

## Fine Tuning of Solid-State Properties of Septithiophenes by Tailoring the Substituents

Andreas Kreyes,<sup>†</sup> Stefan Ellinger,<sup>†</sup> Katharina Landfester,<sup>†,‡</sup> Matthieu Defaux,<sup>§,⊥</sup>  
Dimitri A. Ivanov,<sup>§</sup> Andreas Elschner,<sup>||</sup> Timo Meyer-Friedrichsen,<sup>||</sup> and Ulrich Ziener<sup>\*,†</sup>

<sup>†</sup>University of Ulm, Institute of Organic Chemistry III, Albert-Einstein-Allee 11, D-89081 Ulm, Germany,  
<sup>‡</sup>Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany, <sup>§</sup>Institut de  
Sciences des Matériaux de Mulhouse (CNRS LRC 7228), 15 rue Jean Starcky, B.P. 2488, 68057 Mulhouse  
Cedex, France, <sup>||</sup>H.C. Starck Clevios GmbH, Chemiepark, Geb.B202, D-51368 Leverkusen, Germany.

<sup>⊥</sup>Present address: DWI an der RWTH Aachen, Pauwelsstrasse 8, D-52056 Aachen, Germany.

Received November 11, 2009

A series of five  $\alpha,\omega$ -substituted septithiophenes, which differ in the geometry of the peripheral branched alkyl substituents, is presented. The position of the branching point has a substantial effect on the solubility and melting points of the oligomers. In contrast, organic field-effect transistors (OFETs) that have been prepared from those materials via vapor deposition show all mobilities in the same range (0.18–0.018 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>). The relative unsusceptibility of the mobilities on the molecular structure is attributed to the fact that all septithiophenes form smectic-like structures at room temperature under solid-state conditions, as revealed by temperature-dependent X-ray diffraction. Furthermore, four of the five oligomers exhibit thermotropic liquid crystalline smectic C phases. Strong interactions between the thiophene cores are assumed as driving forces for those structural features. Thus, tailoring the peripheral substituents makes it possible to fine-tune the thermal and solubility properties and, to a certain extent, the ordering under solid-state conditions. The ordering and the electrical properties are mainly dominated by the length of the core of the oligothiophenes.

### Introduction

Organic semiconductors that contain conjugated  $\pi$ -electron systems have been intensively investigated as active materials in electronic applications such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and photovoltaic cells (PVCs).<sup>1–5</sup> The possibility of large area processing from solution on flexible substrates such as polymer foils makes these materials particularly suitable for new low-cost, lightweight applications as electronic papers, radio-frequency identification (RFID) tags, or flexible displays.<sup>6,7</sup> One major advantage of organic semiconductors is the possibility to design the materials on the level of molecular structure to optimize their properties for the desired application.

One very promising class of materials for use in OFETs is based on  $\alpha,\omega$ -substituted oligothiophenes. A huge spectrum

of different derivatives has been synthesized and applied in transistors so far,<sup>8–19</sup> whereas only a few oligomers with more than six thiophene rings are reported.<sup>20–25</sup> Molecular ordering is the key factor for the performance of such devices. The major problems of usually obtained

\*Author to whom correspondence should be addressed. E-mail: Ulrich.Ziener@uni-ulm.de.

- (1) Shimizu, Y.; Oikawa, K.; Nakayama, K. I.; Guillon, D. *J. Mater. Chem.* **2007**, *17*, 4223–4229.
- (2) Roncali, J.; Leriche, P.; Cravino, A. *Adv. Mater.* **2007**, *19*, 2045–2060.
- (3) Sirringhaus, H. *Adv. Mater.* **2005**, *17*, 2411–2425.
- (4) Barbarella, G.; Melucci, M.; Sotgiu, G. *Adv. Mater.* **2005**, *17*, 1581–1593.
- (5) Fichou, D. *J. Mater. Chem.* **2000**, *10*, 571–588.
- (6) Gundlach, D. J. *Nature Mater.* **2007**, *6*, 173–174.
- (7) Berggren, M.; Nilsson, D.; Robinson, N. D. *Nature Mater.* **2007**, *6*, 3–5.
- (8) Meng, Q.; Sun, X.-H.; Lu, Z.; Xia, P.-F.; Shi, Z.; Chen, D.; Wong, M.; Wakim, S.; Lu, J.; Baribeau, J.-M.; Tao, Y. *Chem.–Eur. J.* **2009**, *15*, 3474–3487.

- (9) Melucci, M.; Favaretto, L.; Bettini, C.; Gazzano, M.; Camaioni, N.; Maccagnani, P.; Ostoja, P.; Monari, M.; Barbarella, G. *Chem.–Eur. J.* **2007**, *13*, 10046–10054.
- (10) Zhang, F.; Funahashi, M.; Tamaoki, N. *Appl. Phys. Lett.* **2007**, *91*.
- (11) Funahashi, M.; Zhang, F.; Tamaoki, N. *Adv. Mater.* **2007**, *19*, 353–358.
- (12) Ponomarenko, S. A.; Tatarinova, E. A.; Muzafarov, A. M.; Kirchmeyer, S.; Brassat, L.; Mourran, A.; Moeller, M.; Setayesh, S.; De Leeuw, D. *Chem. Mater.* **2006**, *18*, 4101–4108.
- (13) Van Breemen, A. J. J. M.; Herwig, P. T.; Chlon, C. H. T.; Sweelssen, J.; Schoo, H. F. M.; Setayesh, S.; Hardeman, W. M.; Martin, C. A.; De Leeuw, D. M.; Valetton, J. J. P.; Bastiaansen, C. W. M.; Broer, D. J.; Popa-Merticaru, A. R.; Meskers, S. C. J. *J. Am. Chem. Soc.* **2006**, *128*, 2336–2345.
- (14) Oikawa, K.; Monobe, H.; Takahashi, J.; Tsuchiya, K.; Heinrich, B.; Guillon, D.; Shimizu, Y. *Chem. Commun.* **2005**, 5337–5339.
- (15) Funahashi, M.; Hanna, J. I. *Adv. Mater.* **2005**, *17*, 594–598.
- (16) Facchetti, A.; Musherush, M.; Yoon, M. H.; Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 13859–13874.
- (17) Murphy, A. R.; Fréchet, J. M. J.; Chang, P.; Lee, J.; Subramanian, V. *J. Am. Chem. Soc.* **2004**, *126*, 1596–1597.
- (18) Afzali, A.; Breen, T. L.; Kagan, C. R. *Chem. Mater.* **2002**, *14*, 1742–1746.
- (19) Funahashi, M.; Hanna, J. I. *Phys. Rev. Lett.* **1997**, *78*, 2184–2187.
- (20) Ellinger, S.; Kreyes, A.; Ziener, U.; Hoffmann-Richter, C.; Landfester, K.; Möller, M. *Eur. J. Org. Chem.* **2007**, 5686–5702.
- (21) Ellinger, S.; Ziener, U.; Thewalt, U.; Landfester, K.; Möller, M. *Chem. Mater.* **2007**, *19*, 1070–1075.
- (22) DeLongchamp, D. M.; Jung, Y.; Fischer, D. A.; Lin, E. K.; Chang, P.; Subramanian, V.; Murphy, A. R.; Fréchet, J. M. J. *J. Phys. Chem. B* **2006**, *110*, 10645–10650.

