Synthesis and characterization of structurally defined head-to-tail coupled oligo(3-alkylthiophenes)

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A very efficient and selective synthesis to regioregular HT-coupled oligo(3-alkylthiophenes) has been developed. A series of benzyl ester-capped oligothiophenes up to the decamer has been synthesized using successive iodination/Suzuki-coupling reaction sequences. For the corresponding hexamer it was shown that saponification and decarboxylation to the HT-coupled oligo(3-alkylthiophene) proceeds in high yields. The dependence of the electronic properties on the chain length of the conjugated oligomers was investigated. The oligomers form very stable and well-ordered adsorbates at the solid–liquid interface and these were imaged by scanning tunneling techniques.

Due to their environmental and thermal stability polythiophenes, in both the neutral and the oxidized state, are among the best investigated conducting polymers.[1] The electronic properties of polythiophenes were immensely improved by the controlled chemical synthesis of regioregularly substituted poly(3-alkylthiophenes) (P3AT) that, depending on the alkyl chain length and the synthetic method employed, contain up to 99% head-to-tail (HT) couplings of adjacent monomeric 3-alkylthiophene units.[2] In contrast to regiorandom P3ATs, in HT-P3ATs, due to the regiochemical control, higher conjugation and enhanced conductivities are obtained. In general, the synthesis was carried out using nickel- or palladium-catalyzed cross-coupling reactions to polymerize 3-alkyl-2-halogenothiophenes that are metallated at the 5-position by a magnesium,[3] zinc,[4] tin,[5] or a boronic ester[6] function. In this way mislinkages and defects in the polymeric backbone are minimized. However, due to the typical statistical chain length distribution, these materials are still polydisperse and the physical properties cannot be strictly correlated to the structural parameters.

The synthesis and investigation of well-defined model oligothiophenes has therefore recently become extremely useful to gain insight into the structural and electronic peculiarities of conjugated materials.[7] Various series of oligothiophenes, which are preferably alkylated and therefore soluble, with controlled chain and conjugation length of up to 16 thiophene units[8] have been synthesized by the stepwise assembly of defined units. In these series, the physical properties are now well-correlated to the (conjugated) chain length and thus 'real' structure-property relationships become available.[7] However, these oligothiophene series are not models for HT-P3ATs, since they contain either regiorandom positions of the solubilizing alkyl chains[9] or less than one alkyl chain per thiophene unit,[10] or couplings other than head-to-tail.[11]

As a result of new developments in polythiophene chemistry and of HT-P3ATs, the first examples of monodisperse HT-coupled oligo(3-alkylthiophenes) (HT-O3AT), mainly bi- and terthiophenes, were very recently reported. The synthesis of these model compounds generally faces some inherent problems. Barbarella *et al.*[12] synthesized and assigned the NMR spectra of all possible configurational triads of trialkylated terthiophenes including the HT-HT derivative. The corresponding methyl-substituted regioregular bi- and terthiophenes were obtained by successive nickel-catalyzed cross-coupling reactions. However, Kumada-coupling of the corresponding brominated bithiophene and the Grignard reagent of 2-bromo-4-methylthiophene produced the HT-coupled terthiophene with only a 20% yield, but with an isomeric purity of $>98\%$.[12] This compound (mp 61 °C) had been synthesized earlier by Zimmer and coworkers,[13] but the considerably lower melting point they obtained (mp 39 °C)[13] indicates a far lower isomeric purity. The corresponding 3,4′,4″-trihexyl-2,2′,5′,5″-terthiophene was prepared by Pd^0-catalyzed Stille-type cross-coupling reactions of organotin and brominated units. In this case, the least effective step was the preparation of 3,4′-dihexyl-2,2′-bithiophene, with a yield of only 23%.[14] Analogous cross-coupling of related tetrahydropyranyl-protected hydroxyethyl-substituted derivatives resulted in the formation of a 5 : 1 mixture of the desired 3,4′-disubstituted bithiophene and a 4,4′-disubstituted regioisomer, which is formed in homo-coupling reactions and which could not be completely separated. Finally, the more polar deprotected hydroxyethyl-substituted derivative was purified by chromatography.[15] The problems of modest yields in coupling steps and homo-coupling products, which were difficult to remove, were also present in the synthesis of a HT-coupled terthiophene with aryloxy-protected hexyl side chains.[16]

Very recently, the synthesis of a series of HT-oligo(3-octylthiophenes) up to the hexamer was reported.[17] A chloride substituent was used to protect one of the reactive α positions in the monomer and oligomers. Stepwise elongation by a monothiophene unit was achieved by successive iodination and Suzuki-coupling reaction of the resulting α-iodooligothiophene and a thiophene boronic ester. The deprotected oligomer series was isolated isomerically pure in good yields by hydrogenolysis of the chloro function. For use in block copolymers the synthesis of terminally phenyl-capped oligo(3-octylthiophenes) up to the nonamer was achieved using Negishi-coupling of brominated 3-octylthiophene units and organozinc derivatives.[18] However, the yields for the higher members were rather low and since the terminal phenyl group

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cannot be cleaved off, this strategy is not applicable for the preparation of HT-O3ATs that are non-functionalized in the α position.

This paper reports the efficient synthesis of a complete series of isomerically pure HT-coupled oligo(3-dodecylthiophenes). The advantageous strategy developed perfectly overcomes the inherent problems described above. Firstly, the use of a terminal benzyl ester protecting group in order to block one of the reactive α positions of the oligothiophenes and to simultaneously allow selective halogenation at the other end, circumvents the difficult preparation of isomerically pure 2,4-disubstituted thiophene building blocks.[13] Secondly, Suzuki-cross-coupling reactions proved to be very effective *and* selective. This allowed us to avoid problems with low yields in metal-catalyzed cross-coupling steps,[12–16,18] and the formation of isomeric homo-coupling products.[15,16] The use of the *boronated bithiophene unit* **2b** allowed us quickly to proceed to longer chain lengths, including a HT-coupled decamer, the longest model oligomer for HT-P3ATs so far synthesized. The physical properties of the oligomers were then determined and correlated with chain length. Then, it was shown for the corresponding sexithiophene that removal of the benzyl ester-protecting group to form the 'pure' non-functionalized HT-O3AT proceeds in high yields.

Results

Synthesis of ester-capped HT-coupled oligo(3-dodecylthiophenes)

The starting point of our synthetic route was the synthesis of isomerically pure 3,4′-didodecyl-2,2′-bithiophene (**2**) in 85% yield by palladium-catalyzed coupling of 3-dodecyl-2-iodothiophene (**1a**) and thienylboronate (**1b**), which was prepared from 3-dodecylthiophene in 36% yield without any 2,3-substituted isomer as a byproduct. We found that the latter derivative undergoes a fast deboronation and therefore can be separated from the boronate **1b**. Interestingly, homocoupling of the boronate **1b** to the corresponding 4,4′-substituted bithiophene has not been observed and the bithiophene **2** was isolated with an isomeric purity >99% (HPLC). The only side reaction of the boronate **1b** is deboronation, forming 3-dodecylthiophene, which was easily separated. Selective bromination of the HT-didodecylbithiophene **2** with one equivalent of *N*-bromosuccinimide (NBS) leads selectively to the monobromo derivative **2a** with 85% yield. A small amount of dibrominated byproduct could be separated by flash chromatography. The bromobithiophene **2a** was then, on the one hand, converted with 86% yield to the boronic ester **2b** by metallation with magnesium in refluxing THF, subsequent quenching with 2-methoxy-1,3,2-dioxaborinane[19] at −60 °C, and addition of boron trifluoride etherate. In this way, the use of protic solvents could be avoided, which in the case of electron-rich systems typically lead to considerable amounts of deboronation product. On the other hand, **2a** was transformed with magnesium to the Grignard reagent and reacted with carbon dioxide in 65% yield to give the carboxylic acid **2c**. Subsequent deprotonation with DBU and reaction with benzyl bromide gave the benzyl ester **2e**, which constitutes the smallest member of the homologous series (Scheme 1), in 72% yield.

