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Aggregation Phenomena of Long α- and α,ω-Substituted Oligothiophenes – the Effect of Branched vs. Linear End-Groups

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Five homologous series of α- and α,ω-substituted oligothiophenes up to an undecamer with branched and linear alkyl chains, respectively, are presented. These series are compared with respect to self-organisation in solution and in solid state. UV/Vis absorption data for the long disubstituted branched oligothiophenes indicate the formation of aggregates in solution, expressed by a bathochromic shift of the absorption maximum and the appearance of shoulders. These changes in the spectra are obtained by variation of the solvent quality and/or the temperature. Contrary, the linear disubstituted oligothiophenes exhibit the formation of H-aggregates in solution indicated by a hypsochromic shift in the UV/Vis spectra. Results from fluorescence spectroscopy support the existence of aggregates. No aggregation phenomena were found for the monoalkylated branched oligothiophenes. In contrast, H-aggregation is found for the monoalkylated linear oligomers. This unexpected influence of the branching of the alkyl end groups on the aggregation behaviour in solution is discussed with the aid of mixed substituted oligothiophenes. Further information on shape and size of the aggregates present in solution is found by AFM measurements revealing that the linear substituents rather provoke the formation of anisotropic structures whereas the branched alkyl chains lead to spherical nanoobjects. Investigations of the thermal behaviour in solid state show that some of the oligomers exhibit thermotropic liquid crystalline phases.

Introduction

The synthetic accessibility and structural variability of oligothiophenes in combination with their semiconducting properties gives a high potential to this product class reflected by an increasing number of applications, for instance in the production of cheap solution-processed organic field-effect transistors.[1–3] A crucial prerequisite for high-performance devices is an efficient control over the ordering of the semiconducting oligomers in solid state. Miniaturisation of electronic circuits by a top-down approach requires expensive and time-consuming lithographic techniques. Thus, molecular self-assembling processes (bottom-up) of the electronic materials preferably from solution leading to ordered structures are highly desired. Such organisational phenomena are often supported by preorganisation in solution. Hence, the understanding and control of aggregation processes of oligothiophenes in solution are important steps towards the design of molecular electronics by self-organisation.

The introduction of charged alkylammonium substituents into a sexithiophene promotes the solubility of the oligomers in water and THF/water mixtures which are present as aggregates showing solvatochromic behaviour.[4] These charged oligomers can also be used as building blocks for layered structures with polyelectrolytes.[5,6] Yet polar but neutral ethylene glycol units in α-position in a quaterthiophene lead to vesicles in aqueous solution.[7] Extensive studies on similar oligothiophenes with chiral oligoethylene glycol-derived substituents prove the formation of chiral supramolecular structures in polar solvents.[8–14] Still polar alkylurea substituents in mono- and bithiophene cause the development of fibrous gels in solution[15] or highly ordered two-dimensional structures on graphite through the directionality of intermolecular hydrogen bonds.[16,17] The π–π interactions of the conjugated core and van-der-Waals interactions of dendritic fragments of oligothiophenes with hydrophobic alkyl substituents in β-position and poly(benzyl ether)dendrons as end groups up to a septdecamer cause the formation of supramolecular structures leading to thermochromism in dichloromethane solution.[18–20] Substituents in α-position consisting of fairly apolar polystyrene (degree of polymerisation: 30) in an undecithiophene provoke spherical micellar structures in toluene because of the incompatibility of the two blocks PS and oligothiophene.[21]

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Though there is a vast number of references on oligothiophenes with plain alkyl substituents in α- and ω-position, to the best of our knowledge no investigations are published on their aggregation behaviour in solution. In order to observe self-organisation in solution a strong incompatibility of the (alkyl) substituents and the oligothiophene moiety is requested, thus requiring a suffcient large number of thiophene units in the molecule. It has to be stated that long oligothiophenes exceeding six thiophene units are rarely known due to problems of their synthetic accessibility.

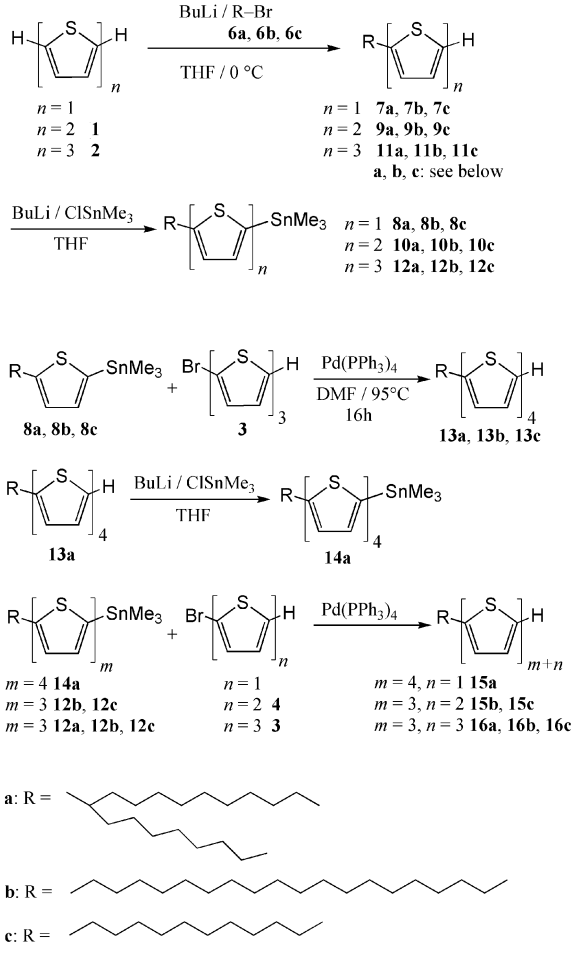
Here we report on the synthesis of long defined α-mono- and α,ω-disubstituted oligothiophenes with linear, branched and mixed alkyl substituents, respectively. The synthetic approach is based on a combination of metal-catalysed Stille-type coupling reactions and a soluble precursor route which we have published recently.[22] Thus, homologous series of oligothiophenes with linear C_{12}, C_{20} and branched C_{20} alkyl chains, respectively, were obtained, which allow us to investigate thoroughly the influence of (i) the conjugation length and (ii) the branching of the substituents on the self-organisation properties in solution. The aggregation behaviour of the oligothiophenes in solution is studied by UV/Vis and fluorescence spectroscopy. Atomic force microscopy (AFM) investigations underline the effect of molecular organisation on the mesoscale in solution. Temperature-dependent ordering phenomena of the different oligomers in solid state are investigated by differential scanning calorimetry (DSC) and polarising optical microscopy (POM) revealing the presence of liquid-crystalline phases of several of the oligothiophenes.

Results and Discussion

Synthesis

The straightforward synthesis based on (palladium-catalysed) coupling reactions and ring-closure steps allows the preparation of a large number of different oligothiophenes in homologues series from a few fundamental building blocks. Combining the different components of this kit for reaction in a statistical way would offer an even larger variety of synthetic approaches but it turned out that the appropriate synthetic pathway has to be adjusted for each compound individually to achieve optimum yields and purity of the final materials.

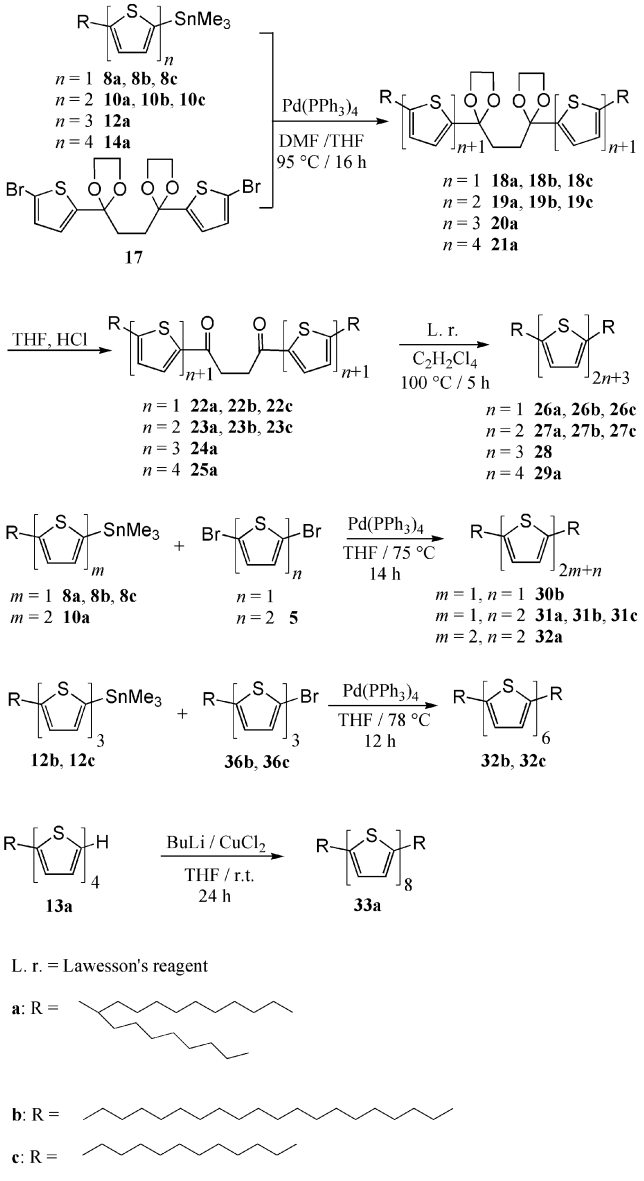
Thus, the α-monosubstituted oligomers up to the sexithiophene derivative **16** were obtained from thiophene, bithiophene (**1**), and terthiophene (**2**), respectively, by direct lithiation and alkylation (leading to the monoalkylated monomer **7**, dimer **9**, and trimer **11**) and subsequent Stille-type coupling of the corresponding stannylated derivatives **8** and **12** with the monobrominated thiophene, bithiophene **4**, and terthiophene **3**, respectively (Scheme 1). Interestingly, the synthesis of the pentamer **15a** with branched C_{20} alkyl chains by coupling the stannylated quaterthiophene **14a** with 2-bromothiophene is superior to the alternative approach by coupling the stannylated terthiophene **12a** with 5-bromobithiophene (**4**) with respect to yield and purity. Limitations in solubility prevent the corresponding synthetic approach for the oligomers with the linear substituents via the tetramers **14b** and **c**.



Scheme 1. Synthesis of the building blocks and the α-substituted oligomers.

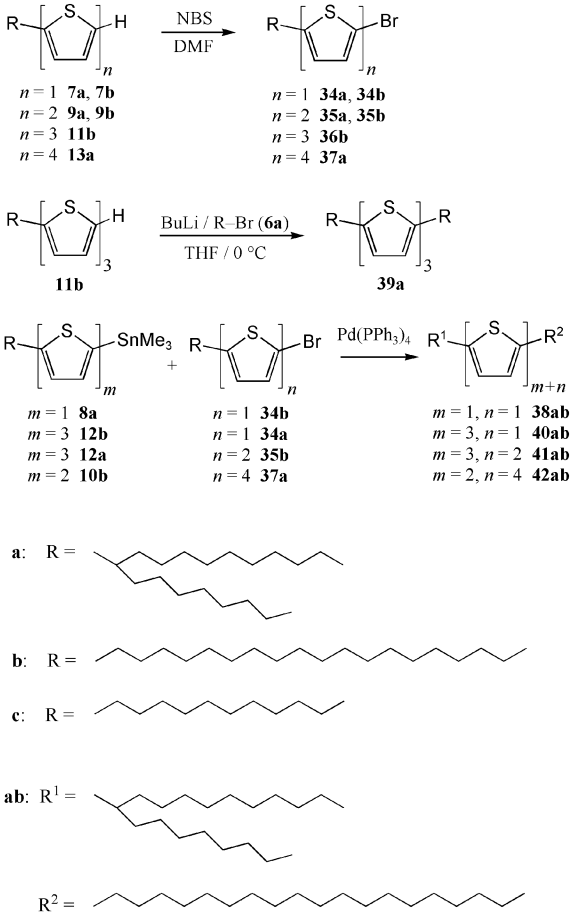
The α,ω-disubstituted oligothiophenes could be obtained with a few exceptions from double Stille-type coupling of the monoalkylated and stannylated thiophene **8**, bithiophene **10**, terthiophene **12**, and quaterthiophene **14a** with either 2,5-dibromothiophene and 5,5′-dibromobithiophene (**5**) or the protected diketone **17** (with subsequent deprotection and ring closure by Lawesson's reagent)[22] leading to the even- and odd-numbered oligomers **26**–**32**, respectively, up to the undecamer **29a** (Scheme 2). The short terthiophene derivative **30a** with branched C_{20} substitutents could be isolated as by-product of the direct alkylation of terthiophene (**2**) with R–Br **6a**. These results confirm findings in the literature that β-unsubstituted oligomers comprising more than six thiophene units are hardly accessible and can be only obtained in reasonable yield and purity via a soluble precursor strategy.[22] This strategy is restricted to the formation of odd numbered oligothiophenes. Hence the synthetic approach to the longer even-numbered sexithiophenes **32b** and **32c** and to the octithiophene **33a** with less solubilising linear substituents has to be adjusted. **32b** and

32c were prepared from mono cross-coupling **12b** and **12c** with the monoalkylated and monobrominated compounds **36b** and **36c**, respectively. The octamer **33a** could be synthesised by oxidative coupling of the lithiated monoalkylated tetramer **13a** with $CuCl_2$ (Scheme 2) according to a known procedure.[23]



Scheme 2. Synthesis of the α,ω-disubstituted oligomers.

To evaluate the influence of the branching of the substituents on optical and self-organisation properties of the oligomers (see below) compounds with mixed substituents were prepared. A similar strategic approach based on lithiation and metal-catalysed coupling reactions was reported recently.[24] In accordance with the synthetic strategy above the oligomers from the dimer **38ab** to the hexamer **42ab** were obtained by Stille-type coupling. The monoalkylated and monostannylated oligomers were treated with the corresponding monobrominated derivatives which were synthesised by bromination of the monoalkylated oligomers **7**, **9**, **11**, and **13** with NBS according to the literature[25] (Scheme 3). The terthiophene compound **39ab** could be accessed more efficiently by direct alkylation of the monoalkylated derivative **11b** with the bromoalkane **6a**. As already stated above and as shown in Scheme 3, the general strategy of coupling reactions has to be adjusted individually for each compound to reach optimum yield and purity. Here, only the optimised combinations of brominated and stannylated components, respectively, are presented.



Scheme 3. Synthesis of the mixed-substituted oligothiophenes.

Optical Properties

Electronic absorption and fluorescence spectra of freshly prepared solutions of the mono- and disubstituted oligomers were investigated in 1,1,2,2-tetrachloroethane (TCE) as it proved to be the best solvent for all, especially the longer oligomers. The oligothiophenes show expectedly an increase of the maximum of absorption and emission, respectively, with increasing chain length. The data correspond very well with the ones of the unsubstituted analogues[26] and there is hardly found any influence of the alkyl substituents on the electronic properties. Exemplarily, the data of the α,ω-disubstituted oligomers with branched C_{20} alkyl substituents is listed in Table 1. The results for the monosubstituted oligomers *n***T** and the compounds with the

Table 1. Absorption and emission spectroscopic data of the α,ω-disubstituted oligomers *n***T** with branched C_{20} and mixed alkyl substitutents, respectively.

Comp.	λ_{abs} [nm][a]	λ_{em} [nm][b]	Comp.	λ_{abs} [nm][a]	λ_{em} [nm][b]	*n***T**[c]	λ_{abs} [nm][a]	λ_{em} [nm][b]
30a	360	452	**39ab**	373	452	3**T**	355	407, 426
31a	390	500	**40ab**	409	500	4**T**	390	437, 478
26a	416	541	**41ab**	428	538	5**T**	416	482, 514
32a	436	570	**42ab**	448	564	6**T**	432	510
27a[d]	453	586				7**T**	440	522, 560
33a[d]	463	598						
28a[d]	472	606						
29a[d]	481	611						

[a] Maximum of the absorption, $c = 5 \times 10^{-5}$ M in $C_2H_2Cl_4$. [b] Maximum of the fluorescence emission, $c = 10^{-5}$ M in $C_2H_2Cl_4$. [c] **T** = thiophene unit. For comparison data of the unsubstituted analogues in $CHCl_3$ is given from reference.[26] [d] From reference.[22]

linear substituents are given in the Supporting Information.

We have reported recently, that solutions of the longer disubstituted oligomers **28a** and **29a** with the branched C_{20} chains show a significant change in colour which we attribute to the formation of aggregates.[22] The effect can be accelerated by lowering the temperature as shown exemplarily for nonathiophene **28a** (Figure 1) or alternatively by adding a poor solvent (e.g. methanol) to the solution. The corresponding shorter oligomers with eight and seven thiophene units **33a** and **27a** exhibit a similar absorption behaviour but only after addition of methanol to the solution. The change of colour is expressed in UV/Vis spectra in a bathochromic shift of the maximum and the development of shoulders on the low energy side. These changes are fully reversible by increasing the temperature or improving the solvent quality, respectively. The even shorter oligomers with one or two branched substituents do not show any hint for aggregation in TCE solution.