polycrystalline films are structural defects and grain boundaries, which act as traps for the charge carriers and, therefore, considerably reduce the obtained mobilities. Liquid crystalline (LC) compounds turn out to be adequate materials to avoid these restrictions. Their capability in self-healing structural defects and the formation of large structurally homogeneous domains is well-known. Smectic phases are of special interest. Here, anisotropic, two-dimensional charge transport through the layers occurs, which is superior to one-dimensional transport in wirelike columnar LC phases.<sup>26</sup> The higher the degree of order in the smectic layer, the higher the obtained mobilities.<sup>14</sup> Many examples of  $\alpha,\omega$ -substituted oligothiophenes forming miscellaneous LC phases are described in the literature.<sup>9,20,27–31</sup> Such mesophases can result from a combination of the rigid rodlike, order-inducing aromatic core and one or two flexible, peripheral substituents, which cause disorder. The thermal behavior (e.g., transition temperatures and the range of mesophase of the oligomers) is strongly affected by the balance between core length and substituent length and the structure of the side chains,<sup>32–34</sup> respectively. Previously, we have described a variety of  $\alpha,\omega$ -oligothiophenes with linear substituents and a branched substituent, respectively.<sup>20,21</sup> The presence of the branching in the side chain has a strong effect on solid-state (and solution) properties such as melting point, ordering, and LC behavior of the oligomers, which are crucial for their application in, e.g., OFETs. To our knowledge, there has been no systematic investigation on how the position of the branching influences, especially, the aforementioned solid-state properties. In a very recent publication, the effect of trimethylsilyl groups on the solid-state ordering and, thus, OFET mobilities in single crystals of oligothiophenes up to 5T could be shown.<sup>35</sup>

Here, we report on a series of five septithiophenes, with branched substituents in the  $\alpha,\omega$ -position, four of which

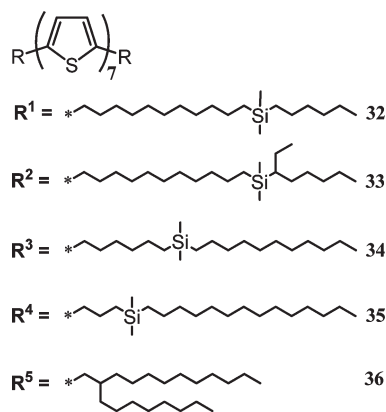


Figure 1. Septithiophenes 32–36 with varying substituents.

are described for the first time (see Figure 1). All the substituents consist of almost the same number of chain atoms, for the reason of comparison. Our approach is to determine the influence on solubility and solid-state properties by a subtle tailoring of the branched substituents. The use of alkyl silanes provides the possibility to design the substituents' structure, in terms of distance of the branching point from the core and length of the branches, as desired. Oligomers 32, 34, and 35 carry isomeric substituents that only differ in the position of the branching point. The synthesis was performed with the well-established strategy to use a protected diketone precursor, which preserves solubility until the very last reaction step and, therefore, simplifies purification.<sup>20,21</sup> The influence of the structure of the substituents on the solid-state properties was studied by differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD). Finally, a series of OFETs was fabricated from compounds 32–35, and the previously published 2-octyldodecyl-disubstituted septithiophene (36)<sup>21</sup> by evaporation deposition on different dielectrics.

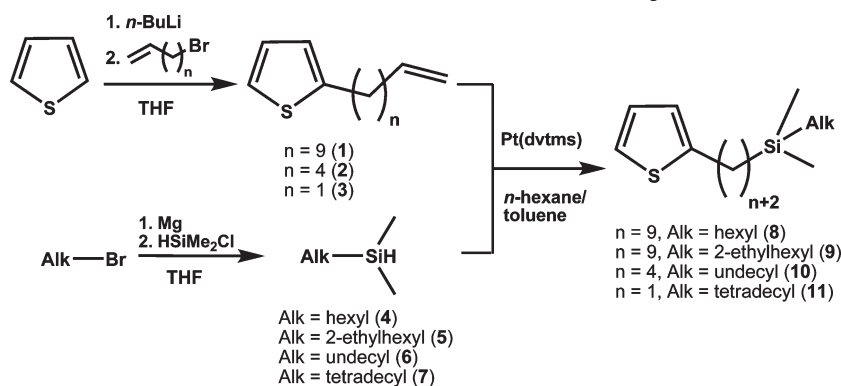
## Results and Discussion

**Synthesis.** The synthesis of the  $\alpha,\omega$ -substituted septithiophenes 32–35 can be divided into three major parts. The first one consists of the attachment of the substituents to thiophene, as shown in Scheme 1. In the second part, soluble septithiophene precursors are prepared by a series of Stille-type coupling reactions (Scheme 2), followed by deprotection of these precursors and subsequent ring closure to the final septithiophenes in the third part (Scheme 3).

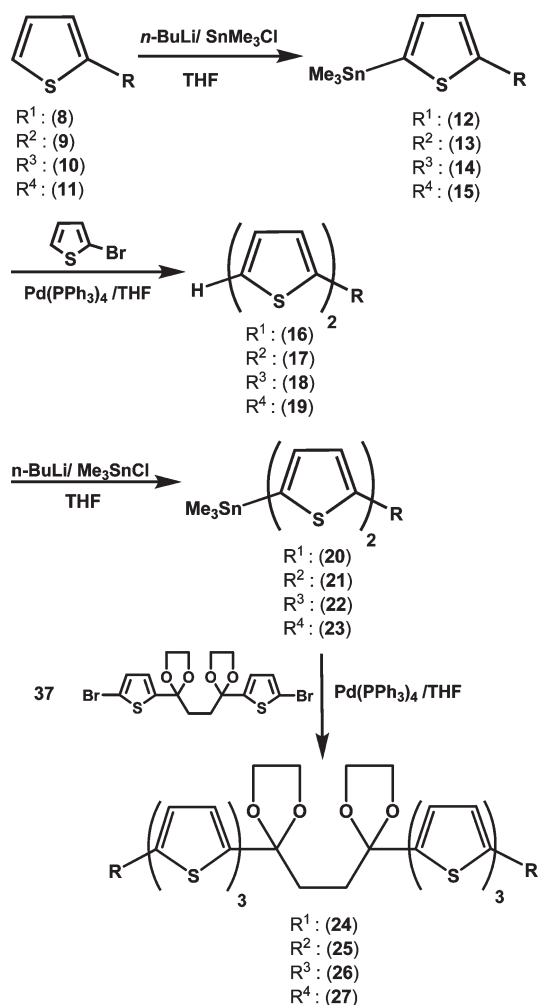
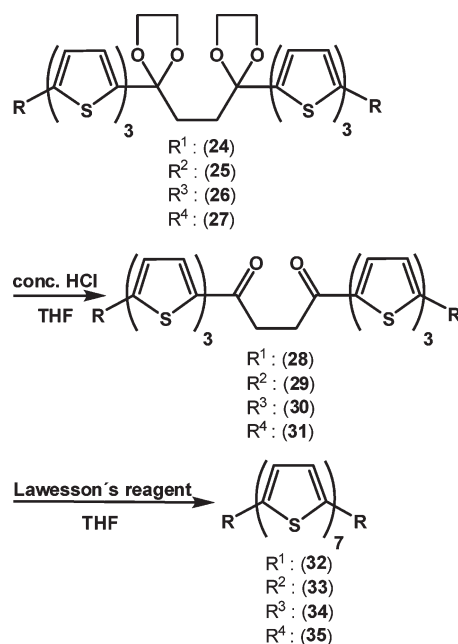
The synthetic route starts with the introduction of the different alkyl substituents to thiophene (Scheme 1). Therefore, thiophene was first lithiated with *n*-BuLi and then monoalkenylated with 11-bromo-1-undecene, 6-bromo-1-hexene and allylbromide, respectively. These monoalkenylated thiophenes (1–3) were then converted to the desired substituted thiophenes (8–11) via hydrosilylation reaction using Karstedt catalyst (1,3-divinyl-1,1,3,3-tetramethyldisiloxaneplatinum(0) (Pt(dvtms))) with silanes 4–7. The latter were synthesized by Grignard