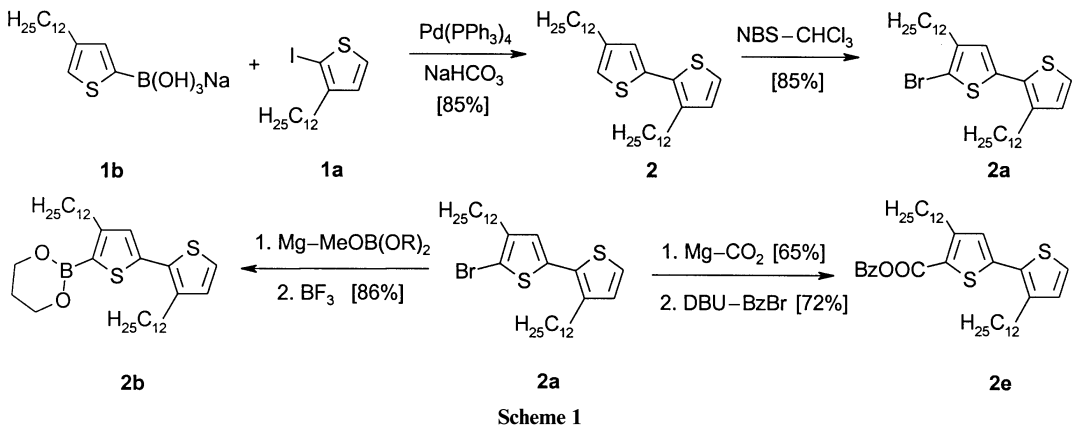
Starting from the benzyl ester-substituted bithiophene **2e**, the longer oligomers were built up by repeated iodination and Suzuki-coupling sequences. Selective iodination of the benzyl ester **2e**, and in the following of the tetrameric (**4e**), hexameric (**6e**) and octameric (**8e**) esters at the free α position, was achieved by adding iodine in the presence of mercuric caproate. The isomerically pure HT-coupled α′-iodobithiophene benzyl ester **3** (95% yield), iodinated tetramer **5** (95% yield), hexamer **7** (95% yield), and octamer **9** (90% yield) were obtained nearly quantitatively. On account of the enhanced solubility produced, especially for the halogenation of the longer oligomers, the use of mercuric caproate instead of mercuric acetate proved to be very important in order to achieve high selectivities and efficiencies of the iodination reaction. The subsequent palladium-catalyzed cross-coupling reaction of the α′-iodobithiophene **3** with the bithiophene boronic ester **2b** was performed under non-aqueous conditions using cesium fluoride in absolute THF[20] as non-nucleophilic base and effectively led to the HT-coupled quaterthiophene benzyl ester **4e** in 77% yield. We found that under these conditions **2b**, which is normally very sensitive to deboronation, was sufficiently stable. Analogously, the α′-iodoquaterthiophene benzyl ester **5** was coupled with the boronic ester **2b** to give the sexithiophene **6e** in 70% yield, the α′-iodosexithiophene **7** to give the octithiophene **8e** in 74% yield, and finally the α′-iodooctithiophene **9** to give the decithiophene **10e** in 50% yield. The iodinated benzyl esters **3**, **5**, **7** and **9** and the benzyl esters **2e**, **4e**, **6e**, **8e** and **10e** are highly soluble in common organic solvents and could be purified by flash chromatography to yield the isomerically pure oligomers in high purity (HPLC >99%) (Scheme 2).

Synthesis of HT-coupled hexadodecylsexithiophene

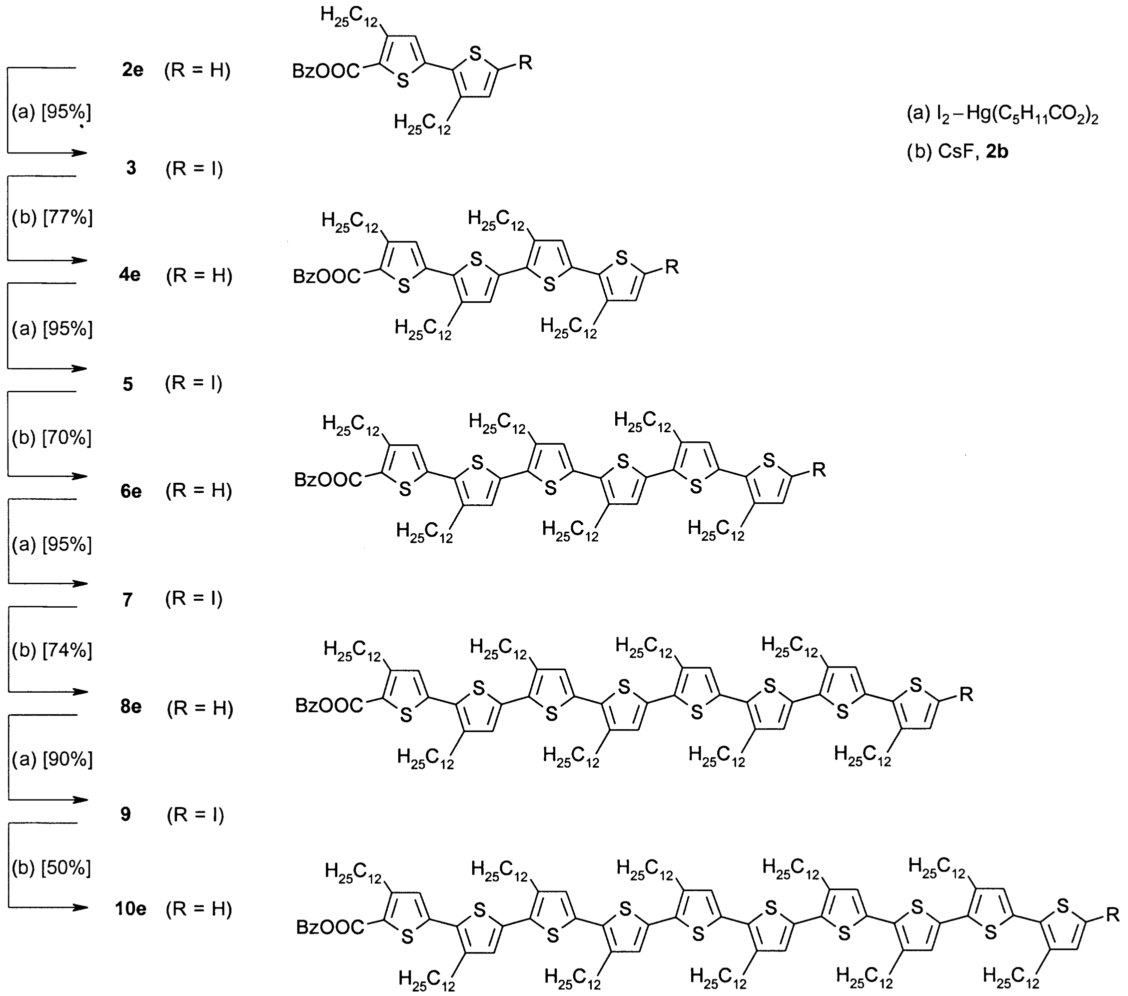
The route to non-functionalized HT-oligo(3-dodecylthiophenes) was demonstrated for the sexithiophene **6**. Cleavage of the benzyl ester-protecting group in the hexamer **6e** with tetrabutylammonium hydroxide resulted in the corresponding sexithiophene carboxylic acid **6c** with a high yield (98%). The carboxylic acid **6c** was decarboxylated cleanly by means of copper powder in quinoline at 190 °C,[21] producing the HT-coupled hexadodecylsexithiophene **6** with 85% yield (HPLC >99%) (Scheme 3).

Electronic properties

In homologous series of oligomers, their properties can be investigated as a function of chain length. Therefore, clear



Scheme 1



Scheme 2

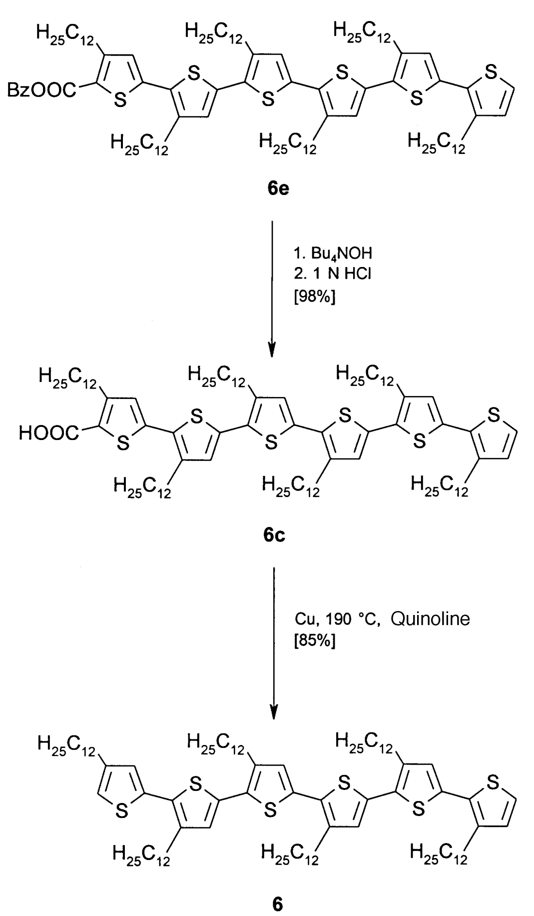
structure-property relationships become observable, which are normally not deducible from the corresponding polydisperse polymeric systems. For conjugated oligomeric systems, as can be shown experimentally[22] and theoretically,[23] indeed nearly all of the (electronic) properties depend linearly on the inverse of the (conjugated) chain length. As examples, a good linear correlation is normally found for the absorption energy of the π–π^* transition or the redox potentials up to a chain length of six[17,24] to eight repeating units.[25] However, very recently it was realized that for longer members of oligothiophene series[8,26] an appreciable deviation from linearity to higher energies occurs when the number of repeating units approaches or exceeds ten. This was later confirmed for other conjugated oligomer systems.[27] This beginning of saturation of the effective conjugation seems to be a general rule for conjugated oligomers and is primarily due to the alternation of bond length in the π system.[26]

For this series of ester-capped oligothiophenes, the physical properties have been investigated as a function of chain length. Starting from the bithiophene ester **2e** (mp 47 °C), the melting point increased linearly by about 4–5 degrees per alkylthiophene unit added, finally reaching 84 °C for the decamer **10e** (Table 1). In contrast to the ester-capped sexithiophene **6e** (mp 66 °C) and the sexithiophene **6** (mp 65 °C), the sexithiophene carboxylic acid **6c** (mp 70 °C) melts at somewhat higher temperatures, because of the presence of intermolecular hydrogen bonds. In the absorption spectra of the ester-capped oligomers **2e**, **4e**, **6e**, **8e** and **10e**, broad and unstructured bands due to the π–π^* transition are observed, reflecting the non-coplanarity and rotational freedom of the

Table 1 Physical properties (melting points, absorption maxima, and redox potentials) of the regioregular HT-coupled oligo(3-dodecylthiophenes) **2e**, **4e**, **6e**, **8e** and **10e** in comparison to the sexithiophene derivatives **6c** and **6**

Oligothiophene	mp/°C	λ_{max}/nm[a] (log ε)	E_{abs}/eV	E°_1/V[b]	E°_2/V[b]	E°_3/V[b]	E°_4/V[b]
2e	47	331 (4.21)	3.75	1.00[c]	—	—	—
4e	55	391 (4.46)	3.17	0.52	0.92[c]	—	—
6e	66	414 (4.64)	3.00	0.35	0.54	1.35[c]	—
8e	77	427 (4.78)	2.90	0.30	0.45	0.92[c]	—
10e	84	433 (4.87)	2.86	0.28	0.37	0.66	0.84
6c	70	414 (4.59)	3.00	n.d.[d]	n.d.[d]	n.d.[d]	—
6	65	404 (4.64)	3.07	0.33	0.48	1.21[c]	—

[a] $c = 5 \times 10^{-6}$ mol L^{-1} in CH$_2$Cl$_2$. [b] $c = 1 \times 10^{-3}$ mol L^{-1} in CH$_2$Cl$_2$–TBAHFP (0.1 M), 100 mV s^{-1}, all potentials *vs.* Fc/Fc$^+$. [c] Irreversible redox process, E° estimated from $i^\circ = 0.855\, i_p$.[40] [d] Not determined.