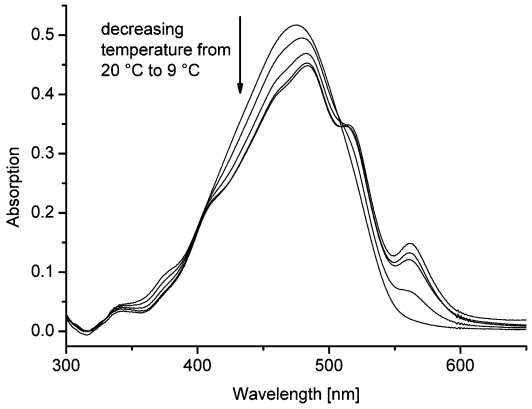


Figure 1. UV/Vis spectra of nonathiophene **28a** in TCE at different temperatures.[22]

Turning to the oligomers with linear substituents reveals that significant changes in the UV/Vis spectra in TCE are found as well. This applies for the oligothiophenes **16c** (monoalkylated), **32c** and **26c** (dialkylated) with C_{12} chains and for the compounds with C_{20} chains even starting from quaterthiophene **13b** (monoalkylated) and terthiophene **30b** (dialkylated). Surprisingly, here the UV/Vis spectra do not exhibit a bathochromic but a strong hypsochromic shift. As shown exemplarily in Figure 2 for the quinquethiophene **26b** with linear C_{20} chains the original peak at 412 nm is vanished almost completely and a new peak is formed at 348 nm after some time in TCE solution. Upon heating the solution the original spectra can be recovered (Figure 2) which denotes full reversibility of the phenomenon. The appearance of an isosbestic point at 369 nm in Figure 2 indicates the stoichiometric transformation between the aggregates and the molecular species at r.t. and at higher temperature, respectively.

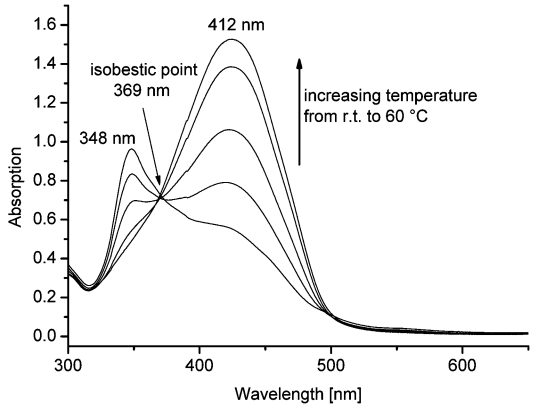


Figure 2. UV/Vis spectra of quinquethiophene **26b** in TCE at different temperatures.

Corresponding results are obtained for the other oligomers with linear alkyl chains as substitutents either by adding a bad solvent (e.g. methanol), lowering the temperature, or waiting some time, respectively.

These two opposing trends of absorption behaviour provoked by the geometric nature of the substituents arose the question how oligomers comprising both substituents the branched and the linear C_{20} alkyl chains behave with respect to optical properties. Table 2 exhibits the absorption and emission properties of freshly prepared solutions in TCE of the non-symmetrically substituted terthiophene **39ab**, quaterthiophene **40ab**, quinquethiophene **41ab**, and sexithiophene **42ab**.

It is conspicuous that the wavelength at the maximum of absorption is shifted between ca. 10 and 20 nm towards lower energy compared to the unsubstituted parent compounds (Table 1) though the pure substituents do not have significant influence on the optical properties (see also the

Table 2. Aggregation behaviour of the oligomers in solution (TCE) after addition of methanol (m), some time period (t), or acceleration of aggregation by lowering the temperature (T).

Comp.[b]	Monoalkylated[a]			Dialkylated[a]		
	C_{20}-lin	C_{12}-lin	C_{20}-br	C_{20}-lin	C_{12}-lin	C_{20}-br, C_{20}-lin
R–3**T**–R	–	–	–	m	–	–
R–4**T**–R	m	–	–	m	–	–
R–5**T**–R	m	–	–	t,m,T	–	m
R–6**T**–R	t,m,T	t,m,T	–	t,m,T	t,m,T	m
R–7**T**–R			m	t,m,T	t,m,T	
R–8**T**–R			m			
R–9**T**–R			t,m,T			
R–11**T**–R			t,m,T			

[a] C_{20}-br: branched C_{20} alkyl chain, C_{20}-lin: linear C_{20} alkyl chain, C_{12}-lin: linear C_{12} alkyl chain, m: aggregation by addition of methanol, t: aggregation after some period of time, T: accelerated aggregation by lowering the temperature. [b] **T** = thiophene unit, R = substituent.

Supporting Information). Such peculiar behaviour might be caused by a kind of preorganisation already in solution though no strong hint for aggregation by any of the above described means can be found for terthiophene **39ab** and quaterthiophene **40ab**. Only the higher homologues **41ab** and **42ab** show a strong change of the UV/Vis spectra in TCE after addition of methanol. Figure 3 shows the corresponding data of **41ab**.

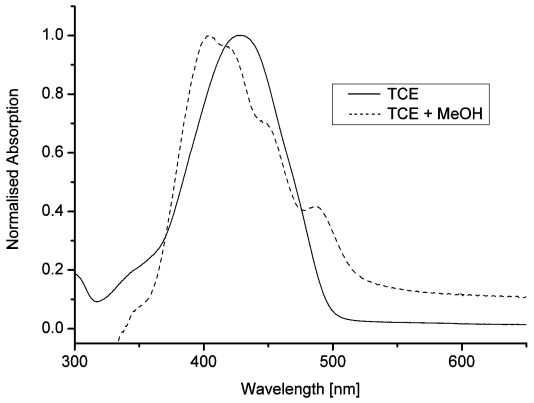


Figure 3. UV/Vis spectra of mixed quinquethiophene **41ab** in TCE at r.t. without and with addition of methanol.

Here, both changes the hypsochromic shift of the maximum and the appearance of shoulders at the low energy side can be found. Apparently, the branched and the linear substituents act independently on the optical properties.

Investigation of the emission behaviour of the oligothiophenes reveals that there is hardly any influence of time, temperature, or solvent quality on the shape and position of the corresponding peaks. It is only the intensity of fluorescence which is strongly reduced by the aforementioned factors as shown exemplarily in Figure 4 for quinquethiophene **26b** equipped with the linear C_{20} chains at different temperatures.

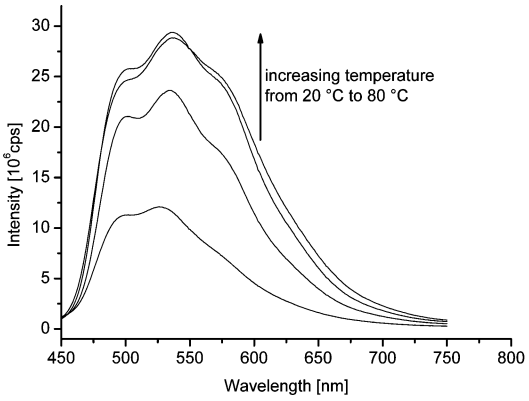


Figure 4. Temperature-dependent fluorescence spectra of quinquethiophene **26b** in TCE (λ_{ex} = 420 nm).

The effects of solvent quality, time, or temperature on the optical properties of the different oligomers are summarised in Table 2. It can be clearly recognised that a certain threshold length of the thiophene moiety is necessary for the above-mentioned effects. Additionally, the substituents play a substantial role for the threshold. In decreasing order of C_{20}-linear, C_{12}-linear, and C_{20}-branched effects on the optical behaviour are observed already for the terthiophene, the sexithiophene, or only the septithiophene derivatives, respectively.

Furthermore, the changes in UV/Vis and fluorescence spectra upon addition of methanol, lowering of temperature or simply after some time are fully in accordance with the presence of aggregates in solution.[22] The hypsochromic shifts of absorption maxima and the decreased fluorescence intensity for the oligomers with linear substituents points to the existence of H-aggregates. Correspondingly, the aggregates of the oligothiophenes with the branched substituents can be described as J-aggregates though for these an increase of fluorescence intensity is predicted. Consequently, the aggregated compounds with the mixed alkyl chains might be regarded as mixed H/J-aggregates.

In Figure 5 we have a closer look on the precise shifts of the absorption maxima for the aggregated structures as a function of the inverse number of thiophene units. It reveals that – except for the short oligomers **30b** and **31b** – (i) the absolute shifts ΔE are only determined by the substituents falling in narrow ranges regardless of the number of thiophene units [0.5–0.7 eV for linear substituents (upper oval), ca. –0.05 eV for the branched substituents (lower oval), and 0.2 eV for the mixed substituents (middle oval)] and (ii) the amounts of the shifts are much more pronounced for the compounds with linear than with branched substituents. These findings are consistent with the higher ability of the linear chains for packing than of the branched homologues. Interestingly, the blue shift of the maxima of the dialkylated oligomers with linear C_{20} chains seem to level off at ca. 0.55 eV whereas the monoalkylated homologues show still an increase of ΔE. Assuming that (i) the situation in the aggregates is a mirror image of the porperties in solid state (thin film) and that (ii) the amount of ΔE is a measure for

the intermolecular interaction (packing effects) and thus for electron transport (mobility) properties it is expected that (a) oligomers with linear substituents are much superior to the homologues with branched alkyl chains[27] and (b) improvement of electronic properties might level off at around five to seven thiophene units for electronic applications like OFETs.[28]

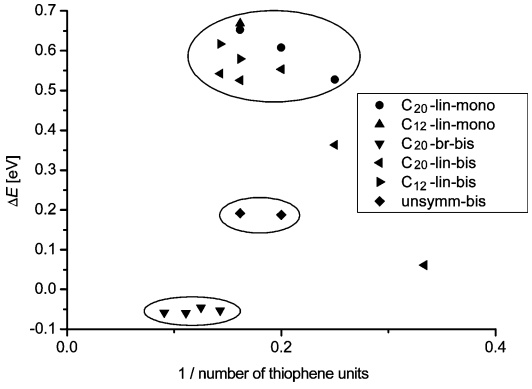


Figure 5. Shifts of the absorption maxima in the UV/Vis spectra of the aggregated species relative to the non-aggregated form in TCE as a function of the inverse number of thiophene units. The ovals comprise all oligomers with only linear, branched, and both linear and branched substituents, respectively, and clarify the close values of ΔE depending only on the geometry of the substituents.

Similar investigations on the influence of branched and linear substitutents attached to a perylene derivative on optical and self-organisation properties were reported recently.[29] Here, branched substituents led to a slight red-shift of the absorption bands in the UV/Vis spectra but no new bands appeared whereas the linear chains provoked mainly a new band at longer wavelength. For both compounds the authors attribute the observed effects to π–π interactions in aggregated state which are more expressed for the compounds with linear than with branched substituents.

AFM Investigations

The optical spectra gave insight to the local arrangement of the molecules in the aggregated state in solution. However, only from the UV/Vis spectroscopic data it cannot be assessed whether dimers or higher aggregates prevail.[30] Furthermore, it was found recently that oligothiophenes in thin films show a distinct influence of geometry of the substituents on film morphology. Oligomers with bulky, branched end groups exhibit a dependence of microstructure on core length, whereas the products with small, linear end groups do not.[31] We undertook AFM measurements to (i) further prove the existence of higher aggregates and (ii) to get information on shape and size of the aggregates depending on the geometry of the substituents. In order to reveal the true morphology of the aggregates the "solutions" were spin-cast onto mica and the substrates were investigated by AFM immediately after to capture the situation in solution at the best. The compounds with linear substituents **26b**, **32b** **27b** and **27c**, and nonathiophene **28a** with branched chains directly spin-cast from solution (c = 40 μg mL^{-1}) which presented the characteristics of aggregation in UV/Vis (see above) show objects with lateral dimensions in the range of hundred to several hundred nanometers (see Supporting Information, Figure S2). Interestingly, the compounds with linear substituents **26b**, **27c**, and **32b** offer highly anisomeric needle- and worm-like morphologies whereas oligomer **28a** with branched alkyl chains shows rather spherical nanoobjects (see Supporting Information, Figure S2). The same morphology is found for all aggregating compounds with branched alkyl substituents. From these findings it can be deduced that the geometry of the substituents determines the morphology of the aggregates regardless of the length of the core. In contrast, septithiophene **27b** with linear chains exhibits spherical aggregates, too, though cylindrical shapes are expected. Obviously, the morphology is strongly influenced by a subtle interplay between the flexible substituents in the periphery and the stiff core. Looking at the height of the aggregates reveals that they are rather flat with a thickness between 3 to 20 nm which falls in the range of molecular dimensions. This could be regarded as a hint for crystallisation processes during spin-casting. In order to exclude that the objects found by AFM on the "dry" substrate are only formed during the spin-casting process preheated solutions which do not indicate the presence of any aggregated species by UV/Vis were investigated as well. These show plate-like objects which were formed by crystallisation during the evaporation process. Hence, the observed structures directly from solution must be present already before sample preparation and can be regarded as the aggregates though we shall not exclude that they are somewhat altered by the drying process and specific interactions with the substrate though there is no strong influence of the highly polar mica on the ordering of the nonpolar oligomers expected. It has to be mentioned that septithiophene **27c** after heating shows still the worm-like morphology yet in a more compact and less ordered structure than deposited directly from solution at room temperature indicating that the self-assembly process of this compound is very fast.

Thermal Behaviour

Investigation of the thermal behaviour in solid state gives further information on ordering phenomena and extent of intermolecular interaction for the differently substituted oligomers. Looking at the temperature of the highest thermal transition (melting or clearing point, respectively, depending on the morphology, see below) in dependence of the number of thiophene units shows clear trends for all oligomers (Figure 6): (i) the longer the oligomers the higher the temperature; (ii) the oligomers with the branched substituents lead to the lowest transition temperatures, followed by the non-symmetrically substituted compounds and the oligomers with linear alkyl chains which show similar behaviour regardless of the length of the alkyl chains;

(iii) the short oligomers up to the dimer show lower melting points than the unsubstituted homologue but for $n > 2$ the unsubstituted compounds exceed the substituted ones; (iv) an approximately linear increase of temperature is found for all oligomers with ca. $n > 3$. Points (iii) and (iv) show that for the short oligomers the thermal transition is determined by the substituents but the longer the oligomers are the more the thiophene moiety dominates the transition temperature. From the linear portion of the curves in Figure 6 an incremental behaviour of the temperature increase can be deduced with ca. 50–60 K per thiophene unit regardless of the substituents. A more precise view at the data reveals that at least for some of the homologous series a slight decrease of the slope for the longer oligomers (ca. for $n > 6$) can be observed, which might lead to a leveling off of the transition temperatures at large numbers of thiophene units. From a polymer chemistry view point such behaviour is not surprising because of chain folding thus even longer thiophene chains do not cause a further increase of the melting point.

Assuming that the transition temperature reflects the intermolecular interactions and to some extent the ordering behaviour in solid state, it can be deduced that linear alkyl substituents are superior (higher degree of order) to the branched ones as already found from the optical properties (see above). More direct evidence for such structure/property relationship could be gained from transition enthalpies but these values do not present clear trends or dependencies from the number of thiophene units because of polymorphism and the existence of amorphous fractions of several oligomers.

A closer look at the thermal properties of the oligomers shows that some of them offer rich phase diagrams. As found in the literature[11,26,33–37] and described in our previous publication,[22] there are several oligothiophenes which show liquid crystalline properties. It is not too surprising to find some more compounds in the presented homologous series. Table 3 gives an overview on the thermal properties of those oligomers which offer multiple phase-transitions. From polarising optical microscopy (POM) the existence of LC phases can be deduced.

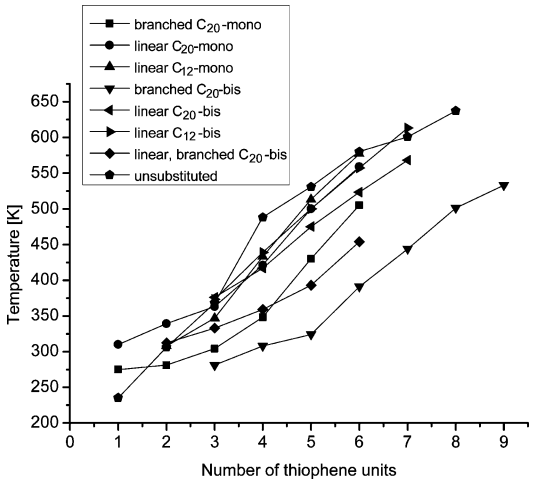


Figure 6. Melting or clearing points, respectively, of the α-mono-, α,ω-bis-, and the unsubstituted[32] oligomers.

It can be clearly seen in Table 3 that there is an onset of appearance of LC phases at the terthiophenes (disubstituted with linear chains), oligomers with less thiophene units simply melt as their thermal behaviour is determined by the substituents. The slightly less ordered monosubstituted oligomers with linear chains show liquid-crystalline properties for the quaterthiophenes. For the compounds with the branched substituents only from the quinquethiophene (monosubstituted) or even sexithiophene (disubstituted), respectively, LC phases can be observed. Such ordering behaviour is consistent with the aggregation properties of the oligomers found in solution (see above). Interestingly,

Table 3. Thermal behaviour of the oligomers (**T** = thiophene unit) with multiple phase transitions: transition temperatures [°C] at a peak maximum in the heating curve. Values in parentheses are the enthalpies of transition [kJ/mol]. Compounds with LC phases are printed in *italics*, for compounds with only one transition (melting) a minus sign is given.