- (23) Henze, O.; Feast, W. J.; Gardebien, F.; Jonkheijm, P.; Lazzaroni, R.; Leclère, P.; Meijer, E. W.; Schenning, A. P. H. J. *J. Am. Chem. Soc.* **2006**, *128*, 5923–5929.
- (24) Hempenius, M. A.; Langeveld-Voss, B. M. W.; Van Haare, J. A. E. H.; Janssen, R. A. J.; Sheiko, S. S.; Spatz, J. P.; Möller, M.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 2798–2804.
- (25) Hajlaoui, R.; Fichou, D.; Horowitz, G.; Nessakh, B.; Constant, M.; Garnier, F. *Adv. Mater.* **1997**, *9*, 557–561.
- (26) Oikawa, K.; Monobe, H.; Nakayama, K. I.; Kimoto, T.; Tsuchiya, K.; Heinrich, B.; Guillon, D.; Shimizu, Y.; Yokoyama, M. *Adv. Mater.* **2007**, *19*, 1864–1868.
- (27) Yasuda, T.; Ooi, H.; Morita, J.; Akama, Y.; Minoura, K.; Funahashi, M.; Shimomura, T.; Kato, T. *Adv. Funct. Mater.* **2009**, *19*, 411–419.
- (28) Lengyel, O.; Hardeman, W. M.; Wondergein, H. J.; De Leenw, D. M.; Van Breemen, A. J. J. M.; Resel, R. *Adv. Mater.* **2006**, *18*, 896–899.
- (29) Wada, H.; Taguchi, T.; Goto, M.; Kambayashi, T.; Mori, T.; Ishikawa, K.; Takezoe, H. *Chem. Lett.* **2006**, *35*, 280–281.
- (30) Ponomarenko, S.; Kirchmeyer, S. *J. Mater. Chem.* **2003**, *13*, 197–202.
- (31) Azumi, R.; Götz, G.; Bäuerle, P. *Synth. Met.* **1999**, *101*, 544–545.
- (32) Leroy, J.; Boucher, N.; Sergeyev, S.; Sferrazza, M.; Geerts, Y. H. *Eur. J. Org. Chem.* **2007**, 1256–1261.
- (33) Janssen, P. G. A.; Pouderoijen, M.; Van Breemen, A. J. J. M.; Herwig, P. T.; Koeckelberghs, G.; Popa-Merticaru, A. R.; Meskers, S. C. J.; Valetton, J. J. P.; Meijer, E. W.; Schenning, A. P. H. J. *J. Mater. Chem.* **2006**, *16*, 4335–4342.
- (34) Yasuda, T.; Kishimoto, K.; Kato, T. *Chem. Commun.* **2006**, 3399–3401.
- (35) Reese, C.; Roberts, M. E.; Parkin, S. R.; Bao, Z. *Adv. Mater.* **2009**, *21*, 3678–3681.

Scheme 1. Introduction of the Substituents to Thiophene



Scheme 2. Stille-Type Coupling Reactions to the Soluble Septithiophene Precursors

Scheme 3. Deprotection of the Precursors and Ring Closure to the Final  $\alpha,\omega$ -Substituted Septithiophenes

coupling reactions, according to a literature procedure beforehand.<sup>36</sup> Alkylated thiophenes **8–11** were then lithiated at the remaining free  $\alpha$ -position with *n*-BuLi, stannylated by trimethyltin chloride, and then coupled with 2-bromothiophene by a Stille-type reaction, using tetrakis(triphenylphosphane)palladium(0) as a catalyst, to obtain the alkylated bithiophenes **16–19**

(see Scheme 2). After repeated lithiation and stannylation, bithiophenes **20–23** were then converted to the septithiophene precursors (**24–27**), which show comparably high solubility because the  $\pi$ -conjugation is still interrupted (Scheme 2). In the next step, the ketal groups are removed by treatment with concentrated hydrochloric acid in THF. This results in the formation of the 1,4-diketones **28–31**, which represent a synthon for thiophene (see Scheme 3). Although these diketones show less solubility, compared to the diketal precursors, they still can be converted easily to the corresponding  $\alpha,\omega$ -substituted septithiophenes **32–35** with Lawesson's reagent, using THF as a solvent.

**Thermal Properties.** The thermal behavior of septithiophenes **32–35** was investigated by DSC, POM, and temperature-dependent XRD. The presence of LC phases of the conducting oligomers is especially interesting, because it allows the oligomers in OFET devices to be aligned, resulting in defect-free films, which are key factors for charge transport.

(36) Suzuki, T.; Lo, P. Y. *J. Organomet. Chem.* **1990**, *391*, 19–25.

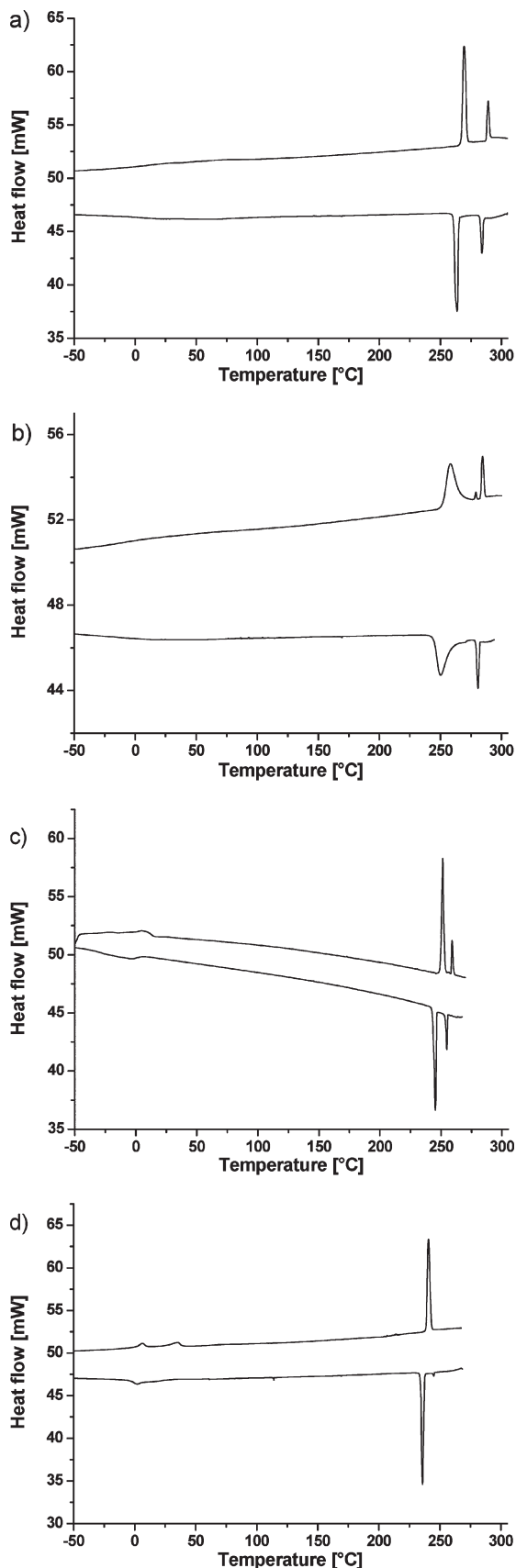


Figure 2. DSC thermograms of (a) **32**, (b) **33**, (c) **34**, and (d) **35**.