Scheme 3

individual thiophene units. Not only the energy of the π–π* band, but also the extinction coefficient gradually increases with increasing chain length of the oligomers (Table 1, Fig. 1). Compared to the carboxy-substituted oligomers **6c** and **6e** (λ_{max} = 414 nm), the absorption maximum of the sexithiophene **6** lies at lower wavelength and higher energy (λ_{max} = 404 nm) and is directly comparable to that of the corresponding octyl-substituted hexamer synthesized by Bidan *et al.* (λ_{max} = 405 nm).[17] The correlation of the absorption energies (E_{abs}) of the ester-capped oligomers with inverse chain length (1/*n*) clearly reveals that in this series the relationship is not linear. A deviation from linearity to higher energies is found for the longer oligomers **8e** and **10e** (Fig. 2). This is another clear example that optical properties cannot be described by a simple linear 1/*n*-relationship. In this series saturation of the conjugation already starts at eight repeating units. This result suggests that due to the high number of alkyl side chains HT-O3ATs adopt a less planar conformation in solution, which decreases the effective conjugation. Therefore, linear extrapolation of the transition energies to an infinite chain length, which was frequently used to estimate, on the one hand, the absorption maxima of the corresponding polymers and, on the other hand, the mean conjugation length,[24,28] clearly overestimates this parameter of the polymer. For this series, linear extrapolation of the π–π* transition energy to $1/n \rightarrow 0$ results in a value of E_{abs} = 2.61 eV (λ_{max} = 475 nm), which is definitely smaller than the experimental values reported for HT-coupled poly(3-dodecylthiophene) (HT-P3DDT, E = 2.69 eV, λ_{max} = 460 nm,[3a] E = 2.74 eV, λ_{max} = 453 nm,[3b]).

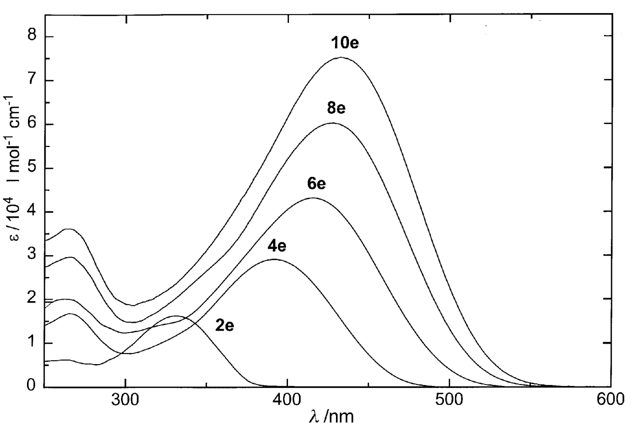


Fig. 1 UV/vis spectra of the HT-benzyl ester-capped oligo(3-alkylthiophenes) **2e**, **4e**, **6e**, **8e** and **10e** in dichloromethane ($c = 5 \times 10^{-6}$ mol L^{-1}).

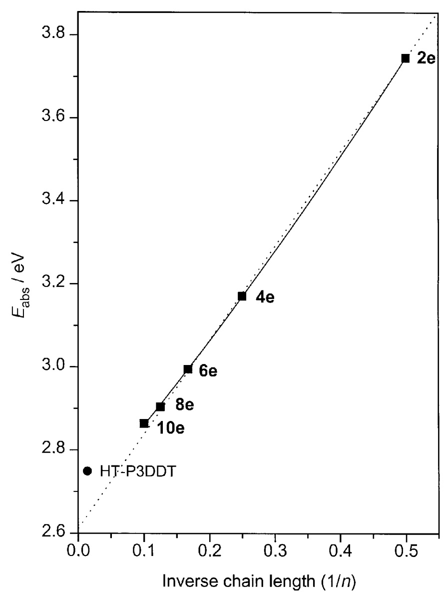


Fig. 2 Correlation of the absorption energies E_{abs} of the HT-benzyl ester-capped oligothiophenes **2e**, **4e**, **6e**, **8e** and **10e** with chain length; E_{abs} is plotted against the reciprocal of the number of thiophene units, 1/*n*. The value for the corresponding HT-poly(3-dodecylthiophene) (circle) is included (*n* was estimated from a GPC measurement).[3b]

Monodisperse conjugated oligomers represent ideal model compounds for the interpretation of electrochemical findings on the corresponding conducting polymers since the redox potentials can be determined in solution and correlated with structural data such as the chain length.[29] The redox properties of the novel ester-capped HT-oligothiophenes **2e**–**10e** were determined by cyclic voltammetry. First of all, as was also found for other oligomeric series,[30] the number of stable redox states increases and the potential difference between adjacent redox states decreases (Table 1) with increasing chain length. Whereas the bithiophene **2e** shows only one redox process (E_1° = 1.00 V *vs.* Fc/Fc$^+$), due to extended conjugation the number of reversible transitions increases to two for the quaterthiophene **4e** ($E_{1,2}^\circ$ = 0.52 V, 0.92 V *vs.* Fc/Fc$^+$), to three for the hexamer **6e** (E_{1-3}° = 0.35 V, 0.54 V, 1.35 V *vs.* Fc/Fc$^+$), and the octamer **8e** (E_{1-3}° = 0.30 V, 0.45 V, 0.92 V *vs.* Fc/Fc$^+$), and finally to four for the decamer **10e** (E_{1-4}° = 0.28 V, 0.37 V, 0.66 V, 0.84 V *vs.* Fc/Fc$^+$). Hence, for HT-decithiophene **10e** up to four reversible oxidation waves were found, indicating stable radical cations to tetracations. In each step one electron is transferred and the first two redox waves nearly merge (Fig. 3). Simultaneously, with increasing chain length of the oligomers the redox potentials are gradually shifted to more cathodic values. Correlations of the redox potentials with the inverse chain length were found to be linear for series of oligothiophenes[24,25] and other oligomeric systems[29] up to six repeating units. In Fig. 4 the first (E_1°) and second (E_2°) oxidation potentials are plotted *vs.* the inverse chain length (1/*n*). In contrast to the previous results and in accordance with the optical properties for this series, it becomes evident that there

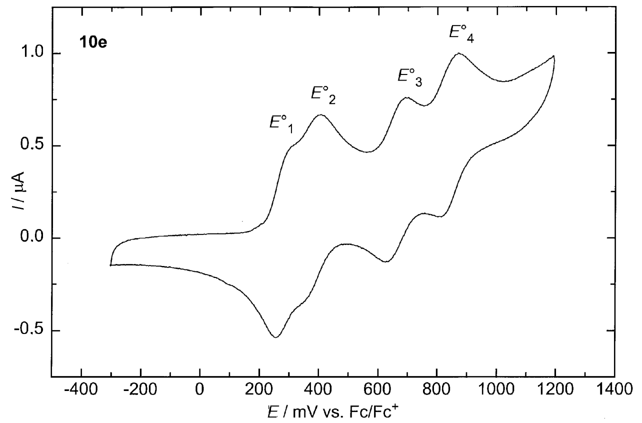


Fig. 3 Cyclic voltammogram of HT-benzyl ester-capped decithiophene **10e** ($c = 1 \times 10^{-4}$ mol L^{-1}) in dichloromethane–TBAHPF (0.1 M) at 100 mV s^{-1}.

is no linear correlation of the redox potentials with $1/n$. These redox transitions of the higher members **8e** and **10e** are clearly displaced to higher values than those estimated from a linear dependence. Linear extrapolation of the potentials to infinite chain length would clearly overestimate the value of the corresponding (ideal) polymer. A comparison of the electrochemical data of this oligomeric series with the redox potential of HT-P3DDT ($E_{pa} = 0.99$ V *vs.* SCE)[2] does not hold in this case, since for polydisperse conjugated polymers broad redox waves are typically found.[31]

Due to the electron-withdrawing effect of the ester group, the redox potentials of the ester-capped sexithiophene **6e** lie, as expected, slightly higher than those of the HT-sexithiophene **6** ($E_1^\circ = 0.33$ V, $E_2^\circ = 0.48$ V *vs.* Fc/Fc^+). The values for both hexaalkylated sexithiophenes **6** and **6e** are directly comparable to the redox potentials of a regioregularly substituted sexithiophene containing only two dodecyl side chains ($E_1^\circ = 0.34$ V, $E_2^\circ = 0.54$ V *vs.* Fc/Fc^+).[32]