R =	C_{12}-mono[a]	C_{20}-lin-mono[a]	C_{20}-br-mono[a]	C_{12}-bis[a]	C_{20}-lin-bis[a]	C_{20}-br-bis[a]	C_{20}-br-lin[a]
R–1**T**–R	–	–4 (3) / 13 (1) / 37 (48)	–	–	–	–	–
R–2**T**–R	–	–	–	–	–	–	39 (64) / 62 (4)
R–3**T**–R	–	89 / 91 (79)[b]	–	*59 (4) / 82 (46) / 100 (27)*	*92 / 99 / 102 (129)*[b]	–	–
R–4**T**–R	*130 (33) / 160 (27)*	*131 (58) / 148 (27)*	–	*107 (46) / 166 (39)*	*89 / 113 / 118 / 129 / 133 / 145 (122)*[b]	–	–
R–5**T**–R	83 (16) / 240 (37)	98 (40) / 227 (28)	*152 (24) / 161 (34)*[c]	*95 (16) / 227 (44)*	100 / 120 (64) / 199 (36)	–	*107 / 113 / 121 (68)*[b]
R–6**T**–R	300 / 304 (44)[b]	100 (43) / 286 (46)	–	118 (20) / 274 / 284 (47)[b]	130 / 134 (61) / 250 (43)	*74 (17) / 84 (5) / 110 (8) / 118 (33)*	–
R–7**T**–R				318 (45) / 340 (20)	99 (59) / 295 (62)	*10 (11) / 63 (5) / 166 / 171 (39)*[b][d]	
R–8**T**–R						*211 (30) / 228 (4)*	
R–9**T**–R						*241 (26) / 257 (6)*[d]	

[a] mono = monosubstituted; lin = linear; br = branched; bis = doubly substituted. [b] Peaks are not resolved, thus the total enthalpy of the preceding transitions is given. [c] Transition in the cooling curve because of low resolution of the heating curve. [d] From ref.[22]

the longer oligomers with at most one branched substituent present no LC phases despite multiple phase transitions (plain in Table 3).

Shearing experiments under the POM reveal the existence of undefined ordered (crystalline) phases but no liquid crystalline properties. These ordered phases might be mainly caused by reordering phenomena of the side chains. Apparently, when the number of thiophene units exceeds a certain value, the tendency of the core to crystallise overwhelmes the fluidising properties of the alkyl substituents. In contrast to the literature[33] where no LC phase was detected for the mono- and disubstituted quaterthiophenes **13c** and **31c** with C_{12} alkyl chains, we assign their mesophases to smectic LC phases despite of the high enthalpy of transition at the clearing point because under shear the compounds show in POM clearly a fluid-like behaviour.

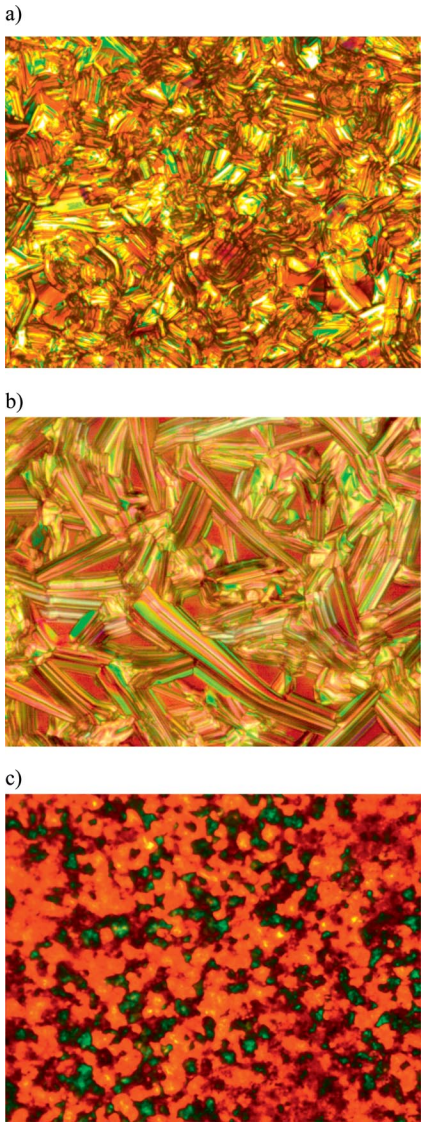


Figure 7. Selected POM images obtained by cooling from the isotropic phase of a) monosubstituted quinquethiophene **15a** at 157 °C, b) disubstituted quinquethiophene **26c** at 207 °C, and c) disubstituted sexithiophene **32a** at 107 °C.

The textures of the mesophases investigated by POM give some hint for the morphology of the LC phases (Figure 7).

From the various textures shown exemplarily in Figure 7 and in accordance with the literature[38] we assume that all the LC phases of the oligomers with linear side chains present smectic phases as supported by the relatively high enthalpy at the clearing point (Table 3) and the stiffness of the rod-like molecules. Only for the disubstituted sexithiophene **32a** (Figure 7, c), septithiophene **27a**,[22] and octithiophene **33a** with branched alkyl chains the typical "Schlieren" texture indicates the presence of nematic phases. As already stated in the recent publication,[22] for the even longer nonathiophene **28a** a smectic phase is suggested. The same applies for the monosubstituted (branched) quinquethiophene **15a** where presumably the thiophene core dominates the arrangement in the mesophase leading to the higher ordered smectic phase.

It shall be mentioned that besides the ring-closed oligomers some of the deprotected diketone derivatives form thermotropic LC phases as well (see Supporting Information).[22] To reveal the precise morphology of the different phases especially the unidentified ordered ones X-ray investigations are essential which are currently under way.

Conclusions

Various homologous series of oligothiophenes with linear and/or branched alkyl substituents in α- and α,ω-position have been synthesised and characterised with respect to self-organisation in solution and solid state. The analysis of the relationship between the structure and the optical properties of these oligomers by UV/Vis and fluorescence spectroscopy shows the different aggregation phenomena induced by the substituents in combination with the length of the thiophene core. The linear substituents cause a strong blue-shift of the main absorption whereas the branched residues lead to a slight red-shift and highly expressed bathochromic shoulders. Consequently, the mixed compounds with both a linear and a branched substituent overtake an intermediate role with a slight blue-shift and shoulders at the low energy side. These fundamental differences caused by the alkyl periphery is somewhat reflected by the shape of the aggregates in solution, i.e. the linear residues rather provoke anisotropic shapes (worm- and needle-like), whereas the branched alkyl chains with a higher steric demand prefer round shaped objects as proved by AFM. The pronounced influence of the molecular geometry on self-organisation properties is found in solid state as well. DSC measurements show that some of the oligomers present liquid crystalline phases depending on a well-balanced interplay between geometry of the alkyl chains and the length of the core. These self-organisation phenomena will play a crucial role in device formation for thin-film applications of this class of compounds where not only molecular properties are essential for optimal performance but especially structure formation and intermolecular interactions will have an extraordinary impact on charge carrier mobility.

Experimental Section

General: *n*-Butyllithium (*n*BuLi, 1.6 M in hexane, Merck), tetrakis-(triphenylphosphane)palladium(0) (Strem), thiophene, 2-bromothiophene, 2,5-dibromothiophene, 2-octyl-1-dodecanol, 1-bromoeicosane (**6b**), and 1-bromododecane (**6c**) (Sigma–Aldrich) were purchased and used without further purification. The solvents were purified and dried by common methods.[39] Bithiophene (**1**), α-terthiophene[40] (**2**), 5-bromo-2,2′:5′,2′′-terthiophene[25] (**3**), 5,5′-bromo-2,2′-bithiophene[25] (**4**), and 5,5′-dibromo-2,2′-bithiophene[25] (**5**) were prepared according to the literature. The preparation of 1-bromo-2-octyldodecane (**6a**), 2-(2-octyldodecyl)thiophene (**7a**), -bithiophene (**9a**), -terthiophene (**11a**), and -quaterthiophene (**13a**), of the corresponding stannylated derivatives **8a**, **10a**, **12a**, and **14a** and of the protected building block **17** was described recently.[22] In the same publication we have reported on the synthesis of the protected alkylated precursors **18a**, **19a**, **20a**, and **21a**, the consequential deprotected derivatives **22a**, **23a**, **24a**, and **25a** and the corresponding 2-octyldodecyl dialkylated quinquethiophene **26a**, septithiophene **27a**, nonathiophene **28a**, and undecathiophene **29a**, respectively.[22] The dodecyl monosubstituted thiophene **7c** and the corresponding disubstituted sexithiophene **32c** were prepared according to the literature.[25] The synthesis of the dodecyl monosubstituted bithiophene **9c**,[41] terthiophene **11c**,[41] quaterthiophene **13c**,[25] and the corresponding disubstituted terthiophene **30c**[25] and quaterthiophene **31c**[42] are already described in the literature, but we prepared them by a slightly different method, thus keeping the experimental description in the Supporting Information. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature – if not otherwise mentioned – on a Bruker AM 400 and AM 500, respectively. All NMR spectra were run in $CDCl_3$ or $C_2D_2Cl_4$, respectively, with the solvent residual peak as internal reference [$CDCl_3$: δ = 7.24 (^{1}H) and 77.0 (^{13}C), $C_2D_2Cl_4$: δ = 6.00 (^{1}H) and 74.0 (^{13}C) ppm]. MALDI-TOF spectra were recorded on a Bruker Daltonic Reflex III. Differential scanning calorimetry (DSC) was performed on a Perkin–Elmer DSC 7. The Polarising optical microscopy (POM) images were taken on a Zeiss Axioskop equipped with a Mettler FP 90 hot stage. The IR spectra were recorded on a Bruker IFS 113v. The UV/Vis spectra were taken with a Perkin–Elmer Lambda 16 and the fluorescence spectra on a Horiba Fluoromax 3. Elemental composition was determined on an Elementar Vario EL and a Perkin–Elmer Analyzer 2400 CHN, respectively. For the AFM measurements samples were prepared by spincoating (500 rpm) a solution (preheated or at room temperature some time after dissolution, see main text) of the oligomer in $C_2H_2Cl_4$ (c = 36–300 μg mL^{-1}) on mica substrates. AFM imaging was performed in tapping mode with a NanoScope IIIa SPM (Digital Instruments, Santa Barbara, CA) with single side Al-coated Si-cantilever (force constant = 1.2–2.5 N/m, f_0 = 61.5–72.8 kHz).

2-Eicosylthiophene (7b): To a solution of thiophene (20.0 mL, 226 mmol) in THF (20.0 mL) *n*BuLi (25.0 mL, 40.0 mmol) is added at 0 °C dropwise. After stirring the solution for 30 min, 1-bromoeicosane (**6b**) (9.75 g, 27.0 mmol) is added. The mixture is stirred for 48 h at 60 °C, cooled to room temperature, poured into water and extracted with dichloromethane. After combining the organic fractions and drying over $MgSO_4$ and removal of the solvent, the product is purified by column chromatography (SiO_2/hexane) to give a white solid (6.72 g, 68%). R_f = 0.47 (hexane); m.p. 36 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.08 [dd, J(H,H) = 1.2 and 5.0 Hz, 1 H, 5-H], 6.90 [dd, J(H,H) = 3.2 and 5.0 Hz, 1 H, 4-H], 6.75 [dd, J(H,H) = 1.2 and 3.6 Hz, 1 H, 3-H], 2.79 [t, ^3J(H,H) = 7.7 Hz, 2 H, 2 H, CH_2, thiophene], 1.68 (m, 2 H, CH_2-CH_2, thiophene), 1.32 (m, 34 H, CH_2, alkyl), 0.87 [t, ^3J(H,H) = 6.9 Hz, 3 H, CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 145.8, 126.6, 123.8, 122.6, 31.9, 31.8, 29.9, 29.7, 29.67, 29.66, 29.64, 29.5, 29.3, 29.1, 22.6, 14.1 ppm. MS (100 eV, CI): m/z (%) = 363 (100) [M$^+$]. $C_{24}H_{44}S_1$ (364.3): calcd. C 79.05, H 12.16; found C 78.86, H 12.07.

2-Dodecylthiophene (7c): To a solution of thiophene (64.0 mL, 0.80 mol) in THF (50.0 mL) *n*BuLi (56.0 mL, 90.0 mmol) is added dropwise in 5 h at 0 °C. After additional stirring of 30 min 1-bromododecane (**6c**) (19.0 mL, 79.0 mmol) is added. The mixture is stirred for 4 d under reflux, cooled to room temperature, poured onto water and extracted with dichloromethane. After the organic phases are combined and dried with $MgSO_4$, the solvent is removed. The product is purified by column chromatography (SiO_2/hexane) to give a colourless liquid (16.6 g, 83%). R_f = 0.43 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.12 [dd, ^3J(H,H) = 5.0, ^4J(H,H) = 1.0 Hz, 1 H, 5-H], 6.94 [dd, ^3J(H,H) = 5.1, ^4J(H,H) = 3.5 Hz, 1 H, 4-H], 6.81 [dd, ^3J(H,H) = 3.6, ^4J(H,H) = 1.0 Hz, 1 H, 3-H], 2.86 [t, ^3J(H,H) = 7.6 Hz, 2 H, α-CH_2], 1.75–1.69 [quint, ^3J(H,H) = 7.6 Hz, 2 H, β-CH_2], 1.38–1.32 (m, 18 H, alkyl-CH_2), 0.94 [t, ^3J(H,H) = 6.6 Hz, 3 H, CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 145.9, 126.6, 123.9, 122.7, 32.0, 31.9, 30.0, 29.77, 29.74, 29.6, 29.47, 29.45, 29.2, 22.8, 14.2 ppm. MS (100 eV, CI): m/z (%) = 253 (100) [M$^+$].

2-Trimethylstannyl-5-eicosylthiophene (8b): Compound **7b** (743 mg, 2.03 mmol) is dissolved in THF(12.0 mL), lithiated slowly with *n*BuLi (1.80 mL, 1.6 M, 2.90 mmol) and stirred for 30 min at room temperature. Then trimethyltin chloride (577 mg, 2.90 mmol) is added. The solution is stirred overnight and the solvent evaporated to give crude compound **8b** (980 mg, 92%) as a white-brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.99 [d, ^3J(H,H) = 3.0 Hz, 1 H, 3-H], 6.88 [d, ^3J(H,H) = 3.0 Hz, 1 H, 4-H], 2.85 [t, ^3J(H,H) = 7.5 Hz, 2 H, CH_2, thiophene], 1.67 (m, 2 H, CH_2-CH_2, thiophene), 1.32 (m, 34 H, CH_2, alkyl), 0.88 [t, ^3J(H,H) = 6.9 Hz, 3 H, CH_3], 0.42 [s, 9 H, Sn-$(CH_3)_3$] ppm. The solid is used directly for the coupling step without further purification.

2-Trimethylstannyl-5-dodecylthiophene (8c): To a solution of compound **7c** (1.0 g, 4.0 mmol) in THF (10 mL) *n*BuLi (3.8 mL, 6.0 mmol) is added and stirred for 30 min at room temperature. Then a solution of trimethyltin chloride (1.2 g, 6.0 mmol) in 5 mL of THF is added. After 3 h of stirring the solvent is evaporated to give crude compound **8c** in quantitative yield, which is used directly for the coupling step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.99 [d, ^3J(H,H) = 3.8 Hz, 1 H, 4-H], 6.87 [d, ^3J(H,H) = 3.8 Hz, 1 H, 4-H], 2.82 [t, ^3J(H,H) = 7.7 Hz, 2 H, α-CH_2], 1.66 [quint, ^3J(H,H) = 7.3 Hz, 2 H, β-CH_2], 1.24 (br. s, 18 H, alkyl-CH_2), 0.86 [t, ^3J(H,H) = 6.8 Hz, 3 H, CH_3], 0.32 [s, 9 H, Sn$(CH_3)_3$] ppm.

5-Eicosyl-2,2′-bithiophene (9b): To a solution of bithiophene (**1**) (4.5 g, 27 mmol) in 40 mL of THF *n*BuLi (8.4 mL, 13.5 mmol) is added at 0 °C over a period of 1 h. After stirring the solution for 30 min, 1-bromoeicosane (**6b**) (4.3 g, 12 mmol) is added. The mixture is stirred overnight at 63 °C, cooled, poured into water, and extracted 3 times with chloroform. After combining the chloroform fractions and drying over $MgSO_4$ and removal of the solvent, the product is washed with acetone to remove bithiophene surpluses. Then the product is purified by column chromatography (SiO_2/hexane/CH_2Cl_2, 5:3) to give **9b** (2.4 g, 45%) as a white-green solid. R_f = 0.71 (hexane/CH_2Cl_2, 5:3); m.p. 65 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.14 [dd, J(H,H) = 1.0 and 5.0 Hz, 1 H, 5′-H], 7.07 [dd, J(H,H) = 1.2 and 3.5 Hz, 1 H, 3′-H], 6.97 [dd, J(H,H) = 3.5 and 5.0 Hz, 1 H, 4′-H], 6.96 [d, ^3J(H,H) = 3.5 Hz, 1 H, 3-H], 6.64 [d, ^3J(H,H) = 3.5 Hz, 1 H, 4-H], 2.79 [t, ^3J(H,H) = 7.7 Hz, 2

H, CH_2, thiophene], 1.67 (m, 2 H, CH_2-CH_2, thiophene), 1.32 (m, 34 H, CH_2, alkyl), 0.87 [t, ^3J(H,H) = 6.9 Hz, 3 H, CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 145.3, 138.0, 134.7, 127.6, 124.6, 123.6, 123.3, 122.9, 31.9, 31.6, 30.1, 29.67, 29.65, 29.5, 29.3, 29.0, 22.7, 14.1 ppm. UV/Vis ($C_2D_2Cl_4$): λ_{max} (ε) = 317 nm (6500 $mol^{-1}\,dm^3\,cm^{-1}$). MS (100 eV, CI): *m*/*z* (%) = 446 (100) [M^+]. $C_{28}H_{46}S_2$ (446.3): calcd. C 75.27, H 10.38; found C 75.12, H 10.40.