Among the described septithiophenes, oligomers **32**, **33**, and **34**, where the branching unit is located rather far away from the aromatic core, show similar DSC thermograms

Table 1. Transition Temperatures of the Septithiophenes with Different Substituents

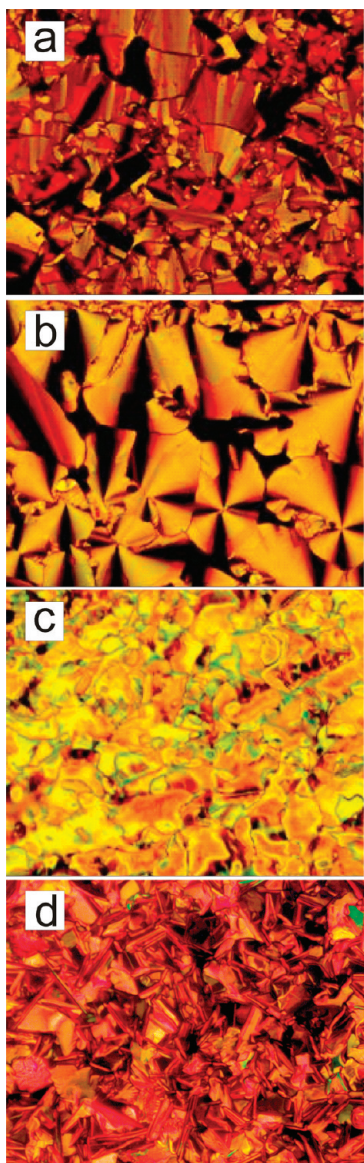
| R-7T-R                                                            | transition temperatures [°C] <sup>a</sup>                                        |
|-------------------------------------------------------------------|----------------------------------------------------------------------------------|
| <b>32</b>                                                         | C 270 (25), LC 290 (8), I                                                        |
| <b>33</b>                                                         | C 258 (16), LC 285 (4), I                                                        |
| <b>34</b>                                                         | C 5 (15), C 252 (27), LC 260 (5), I                                              |
| <b>35</b>                                                         | C 6 (4), C 35 (6), C 241 (38), I                                                 |
| <b>36</b> (2-octyldodecyl) <sup>21</sup><br>eicosyl <sup>20</sup> | C 65 (9), C 166, LC 171 (39 for both transitions), I<br>C 99 (59), C 295 (62), I |

<sup>a</sup> Values in parentheses are the transition enthalpies  $\Delta H$  (given in terms of kJ/mol). Legend: C, crystalline phase; LC, liquid crystalline phase; and I, isotropic phase.

(cf. Figure 2). In all three cases, two high-temperature transitions occur, which are summarized in Table 1.

Compound **32** exhibits the highest transition temperatures, at 270 and 290 °C, respectively. For **33** with the additional branching in the ethylhexyl substituent, both transitions appear at lower temperatures, presumably because of an increased disturbance of the  $\pi$ - $\pi$ -interactions of the thiophene cores, which is expected to dominate the intermolecular cohesive forces in long oligothiophenes. In the case of **34**, where the branching is shifted closer to the aromatic core, the isotropization temperature is decreased by 30 and 25 K, compared to that for **32** and **33**, respectively. In addition, the temperature range between the two transitions is considerably reduced to only 8 K. Moreover, a new broad transition is observed at 5 °C. The transition enthalpy ( $\Delta H$ ) values give further information about the nature of the phases. Upon cooling from the isotropic melt, all the three compounds show similar values for the first transition, from 4 to 8 kJ mol<sup>-1</sup>, and are much lower than the corresponding  $\Delta H$  of the next transition (see Table 1). This is interpreted as a transition from a LC phase to a crystalline phase. Optical micrographs of **32**–**34** were taken in the temperature range between the two transitions upon cooling from the isotropic melt. Typical textures of smectic LC phases were found as can be seen in Figure 3a–c. In addition, shearing experiments were conducted which revealed fluidlike mechanical properties of the oligomers. By cooling below the lower transition, the texture changes again and the fluidlike properties are lost. This shows indeed that the low-temperature phases are solid.

Septithiophene **35** shows a remarkable change in its thermal behavior, compared to the other oligomers. Although the isotropization temperature is reduced once more to 241 °C, which is attributed to the branching point being even closer to the aromatic core than in **34**, two weak low-temperature transitions at 6 and 35 °C appear. Even more important are the measured transition enthalpies. In contrast to compounds **32**–**34**, the  $\Delta H$  value of the high-temperature transition is significantly higher (38 kJ mol<sup>-1</sup>). In this case the presence of an LC phase is not assumed but only the existence of crystalline phases. This assumption is consistent with observations from a previously published (linear) eicosyl disubstituted septithiophene (also see Table 1).<sup>20</sup> Here, a very similar DSC trace was obtained with one low-temperature and one high-temperature transition and both enthalpies being



**Figure 3.** Polarized optical micrographs of oligomers: (a) **32** at 282 °C, (b) **33** at 273 °C, (c) **34** at 253 °C, and (d) **35** at 231 °C.

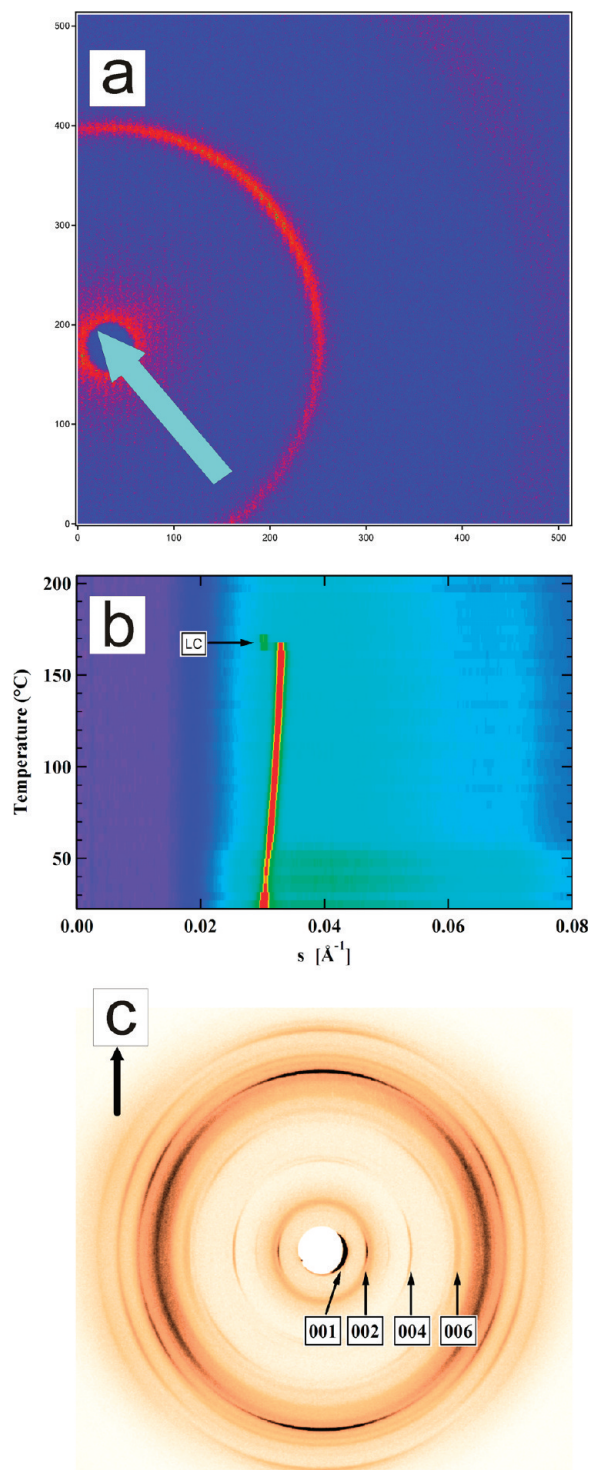
very high, where also no LC phase could be found. POM was used to visualize the different phases of **35**. Upon cooling from the melt, small needlelike crystalline domains form, but they neither fuse during growth nor do they show fluidlike behavior that is similar to that observed for the other septithiophenes (Figure 3d). DSC and POM lead to the conclusion that **35** forms a second, less-ordered crystalline phase instead of an LC phase. For the already described oligomer **36** with the 2-octyldodecyl substituents exhibiting the branching point also close to the thiophene core,<sup>20</sup> the tendency of lowering the transition temperatures and narrowing of the LC phase temperature range is continued and becomes even more pronounced. The temperature range is too narrow to resolve the single transitions and determine the corresponding enthalpies, but it can be seen qualitatively from the DSC thermogram that the second transition to the isotropic phase is much smaller than the melting transition, in agreement with the observations for **32–34**.