Formation of self-assembled monolayers at the solid–liquid interface

Oligothiophenes have successfully advanced as promising materials and active components in electronic devices.[33] Unfortunately, structure determinations in the solid state are scarce due to the poor crystallinity of these oligomers arising from their highly anisotropic shape. However, scanning tunneling microscopy (STM) reveals that organic molecules containing longer alkyl chains are adsorbed from solution onto the surface of pyrolytic graphite (HOPG) or molybdenum disulfide (MoS_2) and form ordered monolayers at the liquid–solid interface.[34] This provides valuable information about the internal molecular arrangement of the molecules, important molecule–molecule and molecule–surface interactions, dynamic processes of domain boundaries, and about defects. Very recently, we found the first two examples in which the 2D molecular arrangement determined in the monolayer by STM coincides with the 3D arrangement in the bulk material.[35]

We and others have reported that various β-alkylated oligothiophenes are physisorbed from solution onto the surface of HOPG and form ordered 2D crystalline monolayers.[8,36] Several general features can be deduced from these STM investigations. Firstly, due to thermodynamic adsorption-desorption equilibrium, dynamic domains of different sizes are observed. The stability and mobility of the domain boundaries clearly depend on the structure of the oligothiophenes.[36b] Secondly, bright areas can be assigned to the heteroaromatic oligothiophene skeletons and the darker regions in between to the alkyl side chains. The rod-like oligothiophene units lie flat on the HOPG surface.[8,36] The molecules are typically ordered in parallel lamella-type stacks in such a way that the alkyl side chains interdigitate and achieve maximum van der Waals interactions. In these lamellae the degree of overlap between two neighboring oligothiophenes decreases with increasing chain length.[8]

The β-alkylated oligothiophenes investigated so far comprised one alkyl side chain per two to three thiophene units. This provides sufficient space for the alkyl side chains to interdigitate and to interact *via* van der Waals forces. However, in the novel series of HT-O3ATs each thiophene ring bears one alkyl side chain. We have investigated the self-assembly behavior of the longest oligomer, the ester-capped decithiophene **10e**, at the solution–substrate interface by the STM technique. In this work, a nearly saturated solution of decamer **10e** in 1,2,4-trichlorobenzene was applied to a freshly cleaved surface of HOPG. The images of the monolayers were recorded at ambient temperature with the aid of a low-current STM equipped with a Pt–Ir tip. In contrast to the hitherto investigated longer oligothiophenes, which hardly achieve thermodynamic equilibrium,[8] the decithiophene **10e** is spontaneously physisorbed and forms well-ordered and very stable monomolecular layers that could be imaged immediately (Fig. 5). By analogy to the previous studies, we attribute the brighter spots to the oligothiophene backbone. Firstly, domains of several tens of nanometers in size can be seen, which mainly take the three different orientations of the molecules. These are aligned with the long molecular axis almost perpendicular to one of the three main crystallographic axes of HOPG (Fig. 5, left). This result indicates that the graphite lattice induces the arrangement of the molecules and the alkyl side chains align along the main crystallographic axes of the substrate. The positions of the domain boundaries change with time, but the dynamics are much slower than in the case of other oligothiophenes.[8] This leads to some defects consisting of one or two missing molecules, in the stacks or at positions where two domains meet. A closer look at the domains clearly reveals that the oligothiophenes form parallel stacks in which the molecules are oriented perpendicular to the stack axis. In contrast to the lamellae-type arrangement of the previously investigated oligomers,[8] the HT-coupled derivatives are perfectly stacked one upon another practically without any displacement of the backbones (Fig. 5, middle). The periodicities of the brighter spots (40–41 Å, 20–21 Å) correspond very well to the calculated long axis of the molecules (40.5 Å) and to the dis-

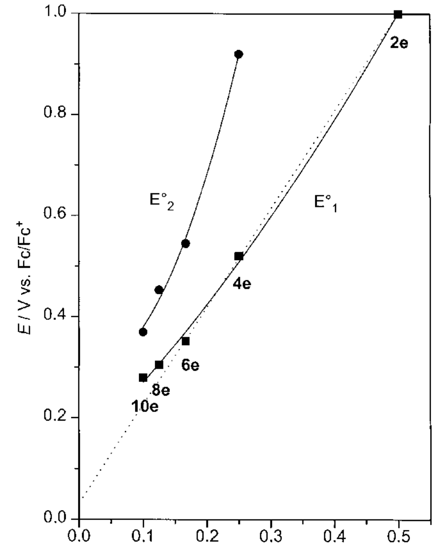


Fig. 4 Correlation of the redox potentials E_1° and E_2° of the HT-benzyl ester-capped oligothiophenes **2e**, **4e**, **6e**, **8e** and **10e** with chain length; E° is plotted against the reciprocal of the number of thiophene units, $1/n$.

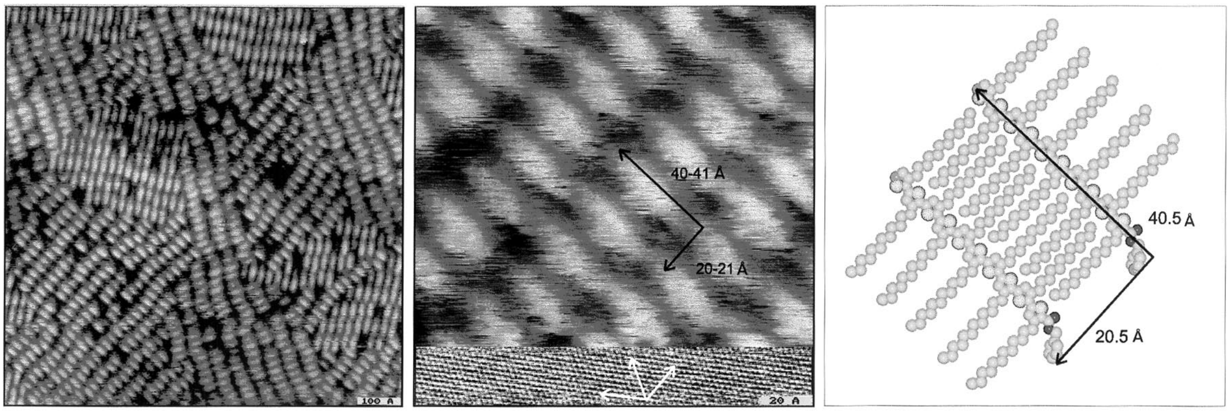


Fig. 5 STM height images of a monolayer of HT-decithiophene **10e** on HOPG. Left: 90 × 90 nm^2, bias voltage = -600 mV, sample is negative, tunnel current = 32 pA. Middle: 16 × 16 nm^2, bias voltage = -570 mV, tunnel current = 19 pA. The inset shows the underlying graphite surface observed at different parameters: bias voltage = -15 mV, tunnel current = 27 pA. The arrows indicate the three main crystallographic axes of the substrate. Right: Calculated model of the molecular arrangement (MM$^+$).

tance between two molecules in a stack (20.5 Å) (Fig. 5, right), which is comparable to the separation of the oligothiophene rods in the lamellae-type arrangement (22 Å).[8] It is very evident from these findings that, due to the substitution pattern in this oligomer (one alkyl chain per thiophene unit), overall more intermolecular forces are active and very stable monolayers are spontaneously formed on a substrate surface. For the first time, we have observed an ideal parallel stacking of the conjugated π systems. This seems to be a general rule for this class of oligomers.[37]

Conclusions

Longer members of the isomerically pure HT-oligo(3-dodecylthiophenes) **2e**–**10e** were very efficiently produced by coupling boronated bithiophenes to iodinated oligothiophene blocks. The improvement achieved by the use of our generally applicable strategy lies with the fact that (*i*) the 2,4-disubstituted thiophene boronate **1b** was obtained isomerically pure, (*ii*) an easily removable benzyl ester protecting group provides chain growth at only one end of the oligothiophene, (*iii*) the use of mercuric caproate in the iodination step guarantees high selectivity and (*iv*) non-aqueous conditions in the cross-coupling step lead to effective conversion since deboronation is suppressed and no homo-coupling products are formed. The investigation of the electronic properties clearly revealed that the correlation of the optical and redox properties with the inverse chain length cannot be described by the usual linear relationship. The effects of the onset of saturation of the conjugation is already evident with eight repeating units. High resolution STM investigations on adsorbed monolayers of the decamer **10e** on HOPG clearly revealed that this type of β-substituted oligothiophene is well-suited to form very stable layers with ideally arranged molecules.

The terminal benzyl ester group was not only used as a protecting group of one reactive α position in order to obtain isomerically pure compounds, but also as a mimicking model of a polymeric resin used in solid phase synthesis. Therefore, the very effective iodination/Suzuki-coupling strategy to the ester-capped oligothiophenes and the successive saponification/decarboxylation to the non-functionalized HT-O3AT was chosen and developed in such a way that the reaction conditions can be directly transferred to solid phase synthesis. The same reaction sequences applied to a corresponding bithiophene-modified Merrifield resin should give nearly quantitative yields in each step, since excesses of reagents can now be used. The quick and efficient synthesis of even longer members of regioregular HT-O3ATs on a solid support is currently under way in our laboratory.