5-Dodecyl-2,2′-bithiophene (9c): To a solution of bithiophene (**1**) (3.5 g, 21 mmol) in 50 mL of THF *n*BuLi (9.4 mL, 15 mmol) is added over a period of 4 h at 0 °C. After stirring the solution for additional 30 min 1-bromododecane (**6c**) is added. The mixture is then stirred under reflux for 3 d, cooled to room temperature, poured onto water, and extracted three times with dichloromethane. After combining and drying the organic phases over $MgSO_4$ the solvent is evaporated. The crude product is first washed with methanol to remove bithiophene (**1**) and then purified by column chromatography (SiO_2/hexane) to give **9c** (1.6 g, 32%) as a white solid. R_f = 0.30 (hexane); m.p. 35 °C, ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.14 [dd, ^3J(H,H) = 5.2, ^4J(H,H) = 1.0 Hz, 1 H, 5′-H], 7.07 [dd, ^3J(H,H) = 3.6, ^4J(H,H) = 1.0 Hz, 1 H, 3′-H], 6.98–6.95 (m, 2 H, 4′-H, 3-H), 6.65 [d, ^3J(H,H) = 3.6 Hz, 1 H, 4-H], 2.76 [t, ^3J(H,H) = 7.6 Hz, 2 H, α-CH_2], 1.66 [quint, ^3J(H,H) = 7.6 Hz, 2 H, β-CH_2], 1.24 (br. s, 18 H, alkyl-CH_2), 0.86 [t, ^3J(H,H) = 6.8 Hz] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 145.4, 138.0, 134.7, 127.6, 124.7, 123.7, 123.4, 123.0, 31.9, 31.6, 30.2, 29.7, 29.6, 29.5, 29.4, 29.1, 22.7, 14.1 ppm. UV/Vis ($C_2D_2Cl_4$): λ_{max} = 315 nm. MS (100 eV, CI): *m*/*z* (%) = 335 (100) [M^+]. $C_{20}H_{30}S_2$ (334.6): calcd. C 71.80, H 9.04; found C 71.62, H 9.22.

5-Trimethylstannyl-5′-eicosyl-2,2′-bithiophene (10b): Compound **9b** (500 mg, 1.22 mmol) is dissolved in THF, lithiated slowly with *n*BuLi (1.1 mL, 1.6 M, 1.82 mmol) and stirred for 30 min at room temperature. Then trimethyltin chloride dissolved in 2 mL of THF (358 mg, 1.82 mmol) is added to the mixture. The solution is stirred overnight and the solvent evaporated to give crude **10b** (380 mg, 93%) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.21 [d, ^3J(H,H) = 3.2 Hz, 1 H, 4-H], 7.07 [d, ^3J(H,H) = 3.2 Hz, 1 H, 3-H], 6.98 [d, ^3J(H,H) = 3.5 Hz, 1 H, 3′-H], 6.66 [d, ^3J(H,H) = 3.5 Hz, 1 H, 4′-H], 2.85 [t, ^3J(H,H) = 7.5 Hz, 2 H, CH_2, thiophene], 1.67 (m, 2 H, CH_2-CH_2, thiophene), 1.32 (3 m, 34 H, CH_2, alkyl), 0.88 [t, ^3J(H,H) = 6.9 Hz, 3 H, CH_3], 0.40 [s, 9 H, Sn-$(CH_3)_3$] ppm. The brown solid is used without further purification.

5-Trimethylstannyl-5′-dodecyl-2,2′-bithiophene (10c): To a solution of compound **9c** (1.0 g, 3.0 mmol) in THF (20 mL) *n*BuLi (2.6 mL, 4.2 mmol) was added and stirred at room temperature for 30 min. Then a solution of trimethyltin chloride (837 mg, 4.2 mmol) in THF (5 mL) was added. After the mixture was stirred for 1 h, the solvent was evaporated to give the crude product **10c** as a brown solid in quantitative yield which is directly used in the coupling step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.18 [d, ^3J(H,H) = 3.3 Hz, 1 H, 3-H], 7.04 [d, ^3J(H,H) = 3.3 Hz, 1 H, 4-H], 6.94 [d, ^3J(H,H) = 3.5 Hz, 1 H, 3′-H], 6.64 [d, ^3J(H,H) = 3.6 Hz, 1 H, 4′-H] 2.76 [t, ^3J(H,H) = 7.6 Hz, 2 H, α-CH_2], 1.65 [quint, ^3J(H,H) = 7.5 Hz, 2 H, β-CH_2], 0.86 [t, ^3J(H,H) = 6.8 Hz, 3 H, CH_3], 0.35 [s, 9 H, Sn$(CH_3)_3$] ppm.

5-Eicosyl-2,2′:5′,2′′-terthiophene (11b): To a solution of terthiophene (**3**) (3.2 g, 12.9 mmol) in THF (40 mL) *n*BuLi (7.6 mL, 1.6 M, 12.2 mmol) is added dropwise. After stirring the solution for 2 h, 1-bromoeicosane (**6b**), (2.2 g, 6.1 mmol) in THF (20 mL) is added to the monolithiated terthiophene. The mixture is stirred for 16 h at 55 °C, cooled, poured into water, and extracted with chloroform. After combining the chloroform fractions, drying over $MgSO_4$, and removal of the solvent, the product is recrystallised from acetone. The product is purified by column chromatography (SiO_2/hexane) to give **11b** (1.6 g, 50%) as a yellow microcrystalline powder. R_f = 0.24 (hexane); m.p. 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.18 [dd, J(H,H) = 1.1 and 5.1 Hz, 1 H, 5′′-H], 7.13 [dd, J(H,H) = 1.1 and 3.6 Hz, 1 H, 3′′-H], 7.03 [d, ^3J(H,H) = 3.8 Hz, 1 H, 3-H or 3′-H or 4′-H], 6.99 [dd, J(H,H) = 3.8 and 5.1 Hz, 1 H, 4′′-H], 6.98 [d, ^3J(H,H) = 3.8 Hz, 1 H, 3-H or 3′-H or 4′-H], 6.96 [d, ^3J(H,H) = 3.5 Hz, 1 H, 3-H or 3′-H or 4′-H], 6.65 [d, ^3J(H,H) = 3.5 Hz, 1 H, 4-H], 2.77 [t, ^3J(H,H) = 7.4 Hz, 2 H, CH_2, thiophene], 1.68 (m, 2 H, CH_2-CH_2, thiophene), 1.32 (m, 34 H, CH_2, alkyl), 0.87 [t, ^3J(H,H) = 6.9 Hz, 3 H, CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 145.9, 137.2, 136.8, 135.4, 134.3, 128.1, 125.0, 124.6, 124.5, 123.7, 123.68, 123.6, 32.0, 31.6, 30.2, 29.84, 29.80, 29.7, 29.6, 29.4, 29.2, 22.8, 14.3 ppm. UV/Vis ($C_2D_2Cl_4$): λ_{max} (ε) = 354 nm (15300 $mol^{-1}\,dm^3\,cm^{-1}$). MS (100 eV, CI): *m*/*z* (%) = 529 (100) [M^+]. $C_{32}H_{48}S_3$ (528.3): calcd. C 72.67, H 9.15; found C 72.36, H 9.06.

5-Dodecyl-2,2′:5′2′′-terthiophene (11c): To a solution of terthiophene (**3**) (5.0 g, 20.1 mmol) in THF (60 mL) *n*BuLi (9.3 mL, 15.0 mmol) is added over a period of 3 h at 0 °C. After stirring the solution for additional 30 min 1-bromododecane (**6c**) is added. The mixture is then stirred under reflux for 2 d, cooled to room temperature, poured onto water, and extracted with dichloromethane. After combining the organic fractions and drying over $MgSO_4$ the solvent is evaporated. The crude product is then purified by column chromatography (SiO_2/hexane) to give **11c** (1.6 g, 24%) as a yellow solid. R_f = 0.16 (hexane); m.p. 74 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.18 [dd, ^3J(H,H) = 5.0, ^4J(H,H) = 1.0 Hz, 1 H, 5′′-H], 7.13 [dd, ^3J(H,H) = 3.7, ^4J(H,H) = 1.0 Hz, 1 H, 3′′-H], 7.04 [d, ^3J(H,H) = 3.8 Hz, 1 H, 4′-H], 6.99 [dd, ^3J(H,H) = 5.2, ^4J(H,H) = 3.7 Hz, 1 H, 4′′-H], 6.97 [d, ^3J(H,H) = 3.8 Hz, 1 H, 3′-H], 6.96 [d, ^3J(H,H) = 3.5 Hz, 1 H, 3-H], 6.66 [d, ^3J(H,H) = 3.6 Hz, 1 H, 4-H], 2.77 [t, ^3J(H,H) = 7.7 Hz, 2 H, α-CH_2], 1.66 [quint, ^3J(H,H) = 7.5 Hz, 2 H, β-CH_2], 1.24 (br. s, 18 H, alkyl-CH_2), 0.86 [t, ^3J(H,H) = 6.8 Hz, 3 H, CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 145.6, 137.2, 136.9, 135.5, 134.5, 127.8, 124.8, 124.3, 123.5, 123.4, 31.9, 31.6, 30.2, 29.7, 29.6, 29.5, 29.4, 29.1, 22.7, 14.1 ppm. UV/Vis ($C_2D_2Cl_4$): λ_{max} = 362 nm. MS (100 eV, CI): *m*/*z* (%) = 417 (100) [M^+]. $C_{24}H_{32}S_3$ (416.7): calcd. C 69.18, H 7.74; found C 68.95, H 7.87.

5-Trimethylstannyl-5′′-eicosyl-2,2′:5′,2′′-terthiophene (12b): The alkylated ter-thiophene **11b** (310 mg, 0.62 mmol) is dissolved in THF(10 mL), lithiated slowly with *n*BuLi (0.75 mL, 1.6 M, 1.24 mmol) and stirred for 30 min at room temperature. Then trimethyltin chloride (239 mg, 1.24 mmol) is added to the dark mixture. The solution is stirred overnight and the solvent evaporated to give crude **12b** (380 mg, 93%) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.28 [d, ^3J(H,H) = 3.5 Hz, 1 H, 3-H], 7.11 [d, ^3J(H,H) = 3.5 Hz, 1 H, 2-H], 7.06 [d, ^3J(H,H) = 3.7 Hz, 1 H, 3′-H or 4′-H], 7.01 [d, ^3J(H,H) = 3.7 Hz, 1 H, 3′-H or 4′-H], 6.99 [d, ^3J(H,H) = 3.5 Hz, 1 H, 3′′-H], 6.68 [d, ^3J(H,H) = 3.5 Hz, 1 H, 4′′-H], 2.74 [t, ^3J(H,H) = 7.5 Hz, 2 H, CH_2, thiophene], 1.68 (m, 2 H, CH_2-CH_2, thiophene), 1.33 (m, 34 H, CH_2, alkyl), 0.88 [t, ^3J(H,H) = 6.9 Hz, 3 H, CH_3], 0.40 [s, 9 H, Sn-$(CH_3)_3$] ppm. The crude oil is used directly for the coupling step without further purification.

5-Trimethylstannyl-5′′-dodecyl-2,2′:5′,2′′-terthiophene (12c): To a solution of compound **11c** (208 mg, 0.5 mmol) in THF (12 mL) *n*BuLi (0.47 mL, 0.8 mmol) was added and stirred at room temperature for 30 min. Then a solution of trimethyltin chloride (150 mg, 0.8 mmol) in THF (3 mL) was added. After stirring the solution for 1 h the solvent was evaporated to give crude product

12c as a brown solid in quantitative yield which is directly used in the coupling step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.24 [d, ^3J(H,H) = 3.5 Hz, 1 H, 3-H], 7.06 [d, ^3J(H,H) = 3.5 Hz, 1 H, 4-H], 7.02 [d, ^3J(H,H) = 3.8 Hz, 1 H, 3′-H or 4′-H], 6.97 [d, ^3J(H,H) = 3.8 Hz, 1 H, 3′-H or 4′-H], 6.95 [d, ^3J(H,H) = 3.6 Hz, 1 H, 3′′-H], 6.65 [d, ^3J(H,H) = 3.6 Hz, 1 H, 4′′-H], 2.77 [t, ^3J(H,H) = 7.6 Hz, 2 H, α-CH_2], 1.83 [quint, ^3J(H,H) = 7.2 Hz, 2 H, β-CH_2], 1.25 (br. s, 18 H, alkyl-CH_2), 0.86 [t, ^3J(H,H) = 6.8 Hz, 3 H, CH_3], 0.37 [s, 9 H, Sn(CH_3)$_3$] ppm.

5-Eicosyl-2,2′:5′,2′′:5′′,2′′′-quaterthiophene (13b): Compound **7b** (980 mg, 1.86 mmol) and monobrominated terthiophene **3** (608 mg, 1.86 mmol) are dissolved in 20 mL of dry DMF. Pd(PPh_3)$_4$ (54 mg, 0.04 mmol) is added and the mixture is stirred for 16 h at 93 °C. After cooling to room temperature the orange-brown precipitate is separated by centrifugation and purified by column chromatography (SiO_2/hexane/$CHCl_3$, 5:3) to give **13b** (635 mg, 56%) as a yellow coarse solid. R_f = 0.62 (hexane/$CHCl_3$, 5:3); m.p. 151 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): δ = 7.28 [dd, J(H,H) = 1.0 and 5.1 Hz, 1 H, 5′′′-H], 7.23 [dd, J(H,H) = 1.2 and 3.6 Hz, 1 H, 3′′′-H], 7.04–7.15 (m, 6 H, 3-H, 3′-H, 4′-H, 3′′-H, 4′′-H and 4′′′-H), 6.67 [d, ^3J(H,H) = 3.4 Hz, 1 H, 4-H], 2.85 [t, ^3J(H,H) = 7.4 Hz, 2 H, CH_2, thiophene], 1.68 (m, 2 H, CH_2-CH_2, thiophene), 1.32 (m, 34 H, CH_2, alkyl), 0.95 [t, ^3J(H,H) = 6.9 Hz, 3 H, CH_3] ppm. ^{13}C NMR (100 MHz; $C_2D_2Cl_4$,100 °C): δ = 146.1, 137.4, 137.2, 136.4, 136.3, 135.3, 134.4, 127.9, 124.9, 124.7, 124.6, 124.4, 124.3, 124.0, 123.8, 123.7, 31.9, 31.4, 30.2, 29.7, 29.6, 29.5, 29.33, 29.30, 29.1, 22.6, 14.0 ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 392 nm (22300 mol^{-1} dm^3 cm^{-1}). MS (MALDI-TOF): m/z = 610 [M$^+$]. $C_{36}H_{50}S_4$ (610.3): calcd. C 70.76, H 8.25; found C 70.42, H 8.31.

5-Dodecyl-2,2′:5′,2′′:5′′,2′′′-quaterthiophene (13c): A solution of **7c** (830 mg, 2.0 mmol), **3** (654 mg, 2.0 mmol) and Pd(PPh_3)$_4$ (58 mg, 50 μmol) in THF (50 mL) is stirred under reflux for 15 h. After cooling to room temperature the orange precipitate is separated by filtration. By addition of acetone (10 mL) to the filtrate a second fraction is precipitated. The combined solids are washed with hot acetone. After filtration the solid is dissolved in THF, a spatula of charcoal is added. The mixture is heated up, filtered and the solvent is evaporated to give **13c** (810 mg, 83%) as a yellow solid. m.p. 160 °C. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 100 °C): δ = 7.27 [dd, ^3J(H,H) = 5.1, ^4J(H,H) = 1.1 Hz, 1 H, 5′′′-H], 7.20 [dd, ^3J(H,H) = 3.7, ^4J(H,H) = 1.1 Hz, 1 H, 3′′′-H], 7.11 [d, ^3J(H,H) = 3.8 Hz, 1 H, 3′-H or 4′-H], 7.09–7.08 (m, 2 H, 3′′-H, 4′′-H), 7.06 [dd, ^3J(H,H) = 3.8, ^3J(H,H) = 5.1 Hz, 1 H, 4′′′-H], 7.03 [d, ^3J(H,H) = 3.8 Hz, 1 H, 3′-H or 4′-H], 7.02 [d, J(H,H) = 3.6 Hz, 1 H, 3-H], 6.72 [d, ^3J(H,H) = 3.6 Hz, 1 H, 4 H], 2.80 [t, ^3J(H,H) = 7.6 Hz, 2 H, α-CH_2], 1.69 [quint, ^3J(H,H) = 7.5 Hz, 2 H, β-CH_2], 1.28 (br. s, 18 H, alkyl-CH_2), 0.89 [t, ^3J(H,H) = 6.8 Hz, 3 H, CH_3] ppm. ^{13}C NMR (100 MHz; $C_2D_2Cl_4$,100 °C): δ = 146.1, 137.4, 137.2, 136.5, 136.4, 135.4, 134.4, 128.0, 124.9, 124.7, 124.6, 124.5, 124.3, 124.0, 123.82, 123.80, 31.9, 31.5, 30.3, 29.7, 29.6, 29.5, 29.33, 29.29, 29.1, 22.6, 14.0 ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} = 390 nm. MS (MALDI-TOF): m/z = 499 [M$^+$]. $C_{28}H_{34}S_4$ (498.8): calcd. C 67.42, H 6.87; found C 67.37, H 6.88.