Apparently, not only the position of the branching point but also the length of the branches has a crucial effect on the presence of LC phases. Based on the texture of the POM of **36**, the LC phase may be assigned to a nematic phase.<sup>20</sup>

However, neither DSC nor POM alone can provide sufficient information to identify with certainty the type of the LC phase. Therefore, temperature-dependent small- and wide-angle X-ray scattering measurements were performed on silane-substituted septithiophenes **32–35** that were preliminarily oriented by extrusion. At room temperature, the X-ray patterns of extruded fibers of **32–35** exhibit crystalline phases in which the longest spacing (*c*-parameter) is oriented in the direction perpendicular to the fiber axis. The X-ray results obtained on these systems are exemplified for compound **36** in Figure 4. At room temperature in the domain of the small-angle X-ray scattering (SAXS), the compound displays (Figure 4a) two orders of the 001 peak, corresponding to the longest distance of 33.9 Å (cf. Table 2). The higher orders of this peak (up to 0012) are distinctly visible in the corresponding WAXS pattern (Figure 4c), which also shows sharp and nicely oriented peaks in the meridional direction (i.e., the fiber axis) and along the layer lines running parallel to the layer normal. It is noteworthy that, in this case the *hk0* peaks pertinent to the organization of the structure in the plane of the smectic layers show up on the meridian. The *c*-parameter slightly contracts upon heating, as shown in Figure 4b, and at the temperature corresponding to the melting peak in the DSC curves shows a stepwise transition to a somewhat larger spacing (Table 2), which is indicated with an arrow in Figure 4b. Within the temperature window comprised between the two high-temperature endothermic peaks in DSC, the sample exhibits a smectic-like mesophase in which the spatial correlations between the molecules of the same layer are largely lost. The isotropization point is reached at the temperature corresponding to the high-temperature peak in DSC, which is consistent with the optical observations discussed previously.

The layer thickness of the studied LC phases is, by far, smaller than the molecular length in the stretched conformation (ca. 70 Å, cf. Table 2). In principle, this could be caused either by the interdigitation of the alkyl chains of the neighboring layers or by a tilt of the molecules, with respect to the layer normal (smectic C phase). For compound **36**, the first possibility is ruled out by the analysis of the Patterson functions (not shown here) calculated for the direction of the layer normal.<sup>37</sup> In addition, the interdigitation of the alkyl chains can be also excluded, because of the bulkiness of the substituents. The general tilt angle of the long molecular axis is ~45°; however, it is possible that the tilt adopted by the rigid aromatic part is different from that of the alkyl chains (Figure 5). Corresponding smectic-like crystalline

(37) Clegg, W., *Crystal Structure Determination*; Oxford University Press: Oxford, U.K., 1998.



**Figure 4.** (a) SAXS pattern of an extruded fiber of **36**, measured at 25 °C; (b) integrated SAXS intensity of **36**, plotted as a function of temperature during a heating ramp at 10 °C min<sup>-1</sup>; and (c) WAXS pattern recorded on a fiber of **36** at 25 °C. The arrows in panels (a) and (c) indicate the fiber axis orientation. The 001 peak is partly masked by the beamstop.

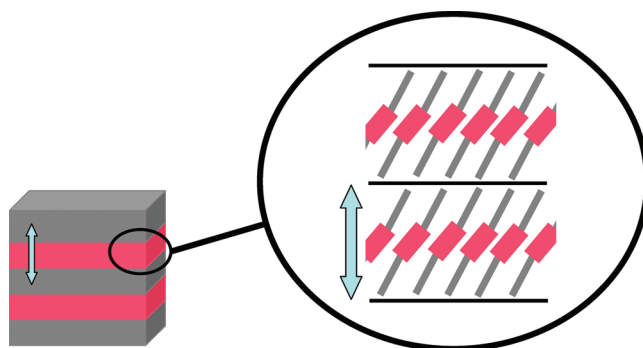
phases at room temperature (rt) and smectic-C LC phases at high temperature were also found for the other oligomers **32–34**. More studies are required to address the structural details of the compounds in the crystalline and LC phases.

**OFET Measurements.** Despite the increasing solubility by introducing branched substituents and by moving the branching point of the substituents closer to the thiophene

**Table 2.** The *c*-Parameters of the Lattice of Septithiophenes **32–36**, as Determined by SAXS/WAXS

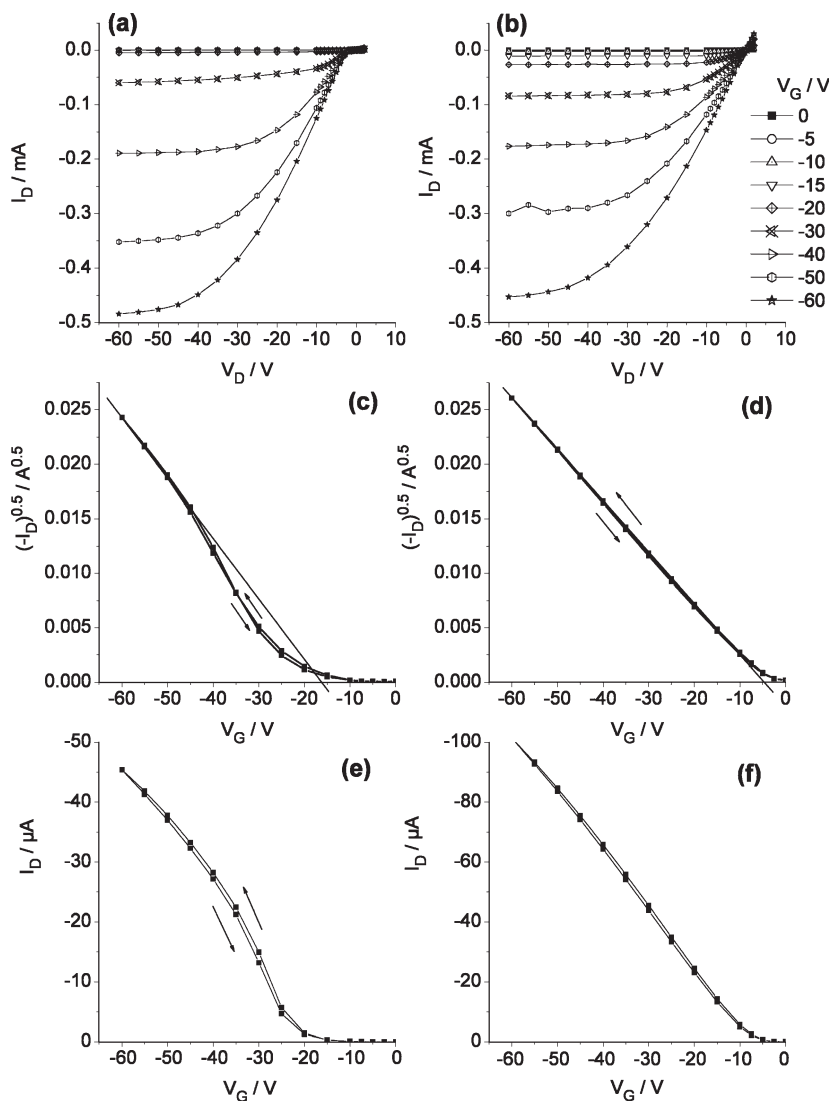
| sample    | layer thickness [Å] <sup>a</sup> | molecule length [Å] <sup>b</sup> |
|-----------|----------------------------------|----------------------------------|
| <b>32</b> | 48.2 (r.t.; C)/45.2 (272; LC)    | 71                               |
| <b>33</b> | 46.8 (r.t.; C)/46.4 (262; LC)    | 70                               |
| <b>34</b> | 49.9 (r.t.; C)/42.6 (252; LC)    | 70                               |
| <b>35</b> | 54.2 (r.t.; C)/47.0 (230; C)     | 70                               |
| <b>36</b> | 33.9 (r.t.; C)/32.9 (165; LC)    | 49                               |