Experimental

General

Methods. Prior to use, solvents and reagents were purified and dried by the usual methods. Thin layer chromatography (TLC) was carried out on Polygram SIL plastic plates from Macherey & Nagel. Preparative column chromatography was performed on glass columns of different sizes packed with silica gel 60 and 200 (Merck). Melting points were determined with a Buechi SMP 20 melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Bruker AMX 500 (500 MHz) and ACF 200 (200 MHz) spectrometers (with deuteriated solvent as lock and tetramethylsilane as internal reference). ^{13}C NMR spectra were recorded on Bruker AMX 500 (126 MHz) and AC 200 (50 MHz) spectrometers. Elemental analyses were performed with an Elementar Vario EL. HPLC analyses were performed with a Nucleosil 100 nitrophenyl column (Knaur) and *n*-hexane–dichloromethane as eluent. Mass spectra were recorded with Varian MAT 711, SSQ 7000, and MALDI-TOF MS Bruker Reflex 2 (matrix dithranol) spectrometers. UV/vis spectra were recorded on a Perkin Elmer Lambda 19 with cuvettes of 1 cm. The cyclic voltammetry experiments were performed with a computer-controlled EG&G PAR 273 potentiostat in a three-electrode single compartment cell (5 mL). The platinum working electrodes consisted of platinum wires sealed in a soft glass tube with a surface of $A = 0.785$ mm^2, which prior to use were polished down to 0.5 μm (Buehler polishing paste) in order to get reproducible surfaces. The counter electrode consisted of a platinum wire, the reference was an Ag/AgCl secondary electrode. All potentials were internally referenced to the ferrocene/ferricenium couple. Argon was used to purge the electrolyte before use. Routinely, a concentration of 2.5–5 × 10^{-4} M of electroactive species was used. The electrolyte consisted of either dichloromethane (p.a., Riedel de Haën), which was refluxed and distilled over CaH_2 under nitrogen. The solvent was directly transferred by means of a syringe to the electrochemical cell. The supporting salt was 0.1 M tetrabutylammonium hexafluorophosphate (TBAHPF, Fluka), which was recrystallized twice from ethanol–water and dried under high vacuum.

Nearly saturated solutions of **10e** in 1,2,4-trichlorobenzene (Aldrich, >99%) were applied to the basal surface of highly oriented pyrolytic graphite (HOPG) with a Pasteur pipette. The tunnel tips were mechanically cut Pt–Ir wires. Adsorption occurred instantaneously and did not need to be induced by a potential pulse. The height images were made under ambient conditions without any digital filtering using a RHK STM regulated by a RHK STM 1000 control system.

Geometry optimizations were made with a molecular mechanics method (MM+, Hyperchem 4.5, Hypercube, Inc.).

Chemicals. Benzyl bromide (Fluka), 3-bromothiophene (Avocado), 1,2-dimethoxyethane (Merck), dodecyl bromide (Fluka), iodine (Fluka), lithium diisopropylamide (LDA, 2.0 M in THF, Fluka), tetrabutylammonium hydroxide (Fluka), sodium thiosulfate (Merck) and trimethylborate (Fluka) were purchased and used without further purification. 3-Dodecylthiophene,[38] 2-bromo-3-dodecylthiophene[38] and tetrakis(triphenylphospino)palladium(0)[39] were prepared following published procedures.

Syntheses

3-Dodecyl-2-iodothiophene (1a). A solution of 2-bromo-3-dodecylthiophene (10.0 g, 30 mmol) in 100 ml dry THF was added to magnesium turnings (0.8 g, 33 mmol) and refluxed until the magnesium was dissolved. The resulting mixture was cooled down to −60 °C and a solution of iodine (7.5 g, 30 mmol) in 100 ml dry THF was slowly added. The mixture was stirred for 2 h and allowed to warm to room temperature. After dilution with 50 ml diethyl ether the mixture was hydrolyzed with aqueous HCl and extracted twice with 50 ml diethyl ether. The organic layers were washed with aqueous sodium thiosulfate and dried over sodium sulfate. After evaporation of the solvent the residue was distilled *in vacuo* to afford 3-dodecyl-2-iodothiophene (**1a**) as a slightly yellow liquid. Yield: 9.40 g (83%). Bp: 125 °C/1 × 10^{-3} mbar (GC >96%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.36 (d, 1H, $^3J_{(5,4)} = 5.2$ Hz, 5-H), 6.74 (d, 1H, $^3J_{(4,5)} = 5.2$ Hz, 4-H), 2.54 (t, 2H, $^3J_{(H,H)} = 7.6$ Hz, α-CH_2), 1.58–1.50 (m, 2H, β-CH_2), 1.29–1.26 (m, 18H, —CH_2), and 0.87 (t, 3H, $^3J_{(H,H)} = 6.6$ Hz, —CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 147.1, 130.3, 127.9, 73.9, 32.1, 31.9, 30.0, 29.68, 29.65, 29.57, 29.43, 29.34, 29.21, 22.7. MS: *m/z* 378 [M^+]. $C_{16}H_{27}IS$ (378.4); calcd: C 50.79, H 7.19; found: C 51.09, H 6.86.

Sodium 4-dodecyl-2-thienylboronate (1b). At −60 °C a LDA-solution (63 ml, 126 mmol, 2 M in *n*-hexane) was added dropwise to a stirred solution of 3-dodecylthiophene (32.0 g, 126 mmol) in 200 ml dry THF. The resulting mixture was stirred for 1 h and was allowed to warm up to room temperature over a 2 h period. After cooling the mixture down to −60 °C trimethylborate (30 ml, 240 mmol) was slowly added. The mixture was allowed to come to room temperature over night and was hydrolyzed with aqueous HCl. After extraction with 150 ml diethyl ether the organic phase was dried over sodium sulfate and stirred with 20 g sodium hydroxide. The resulting precipitate was filtered off and washed with cold diethyl ether to get sodium 4-dodecyl-2-thienylboronate (**1b**) as a colorless solid. The product was used without further purification. Yield 15.0 g (36%). Mp: 128 °C (dec). ^{1}H NMR (200 MHz, CD_3OD): δ 6.82 (s, 1H, $^4J_{(5,3)} = 1.1$ Hz, 5-H), 6.73 (s, 1H, $^4J_{(3,5)} = 1.1$ Hz, 3-H), 2.59 (t, 2H, $^3J_{(H,H)} = 7.3$ Hz, α-CH_2), 1.62–1.53 (m, 2H, β-CH_2), 1.29 (m, 18H_2, CH_2), 0.87 (t, 3H, $^3J_{(H,H)} = 6.7$ Hz, CH_3), OH not resolved. ^{13}C NMR (50 MHz, CD_3OD): δ 143.89, 130.9, 120.0, 33.4, 32.4, 31.3, 31.1, 31.0, 30.9, 30.8, 24.5, 24.0, 14.2.

3,4′-Didodecyl-2,2′-bithiophene (2). Tetrakis(triphenylphosphino)palladium(0) (0.33 g, 0.3 mmol) was added to a solution of **1a** (4.00 g, 10 mmol) in 50 ml dimethoxyethane and the mixture was carefully degassed. After addition of **1b** (3.30 g, 10 mmol) the mixture was heated to reflux and a saturated aqueous solution of $NaHCO_3$ (1.80 g, 20 mmol) was slowly added. After 3 h the coupling reaction was completed and the mixture was diluted with 50 ml diethyl ether. The mixture was washed with aqueous HCl and repeatedly with a saturated NaCl solution. After drying the solution over sodium sulfate and evaporation of the solvent the remaining oil was purified by chromatography (silica gel, cyclohexane) to yield the bithiophene **2** as a slightly yellow oil (3.9 g, 85%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.12 (d, 1H, $^3J_{(5',4')} = 5.2$ Hz, 5′-H), 6.92 (s, 1H, $^4J_{(5,3)} = 1.5$ Hz, 5-H), 6.90 (d, 1H, $^3J_{(4',5')} = 5.2$ Hz, 4′-H), 6.86 (d, 1H, $^4J_{(3,5)} = 1.5$ Hz, 3-H), 2.72 (t, 2H, $^3J_{(a',b')} = 7.7$ Hz, α′-CH_2), 2.58 (t, 2H, $^3J_{(a,b)} = 7.7$ Hz, α-CH_2), 1.60–1.54 (m, 4H, β,β′-CH_2), 1.29–1.25 (m, 36H, CH_2), 0.87 (t, 6H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 143.6, 139.4, 135.9, 131.0, 129.9, 127.3, 123.4, 119.9, 31.7, 30.8, 30.6, 30.5, 29.7, 29.6, 29.55, 29.52, 29.4, 29.2, 22.8, 14.2. $C_{32}H_{54}S_2$ (502.9); calcd: C 76.43, H 10.82; found: C 76.50, H 10.77.

5-Bromo-3′,4-didodecyl-2,2′-bithiophene (2a). **2** (3.00 g, 6 mmol) was dissolved in 20 ml dry $CHCl_3$ and cooled down to 0 °C. Under exclusion of light a solution of *N*-bromosuccinimide (1.18 g, 6.6 mmol) in 50 ml $CHCl_3$ was slowly added and stirred for 3 h. The mixture was allowed to warm up to room temperature and was stirred for 1 day. Then the mixture was diluted with diethyl ether and poured into water. The organic phase was washed several times with aqueous HCl and water and finally dried over sodium sulfate. After evaporation of the solvent the remaining residue was purified with column chromatography (silica gel, *n*-hexane) to afford the bromobithiophene **2a** as a yellow solid (2.90 g, 85%). Mp: 31 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.14 (d, 1H, $^3J_{(5',4')} = 5.2$ Hz, 5′-H), 6.89 (d, 1H, $^3J_{(4',5')} = 5.2$ Hz, 4′-H), 6.77 (s, 1H, 3-H), 2.69 (t, 2H, $^3J_{(H,H)} = 7.8$ Hz, α′-CH_2), 2.54 (t, 2H, $^3J_{(H,H)} = 7.6$ Hz, α-CH_2), 1.62–1.53 (m, 4H, β,β′-CH_2), 1.32–1.25 (m, 36H, CH_2), 0.87 (t, 6H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 142.3, 139.9, 130.0, 129.9, 126.8, 123.9, 108.8, 32.0, 31.6, 30.3, 29.7, 29.6, 29.54, 29.39, 29.25, 29.1, 22.27, 22.67, 14.1. $C_{32}H_{53}BrS_2$ (582.9); calcd: C 66.06, H 9.18; found C 65.88, H 9.14.