5-(2-Octyldodecyl)-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′-quinquethiophene (15a): Compound **14** (420 mg, 0.54 mmol) and 2-bromothiophene (90 mg, 0.54 mmol) are dissolved in 25 mL of dry DMF. Pd(PPh_3)$_4$ (20 mg, 0.017 mmol) is added and the mixture is stirred for 10 h at 93 °C. After cooling to room temperature the orange-brown precipitate is separated by centrifugation and purified by column chromatography (SiO_2/hexane/dichloromethane, 5:3) to give **15** (126 mg, 34%) as a red-brown solid. R_f = 0.63 (hexane/dichloromethane, 5:3); m.p. 157 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.27 [dd, J(H,H) = 1.1 and 5.1 Hz, 1 H, 5′′′′-H], 7.21 [dd, J(H,H) = 1.1 and 3.5 Hz, 1 H, 3′′′′-H], 7.14–7.04 (m, 8 H, 3-H, 3′-H, 4′-H, 3′′-H, 4′′-H, 3′′′-H, 4′′′-H, 4′′′′-H), 6.69 [d, ^3J(H,H) = 3.5 Hz, 1 H, 4-H], 2.75 [d, ^3J(H,H) = 6.5 Hz, 2 H, CH_2, thiophene], 1.61 (br. s, 1 H, CH-CH_2, thiophene), 1.27 (m, 32 H, CH_2, alkyl), 0.89 [t, ^3J(H,H) = 6.7 Hz, 6 H, CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 144.7, 137.5, 137.1, 136.7, 136.5, 136.1, 136.0, 135.2, 134.6, 127.9, 125.9, 124.8, 124.65, 124.60, 124.5, 124.5, 124.3, 124.0, 123.77, 123.75, 40.1, 34.9, 33.6, 31.91, 31.90, 29.9, 29.64, 29.62, 29.60, 29.5, 29.29, 29.25, 26.7, 22.6, 13.9 ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 422 nm (38300 mol^{-1} dm^3 cm^{-1}). MS (MALDI-TOF): m/z = 692 [M$^+$]. $C_{40}H_{52}S_5$ (692.7): calcd. C 69.31, H 7.56; found C 69.09, H 7.29.

5-Eicosyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′-quinquethiophene (15b): Compound **12b** (380 mg, 0.55 mmol) and 5-bromo-2,2′-bithiophene (**4**) (132 mg, 0.55 mmol) are dissolved in 25 mL of dry THF. Pd(PPh_3)$_4$ (10 mg, 0.008 mmol) is added and the mixture is stirred for 14 h at 74 °C. After cooling to room temperature the orange-brown precipitate is separated by centrifugation and recrystallised from THF/CH_2Cl_2 (1:3). The obtained solid is dissolved in tetrachloroethane, activated carbon is added and filtered off. Removal of the solvent gives **15b** (150 mg, 40%) as an orange-red solid. m.p. 225 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): δ = 7.28 [dd, J(H,H) = 1.1 and 5.1 Hz, 1 H, 5′′′′-H], 7.23 [dd, J(H,H) = 1.1 and 3.4 Hz, 1 H, 3′′′′-H], 7.14–7.04 (m, 8 H, 3-H, 3′-H, 4′-H, 3′′-H, 4′′-H, 3′′′-H, 4′′′-H, 4′′′′-H), 6.75 [d, ^3J(H,H) = 3.5 Hz, 1 H, 4-H], 2.85 [t, ^3J(H,H) = 7.3 Hz, 2 H, CH_2, thiophene], 1.74 (m, 2 H, CH_2-CH_2, thiophene), 1.34 (m, 34 H, CH_2, alkyl), 0.95 [t, ^3J(H,H) = 6.9 Hz, 3 H, CH_3] ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 408 nm (25300 mol^{-1} dm^3 cm^{-1}). MS (MALDI-TOF): m/z = 692 [M$^+$]. $C_{40}H_{52}S_5$ (692.7): calcd. C 69.31, H 7.56; found C 69.56, H 7.26.

5-Dodecyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′-quinquethiophene (15c): A solution of compounds **10c** (373 mg, 0.75 mmol), **3** (245 mg, 0.75 mmol) and Pd(PPh_3)$_4$ (22 mg, 19 μmol) in THF (15 mL) is stirred under reflux for 15 h. After cooling to room temperature the orange precipitate is separated by filtration, suspended in hot acetone for 1 h. The solid is then filtered and dissolved in tetrachloroethane. After addition of a spatula of charcoal the mixture is heated and filtered. Acetone is added to the filtrate to precipitate the product. After filtration and removal of the solvent **15c** (290 mg, 67%) is obtained as an orange solid. m.p. 240 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): δ = 7.29 [dd, ^3J(H,H) = 5.1, ^4J(H,H) = 1.0 Hz, 1 H, 5′′′′-H], 7.24 [dd, ^3J(H,H) = 3.6, ^4J(H,H) = 1.0 Hz, 1 H, 3′′′′-H], 7.15–7.12 (m, 4 H, 3′′-H, 4′′-H, 3′′′-H, 4′′′-H), 7.12 [d, ^3J(H,H) = 3.8 Hz, 1 H, 3′-H or 4′-H], 7.08 [dd, ^3J(H,H) = 5.1, ^3J(H,H) = 3.8 Hz, 1 H, 4′′′′-H], 7.06 [d, ^3J(H,H) = 3.6 Hz, 1 H, 3′-H or 4′-H], 7.05 [d, ^3J(H,H) = 3.6 Hz, 1 H, 3-H], 6.75 [d, ^3J(H,H) = 3.6 Hz, 1 H, 4-H], 2.86 [t, ^3J(H,H) = 7.5 Hz, 2 H, α-CH_2], 1.77 [quint, ^3J(H,H) = 7.4 Hz, 2 H, β-CH_2], 1.36 (br. s, 18 H, alkyl-CH_2), 0.96 [t, ^3J(H,H) = 6.9 Hz, 3 H, CH_3] ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} = 423 nm. MS (MALDI-TOF): m/z = 580.1 (100) [M$^+$]. $C_{32}H_{36}S_5$ (580,9): calcd. C 66.16, H 6.25; found C 65.91, H 6.31.

5-(2-Octyldodecyl)-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′-sexithiophene (16a): Compound **12a** (385 mg, 0.55 mmol) and compound **3** (163 mg, 0.54 mmol) are dissolved in 25 mL of dry THF. Pd(PPh_3)$_4$ (18 mg, 0.016 mmol) is added and the mixture is stirred for 12 h at 78 °C. After cooling to room temperature the orange-brown precipitate is separated by centrifugation and washed with THF. The obtained solid is dissolved in tetrachloroethane activated carbon is added and filtered off. Removal of the solvent gives **16a** (198 mg, 47%) as a red-brown solid. m.p. 233 °C. ^{1}H NMR (400 MHz,

$CDCl_3$, 25 °C): δ = 7.29 [dd, J(H,H) = 1.1 and 5.0 Hz, 1 H, 5′′′′′-H], 7.24 [dd, J(H,H) = 1.1 and 3.6 Hz, 1 H, 3′′′′′-H], 7.12–7.01 (m, 10 H, 3-H, 3′-H, 4′-H, 3′′-H, 4′′-H, 3′′′-H, 4′′′-H, 3′′′′-H, 4′′′′-H, 4′′′′′-H), 6.72 [d, ^3J(H,H) = 3.6 Hz, 1 H, 4-H], 2.80 [d, ^3J(H,H) = 6.5 Hz, 2 H, CH_2, thiophene], 1.71 (br. s, 1 H, CH-CH_2, thiophene), 1.30 (m, 32 H, CH_2, alkyl), 0.95 [t, ^3J(H,H) = 6.8 Hz, 6 H, CH_3] ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 433 nm (45400 $mol^{-1}\,dm^3\,cm^{-1}$). MS (MALDI-TOF): m/z (%) = 774 (100) [M^+]. $C_{44}H_{54}S_6$ (774.3): calcd. C 68.16, H 7.02; found C 68.07, H 7.19.

5-Eicosyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′-sexithiophene (16b): Compound **12b** (200 mg, 0.29 mmol) and compound **3** (94 mg, 0.29 mmol) are dissolved in 25 mL of dry THF. $Pd(PPh_3)_4$ (8 mg, 0.006 mmol) is added and the mixture is stirred for 12 h at 78 °C. After cooling to room temperature the orange-brown precipitate is separated by centrifugation and washed with hot THF. The obtained solid is dissolved in tetrachloroethane, activated carbon is added and filtered off. After adding methanol to the solution the product precipitates and the removal of the solvent gives **16b** (128 mg, 56%) as an orange-brown solid. m.p. 297 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): δ = 7.29 [dd, J(H,H) = 1.1 and 5.1 Hz, 1 H, 5′′′′-H], 7.24 [dd, J(H,H) = 1.1 and 3.4 Hz, 1 H, 3′′′′-H], 7.15–7.04 (m, 10 H, 3-H, 3′-H, 4′-H, 3′′-H, 4′′-H, 3′′′-H, 4′′′-H, 3′′′′-H, 4′′′′-H, 4′′′′′-H), 6.75 [d, ^3J(H,H) = 3.5 Hz, 1 H, 4-H], 2.86 [t, ^3J(H,H) = 7.3 Hz, 2 H, CH_2, thiophene], 1.74 (m, 2 H, CH_2-CH_2, thiophene), 1.36 (m, 34 H, CH_2, alkyl), 0.95 [t, ^3J(H,H) = 6.8 Hz, 3 H, CH_3] ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 426 nm (30500 $mol^{-1}\,dm^3\,cm^{-1}$). MS (MALDI-TOF): m/z = 774 [M^+]. $C_{44}H_{54}S_6$ (774.3): calcd. C 68.16, H 7.02; found C 68.07, H 7.19.

5-Dodecyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′-sexithiophene (16c): A solution of compounds **12c** (289 mg, 0.5 mmol), **3** (163 mg, 0.5 mmol) and $Pd(PPh_3)_4$ (15 mg, 13 μmol) in THF (15 mL) is stirred under reflux for 15 h. After cooling to room temperature, the crude product is collected by filtration. Then the solid is suspended in acetone and stirred under reflux for 1 h. After filtration it is dissolved in tetrachloroethane. A spatula of charcoal is added, the mixture is heated up and filtered. The product is precipitated by addition of acetone, filtered and dried in vacuo. **16c** (170 mg, 51%) is obtained as a light red solid. m.p. 304 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): δ = 7.29 [dd, ^3J(H,H) = 5.1, ^4J(H,H) = 1.1 Hz, 1 H, 5′′′′′-H], 7.25 [dd, ^3J(H,H) = 3.6, ^4J(H,H) = 1.2 Hz, 1 H, 3′′′′′-H], 7.15 (br. s, 4 H, 3′′-H, 4′′-H, 3′′′-H, 4′′′-H), 7.15 [d, ^3J(H,H) = 3.8 Hz, 1 H, 3′′′′-H or 4′′′′-H], 7.13 [d, ^3J(H,H) = 3.7 Hz, 1 H, 3′′′′-H or 4′′′′-H], 7.12 [d, ^3J(H,H) = 3.7 Hz, 1 H, 3′-H or 4′-H], 7.09 [dd, ^3J(H,H) = 5.1, ^3J(H,H) = 3.6 Hz, 1 H, 4′′′′′-H], 7.07 [d, ^3J(H,H) = 3.8 Hz, 1 H, 3′-H or 4′-H], 7.05 [d, ^3J(H,H) = 3.5 Hz, 1 H, 3-H], 6.75 [d, ^3J(H,H) = 3.5 Hz, 1 H, 4-H], 2.86 [t, ^3J(H,H) = 7.6 Hz, 2 H, α-CH_2], 1.77 [quint, ^3J(H,H) = 7.6 Hz, 1 H, β-CH_2], 1.36 (br. s, 18 H, alkyl-CH_2), 0.96 [t, ^3J(H,H) = 7.0 Hz, 3 H, CH_3] ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} = 436 nm. MS (MALDI-TOF): m/z (%) = 662.0 (100) [M^+]. $C_{36}H_{38}S_6$ (663.1): calcd. C 65.21, H 5.78; found C 64.84, H 5.83.

Protected Alkylated Quinquethiophene Precursor 18b: Compound **8b** (263 mg, 0.5 mmol) and compound **17** (124 mg, 0.25 mmol) are dissolved in 25 mL of dry DMF. $Pd(PPh_3)_4$ (23 mg, 0.019 mmol) is added and the mixture is stirred for 14 h at 92 °C. After cooling to room temperature the precipitate is separated by centrifugation, washed three times with acetone and dried in vacuo yielding **18b** as a grey-white microcrystalline solid (202 mg, 77%). ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): δ = 7.00 [d, ^3J(H,H) = 3.5 Hz, 2 H, 3′′-H, 3′′′′-H], 6.99 [d, ^3J(H,H) = 3.7 Hz, 2 H, 4′-H, 4′′′-H], 6.93 [d, ^3J(H,H) = 3.7 Hz, 2 H, 3′-H, 3′′′-H], 6.73 [d, ^3J(H,H) = 3.5 Hz, 2 H, 4′′-H, 4′′′′-H], 4.07–4.00 (m, 8 H, protecting group.), 2.91 [t, ^3J(H,H) = 7.3 Hz, 4 H, CH_2, thiophene], 2.24 (s, 4 H, 2-H, 3-H), 1.89 (m, 4 H, CH_2-CH_2, thiophene), 1.36 (m, 68 H, CH_2, alkyl), 0.86 [t, ^3J(H,H) = 6.9 Hz, 6 H, CH_3] ppm. The crude product is used without further purification for the next step.

Protected Alkylated Quinquethiophene Precursor 18c: Compounds **8c** (1.7 g, 4.0 mmol) and **17** (1.0 g, 2.0 mmol) and $Pd(PPh_3)_4$ (30 mg, 26 μmol) are dissolved in THF (30 mL). The solution is stirred under reflux for 20 h. After cooling to room temperature methanol (10 mL) is added and the resulting brown solid is filtered. The crude product is recrystallised from acetone and dried in vacuo to obtain **18c** (770 mg, 46%) as a white solid. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 25 °C): δ = 6.96 (m, 4 H, 3′′-H, 3′′′′-H, 4′-H, 4′′′-H), 6.88 [d, ^3J(H,H) = 3.6 Hz, 2 H, 3′-H, 3′′′-H], 6.68 [d, ^3J(H,H) = 3.6 Hz, 2 H, 4′′-H, 4′′′′-H], 4.04–3.95 (m, 8 H, protecting group), 2.78 [t, ^3J(H,H) = 7.6 Hz; α-CH_2], 2.17 (s, 4 H, 2-H, 3-H), 1.67 [quint, ^3J(H,H) = 7.3 Hz, 4 H, β-CH_2], 1.27 (br. s, 36 H, alkyl-CH_2), 0.89 [t, ^3J(H,H) = 6.8 Hz, 6 H, CH_3] ppm. ^{13}C NMR (126 MHz, $C_2D_2Cl_4$, 25 °C): δ = 145.7, 144.7, 137.6, 134.6, 125.3, 125.0, 123.5, 122.8, 108.5, 65.3, 34.7, 32.0, 31.7, 30.2, 29.8, 29.5, 29.2, 22.8, 14.4 ppm. $C_{48}H_{70}O_4S_4$ (839.3): calcd. C 68.69, H 8.41; found C 68.48, H 8.37.

Protected Septithiophene 19b: Compound **10b** (192 mg, 0.32 mmol) and compound **17** (79 mg, 0.16 mmol) are dissolved in 25 mL of DMF/THF (1:1). $Pd(PPh_3)_4$ (15 mg, 0.013 mmol) is added and the mixture is stirred for 14 h at 93 °C. After cooling to room temperature the precipitate is separated by centrifugation, washed with acetone, ethyl acetate and dried in vacuo yielding **19b** as yellowish-brown powder (178 mg, 49%). ^{1}H NMR (400 MHz; $C_2D_2Cl_4$, 25 °C): δ = 6.97–6.94 (m, 8 H, 4′-H, 3′′-H, 4′′-H, 3′′′-H, 4′′′′-H, 3′′′′′-H, 4′′′′′-H, 3′′′′′′-H), 6.85 [d, ^3J(H,H) = 3.5 Hz, 2 H, 3′-H, 3′′′′-H], 6.64 [d, ^3J(H,H) = 3.5 Hz, 2 H, 4′′′-H, 4′′′′′′-H], 4.01–3.95 (m, 8 H, protecting groups.), 2.70 [t, ^3J(H,H) = 6.5 Hz, 4 H, CH_2, thiophene], 2.16 (s, 4 H, 2-H, 3-H), 1.60 (m, 4 H, CH_2-CH_2, thiophene), 1.25 (m, 68 H, CH_2 alkyl), 0.86 [t, J(H,H) = 6.9 Hz, 6 H, CH_3] ppm. The crude product is used without further purification for the next step.

Protected Septithiophene 19c: Compounds **10c** (1.5 g, 3.0 mmol), **17** (744 mg, 1.5 mmol) and $Pd(PPh_3)_4$ (50 mg, 43 μmol) are dissolved in THF (50 mL). The solution is stirred under reflux for 20 h. After cooling to room temperature methanol (10 mL) is added and the resulting yellow solid is filtered, washed with acetone and dried in vacuo. The crude product **19c** (740 mg, 49%) is used without further purification in the next step. ^{1}H NMR (500 MHz; $C_2D_2Cl_4$, 100 °C): δ = 7.08 [d, ^3J(H,H) = 3.7 Hz, 2 H, 3′′-H, 3′′′′′-H or 4′′-H, 4′′′′′-H], 7.06 [d, ^3J(H,H) = 3.7 Hz, 2 H, 4′-H, 4′′′′-H], 7.05 [d, ^3J(H,H) = 3.7 Hz, 2 H, 3′′-H, 3′′′′′-H or 4′′-H, 4′′′′′-H], 7.04 [d, ^3J(H,H) = 3.6 Hz, 2 H, 3′′′-H, 3′′′′′′-H], 6.97 [d, ^3J(H,H) = 3.7 Hz, 2 H, 3′-H, 3′′′′-H], 6.76 [d, ^3J(H,H) = 3.6 Hz, 2 H, 4′′′-H, 4′′′′′′-H], 4.10–4.03 (m, 8 H, protecting groups), 2.87 [t, ^3J(H,H) = 7.5 Hz, 4 H, α-CH_2], 2.26 (s, 4 H, 2-H, 3-H), 1.78 [quint, ^3J(H,H) = 7.3 Hz, 4 H, β-CH_2], 1.35 (br. s, 36 H, alkyl-CH_2), 0.97 [t, ^3J(H,H) = 6.8 Hz, 6 H, CH_3] ppm. ^{13}C NMR (126 MHz, $C_2D_2Cl_4$, 100 °C): δ = 146.0, 137.2, 137.0, 135.8, 134.5, 125.3, 124.9, 124.3, 123.73, 123.70, 123.4, 108.8, 67.9, 65.3, 34.8, 31.9, 31.5, 30.2, 29.64, 29.62, 29.5, 29.33, 29.29, 29.1, 25.7, 22.6, 14.0 ppm.