<sup>a</sup> Values in parentheses are the corresponding temperatures [°C]. C: crystalline phase, LC: liquid crystalline phase. <sup>b</sup> End-to-end distance for geometry-optimized structures determined in the gas phase by mm+ force field of Hyperchem version 7.52 (Hypercube, Inc. 2002).



**Figure 5.** Structural model of the LC phases formed by compounds **32**, **33**, **34**, and **36**.

core, none of compounds **32–36** showed sufficient solubilities to fabricate OFETs from solution. Therefore, thin films of these oligomers were produced by evaporation. The materials were deposited on ODMS and PS dielectrics. Measurements directly after preparation did not show the typical OFET characteristics. At low source–drain voltage ( $V_D$ ), almost no source–drain current ( $I_D$ ) can be detected independent of the gate voltage ( $V_G$ ) (see Figure 6a). A set-on voltage of  $V_D < -2.5$  V must be applied to observe amplification. The corresponding transistor transfers do not reveal a straight line but rather an S-shaped curve, regardless of whether the data were taken in the linear regime or in the saturation regime. The curves exhibit linearity only at very high voltages. In addition, a pronounced hysteresis between forward and back  $V_G$ -sweep was observed on some transistors. Despite these observations, the curves could be evaluated to obtain the mobilities between 0.03 and 0.18 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> by fitting the high-voltage part, on–off ratios for the source–drain current around 10<sup>5</sup>, and the threshold voltages between -16 V and -40 V (see Table 3). Measurements conducted on the OFETs after storing them for 13 days at room temperature, in darkness, and in air exhibited the usual OFET characteristics, as can be seen in Figure 6b. This “annealing” caused a slight decrease of the mobilities, by a factor of ~2–3; however, at the same time, the threshold voltages were also dramatically reduced by a factor of 2–4 to a range of -4 V to -20 V. We attribute these changes to a healing of structural defects that might act as traps for free charge carriers. This is supported by the observation that the transistor transfers become linear within the entire sweep range and that the hysteresis almost vanishes (see Figures 6d and 6f). Interestingly, although the devices were



**Figure 6.** Exemplary OFET characteristics of **32** on PS: (a, c, e) after deposition and (b, d, f) after 13 days. The transistor transfers at  $V_D = -60$  V (saturation) are depicted in panels (c) and (d), and transistor transfers at  $V_D = -5$  V (linear) are depicted in panels (e) and (f).

**Table 3.** OFET Characteristics of the Septithiophenes Directly after Preparation

| sample    | dielectric <sup>a</sup> | $\mu_{\text{sat}}^{\text{cm}^2 \text{V}^{-1} \text{s}^{-1}}$ | $I_{\text{on}}/I_{\text{off}}$ | threshold voltage, $V_t$ |
|-----------|-------------------------|--------------------------------------------------------------|--------------------------------|--------------------------|
| <b>32</b> | ODMS                    | 0.094                                                        | $1.9 \times 10^5$              | -29.7                    |
|           | PS                      | 0.040                                                        | $1.0 \times 10^5$              | -16.8                    |
| <b>33</b> | ODMS                    | 0.182                                                        | $2.4 \times 10^5$              | -38.2                    |
|           | PS                      | 0.068                                                        | $7.7 \times 10^4$              | -39.8                    |
| <b>34</b> | ODMS                    | 0.161                                                        | $2.7 \times 10^5$              | -37.9                    |
|           | PS                      | 0.026                                                        | $1.1 \times 10^5$              | -15.5                    |
| <b>35</b> | ODMS                    | 0.018                                                        | $8.1 \times 10^4$              | -26.1                    |
|           | PS                      | 0.074                                                        | $9.3 \times 10^4$              | -17.7                    |
| <b>36</b> | ODMS                    | 0.064                                                        | $7.8 \times 10^4$              | -32.2                    |
|           | PS                      | 0.058                                                        | $1.7 \times 10^5$              | -25.1                    |

<sup>a</sup>Legend: ODMS, octyldimethylchlorosilane; PS, polystyrene.

not optimized but prepared under standard conditions, the mobilities (i) are among the highest values found for polycrystalline materials within this class of compounds and (ii) show hardly any influence of the structure of the substituents on the OFET mobilities within the experimental errors. The impact of the choice of the dielectric exceeds the influence of the substituents' structures. This is consistent with the

solid-state ordering determined by XRD (see above), i.e., despite the variation in the structure of the substituents, the smectic arrangement of the molecules is maintained. On the other side, by a subtle tailoring of the substituents' nature, the processing properties—such as transition temperatures and the presence and temperature range of the LC phase—can be fine-tuned. Interestingly, the mobilities of our oligomers cover almost exactly the same range as that found for single crystals of 4T and trimethylsilyl-substituted derivatives.<sup>35</sup> While the single-crystal analysis allows a precise correlation between solid-state ordering and electrical properties, the more-complicated polycrystalline system of the septithiophenes hampers a direct correlation between the mobilities and the molecular structure. Hence, contrary to the literature,<sup>35</sup> we do not regard the mobility values in the series of the septithiophenes as significantly different (see above).

## Conclusion

In summary, we have demonstrated the synthesis of carbosilane-substituted septithiophenes. The platinum-catalyzed hydrosilylation reaction provides a facile way

to synthesize a large number of substituents. Regulation of the side-chains' structures regarding the distance of the branching point from the heteroaromatic core and the length and number of the branches can be easily performed. The solid-state properties were explored by DSC, POM, and XRD. A strong impact of the structure of the substituents on the thermal properties in solid state was observed. Dimethylsilyl branching units rather far away from the core in compounds **32–34** lead to relatively high transition temperatures above 250 °C and the formation of smectic C mesophases, whereas compound **35** with the branching point closest to the thiophene core melts at the lowest temperature within the alkyl-dimethylsilyl branched oligothiophenes but does not exhibit an LC phase. This similarity to the dieicosyl-substituted septithiophene is addressed to the long C<sub>14</sub> chain behind the branching point, which causes the much lower melting point. Not only the branching distances but also the bulkiness of the side chains influences the thermal behavior. 2-Octyldodecyl-substituted compound **36** also exhibits a smectic C phase, although only in a very small range, with the lowest clearing point in the presented series of septithiophenes. OFETs fabricated from those materials yielded field-effect mobilities up to 0.18 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and on/off ratios of ~10<sup>5</sup>, which is as good as that for comparable systems reported in the literature. Here, in contrast to the thermal behavior, the substituents do not play an important role but rather the dielectric does.