4,3′-Didodecyl-2,2′-bithiophene-5-boronic acid propane-1,3-diol ester (2b). A solution of **2a** (2.00 g, 3.4 mmol) in 50 ml dry THF was mixed with magnesium turnings (0.10 g, 3.8 mmol) and was refluxed until the magnesium had reacted. The mixture was cooled down to −60 °C and treated with 2-methoxy-1,3,2-dioxaborinane (0.40 g, 3.5 mmol) and stirred for 2 h. The reaction mixture was allowed to come to room temperature and then cooled down again to −60 °C; boron trifluoride etherate (0.24 g, 3.5 mmol) was added dropwise. After reaching room temperature the solvent was evaporated *in vacuo*. The remaining residue was dissolved in dry petroleum ether and filtered over Celite to afford the bithiophene boronic acid propanediol ester **2b** in 85% purity as a yellow oil (1.70 g, 3.0 mmol), which was used without further purification. ^{1}H NMR (200 MHz, $CDCl_3$): δ 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, $^3J_{(H,H)} = 6.6$ Hz, —OCH_2CH_2CH_2O—), 2.85 (m, 4H, α,α′-CH_2), 2.05 (q, 2H, $^3J_{(H,H)} = 5.5$ Hz, —OCH_2CH_2CH_2O—), 1.64–1.55 (m, 4H, β,β′-CH_2), 1.31 (m, 32H, —CH_2—), 0.87 (t, 6H, CH_3). ^{13}C NMR (50 MHz, CDCl$_3$): δ 153.0, 140.4, 139.4, 131.27, 130.4, 129.9, 123.37, 61.9, 31.9, 31.6, 29.9, 29.7, 29.5, 27.4, 22.7, 14.1. MS: *m*/*z* 586 [M$^+$].

4,3′-Didodecyl-2,2′-bithiophene-5-carboxylic acid (2c). A solution of **2a** (3.70 g, 6.4 mmol) in 50 ml dry THF was added to magnesium turnings (0.30 g, 10.3 mmol) and was refluxed until the magnesium disappeared. The mixture was cooled down to 0 °C and solid carbon dioxide was added. After reaching room temperature the mixture was hydrolyzed with aqueous HCl and the organic phase washed several times with water. Finally, the organic layer was dried over sodium sulfate and after evaporation of the solvent the remaining residue was purified with column chromatography (silica gel, dichloromethane–ethyl acetate [80 : 20]) to afford the bithiophene carboxylic acid **2c** (1.70 g, 65%) as a yellow solid. Mp: 79 °C. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.28 (d, 1H, $^3J_{(5',4')}$ = 5.2 Hz, 5′-H), 7.0 (s, 1H, 3-H), 6.93 (d, 1H, $^3J_{(4',5')}$ = 5.2 Hz, 4′-H), 3.05 (t, 2H, $^3J_{(\mathrm{H,H})}$ = 7.6 Hz, α-CH_2), 2.81 (t, 2H, $^3J_{(\mathrm{H,H})}$ = 7.8 Hz, α′-CH_2), 1.71–1.64 (m, 4H, β,β′-CH_2), 1.41–1.21 (m, 36H, —CH_2—), 0.87 (t, 6H, CH_3), OH not resolved. ^{13}C NMR (CDCl$_3$): δ 168.2, 153.9, 142.8, 141.3, 130.4, 129.4, 128.6, 124.9, 124.8, 31.9, 30.4, 29.6, 29.5, 22.7, 14.1. MS: *m*/*z* 546 [M$^+$], 502 [M$^+$ − COOH]. $C_{33}H_{54}O_2S_2$ (545.8); calcd: C 72.47, H 9.95; found: C 72.35, H 9.97.

4,3′-Didodecyl-2,2′-bithiophene-5-carboxylic acid benzyl ester (2e). To a solution of **2c** (0.90 g, 1.7 mmol) in 50 ml dry toluene DBU (0.25 g, 1.7 mmol) was slowly added. The mixture was stirred for half an hour at room temperature and benzyl bromide (0.30 g, 1.7 mmol) was added dropwise. After stirring for 3 h at room temperature the mixture was washed with water and extracted several times with diethyl ether. The combined organic layers were washed with aqueous HCl, water and dried over sodium sulfate. The evaporation of the solvent and purification with column chromatography over silica gel (*n*-hexane–dichloromethane [80 : 20]) yielded the bithiophene benzyl ester **2e** (0.75 g, 72%) as a yellow solid. Mp: 47 °C. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.48–7.32 (m, 5H, Ph—*H*), 7.20 (d, 1H, $^3J_{(5',4')}$ = 5.2 Hz, 5′-H), 6.95 (s, 1H, 3-H), 6.94 (d, 1H, $^3J_{(4',5')}$ = 5.2 Hz, 4′-H), 5.35 (s, 2H, PhCH_2O—), 2.99 (t, 2H, $^3J_{(\mathrm{H,H})}$ = 7.6 Hz, α-CH_2), 2.78 (t, 2H, $^3J_{(\mathrm{H,H})}$ = 7.8 Hz, α′-CH_2), 1.68–1.58 (m, 4H, β,β′-CH_2), 1.38–1.28 (m, 36H, —CH_2—), 0.87 (t, 6H, CH_3). ^{13}C NMR (50 MHz, CDCl$_3$): δ 163.2, 152.2, 140.9, 130.3, 136.6, 136.1, 129.8, 128.9, 128.5, 128.0, 124.9, 124.2, 66.2, 31.9, 30.5, 29.6, 29.5, 29.36, 22.6, 14.2. MS: *m*/*z* 636 [M$^+$], 502 [M$^+$ − Bz]. $C_{40}H_{60}O_2S_2$ (636.9); calcd: C 75.36, H 9.48; found: C 75.42, H 9.57.

4,3′-Didodecyl-5′-iodo-2,2′-bithiophene-5-carboxylic acid benzyl ester (3). To a solution of **2e** (1.20 g, 1.90 mmol) in CHCl$_3$–acetic acid (95 : 5) mercuric caproate (0.81 g, 2.00 mmol) was added and the solution was then cooled down to 0 °C. After slow dropwise addition of iodine (0.51 g, 2.00 mmol) in the same solvent (over a period of 2 h) the reaction mixture was allowed to warm up to room temperature and was washed several times with aqueous NaHCO$_3$, aqueous sodium thiosulfate, and finally with water. After drying the organic phase over sodium sulfate the solvent was evaporated and the residue filtered through silica gel (petroleum ether–dichloromethane [75 : 25]) to afford the α-iodobithiophene benzyl ester **3** (1.45 g, 95%) as a yellow solid. Mp: 47 °C. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.43–7.34 (m, 5H, Ph—*H*), 7.07 (s, 1H, 4′-H), 6.89 (s, 1H, 3-H), 5.32 (s, 2H, PhCH_2O—), 2.96 (t, 2H, $^3J_{(\mathrm{H,H})}$ = 7.8 Hz, α-CH_2), 2.71 (t, 2H, $^3J_{(\mathrm{H,H})}$ = 7.8 Hz, α′-CH_2), 1.61–1.54 (m, 4H, β,β′-CH_2), 1.25 (m, 36H, —CH_2—), 0.87 (t, 6H, CH_3). ^{13}C NMR (CDCl$_3$): δ 162.1, 151.9, 142.7, 139.9, 139.4, 135.9, 135.8, 129.25, 127.9, 125.7, 72.9, 66.3, 31.9, 30.4, 29.7, 29.53, 22.66, 14.08. MS: *m*/*z* 762 [M$^+$]. $C_{40}H_{60}IO_2S_2$ (763.9); calcd: C 62.96, H 7.79; C 62.76, H 8.04.

4,3′,3″,3‴-Tetradodecyl-2,2′:5′,2″:5″,2‴-quaterthiophene-5-carboxylic acid benzyl ester (4e). To a solution of **3** (1.00 g, 1.30 mmol) in 30 ml dry THF tetrakis(triphenylphosphino)palladium(0) (0.07 g, 0.065 mmol, 5 mol%) and cesium fluoride (1.00 g, 6.00 mmol) were added. The mixture was refluxed under an inert gas atmosphere. To the refluxing suspension a solution of **2b** (1.16 g, 2.00 mmol) in dry THF was added dropwise. The mixture was refluxed for 3 h and the coupling rate was controlled by thin layer chromatography. After evaporation of the solvent the residue was purified by column chromatography (silica gel, *n*-hexane–dichloromethane [80 : 20]) to afford the quaterthiophene benzyl ester **4e** (1.13 g, 77%) as an orange solid. Mp: 55 °C. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.45–7.35 (m, 5H, Ph—*H*), 7.15 (d, 1H, $^3J_{(5''',4''')}$ = 5.2 Hz, 5‴-H), 6.98 (s, 1H, 4-H), 6.96 (s, 1H, 4′-H), 6.33 (s, 1H, 4″-H), 6.22 (d, 1H, $^3J_{(4''',5''')}$ = 5.2 Hz, 4‴-H), 5.32 (s, 2H, PhCH_2O—), 3.01 (t, 2H, $^3J_{(\mathrm{H,H})}$ = 7.8 Hz, α-CH_2), 2.78 (t, 6H, $^3J_{(\mathrm{H,H})}$ = 7.8 Hz, α′-α‴-CH_2), 1.65–1.55 (m, 8H, β-β‴-CH_2), 1.28 (m, 72H, —CH_2—), 0.87 (t, 12H, CH_3). ^{13}C NMR (50 MHz, CDCl$_3$): δ 162.2, 152.1, 141.3, 140.7, 140.1, 139.7, 136.1, 135.0, 134.5, 132.2, 131.9, 130.3, 130.1, 129.8, 129.6, 128.5, 127.9, 124.9, 123.6, 66.3, 31.9, 30.5, 29.6, 29.5, 29.3, 22.6, 14.1. MS: *m*/*z* = 1137 [M$^+$]. $C_{72}H_{112}O_2S_4$ (1137.9); calcd: C 76.00, H 9.91; found: C 75.83, H 9.94.