Deprotected Alkylated Quinquethiophene Precursor 22b: Compound **18b** (120 mg, 0.11 mmol) is dissolved in hot THF (60 mL) and 2 mL of conc. HCl are added to this solution. After stirring the mixture for 1 h the product is formed as precipitate. The brown product is washed with saturated aq. $NaHCO_3$ and purified by recrystallisation from acetone/ethyl acetate (3:6) to give **22b** as a

white-yellow solid (92 mg, 82%). m.p. 166 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): δ = 7.71 [d, J(H,H) = 4.0 Hz, 2 H, 3′-H, 3‴-H], 7.19 [d, ^3J(H,H) = 3.7 Hz, 2 H, 3″-H, 3⁗-H], 7.16 [d, ^3J(H,H) = 4.0 Hz, 2 H, 4′-H, 4‴-H], 6.78 [d, ^3J(H,H) = 3.7 Hz, 2 H, 4″-H, 4⁗-H], 3.37 (s, 4 H, 2-H, 3-H), 2.87 [t, ^3J(H,H) = 7.3 Hz, 4 H, CH_2, thiophene], 1.70 (m, 4 H, CH_2-CH_2, thiophene), 1.34 (m, 68 H, CH_2, alkyl), 0.86 [t, ^3J(H,H) = 6.9 Hz, 6 H, CH_3] ppm. IR (KBr): $\tilde{\nu}$ = 1653 cm^{-1} (C=O). UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 416 nm (34600 mol^{-1} dm^3 cm^{-1}). MS (MALDI-TOF): m/z = 975 [M$^+$ + H], 529 [M$^+$ – $C_{32}H_{49}O_2S_2$]. $C_{60}H_{94}O_2S_4$ (974.6): calcd. C 73.86, H 9.71; found C 73.51, H 9.61.

Deprotected Alkylated Quinquethiophene Precursor 22c: Compound **18c** (600 mg, 0.7 mmol) is dissolved in THF (50 mL). Then conc. HCl (4 mL) is added. After 3 h of stirring and cooling to room temperature the resulting precipitate is filtered, washed with acetone and dried in vacuo. **22c** is obtained as a white-yellow solid (450 mg, 84%). m.p. 182 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): δ = 7.71 [d, ^3J(H,H) = 4.1 Hz, 2 H, 3′-H, 3‴-H], 7.19 [d, ^3J(H,H) = 3.7 Hz, 2 H, 3″-H, 3⁗-H], 7.16 [d, ^3J(H,H) = 3.9 Hz, 2 H, 4′-H, 4‴-H], 6.78 [d, ^3J(H,H) = 3.7 Hz, 2 H, 4″-H, 4⁗-H], 3.36 (s, 4 H, 2-H, 3-H), 2.87 [t, ^3J(H,H) = 7.4 Hz, 4 H, α-CH_2], 1.77 [quint, ^3J(H,H) = 7.4 Hz, 4 H, β-CH_2], 1.35 (br. s, 36 H, alkyl-CH_2), 0.96 [t, ^3J(H,H) = 7.1 Hz, CH_3] ppm. MS (MALDI-TOF): m/z (%) = 752 (100) [M$^+$ + H]. $C_{44}H_{62}O_2S_4$ (751.2): calcd. C 70.35, H 8.32; found C 70.06, H 8.27.

Deprotected Alkylated Septithiophene Precursor 23b: Compound **19b** (178 mg, 0.14 mmol) is dissolved in hot THF (70 mL) and 3 mL of conc. HCl are added to the solution. After stirring the mixture for 1 h the product is formed as precipitate. The brown product is washed with water, purified by recrystallisation THF/ethyl acetate (5:2) to give **23b** as a yellow solid (12 mg, 7%). m.p. 207 °C. ^{1}H NMR (500 MHz, $C_2H_2Cl_4$, 100 °C): δ = 7.73 [d, ^3J(H,H) = 3.9 Hz, 2 H, 3′-H, 3⁗′-H], 7.25 [d, ^3J(H,H) = 3.7 Hz, 2 H, 3″-H, 3⁗″-H], 7.21 [d, ^3J(H,H) = 3.9 Hz, 2 H, 4′-H, 4⁗′-H], 7.08 [d, ^3J(H,H) = 3.7 Hz, 2 H, 4″-H, 4⁗″-H or 3‴-H, 3⁗‴-H], 7.07 [d, ^3J(H,H) = 3.2 Hz, 2 H, 4″-H, 4⁗″-H or 3‴-H, 3⁗‴-H], 6.75 [d, ^3J(H,H) = 3.7 Hz, 2 H, 4‴-H, 4⁗‴-H], 3.38 (s, 2 H, 2-H, 3-H), 2.87 [t, ^3J(H,H) = 6.5 Hz, 4 H, CH_2, thiophene], 1.75 (m, 4 H, CH_2-CH_2, thiophene), 1.37 (m, 68 H, CH_2, alkyl), 0.93 [t, ^3J(H,H) = 6.9 Hz, 6 H, CH_3] ppm. IR (KBr): $\tilde{\nu}$ = 1649 cm^{-1} (C=O). UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 440 nm (150300 mol^{-1} dm^3 cm^{-1}). MS (MALDI-TOF): m/z = 1138 [M$^+$], 611 [M$^+$ – $C_{36}H_{51}O_2S_3$].

Deprotected Alkylated Septithiophene Precursor 23c: Compound **19c** (300 mg, 0.3 mmol) is dissolved in hot THF (100 mL). Then conc. HCl (2 mL) is added. After stirring the mixture for 5 h and cooling to room temperature the resulting precipitate is filtered and dried in vacuo. **23c** (190 mg, 69%) is obtained as a yellow solid. m.p. 269 °C. ^{1}H NMR (500 MHz, $C_2H_2Cl_4$, 100 °C): δ = 7.74 [d, ^3J(H,H) = 2.9 Hz, 2 H, 3′-H, 3⁗′-H], 7.26 [d, ^3J(H,H) = 2.7 Hz, 2 H, 3″-H, 3⁗″-H], 7.22 [d, ^3J(H,H) = 2.9 Hz, 2 H, 4′-H, 4⁗′-H], 7.09–7.08 (m, 4 H, 4″-H, 4⁗″-H, 3‴-H, 3⁗‴-H), 6.76 [d, ^3J(H,H) = 2.5 Hz, 2 H, 4‴-H, 4⁗‴-H], 3.38 (s, 4 H, 2-H, 3-H), 2.86 [t, ^3J(H,H) = 7.4 Hz, 4 H, α-CH_2], 1.77 [quint, ^3J(H,H) = 7.5 Hz, 4 H, β-CH_2], 1.35 (br. s, 36 H, alkyl-CH_2), 0.96 [t, ^3J(H,H) = 7.0 H; 6 H, CH_3] ppm. ^{13}C NMR (126 MHz, $C_2D_2Cl_4$, 100 °C): δ = 190.6, 146.8, 145.5, 141.7, 139.6, 134.4, 134.0, 132.9, 126.5, 125.1, 124.4, 124.1, 124.0, 33.4, 31.9, 31.5, 30.3, 29.64, 29.61, 29.5, 29.32, 29.29, 29.1, 22.6, 14.0 ppm. MS (MALDI-TOF): m/z (%) = 913.4 (100) [M$^+$ – H]. $C_{52}H_{66}O_2S_6$ (915.5): calcd. C 68.22, H 7.27; found C 67.78, H 7.38.

5,5⁗′-Dieicosyl-2,2′:5′,2″:5″,2‴:5‴,2⁗′-quinquethiophene (26b): A mixture of **22b** (80 mg, 0.08 mmol), Lawesson′s reagent (60 mg, 0.15 mmol) and dry THF (70 mL) is heated to 83 °C and maintained for ca 6 h until H_2S formation has ceased. After cooling to room temperature the precipitate is separated by centrifugation and washed with acetone. The crude product is purified by recrystallisation from CH_2Cl_2/ethyl acetate (8:2) to give **26b** as a red-brown solid (51 mg, 65%). m.p. 198 °C. ^{1}H NMR (500 MHz, C_2DCl_4, 100 °C): δ = 7.13 (s, 2 H, 3″-H, 4″-H), 7.11 [d, ^3J(H,H) = 3.5 Hz, 2 H, 4′-H, 3‴-H], 7.06 [d, ^3J(H,H) = 3.5 Hz, 2 H, 3′-H, 4‴-H], 7.05 [d, ^3J(H,H) = 2.7 Hz, 2 H, 3-H, 3⁗′-H], 6.72 [d, ^3J(H,H) = 2.7 Hz, 2 H, 4-H, 4⁗′-H], 2.89 [t, ^3J(H,H) = 7.7 Hz, 4 H, CH_2, thiophene], 1.60 (m, 4 H, CH_2-CH_2, thiophene), 1.27 (m, 68 H, CH_2, alkyl), 0.86 [t, ^3J(H,H) = 6.9 Hz, 6 H, CH_3] ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 412 nm (29500 mol^{-1} dm^3 cm^{-1}). MS (MALDI-TOF): m/z = 973 [M$^+$]. $C_{60}H_{92}S_5$ (972.6): calcd. C 74.01, H 9.52; found C 73.88, H 9.45.

5,5⁗′-Didodecyl-2,2′:5′,2″:5″,2‴:5‴,2⁗′-quinquethiophene (26c): Compound **22c** (300 mg, 0.4 mmol) and Lawesson's reagent (650 mg, 1.6 mmol) are dissolved in dry tetrachloroethane (60 mL). The mixture is stirred for 18 h under reflux. After cooling to room temperature the resulting precipitate is filtered, resuspended in hot THF and stirred for 1 h. After filtration and drying in vacuo **26c** (194 mg, 65%) is obtained as an orange solid. m.p. 227 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): δ = 7.11 (s, 2 H, 3″-H, 4″-H), 7.11 (bd, 2 H, 3′-H, 4‴-H or 4′-H, 3‴-H), 7.06 [d, ^3J(H,H) = 3.6 Hz, 2 H, 3′-H, 4‴-H or 4′-H, 3‴-H], 7.05 [d, ^3J(H,H) = 3.5 Hz, 2 H, 3-H, 3⁗′-H], 6.75 [d, ^3J(H,H) = 3.5 Hz, 2 H, 4-H, 4⁗′-H], 2.86 [t, ^3J(H,H) = 7.5 Hz, 6 H, α-CH_2], 1.77 [quint, ^3J(H,H) = 7.3 Hz, 4 H, β-CH_2], 1.36 (br. s, 36 H, alkyl-CH_2), 0.96 [t, ^3J(H,H) = 7.0 Hz, 6 H, CH_3] ppm. ^{13}C NMR (126 MHz, $C_2D_2Cl_4$, 100 °C): δ = 146.1, 137.4, 136.3, 135.4, 134.4.124.9, 124.5, 124.4, 123.8, 31.9, 31.5, 30.3, 29.7, 29.6, 29.5, 29.34, 29.30, 29.1, 22.6, 14.0 ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} = 424 nm. MS (MALDI-TOF): m/z = 748.2 [M$^+$ – H]. $C_{44}H_{60}S_5$ (749.3): calcd. C 70.53, H 8.07; found C 70.40, H 8.11.

5,5⁗″-Dieicosyl-2,2′:5′,2″:5″,2‴:5‴,2⁗′:5⁗′,2⁗″:5⁗″,2⁗‴-septithiophene (27b): A mixture of **23b** (100 mg, 0.09 mmol), Lawesson's reagent (64 mg, 0.16 mmol) and tetrachloroethane (40 mL) is heated to 100 °C and maintained for ca. 5 h until H_2S formation has ceased. After adding some mL of methanol the precipitate is separated by centrifugation and washed with acetone and ethyl acetate. The crude product was purified by recrystallization from THF/dichloromethane (2:1) to give **27b** as red solid (60 mg, 59%). m.p. 299 °C. ^{1}H NMR (500 MHz; $C_2D_2Cl_4$, 100 °C): δ = 7.14–7.12 (m, 8 H), 7.06 [d, ^3J(H,H) = 3.7 Hz, 2 H], 7.05 [d, ^3J(H,H) = 3.5 Hz, 2 H], 6.75 [d, ^3J(H,H) = 3.5 Hz, 2 H, 4-H, 4⁗″-H], 2.87 [t, ^3J(H,H) = 6.5 Hz, 4 H, CH_2, thiophene], 1.61 (m, 4 H, CH_2-CH_2, thiophene), 1.26 (m, 68 H, CH_2, alkyl), 0.86 [t, ^3J(H,H) = 6.9 Hz, 6 H, CH_3] ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 450 nm (38000 mol^{-1} dm^3 cm^{-1}). MS (MALDI-TOF): m/z (%) = 1137 (100) [M$^+$]. $C_{68}H_{96}S_7$ (1137.9): calcd. C 71.77, H 8.50; found C 71.42, H 8.43.

5,5⁗″-Didodecyl-2,2′:5′,2″:5″,2‴:5‴,2⁗′:5⁗′,2⁗″:5⁗″,2⁗‴-septithiophene (27c): A solution of compound **23c** (190 mg, 0.2 mmol) and Lawesson's reagent (323 mg, 0.8 mmol) in tetrachloroethane (80 mL) is stirred under reflux for 18 h. After cooling to room temperature the resulting precipitate is separated by filtration and washed with acetone. Then it is suspended in hot THF, stirred for 1 h, filtered and dried in vacuo. **27c** (105 mg, 57%) is obtained as a red solid. m.p. 340 °C. ^{1}H NMR (500 MHz; $C_2D_2Cl_4$, 100 °C): δ = 7.14–7.12 (m, 8 H), 7.06 [d, ^3J(H,H) = 2.4 Hz, 2 H], 7.05 [d, ^3J(H,H) = 2.4 Hz, 2 H, 3-H, 3⁗″-H], 6.75 [d, ^3J(H,H) = 2.4 Hz, 2 H, 4-H, 4⁗″-H], 2.86 [t, ^3J(H,H) =

7.4 Hz, 4 H, α-CH_2], 1.77 [quint, ^3J(H,H) = 7.4 Hz, 4 H, β-CH_2], 1.34 (br. s, 36 H, alkyl-CH_2), 0.96 [t, ^3J(H,H) = 6.9 Hz, 6 H, CH_3] ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} = 449 nm. MS (MALDI-TOF): *m/z* = 912.6 [M^+ – H]. $C_{52}H_{64}S_7$ (913.5): calcd. C 68.37, H 7.06; found C 67.42, H 7.07.

5,5′′-Bis(2-octyldodecyl)-2,2′:5′,2′′-terthiophene (30a): Monoalkylated compound **30a** is isolated as byproduct of the synthesis of dialkylated **11a** during the purification process by column chromatography (SiO_2/hexane). After removal of the solvent **30a** is received as a semifluid green-brown oil (0.3 g, 0.37 mmol). R_f = 0.41 (hexane); m.p. 6 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.95 (s, 2 H, 3′-H, 4′-H), 6.94 [d, ^3J(H,H) = 3.5 Hz, 2 H, 3-H, 3′′-H], 6.63 [d, ^3J(H,H) = 3.5 Hz, 2 H, 4-H, 4′′-H], 2.71 [d, ^3J(H,H) = 6.5 Hz, 4 H, CH_2, thiophene], 1.56 (br. s, 2 H, CH_2-CH_2, thiophene), 1.26 (m, 64 H, CH_2, alkyl), 0.86 [t, ^3J(H,H) = 6.9 Hz, 12 H, CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 143.9, 136.1, 134.8, 125.8, 123.3, 123.0, 39.9, 34.5, 33.1, 31.93, 31.91, 29.9, 29.66, 29.65, 29.61, 29.35, 29.32, 26.6, 22.6, 14.1 ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 360 nm (19100 $mol^{-1}\,dm^3\,cm^{-1}$). MS (MALDI-TOF): *m/z* (%) = 808 (100) [M^+]. $C_{52}H_{88}S_3$ (808.6): calcd. C 77.16, H 10.96; found C 77.52, H 10.73.