Our next aim will be to synthesize long oligothiophenes that carry higher-branched carbosilane side chains. This will have a strong impact on solubility. Hence, it is expected that deposition from solution under standard conditions for the preparation of OFETs is possible. Higher solubility will also provide the synthesis of even longer oligothiophenes, which should lead to higher mobilities, because of the extended  $\pi$ -electron system. A concomitant reduction of the transition temperatures of the LC phases below 100 °C might make it possible to improve ordering in films and therefore increase the mobilities by quick annealing of the films at feasible temperatures.

### Experimental Section

**X-ray Scattering.** Room-temperature wide-angle X-ray scattering (WAXS) experiments were conducted using a rotating anode generator (Rigaku Model MicroMax-007 HF) operated at 40 kV and 30 mA. The brilliance of the focal spot ~70  $\mu\text{m}$  in diameter equals  $8 \times 10^{10}$  cps mm<sup>-2</sup>. The optical system of the device is composed of high-performance adjustable confocal mirrors (Osmic VariMax) and three pinholes. The first two pinholes define the beam size and divergence, while the third one removes the parasitic scattering. For the configuration used in this work, the X-ray spot on the sample was ~200  $\mu\text{m}$ . The data was collected in transmission using X-ray-sensitive Fuji image plates with a pixel size of 100  $\mu\text{m} \times 100 \mu\text{m}$ . The samples were sealed between two Kapton windows. The sample-to-detector distance was determined using silver behenate powder.

Temperature-resolved small- and wide-angle X-ray scattering experiments (SAXS/WAXS) were performed on the BM26 and ID02 beamlines of the European Synchrotron Radiation Facility, ESRF (Grenoble, France). The energy of the X-ray

photons was 10 keV. The scattering patterns were collected in transmission using a CCD camera for WAXS and a gas detector for SAXS. The  $s$ -axis ( $s = 2 \sin(\theta)/\lambda$ , where  $\theta$  is the Bragg angle and  $\lambda$  is the wavelength) was calibrated using several diffraction orders of silver behenate. The setup was equipped with a Linkam heating stage coupled to a liquid nitrogen cooling system. Oriented samples were prepared by extrusion using a home-built mini-extruder at 70 °C to obtain fibers of 0.7 mm in diameter.

**OFET Preparation.** Polished silicon wafers were employed as substrates for OFETs comprising a thermally grown oxide layer 300 nm thick. The substrates were cut to squares of 2.5 cm size and were cleaned in an ultrasonic bath at 60 °C filled with deionized (DI) water and 0.3% glass detergent (Mucosol). After rinsing with pure DI water and drying in a spin dryer, the substrates were left in a ultraviolet/ozone reactor for 15 min. A dielectrical layer was deposited successively. In the case of polystyrene (PS), a 1 wt % solution in xylene was spin-coated at 2000 rpm for 30 s. The predried film was baked for 3 min on a hot plate at 70 °C. In the case of octyldimethylchlorosilane (ODMS), the substrates were kept in a turned-over beaker mounted on top of a Petri dish filled with ODMS. The substrates were maintained for 1 h in a saturated ODMS atmosphere at 70 °C. The substrates were conveyed into a sublimation chamber (Leybold Univex 350) and ~25 mg of the 7T molecules were sublimed at a base pressure of  $2 \times 10^{-4}$  Pa. The sublimation temperature of the molybdenum crucible was monitored and did not exceed  $T = 350$  °C while the substrates were kept at room temperature. Following the deposition, the organic layers were not further annealed but kept at room temperature. Finally, source–drain electrodes were deposited by subliming gold through a shadow mask of interdigitating fingers creating four individual addressable OFETs on each substrate. The channel length  $L$  and width  $W$  were  $L = 100 \mu\text{m}$  and  $W = 14.8 \mu\text{m}$ , respectively.

**OFET Characterization.** OFET characteristics were acquired by combining two SMUs (Keithley 238 and 2400) addressed via a LabView program. One SMU controls the source–drain bias ( $V_D$ ) by monitoring the current ( $I_D$ ) whereas the second controls the gate voltage ( $V_G$ ) with source as the common ground.  $I_D$ – $V_D$  curves were obtained by sweeping  $V_D$  from +5 V to –60 V at various  $V_G$  settings from 0 V to –60 V. Transistor transfer curves were measured by monitoring  $I_D$  while sweeping  $V_G$  from –60 V to +10 V and back to –60 V. The drain voltage has been set at –5 V and –60 V to determine the transfer in the linear and saturation regime, respectively. The mobility ( $\mu$ ) is determined by the slope of the plot of  $I_D$  vs  $V_G$ , according to

$$I_D = \frac{WC_i}{L} \mu \left( V_G - V_T - \frac{V_D}{2} \right) V_D$$

in the linear regime with  $V_T$  the threshold voltage.<sup>38</sup>  $C_i$  is the capacitance per unit area of the insulating layer, which has been determined to be 10.8 nF cm<sup>-2</sup> and 6.84 nF cm<sup>-2</sup> for PS and ODMS, respectively. The slope of  $(I_D)^{1/2}$  vs  $V_G$  reveals the mobility in the saturation regime, as modeled in the equation

$$I_D = \frac{WC_i}{2L} \mu (V_G - V_T)^2$$

The error of determination of mobility and threshold voltage within the 4 parallel processed OFETs was < 20%.

(38) Dimitrakopoulos, C. D.; Mascaro, D. J. *IBM J. Res. Develop.* **2001**, *45*, 11–28.



**Synthesis.** *General.* *n*-Butyllithium (*n*-BuLi, 1.6 M in *n*-hexane), tetrakis(triphenylphosphane)palladium(0) (Strem), 2-bromothiophene, allylbromide, chlorodimethylsilane, 1-bromohexane, 2-ethylhexylbromide (Acros), 1-bromoundecane, 1-bromotetradecane, thiophene, trimethyltin chloride, Lawesson's reagent, and 1,3-divinyl-1,1,3,3-tetramethyldisiloxaneplatinum(0) (Pt(dvtms), 0.1 M in xylene) (all Aldrich) were purchased and used without further purification. Tetrahydrofuran (THF), toluene, and *n*-hexane were dried over sodium and stored under argon. 6-bromo-1-hexene,<sup>39</sup> 11-bromo-1-undecene,<sup>39</sup> 2-chloromethylthiophene,<sup>40</sup> hexyldimethylsilane, (2-ethylhexyl)dimethylsilane, dimethylundecylsilane,<sup>36</sup> 2-allylthiophene,<sup>41</sup> and 1,2-bis(2-(5-bromothiophen-2-yl)-1,3-dioxolan-2-yl)ethane<sup>21</sup> were prepared according to the literature. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at room temperature, if not otherwise mentioned, on a Bruker AMX 400 and Bruker AMX 500. All NMR measurements were done in CDCl<sub>3</sub> or C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, respectively, with the solvent residual peak as an internal reference [CDCl<sub>3</sub>: δ = 7.24 (<sup>1</sup>H) and δ = 77.0 (<sup>13</sup>C), C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>: δ = 6.00 (<sup>1</sup>H) ppm]. Mass spectrometry was performed on Bruker Reflex III (MALDI-TOF) and Finnigan Mat S50 (CI), respectively. Differential scanning calorimetry (DSC) was performed on a Perkin–Elmer Model DSC 7 system. Polarizing optical microscopy was done with a Zeiss Model Axioskop device equipped with a Mettler Model FP90 hot stage. UV/vis spectra were taken with a Perkin–Elmer Lambda 16 system. The elemental composition was determined with a Elementar Vario EL system.