5‴-Iodo-4,3′,3″,3‴-tetradodecyl-2,2′ : 5′,2″ : 5″,2‴-quaterthiophene-5-carboxylic acid benzyl ester (5). Following the synthetic method for **3**, **4e** (0.91 g, 0.80 mmol) was reacted with mercuric caproate (0.34 g, 0.84 mmol) and iodine (0.21 g, 0.84 mmol). After chromatographic work-up (silica gel, petroleum ether–dichloromethane [75 : 25]) benzyl ester **5** was obtained as an orange solid (0.96 g, 95%). Mp: 71 °C. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.43–7.34 (m, 5H, Ph—*H*), 7.05 (s, 1H, 4‴-H), 6.98 (s, 1H, 4″-H), 6.97 (s, 1H, 4′-H), 6.78 (s, 1H, 3-H), 5.32 (s, 2H, PhCH_2O—), 2.96 (t, 2H, $^3J_{(\mathrm{H,H})}$ = 7.8 Hz, α-CH_2), 2.71 (m, 4H, α′-α‴-CH_2), 1.61–1.54 (m, 8H, β-β‴-CH_2), 1.25 (m, 72H, —CH_2—), 0.87 (t, 12H, CH_3). ^{13}C NMR (126 MHz, CDCl$_3$): δ 162.2, 152.1, 141.4, 141.3, 140.06, 140.1, 136.40, 136.0, 134.7, 132.9, 130.5, 129.8, 128.5, 128.1, 125.1, 71.6, 66.2, 31.9, 30.5, 30.4, 29.7, 29.6, 29.5, 29.4, 29.3, 28.9, 22.9, 14.1. MS: *m*/*z* 1262.6 [M$^+$]. $C_{72}H_{111}IO_2S_4$ (1263.2); calcd: C 68.43, H 8.85; found: 68.16, H 8.72.

4,3′,3″,3‴,3⁗,3′′′′′-Hexadodecyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′-sexithiophene-5-carboxylic acid benzyl ester (6e). Following the synthetic method for **4e**, **5** (0.30 g, 0.24 mmol), tetrakis(triphenylphosphino)palladium(0) (0.015 g, 0.012 mmol, 5 mol%), cesium fluoride (0.45 g, 3.00 mmol), and **2b** (0.42 g, 0.72 mmol) were reacted. After chromatographic work-up (silica gel, petroleum ether–dichloromethane [75 : 25]) the benzyl ester **6e** was obtained as a red solid (0.37 g, 70%). Mp: 66 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.46–7.32 (m, 5H, Ph—*H*), 7.16 (d, 1H, $^3J_{(5''''',4''''')}$ = 5.2 Hz, 5′′′′′-H), 6.99 (s, 1H, 4⁗-H), 6.97 (s, 1H, 4‴-H), 6.97 (s, 1H, 4″-H), 6.96 (s, 1H, 4′-H), 6.94 (s, 1H, 3-H), 6.92 (d, 1H, $^3J_{(4''''',5''''')}$ = 5.2 Hz, 4⁗-H), 5.35 (s, 2H, PhCH_2O—), 2.99 (t, 2H, $^3J_{(\mathrm{H,H})}$ = 7.8 Hz, α-CH_2), 2.78 (t, 10H, $^3J_{(\mathrm{H,H})}$ = 7.8 Hz, α′-α⁗-CH_2), 1.75–1.6 (m, 12H, β-β⁗-CH_2), 1.45–1.2 (m, 108H, —CH_2—), 0.87 (t, 12H, CH_3). ^{13}C NMR (126 MHz, CDCl$_3$): δ 162.2, 152.1, 141.3, 140.7, 140.1, 139.7, 139.81, 139.6, 136.1, 135.0, 134.5, 133.9, 133.8, 132.2, 131.9, 130.5, 130.3, 130.1, 129.8, 129.6, 128.5, 128.1, 128.0, 127.9, 124.9, 123.6, 66.3, 31.9, 30.5, 29.6, 29.5, 29.57, 29.51, 29.3, 29.2, 22.6, 14.1. $C_{104}H_{164}O_2S_6$ (1638.8); calcd: C 76.22, H 10.09; found: C 76.40, H 10.09. MALDI-TOF MS: ($C_{104}H_{164}O_2S_6$) found: 1638.7.

4,3′,3′′,3′′′,3′′′′,3′′′′′-Hexadodecyl-2,2′ : 5′,2′′ : 5′′,2′′′ : 5′′′, 2′′′′ : 5′′′′,2′′′′′-sexithiophene-5-carboxylic acid (6c). To a solution of **6e** (50 mg, 0.03 mmol) in dry THF, tetrabutylammonium hydroxide (16 mg, 0.06 mmol) was added and the mixture was refluxed for 1 h. After dilution with diethyl ether it was washed several times with aqueous HCl and water. The organic phase was dried over sodium sulfate and after evaporation of the solvent the remaining residue was purified with column chromatography (silica gel, dichloromethane) to afford the sexithiophene carboxylic acid **6c** (46 mg, 98%) as a red solid. Mp: 70 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.16 (d, 1H, $^3J_{(5''''',4''''')} = 5.1$ Hz, 5′′′′′-H), 7.03 (s, 1H, 4′′′′-H), 6.99 (s, 1H, 4′′′-H), 6.97 (s, 1H, 4′′-H), 6.96 (s, 1H, 4′), 6.93 (s, 1H, 3-H), 6.92 (d, 1H, $^3J_{(4''''',5''''')} = 5.2$ Hz, 4′′′′′-H), 2.99 (t, 2H, $^3J_{(H,H)} = 7.8$ Hz, α-CH_2), 2.78 (m, 10H, $^3J_{(H,H)} = 7.8$ Hz, α′-α′′′′′-CH_2), 1.75–1.6 (m, 12H, β-β′′′′′-CH_2), 1.45–1.2 (m, 108H, —CH_2—), 0.87 (t, 12H, CH_3), OH not resolved. ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.8, 153.5, 142.0, 141.7, 140.4, 140.0, 139.8, 139.6, 135.3, 134.2, 134.1, 133.9, 130.5, 130.3, 130.2, 130.0, 129.9, 129.5, 128.8, 128.7, 128.63, 128.62, 124.2, 123.6, 31.9, 30.6, 30.5, 30.4, 30.3, 29.8, 29.7, 29.66, 29.62, 29.56, 29.5, 29.41, 29.3, 29.2, 22.6, 14.0. $C_{97}H_{158}O_2S_6$ (1548.7); calcd: C 75.23, H 10.28; found: C 74.95, H 10.11.

4,3′,3′′,3′′′,3′′′′,3′′′′′-Hexadodecyl-2,2′ : 5′,2′′ : 5′′,2′′′ : 5′′′, 2′′′′ : 5′′′′,2′′′′′-sexithiophene (6). To a solution of **6c** (45 mg, 0.029 mmol) in 10 ml dry quinoline, copper powder (100 mg) was added. Under an inert gas atmosphere the mixture was heated to 190 °C for 1 h and then poured in aqueous HCl. After several extractions with diethyl ether the combined organic layers were washed with water. The organic phase was dried over sodium sulfate and after evaporation of the solvent the remaining residue was purified with column chromatography (silica gel, petroleum ether) to yield the sexithiophene **6** (37 mg, 85%) as an orange solid. Mp: 65 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 (d, 1H, $^3J_{(5''''',4''''')} = 5.1$ Hz, 5′′′′′-H), 6.97 (s, 1H, 4′′′′-H), 6.96 (s, 1H, 4′′′-H), 6.95 (s, 1H, 4′′-H), 6.95 (s, 1H, 4′-H), 6.93 (s, 1H, 3-H), 6.92 (d, 1H, $^3J_{(4''''',5''''')} = 5.2$ Hz, 4′′′′′-H, 6.88 (d, 1H, $^4J_{(5,3)} = 1.1$ Hz, 5-H), 2.78 (m, 10H, α′-α′′′′′-CH_2), 2.6 (t, 2H, $^3J_{(H,H)} = 7.8$ Hz, α-CH_2), 1.75–1.6 (m, 12H, β-β′′′′′-CH_2), 1.45–1.2 (m, 108H, —CH_2—), 0.87 (t, 12H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.6, 139.8, 139.7, 139.64, 139.62, 135.5, 134.1, 133.7, 133.6, 133.5, 131.0, 130.58, 130.56, 130.4, 130.0, 128.7, 128.5, 128.4, 127.1, 123.5, 119.9, 31.9, 30.66, 30.61, 30.5, 30.4, 29.6, 29.58, 29.5, 29.4, 29.37, 29.3, 29.2, 22.6, 14.0. $C_{96}H_{158}S_6$ (1504.7); calcd: C 76.63, H 10.58; found: C 76.58, H 10.69. MALDI-TOF MS: ($C_{96}H_{158}S_6$); found: 1504.5.