5,5′′-Dieicosyl-2,2′:5′,2′′-terthiophene (30b): Compound **8b** (420 mg, 0.79 mmol) and 2,5-dibromothiophene (96 mg, 0.39 mmol) are dissolved in 40 mL of dry DMF. $Pd(PPh_3)_4$ (18 mg, 0.015 mmol) is added and the mixture is stirred overnight at 92 °C. After cooling to room temperature the orange-brown precipitate is separated by centrifugation and washed with acetone and recrystallized from THF/ethyl acetate (2:3). The crude product is purified by column chromatography (SiO_2/CH_2Cl_2) to give **30b** as a yellow solid (136 mg, 42%). R_f = 0.82 (CH_2Cl_2); m.p. 100 °C. ^{1}H NMR (400 MHz, $C_2H_2Cl_4$, 100 °C): δ = 7.01 (s, 2 H, 3′-H, 4′-H), 7.00 [d, ^3J(H,H) = 3.5 Hz, 2 H, 3-H, 3′′-H], 6.72 [d, ^3J(H,H) = 3.5 Hz, 2 H, 4-H, 4′′-H], 2.83 [t, ^3J(H,H) = 7.5 Hz, 4 H, CH_2, thiophene], 1.75 (m, 4 H, CH_2-CH_2, thiophene), 1.36 (m, 68 H, CH_2, alkyl), 0.95 [t, ^3J(H,H) = 6.9 Hz, 6 H, CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 100 °C): δ = 143.9, 136.1, 134.8, 125.8, 123.3, 123.0, 39.95, 34.5, 33.1, 31.93, 31.91, 29.9, 29.66, 29.65, 29.61, 29.35, 29.32, 26.6, 22.6, 14.1 ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 352 nm (16800 $mol^{-1}\,dm^3\,cm^{-1}$). MS (MALDI-TOF): *m/z* = 808 [M^+]. $C_{52}H_{88}S_3$ (808.6): calcd. C 77.16, H 10.96; found C 76.97, H 11.06.

5,5′′′-Bis(2-octyldodecyl)-2,2′:5′,2′′:5′′,2′′′-quaterthiophene (31a): Compound **8a** (850 mg, 1.6 mmol) and 5,5′-dibromo-2,2′-bithiophene (**5**) (290 mg, 0.89 mmol) are dissolved in 20 mL of dry DMF. $Pd(PPh_3)_4$ (35 mg, 0.04 mmol) is added and the mixture is stirred overnight at 93 °C. After cooling to room temperature the product is poured into water and extracted 3 times with chloroform. After combining the chloroform fractions and drying over Na_2SO_4 and removal of the solvent, the product is purified by column chromatography (SiO_2/hexane/CH_2Cl_2, 8:2) to give **31a** (573 mg, 67%) as a light yellow solid. R_f = 0.67 (hexane/CH_2Cl_2, 8:2); m.p. 35 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.01 [d, ^3J(H,H) = 3.7 Hz, 2 H, 4′-H, 3′′-H], 6.97 [d, ^3J(H,H) = 3.7 Hz, 2 H, 3′-H, 4′′-H], 6.95 [d, ^3J(H,H) = 3.7 Hz, 2 H, 3-H, 3′′′-H], 6.63 [d, ^3J(H,H) = 3.5 Hz, 2 H, 4-H, 4′′′-H], 2.70 [d, ^3J(H,H) = 6.5 Hz, 4 H, CH_2, thiophene], 1.60 (br. s, 2 H, CH-CH_2, thiophene), 1.27 (m, 64 H, CH_2, alkyl), 0.86 [t, ^3J(H,H) = 6.9 Hz, 12 H, CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 144.2, 136.8, 135.3, 134.6, 125.9, 123.9, 123.5, 123.2, 39.9, 34.5, 33.1, 31.92, 31.91, 29.9, 29.7, 29.65, 29.6, 29.4, 29.3, 26.6, 22.6, 14.1 ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 390 nm (26000 $mol^{-1}\,dm^3\,cm^{-1}$). MS (MALDI-TOF): *m/z* = 890 [M^+]. $C_{56}H_{90}S_4$ (891.57): calcd. C 75.44, H 10.17; found C 75.72, H 10.17.

5,5′′′-Dieicosyl-2,2′:5′,2′′:5′′,2′′′-quaterthiophene (31b): Compound **8b** (420 mg, 079 mmol) and 5,5′-dibromo-2,2′-bithiophene (**5**) (126 mg, 0.39 mmol) are dissolved in 40 mL of dry DMF. $Pd(PPh_3)_4$ (35 mg, 0.04 mmol) is added and the mixture is stirred overnight at 93 °C. After cooling to room temperature the orange-brown precipitate is separated by centrifugation and washed with acetone and recrystallized from THF/ethyl acetate (2:3). The crude product is purified by column chromatography (SiO_2/$C_2H_2Cl_4$/$C_6H_4Cl_2$, 1:2) to give **31b** as a yellow-brown solid (42 mg, 12%). m.p. 146 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): δ = 7.08 [d, ^3J(H,H) = 3.7 Hz, 2 H, 4′-H, 3′′-H], 7.04 [d, ^3J(H,H) = 3.7 Hz, 2 H, 3′-H, 4′′-H], 7.03 [d, ^3J(H,H) = 3.7 Hz, 2 H, 3-H, 3′′′-H], 6.74 [d, ^3J(H,H) = 3.7 Hz, 2 H, 4-H, 4′′′-H], 2.85 [t, ^3J(H,H) = 7.5 Hz, 4 H, CH_2, thiophene], 1.74 (m, 4 H, CH_2-CH_2, thiophene), 1.27 (m, 68 H, CH_2, alkyl), 0.96 [t, ^3J(H,H) = 6.9 Hz, 6 H, CH_3] ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 390 nm (26000 $mol^{-1}\,dm^3\,cm^{-1}$). MS (MALDI-TOF): *m/z* = 891 [M^+]. $C_{56}H_{90}S_4$ (890.6): calcd. C 75.44, H 10.17; found C 75.51, H 10.26.

5,5′′′-Didodecyl-2,2′:5′,2′′:5′′,2′′′-quaterthiophene (31c): Compound **8c** (664 mg, 1.6 mmol), 5,5′-dibromo-2,2′-bithiophene (**5**) (259 mg, 0.8 mmol) and $Pd(PPh_3)_4$ (35 mg, 30 μmol) are dissolved in THF (20 mL) and stirred under reflux for 18 h. After cooling to room temperature the orange precipitate is filtered, suspended in acetone (40 mL) and stirred under reflux for 1 h. After filtration the solid is dissolved in hot THF and a spatula of charcoal is added. The mixture is then filtered hot. Methanol is added to the filtrate to precipitate **31c**, which is filtered and dried in vacuo. **31c** (410 mg, 77%) is obtained as a yellow solid. m.p. 166 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): δ = 7.09 [d, ^3J(H,H) = 3.9 Hz, 2 H, 3′-H, 4′′-Hor 4′-H, 3′′-H], 7.05 [d, ^3J(H,H) = 3.8 Hz, 2 H, 3′-H, 4′′-H or 4′-H, 3′′-H], 7.04 [d, ^3J(H,H) = 3.8 Hz, 2 H, 3-H, 3′′′-H], 6.74 [d, ^3J(H,H) = 3.8 Hz, 2 H, 4-H, 4′′′-H], 2.86 [t, ^3J(H,H) = 7.6 Hz, 4 H, α-CH_2], 1.76 [quint, ^3J(H,H) = 7.5 Hz, 4 H, β-CH_2], 1.35 (br. s, 36 H, alkyl-CH_2), 0.96 [t, ^3J(H,H) = 6.9 Hz, 6 H, CH_3] ppm. ^{13}C NMR (126 MHz, $C_2D_2Cl_4$, 100 °C): δ = 146.0, 137.2, 135.6, 134.5, 124.9, 124.3, 123.8, 123.7, 31.9, 31.5, 30.3, 29.64, 29.62, 29.5, 29.33, 29.29, 29.1, 22.6, 14.0 ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} = 403 nm. MS (MALDI-TOF): *m/z* (%) = 666.2 (100) [M^+ – H]. $C_{40}H_{58}S_4$ (667.2): calcd. C 72.01, H 8.75; found C 72.04, H 8.74.

5,5′′′′′-Bis(2-octyldodecyl)-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′-sexithiophene (32a): Compound **10a** (100 mg, 0.16 mmol) and 5,5′-dibromo-2,2′-bithiophene (**5**) (22 mg, 0.08 mmol) are dissolved in 15 mL of dry DMF. $Pd(PPh_3)_4$ (8 mg, 0.006 mmol) is added and the mixture is stirred for 14 h at 93 °C. After cooling to room temperature the precipitate is separated by centrifugation, washed with acetone and purified by column chromatography (SiO_2/hexane/ethyl acetate, 4:1) to give **32a** as red-brown solid (35 mg, 41%). R_f = 0.72 (hexane/ethyl acetate, 4:1); m.p. 117 °C. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 25 °C): δ = 7.13 [d, ^3J(H,H) = 3.8 Hz, 2 H, 4′′-H, 3′′′-H], 7.12 [d, ^3J(H,H) = 3.8 Hz, 2 H, 3′′-H, 4′′′-H], 7.11 [d, ^3J(H,H) = 3.8 Hz, 2 H, 4′-H, 3′′′′-H], 7.07 [d, ^3J(H,H) = 3.8 Hz, 2 H, 3′-H, 4′′′′-H], 7.05 [d, ^3J(H,H) = 3.5 Hz, 2 H, 3-H, 3′′′′′-H], 6.73 [d, ^3J(H,H) = 3.5 Hz, 2 H, 4-H, 4′′′′′-H], 2.80 [d, ^3J(H,H) = 6.5 Hz, 4 H, CH_2, thiophene], 1.70 (br. s, 2 H, CH-CH_2, thiophene), 1.35 (m, 64 H, CH_2, alkyl), 0.95 [t, ^3J(H,H) = 6.9 Hz, 12 H, CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 144.7, 137.5, 136.6, 136.0, 135.2, 134.6, 125.9, 124.5, 124.5, 124.3, 123.78, 123.76, 40.1, 34.9, 33.6, 31.92, 31.91, 29.9, 29.65, 29.62, 29.61,29.5, 29.3, 29.2, 26.8, 22.6, 13.9 ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 436 nm (46200 $mol^{-1}\,dm^3\,cm^{-1}$). MS (MALDI-TOF): *m/z* = 1054 [M^+]. $C_{64}H_{94}S_6$ (1054.5): C 72.80; H 8.97; gef. C 72.63, H 8.84.

5,5‴″-Dieicosyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2‴″-sexithiophene (32b): Com-pounds **12b** (218 mg, 0.31 mmol) and **36b** (191 mg, 0.31 mmol) are dissolved in 20 mL of dry THF. $Pd(PPh_3)_4$ (17 mg, 0.014 mmol) is added and the mixture is stirred for 12 h at 85 °C. After cooling to room temperature the precipitate is separated by centrifugation, washed three times with acetone, THF and methanol and dried in vacuo yielding **32b** as an orange-red solid (106 mg, 32%). m.p. 250 °C. ^{1}H NMR (400 MHz, $C_2H_2Cl_4$, 100 °C): δ = 7.15 [d, ^3J(H,H) = 3.8 Hz, 2 H, 4″-H, 3‴-H], 7.14 [d, ^3J(H,H) = 3.8 Hz, 2 H, 3″-H, 4‴-H], 7.13 [d, ^3J(H,H) = 3.8 Hz, 2 H, 4′-H, 3⁗-H], 7.07 [d, ^3J(H,H) = 3.8 Hz, 2 H, 3′-H, 4⁗-H], 7.05 [d, ^3J(H,H) = 3.5 Hz, 2 H, 3-H, 3‴″-H], 6.75 [d, ^3J(H,H) = 3.5 Hz, 2 H, 4-H, 4‴″-H], 2.85 [t, ^3J(H,H) = 7.4 Hz, 4 H, CH_2, thiophene], 1.78 (m, 4 H, CH_2-CH_2, thiophene), 1.39 (m, 68 H, CH_2, alkyl), 0.95 [t, ^3J(H,H) = 6.9 Hz, 6 H, CH_3] ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 436 nm (32800 mol^{-1} dm^3 cm^{-1}). MS (MALDI-TOF): *m*/*z* = 1054 [M$^+$]. $C_{64}H_{94}S_6$ (1054.5): calcd. C 72.80, H 8.97; found C 72.71, H 8.88.

5,5‴″-Didodecyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2‴″-sexithiophene (32c): Compounds **12c** (290 mg, 0.5 mmol), **36c** (248 mg, 0.5 mmol) and $Pd(PPh_3)_4$ (15 mg, 13 μmol) are dissolved in dry THF (15 mL) and stirred under reflux for 15 h. After cooling to room temperature the resulting red precipitate is collected by filtration. The solid is then suspended in acetone and stirred under reflux for 1 h. After filtration the solid is dissolved in hot tetrachloroethane, a spatula of charcoal is added and the mixture is filtered hot. Addition of methanol precipitates **32c** (170 mg, 41%), which is obtained as a red solid after filtration and drying in vacuo. m.p. 284 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): δ = 7.14 [d, ^3J(H,H) = 3.8 Hz, 2 H, 3″-H, 4‴-H or 4″-H, 3‴-H], 7.12 [d, ^3J(H,H) = 3.8 Hz, 2 H, 3″-H, 4‴-H or 4″-H, 3‴-H], 7.12 [d, ^3J(H,H) = 3.7 Hz, 2 H, 3′-H, 4⁗-H or 4′-H, 3⁗-H], 7.06 [d, ^3J(H,H) = 3.7 Hz, 2 H, 3′-H, 4⁗-H or 4′-H, 3⁗-H], 7.05 [d, ^3J(H,H) = 3.6 Hz, 2 H, 3-H, 3‴″-H], 6.75 [d, ^3J(H,H) = 3.5 Hz, 2 H, 4-H, 4‴″-H], 2.86 [t, ^3J(H,H) = 7.6 Hz, 4 H, α-CH_2], 1.76 [quint, ^3J(H,H) = 7.4 Hz, 4 H, β-CH_2], 1.35 (br. s, 36 H, alkyl-CH_2), 0.96 [t, ^3J(H,H) = 7.1 Hz, 6 H, CH_3] ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} = 440 nm. MS (MALDI-TOF): *m*/*z* (%) = 830.1 (100) [M$^+$ – H]. $C_{48}H_{62}S_6$ (831.4): calcd. C 69.34, H 7.52; found C 68.63, H 7.53.

5,5‴″-Bis(2-octyldodecyl)2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2‴″:5‴″,2⁗″:5⁗″,2‴″″-octithiophene (33a): To a solution of **13a** (572 mg, 0.93 mmol) in 17 mL of anhydrous THF *n*BuLi (0.94 mL, 1.5 mmol) is added. The mixture is stirred for 1 h at room temperature before $CuCl_2$ (300 mg, 1.87 mmol) is added. The mixture is allowed to react overnight at room temperature. The solvent is evaporated and the residue washed successively by water, ethyl acetate and THF in order to eliminate soluble side products together with unreacted **13**. The obtained solid is dissolved in chloroform. By adding methanol product **33a** precipitates and is collected by centrifugation. Removal of the solvent gives **33a** (187 mg, 26%) as a dark-red solid. m.p. 225 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): δ = 7.15–7.14 (m, 6 H), 7.13 [d, *J*(H,H) = 3.5 Hz, 2 H], 7.12 [d, ^3J(H,H) = 3.7 Hz, 2 H], 7.07 [d, ^3J(H,H) = 4.0 Hz, 2 H], 7.06 [d, ^3J(H,H) = 3.5 Hz, 2 H], 6.67 [d, ^3J(H,H) = 3.7 Hz, 2 H, 4-H, 4‴″″-H], 2.80 [d, ^3J(H,H) = 6.5 Hz, 4 H, CH_2, thiophene], 1.72 (br. s, 2 H, CH-CH_2, thiophene), 1.36 (m, 64 H, CH_2 alkyl), 0.95 [t, ^3J(H,H) = 6.9 Hz, 12 H, CH_3] ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 466 nm (53000 mol^{-1} dm^3 cm^{-1}). MS (MALDI-TOF): *m*/*z* (%) = 1218 (100) [M$^+$]. $C_{72}H_{98}S_8$ (1218.5): calcd. C 70.88, H 8.10; found C 70.44, H 7.96.

2-Bromo-5-(2-octyldodecyl)thiophene (34a): Compound **7a** (350 mg, 0.82 mmol) is dissolved in 25 mL of chloroform, 10 mL of acetic acid and NBS (172 mg, 0.94 mmol) is slowly added. The mixture is stirred for 90 min at room temperature under light protection, washed with saturated aq. $NaHCO_3$ and extracted with chloroform. After combining the organic fractions, drying over $MgSO_4$ and removal of the solvent, the product is purified by column chromatography (SiO_2/hexane) to give **34a** as a brown oil (345 mg, 98%). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 25 °C): δ = 6.88 [d, ^3J(H,H) = 3.5 Hz, 1 H, 3-H], 6.55 [d, ^3J(H,H) = 3.5 Hz, 1 H, 4-H], 2.71 [d, ^3J(H,H) = 6.5 Hz, 2 H, CH_2, thiophene], 1.56 (br. s, 1 H, CH-CH_2, thiophene), 1.28 (m, 32 H, CH_2, alkyl), 0.90 [t, ^3J(H,H) = 6.9 Hz, 6 H, CH_3] ppm. ^{13}C NMR (400 MHz, $C_2D_2Cl_4$, 25 °C): δ = 146.3, 129.5, 125.6, 108.6, 39.8, 34.7, 33.2, 32.07, 32.05, 30.0, 29.81, 29.80, 29.78, 29.74, 29.5, 29.4, 26.6, 22.8, 14.3 ppm. $C_{24}H_{43}Br_1S_1$ (442.2): calcd. C 64.99, H 9.77; found C 64.70, H 9.63.