4,3′,3′′,3′′′,3′′′′,3′′′′′-Hexadodecyl-5′′′′′-iodo-2,2′ : 5′,2′′ : 5′′, 2′′′ : 5′′′′,2′′′′ : 5′′′′,2′′′′′-sexithiophene-5-carboxylic acid benzyl ester (7). Following the synthetic method for **3**, **6e** (0.35 g, 0.21 mmol) was reacted with mercuric caproate (0.09 g, 0.21 mmol) and iodine (0.06 g, 0.23 mmol). After chromatographic work-up (silica gel, petroleum ether–dichloromethane [75 : 25]) the benzyl ester **7** was obtained as a red solid (0.37 g, 95%). Mp: 69 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43–7.34 (m, 5H, Ph—H), 7.05 (s, 1H, 4′′′′′-H), 6.98 (s, 1H, 4′′′′-H), 6.97 (s, 1H, 4′′′-H), 6.96 (s, 1H, 4′′-H), 6.94 (s, 1H, 4′-H), 6.87 (s, 1H, 3-H), 5.33 (s, 2H, PhCH_2O—), 2.96 (t, 2H, $^3J_{(H,H)} = 7.8$ Hz, α-CH_2), 2.71 (m, 10H, α′-α′′′′′- CH_2), 1.7–1.59 (m, 12H, β-β′′′′′-CH_2), 1.25 (m, 108H, —CH_2—), 0.87 (t, 18H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.2, 152.1, 141.4, 140.7, 140.2, 140.0, 139.8, 136.5, 136.1, 135.0, 134.0, 133.6, 132.6, 130.9, 130.5, 130.1, 129.7, 129.1, 128.77, 128.71, 128.5, 128.1, 128.0, 125.1, 71.6, 66.9, 31.9, 30.5, 30.4, 29.8, 29.7, 29.6, 29.56, 29.5, 29.4, 29.3, 28.9, 22.6, 14.1. $C_{104}H_{163}IO_2S_6$ (1764.7); calcd: C 70.78, H 9.31; found: C 70.55, H 9.26. MALDI-TOF MS: ($C_{104}H_{163}IO_2S_6$) found: 1764.4.

4,3′,3′′,3′′′,3′′′′,3′′′′′,3′′′′′′′-Octadodecyl-2,2′ : 5′,2′′ : 5′′,2′′′ : 5′′′,2′′′′ : 5′′′′,2′′′′′ : 5′′′′′,2′′′′′′ : 5′′′′′′,2′′′′′′′-octithiophene-5-carboxylic acid benzyl ester (8e). Following the synthetic method for **4e**, **7** (0.30 g, 0.17 mmol), tetrakis(triphenylphosphino)palladium(0) (0.01 g, 0.01 mmol, 5 mol%), cesium fluoride (0.30 g, 2.00 mmol), and **2b** (0.30 g, 0.50 mmol) were reacted. After chromatographic work-up (silica gel, petroleum ether–dichloromethane [75 : 25]) the benzyl ester **8e** was obtained as a dark red solid (0.27 g, 74%). Mp: 77 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46–7.32 (m, 5H, Ph—H), 7.16 (d, 1H, $^3J_{(5''''''',4''''''')} = 5.2$ Hz, 5′′′′′′′-H), 6.98 (s, 1H, 4′′′′′′-H), 6.97 (s, 1H, 4′′′′′-H), 6.97 (s, 1H, 4′′′′-H), 6.97 (s, 1H, 4′′′-H), 6.96 (s, 1H, 4′′-H), 6.95 (s, 1H, 4′-H), 6.93 (s, 1H, 3-H), 6.92 (d, 1H, $^3J_{(4''''''',5''''''')} = 5.2$ Hz, 4′′′′′′′-H), 5.35 (s, 2H, PhCH_2O—), 2.99 (t, 2H, $^3J_{(H,H)} = 7.8$ Hz, α-CH_2), 2.79 (m, 14H, α′-α′′′′′′′-CH_2), 1.75–1.6 (m, 16H, β-β′′′′′′′-CH_2), 1.45–1.2 (m, 144H, —CH_2—), 0.87 (t, 12H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.3, 152.2, 141.1, 140.7, 140.3, 140.0, 139.9, 139.89, 139.81, 139.6, 136.1, 135.0, 134.17, 134.15, 133.9, 133.8, 130.5, 130.43, 130.41, 130.3, 130.0, 129.7, 128.79, 128.7, 128.6, 128.5, 128.1, 128.0, 125.1, 123.5, 66.6, 31.9, 30.6, 30.5, 29.8, 29.7, 29.6, 29.57, 29.51, 29.4, 29.3, 29.2, 22.6, 14.0. $C_{136}H_{216}O_2S_8$ (2139.7); calcd: C 76.34, H 10.18; found: C 76.19, H 10.02. MALDI-TOF MS: ($C_{136}H_{216}O_2S_8$) found: 2140.1.

4,3′,3′′,3′′′,3′′′′,3′′′′′,3′′′′′′,3′′′′′′′- Octadodecyl - 5′′′′′′′ - iodo - 2,2′ : 5′,2′′ : 5′′,2′′′ : 5′′′,2′′′′ : 5′′′′,2′′′′′ : 5′′′′′,2′′′′′′ : 5′′′′′′,2′′′′′′′-octithiophene-5-carboxylic acid benzyl ester (9). Following the synthetic method for **3**, **8e** (0.11 g, 0.05 mmol) was reacted with mercuric caproate (0.02 g, 0.05 mmol) and iodine (0.01g, 0.05 mmol). After chromatographic work-up (silica gel, petroleum ether–dichloromethane [75 : 25]) the benzyl ester **9** was obtained as a dark red solid (0.11 g, 90%). Mp: 75 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43–7.34 (m, 5H, Ph—H), 7.06 (s, 1H, 4′′′′′′′-H), 6.98 (s, 1H, 4′′′′′′-H), 6.97 (s, 1H, 4′′′′′-H), 6.96 (m, 2H, 4′′′′,4′′′-H), 6.96 (s, 1H, 4′′-H), 6.95 (s, 1H, 4′-H), 6.87 (s, 1H, 3-H), 5.33 (s, 2H, PhCH_2O—), 2.96 (t, 2H, $^3J_{(H,H)} = 7.8$ Hz, α-CH_2), 2.71 (m, 14H, α′-α′′′′′′′-CH_2), 1.7–1.59 (m, 16H, β-β′′′′′′′-CH_2), 1.25 (m, 144H, —CH_2—), 0.87 (t, 24H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.3, 152.1, 141.4, 140.7, 140.4, 140.3, 140.0, 139.95, 139.91, 139.8, 136.6, 136.1, 135.0, 134.1, 133.8, 133.7, 133.4, 132.6, 131.0, 130.8, 130.6, 130.5, 130.3, 130.0, 129.7, 129.1, 128.8, 128.78, 128.7, 128.66, 128.63, 128.5, 128.1, 128.0, 125.1, 71.4, 66.3, 38.7, 31.9, 30.57, 30.53, 30.49, 30.42, 29.8, 29.7, 29.6, 29.57, 29.51, 29.4, 29.3, 28.9, 22.6, 14.0. $C_{136}H_{215}IO_2S_8$ (2265.6); calcd: C 72.10, H 9.57; found: C 72.30, H 9.65. MALDI-TOF MS: ($C_{136}H_{215}IO_2S_8$) found: 2265.4.

4,3′,3′′,3′′′,3′′′′,3′′′′′,3′′′′′′,3′′′′′′′,3′′′′′′′′,3′′′′′′′′′- Decadodecyl-2,2′ : 5′,2′′ : 5′′,2′′′ : 5′′′,2′′′′ : 5′′′′,2′′′′′ : 5′′′′′,2′′′′′′ : 5′′′′′′,2′′′′′′′ : 5′′′′′′′,2′′′′′′′′ : 5′′′′′′′′,2′′′′′′′′′-decithiophene-5-carboxylic acid benzyl ester (10e). Following the synthetic method for **4e**, **9** (0.01 g, 0.04 mmol), tetrakis(triphenylphosphino)palladium(0) (0.025 g, 0.002 mmol, 5 mol%), cesium fluoride (0.10 g, 0.60 mmol), and **2b** (0.10 g, 0.18 mmol) were reacted. After chromatographic work-up (silica gel, petroleum ether–dichloromethane [75 : 25]) the benzyl ester **8e** was obtained as a purple solid (0.06 g, 50%). Mp: 84 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46–7.32 (m, 5H, Ph—H), 7.16 (d, 1H, $^3J_{(5''''''''',4''''''''')} = 5.2$ Hz, 5′′′′′′′′′-H), 6.99 (s, 1H, 4′′′′′′′′-H), 6.98 (s, 1H, 4′′′′′′′-H), 6.97 (m, 4H, 4′′′′′′,4′′′′′,4′′′′,4′′′-H), 6.97 (s, 1H, 4′′-H), 6.96 (s, 1H, 4′-H), 6.94 (s, 1H, 3-H), 6.93 (d, 1H, $^3J_{(4''''''''',5''''''''')} = 5.2$ Hz, 4′′′′′′′′′-H), 5.35 (s, 2H, PhCH_2O—), 2.99 (t, 2H, $^3J_{(H,H)} = 7.8$ Hz, α-CH_2), 2.79 (m, 18H, α′-α′′′′′′′′′-CH_2), 1.75–1.6 (m, 20H, β-β′′′′′′′′′-CH_2), 1.45–1.2 (m, 180H,

—CH_2—), and 0.87 (t, 12H, CH_3). $C_{168}H_{268}O_2S_{10}$ (2640.6); calcd: C 76.42, H 10.23; found: C 76.34, H 10.18. MALDI-TOF MS: ($C_{168}H_{268}O_2S_{10}$) found: 2641.2.

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