2-Bromo-5-eicosylthiophene (34b): Compound **7b** (1 g, 2.74 mmol) is dissolved in 25 mL of DMF and NBS (480 mg, 2.74 mmol) is added. The mixture is stirred for 5 h at room temperature under light protection, washed with saturated aq. $NaHCO_3$ and extracted with dichloromethane. After combining the organic fractions, drying over $MgSO_4$ and removal of the solvent, the product is purified by column chromatography (SiO_2/hexane) to give a off-white solid (345 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.81 [d, ^3J(H,H) = 3.5 Hz, 1 H, 3-H], 6.50 [d, ^3J(H,H) = 3.5 Hz, 1 H, 4-H], 2.71 [t, ^3J(H,H) = 7.6 Hz, 2 H, CH_2, thiophene], 1.53 (m, 2 H, CH_2-CH_2, thiophene), 1.23 (m, 34 H, CH_2, alkyl), 0.86 [t, ^3J(H,H) = 6.9 Hz, 3 H, CH_3] ppm. ^{13}C NMR (100 MHz, $C_2D_2Cl_4$, 25 °C): δ = 147.6, 129.3, 124.3, 108.5, 31.9, 31.4, 30.3, 29.67, 29.65, 29.63, 29.60, 29.5, 29.3, 29.0, 22.6, 14.0 ppm. $C_{24}H_{43}Br_1S_1$ (442.2): calcd. C 64.99, H 9.77; found C 65.32, H 9.87.

5-Bromo-5′-(2-octyldodecyl)-2,2′-bithiophene (35a): Compound **10a** (200 mg, 0.45 mmol) is dissolved in 20 mL of DMF and NBS (172 mg, 0.94 mmol) is added. The mixture is stirred for 90 min at room temperature under light protection, washed with saturated aq. $NaHCO_3$ and extracted with chloroform. After combining the organic fractions, drying over $MgSO_4$ and removal of the solvent, the product is purified by column chromatography (SiO_2/hexane) to give **35a** as yellow oil (142 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.91 [d, ^3J(H,H) = 3.7 Hz, 1 H, 3-H], 6.89 [d, ^3J(H,H) = 3.5 Hz, 1 H, 3′-H], 6.80 [d, ^3J(H,H) = 3.7 Hz, 1 H, 4-H], 6.62 [d, ^3J(H,H) = 3.5 Hz, 1 H, 4′-H], 2.69 [d, ^3J(H,H) = 6.5 Hz, 2 H, CH_2, thiophene], 1.60 (br. s, 1 H, CH-CH_2, thiophene), 1.26 (m, 32 H, CH_2, alkyl), 0.86 [t, ^3J(H,H) = 7.1 Hz, 6 H, CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 144.4, 139.5, 134.0, 130.4 125.8, 123.5, 122.9, 110.1, 39.9, 34.5, 33.2, 31.97, 31.96, 29.9, 29.71, 29.70, 29.65, 29.4, 29.3, 26.6, 22.7, 14.1 ppm. $C_{28}H_{45}BrS_2$ (524.2): calcd. C 63.97, H 8.63; found C 63.72, H 8.68.

5-Bromo-5′-eicosyl-2,2′-bithiophene (35b): Compound **9b** (300 mg, 0.67 mmol) is dissolved in 20 mL of DMF at 80 °C and NBS (119 mg, 0.67 mmol) is added. The mixture is stirred for 90 min at 80 °C under light protection, washed with saturated aq. $NaHCO_3$ and extracted with chloroform. Combining the organic fractions, drying over $MgSO_4$ and removal of the solvent gives **35b** as a white-yellow solid (311 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.97 [d, ^3J(H,H) = 3.7 Hz, 1 H, 3′-H], 6.94 [d, ^3J(H,H) = 3.5 Hz, 1 H, 3-H], 6.86 [d, ^3J(H,H) = 3.7 Hz, 1 H, 4′-H], 6.64 [d, ^3J(H,H) = 3.5 Hz, 1 H, 4-H], 2.79 [t, ^3J(H,H) = 7.7 Hz, 2 H, CH_2, thiophene], 1.67 (m, 2 H, CH_2-CH_2, thiophene), 1.32 (m, 34 H, CH_2, alkyl), 0.87 [t, ^3J(H,H) = 6.9 Hz, 3 H, CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 144.4, 139.5, 134.0, 130.4, 125.8, 123.5, 122.9, 110.1, 39.9, 34.5, 33.2, 31.97, 31.96, 29.9, 29.71, 29.70, 29.6, 29.4, 29.3, 26.6, 22.7, 14.1 ppm. $C_{28}H_{45}Br_1S_2$ (524,2): calcd. C 63.97, H 8.63; found C 63.66, H 8.70.

5-Bromo-5′′-eicosyl-2,2′:5′,2′′-terthiophene (36b): Compound **11b** (200 mg, 0.37 mmol) is dissolved in 30 mL of DMF at 80 °C and NBS (68 mg, 0.38 mmol) is added. The mixture is stirred for 14 h at 80 °C under light protection, washed with saturated aq. $NaHCO_3$ and extracted with chloroform. Combining the organic fractions, drying over $MgSO_4$ and removal of the solvent gives **36b** as a yellow solid (146 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.04–7.02 (m, 4 H, 4-H, 3′-H, 4′-H, 3′′-H), 6.95 [d, ^3J(H,H) = 3.7 Hz, 1 H, 3-H], 6.74 [d, ^3J(H,H) = 3.5 Hz, 1 H, 4-H], 2.85 [t, ^3J(H,H) = 7.4 Hz, 2 H, CH_2, thiophene], 1.67 (m, 2 H, CH_2-CH_2, thiophene), 1.32 (m, 34 H, CH_2, alkyl), 0.87 [t, ^3J(H,H) = 6.9 Hz, 3 H, CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 144.5, 138.8, 137.4, 134.4, 134.3, 130.6, 125.9, 124.5, 123.5, 123.4, 123.4, 110.7, 39.9, 34.5, 33.1, 31.93, 31.91, 29.9, 29.66, 29.65, 29.60, 29.3, 29.2, 26.6, 22.6, 14.1 ppm. $C_{28}H_{45}Br_1S_2$ (524.2): calcd. C 63.23, H 7.79; found C 63.36, H 7.52.

5-Bromo-5′′′-(2-octyldodecyl)-2,2′:5′,2′′:5′′,2′′′-quaterthiophene (37a): Compound **13a** (200 mg, 0.32 mmol) is dissolved in 40 mL of DMF. After addition of NBS (36 mg, 0.19 mmol) the resulting suspension is stirred overnight at 80 °C under light protection. The suspension is poured into water, washed with saturated aq. $NaHCO_3$ and extracted with chloroform. Combining the organic fractions, drying over $MgSO_4$ and removal of the solvent gives a yellow-brown solid (191 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.11 [d, ^3J(H,H) = 3.7 Hz, 1 H], 7.10 [d, ^3J(H,H) = 3.7 Hz, 1 H], 7.07–7.05 (m, 3 H), 7.04 [d, ^3J(H,H) = 3.7 Hz, 1 H], 6.97 [d, ^3J(H,H) = 3.7 Hz, 1 H, 4-H], 6.73 [d, ^3J(H,H) = 3.7 Hz, 1 H, 4′′′-H], 2.81 [d, ^3J(H,H) = 6.5 Hz, 2 H, CH_2, thiophene], 1.72 (br. s, 1 H, CH-CH_2, thiophene), 1.35 (m, 32 H, CH_2, alkyl), 0.95 [t, ^3J(H,H) = 6.9 Hz, 6 H, CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 144.8, 138.8, 137.7, 136.9, 135.2, 135.0, 134.5, 130.9, 125.9, 124.9, 124.7, 124.2, 124.0, 123.8, 123.7, 111.3, 40.1, 34.9, 33.6, 31.93, 31.91, 29.9, 29.66, 29.65, 29.60, 29.3, 29.2, 26.6, 22.6, 14.1 ppm. $C_{36}H_{49}Br_1S_4$ (688.2): calcd. C 62.67, H 7.16; found C 62.53, H 7.02.

5-Eicosyl-5′-(2-octyldodecyl)-2,2′-bithiophene (38ab): 2-Trimethylstannyl-5-(2-octyldodecyl)-thiophene (**8a**) (315 mg, 0.60 mmol) and 2-bromo-5-eicosylthiophene (**34b**) (264 mg, 0.60 mmol) are dissolved in 25 mL of dry DMF. $Pd(PPh_3)_4$ (15 mg, 0.012 mmol) is added and the mixture is stirred for 12 h at 93 °C. After cooling to room temperature the precipitate is separated by filtration and washed with acetone. The obtained solid is dissolved in THF, activated carbon is added and filtered off. Removal of the solvent and drying in vacuo yields **38ab** as a green-yellow microcrystalline powder (273 mg, 63%). m.p. 43 °C. ^{1}H NMR (400 MHz, $CHCl_3$, 25 °C): δ = 6.87 [d, ^3J(H,H) = 3.5 Hz, 2 H, 3-H, 3′-H], 6.61 [d, ^3J(H,H) = 3.5 Hz, 1 H, 4-H], 6.59 [d, ^3J(H,H) = 3.5 Hz, 1 H, 4′-H], 2.74 [t, ^3J(H,H) = 7.3 Hz, 2 H, CH_2, thiophene–R_{lin}], 2.75 [d, ^3J(H,H) = 6.5 Hz, 2 H, CH_2, thiophene–R_{br}] 1.66 (m, 3 H, CH_2-CH_2, thiophene–R_{lin} and CH-CH_2, thiophene–R_{br}), 1.28 (m, 66 H, CH_2, alkyl), 0.87 [t, ^3J(H,H) = 6.9 Hz, 9 H, CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 144.6, 143.2, 135.5, 135.3, 125.6, 124.5, 122.5, 122.4, 39.9, 34.5, 33.1, 31.9, 31.3, 30.2, 29.9, 29.7, 29.6, 29.6, 29.5, 29.35, 29.3, 29.0, 26.6, 22.6, 14.0 ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 317 nm (15400 $mol^{-1}\,dm^3\,cm^{-1}$). MS (MALDI-TOF): *m*/*z* = 727 [M$^+$]. $C_{48}H_{86}S_2$ (726.6): calcd. C 79.26, H 11.92; found C 79.35, H 11.89.

5-Eicosyl-5′′-(2-octyldodecyl)-2,2′:5′,2′′-terthiophene (39ab): To a solution of **11b** (1.10 g, 2.08 mmol) in THF (20 mL) *n*BuLi (1.68 mL, 2.72 mmol) is added dropwise. After stirring the solution for 1 h, 1-bromo-2-octyldodecane (**6a**) (975 mg, 2.7 mmol) in THF (10 mL) is added to monolithiated **11b**. The mixture is stirred for 29 h at 70 °C, cooled to room temperature, poured into water and extracted with chloroform. After combining the organic fractions, drying over $MgSO_4$ and removal of the solvent, the product is purified by column chromatography (SiO_2/hexane) to give **39ab** (484 mg, 29%) as a yellow microcrystalline powder. R_f = 0.34 (hexane); m.p. 60 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.94 (s, 2 H, 3′-H, 4′-H), 6.94 [d, ^3J(H,H) = 3.5 Hz, 1 H, 3-H or 3′′-H], 6.93 [d, ^3J(H,H) = 3.5 Hz, 1 H, 3-H or 3′′-H], 6.65 [d, ^3J(H,H) = 3.5 Hz, 1 H, 4-H], 6.62 [d, ^3J(H,H) = 3.5 Hz, 1 H, 4′′-H], 2.78 [t, ^3J(H,H) = 7.4 Hz, 2 H, CH_2, thiophene–R_{lin}], 2.71 [d, ^3J(H,H) = 6.5 Hz, 2 H, CH_2, thiophene–R_{br}], 1.69–1.65 (m, 3 H, CH_2-CH_2, thiophene–R_{lin} and CH-CH_2, thiophene–R_{br}), 1.28 (m, 66 H, CH_2, alkyl), 0.86 [t, ^3J(H,H) = 6.9 Hz, 9 H, CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 143.9, 134.8, 134.6, 125.8, 124.7, 123.4, 123.3, 123.1, 123.0, 39.95, 36.2, 34.5, 33.1, 31.93, 31.91, 31.5, 30.1, 29.9, 29.66, 29.65, 29.60, 29.35, 29.32, 29.0, 26.61, 22.6, 14.1 ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 373 nm (24700 $mol^{-1}\,dm^3\,cm^{-1}$). MS (MALDI-TOF): *m*/*z* = 808 [M$^+$]. $C_{52}H_{88}S_3$ (808.6): calcd. C 77.16, H 10.96; found C 76.90, H 11.07.

5-Eicosyl-5′′′-(2-octyldodecyl)-2,2′:5′,2′′:5′′,2′′′-quaterthiophene (40ab): Compound **12b** (196 mg, 0.28 mmol) and compound **34a** (125 mg, 0.28 mmol) are dissolved in 10 mL of dry DMF. $Pd(PPh_3)_4$ (16 mg, 0.014 mmol) is added and the solution is stirred overnight at 93 °C. After cooling to room temperature the reaction mixture is poured into water and extracted with chloroform. After combining the chloroform fractions, drying over $MgSO_4$ and removal of the solvent, the product is purified by column chromatography (SiO_2/hexane/CH_2Cl_2, 5:3) to give **40ab** (22 mg, 9%) as a bright yellow powder. R_f = 0.85 (hexane/CH_2Cl_2, 5:3); m.p. 86 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.01 [d, ^3J(H,H) = 3.7 Hz, 2 H, 3-H, 3′′′-H], 6.97–6.94 (m, 4 H, 3′-H, 4′-H, 3′′-H, 4′′-H), 6.66 [d, ^3J(H,H) = 3.7 Hz, 1 H, 4-H], 6.63 [d, ^3J(H,H) = 3.7 Hz, 1 H, 4′′′-H], 2.76 [t, ^3J(H,H) = 7.7 Hz, 2 H, CH_2, thiophene–R_{lin}], 2.69 [d, ^3J(H,H) = 6.5 Hz, 2 H, CH_2, thiophene–R_{br}], 1.64 (m, 3 H, CH_2-CH_2, thiophene–R_{lin} and CH_2-CH_2, thiophene–R_{br}), 1.27 (m, 66 H, CH_2, alkyl), 0.86 [t, ^3J(H,H) = 6.9 Hz, 9 H, CH_3] ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 409 nm (32100 $mol^{-1}\,dm^3\,cm^{-1}$). MS (MALDI-TOF): *m*/*z* = 890 [M$^+$]. $C_{56}H_{90}S_4$ (891.6): calcd. C 75.44, H 10.17; found C 75.25, H 10.22.

5-Eicosyl-5′′′-(2-octyldodecyl)-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′-quinquethiophene (41ab): Compound **12a** (175 mg, 0.25 mmol) and compound **35b** (132 mg, 0.25 mmol) are dissolved in 25 mL of dry THF/DMF (1:1). $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) is added and the mixture is stirred for 14 h at 80 °C. After cooling to room temperature the precipitate is separated by centrifugation and washed with acetone. The obtained solid is dissolved in tetrachloroethane, activated carbon is added and filtered off. Removal of the solvent gives **41ab** (84 mg, 34%) as a yellow-brown solid. m.p. 121 °C. ^{1}H NMR (400 MHz, $C_2H_2Cl_4$, 100 °C): δ = 7.11–710 (m, 4 H), 7.08–7.04 (m, 4 H), 6.75 [d, ^3J(H,H) = 3.7 Hz, 1 H, 4-H], 6.73 [d, ^3J(H,H) = 3.7 Hz, 1 H, 4′′′-H], 2.76 [t, ^3J(H,H) = 7.7 Hz, 2 H, CH_2, thiophene–R_{lin}], 2.69 [d, ^3J(H,H) = 6.5 Hz, 2 H, CH_2, thiophene–R_{br}], 1.64 (m, 3 H, CH_2-CH_2, thiophene–R_{lin} and CH_2-CH_2, thiophene–R_{br}), 1.27 (m, 66 H, CH_2 alkyl), 0.86 [t, ^3J(H,H) = 6.9 Hz, 9 H, CH_3] ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 428 nm (34500 $mol^{-1}\,dm^3\,cm^{-1}$). MS (MALDI-TOF): *m*/*z* = 973 [M$^+$]. $C_{60}H_{92}S_5$ (972.6): calcd. C 74.01, H 9.52; found C 3.95, H 9.35.

5-Eicosyl-5′′′-(2-octyldodecyl)-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′-sexithiophene (42ab): Compound **10b** (67 mg, 0.11 mmol) and compound **37a** (76 mg, 0.11 mmol) are dissolved in 10 mL of dry THF/DMF (1:2). $Pd(PPh_3)_4$ (6 mg, 0.005 mmol) is added and the mixture is stirred for 6 h at 94 °C. After cooling

to room temperature the precipitate is separated by centrifugation and washed with acetone and ethyl acetate. The obtained solid is dissolved in tetrachloroethane, activated carbon is added and filtered off. Removal of the solvent gives **42ab** (48 mg, 42%) as a red-brown solid. m.p. 181 °C. ^{1}H NMR (400 MHz, $C_2H_2Cl_4$, 100 °C): δ = 7.15–7.11 (m, 6 H), 7.07–7.04 (m, 4 H), 6.75 [d, ^3J(H,H) = 3.7 Hz, 1 H, 4-H], 6.73 [d, ^3J(H,H) = 3.7 Hz, 1 H, 4′′′′′-H], 2.86 [t, ^3J(H,H) = 7.7 Hz, 2 H, CH_2, thiophene–R_{lin}], 2.81 [d, ^3J(H,H) = 6.5 Hz, 2 H, CH_2, thiophene–R_{br}], 1.64 (m, 3 H, CH_2-CH_2, thiophene–R_{lin} and CH_2-CH_2, thiophene–R_{br}), 1.27 (m, 66 H, CH_2, alkyl), 0.86 [t, ^3J(H,H) = 6.9 Hz, 9 H, CH_3] ppm. UV/Vis ($C_2H_2Cl_4$): λ_{max} (ε) = 448 nm (38500 mol^{-1} dm^3 cm^{-1}). MS (MALDI-TOF): m/z = 1054 [M$^+$].

Supporting Information (see also the footnote on the first page of this article): Additional UV/Vis, fluorescence, DSC data and POM and AFM images of some oligothiophenes.

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