**2-(Undec-10-enyl)thiophene (1).** To a solution of thiophene (54 mL, 672 mmol) in dry THF (65 mL), *n*-BuLi (60 mL, 96 mmol) was added dropwise at 0 °C. After stirring the solution for 20 min, 11-bromo-1-undecene (19.7 mL, 90.0 mmol) was added and the mixture was stirred under reflux for 4 d. After cooling to room temperature, water was added and the organic phase was separated. The aqueous phase was extracted with dichloromethane (3 × 50 mL). After drying the combined organic phases over anhydrous MgSO<sub>4</sub> and removal of the solvent, the product was purified by column chromatography (SiO<sub>2</sub>/hexane, *R*<sub>f</sub> = 0.51) to give **1** as colorless liquid (19.7 g, 93%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ [ppm]: 7.09 (dd, <sup>3</sup>*J*(5,4) = 5.2 Hz, <sup>4</sup>*J*(5,3) = 1.1 Hz, 1 H, 5-H), 6.90 (dd, <sup>3</sup>*J*(4,5) = 5.0 Hz, <sup>3</sup>*J*(4,3) = 3.5 Hz, 1 H, 4-H), 6.76 (dd, <sup>3</sup>*J*(3,4) = 3.5 Hz, <sup>4</sup>*J*(3,5) = 1.0 Hz, 1 H, 3-H), 5.80 (tdd, <sup>3</sup>*J*(10<sup>alk</sup>,11a<sup>alk</sup>) = 17.0 Hz, <sup>3</sup>*J*(10<sup>alk</sup>,11b<sup>alk</sup>) = 10.2 Hz, <sup>3</sup>*J*(10<sup>alk</sup>,9<sup>alk</sup>) = 6.7 Hz, 1 H, 10<sup>alk</sup>-H), 4.98 (tdd, <sup>2</sup>*J*(11a<sup>alk</sup>,11b<sup>alk</sup>) = 2.1 Hz, <sup>3</sup>*J*(11a<sup>alk</sup>,10<sup>alk</sup>) = 17.1 Hz, <sup>4</sup>*J*(11a<sup>alk</sup>,9<sup>alk</sup>) = 1.6 Hz, 1 H, 11a<sup>alk</sup>-H), 4.91 (tdd, <sup>2</sup>*J*(11b<sup>alk</sup>,11a<sup>alk</sup>) = 2.1 Hz, <sup>3</sup>*J*(11b<sup>alk</sup>,10<sup>alk</sup>) = 10.2 Hz, <sup>4</sup>*J*(11b<sup>alk</sup>,9<sup>alk</sup>) = 1.2 Hz, 1 H, 11b<sup>alk</sup>-H), 2.80 (t, <sup>3</sup>*J*(α,β) = 7.7 Hz, 2 H, α-CH<sub>2</sub>), 2.02 (m, 2 H, 9-H), 1.65 (m, 2 H, β-CH<sub>2</sub>), 1.36–1.26 (m, 12 H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ [ppm]: 145.9, 139.3, 126.7, 123.9, 122.7, 114.2, 33.9, 31.9, 30.0, 29.54, 29.51, 29.4, 29.2, 28.9. MS (CI, 100 eV) *m/z* (%): 237 (100) [M+H]<sup>+</sup>, 97 (58) [M-C<sub>10</sub>H<sub>19</sub>]<sup>+</sup>. Elemental analysis: Calcd. for C<sub>15</sub>H<sub>24</sub>S (236.42): C 76.20, H 10.23; Found: C 76.10, H 10.13.

**2-(Hex-5-enyl)thiophene (2).** To a solution of thiophene (22 mL, 275 mmol) in dry THF (20 mL), *n*-BuLi (27 mL, 43 mmol) was added dropwise at 0 °C. The reaction then was allowed to warm to room temperature and stirred for an additional 20 min. Then, 6-bromo-1-hexene (6.5 g, 40 mmol) was added and the mixture was stirred under reflux for 3 d. After

cooling to room temperature, water was added and the organic phase was separated. The aqueous phase was extracted with dichloromethane (3 × 50 mL). After drying the combined organic phases over MgSO<sub>4</sub> and evaporation of the solvent, the product was purified by column chromatography (SiO<sub>2</sub>/hexane, *R*<sub>f</sub> = 0.51) to give **2** as a colorless liquid (5.1 g, 77%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ [ppm]: 7.09 (dd, <sup>3</sup>*J*(5,4) = 5.2 Hz, <sup>4</sup>*J*(5,3) = 1.1 Hz, 1 H, 5-H), 6.90 (dd, <sup>3</sup>*J*(4,5) = 5.2 Hz, <sup>3</sup>*J*(4,3) = 3.4 Hz, 1 H, 4-H), 6.76 (dd, <sup>3</sup>*J*(3,4) = 3.4 Hz, <sup>4</sup>*J*(3,5) = 1.2 Hz, 1 H, 3-H), 5.79 (tdd, <sup>3</sup>*J*(5<sup>alk</sup>,6a<sup>alk</sup>) = 16.9 Hz, <sup>3</sup>*J*(5<sup>alk</sup>,6b<sup>alk</sup>) = 10.5 Hz, <sup>3</sup>*J*(5<sup>alk</sup>,4<sup>alk</sup>) = 6.7 Hz, 1 H, 5<sup>alk</sup>-H), 4.99 (tdd, <sup>2</sup>*J*(6a<sup>alk</sup>,6b<sup>alk</sup>) = 2.1 Hz, <sup>3</sup>*J*(6a<sup>alk</sup>,5<sup>alk</sup>) = 16.9 Hz, <sup>4</sup>*J*(6a<sup>alk</sup>,4<sup>alk</sup>) = 1.1 Hz, 1 H, 6a<sup>alk</sup>-H), 4.93 (tdd, <sup>2</sup>*J*(6b<sup>alk</sup>,6a<sup>alk</sup>) = 2.1 Hz, <sup>3</sup>*J*(6b<sup>alk</sup>,5<sup>alk</sup>) = 10.4 Hz, <sup>4</sup>*J*(6b<sup>alk</sup>,4<sup>alk</sup>) = 1.1 Hz, 1 H, 6b<sup>alk</sup>-H), 2.82 (t, <sup>3</sup>*J*(α,β) = 7.6 Hz, 2 H, α-CH<sub>2</sub>), 2.07 (m, 2 H, 4<sup>alk</sup>-H), 1.68 (m, 2 H, β-CH<sub>2</sub>), 1.45 (m, 2 H, 3<sup>alk</sup>-H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ [ppm]: 145.6, 138.7, 126.7, 124.0, 122.8, 114.5, 33.5, 31.2, 29.8, 28.4. MS (CI, 100 eV) *m/z* (%): 167 (40) [M+H]<sup>+</sup>, 125 (18) [M-C<sub>3</sub>H<sub>5</sub>]<sup>+</sup>, 97 (100) [M-C<sub>5</sub>H<sub>9</sub>]<sup>+</sup>.

**2-(11-(Hexyldimethylsilyl)undec-1-yl)thiophene (8).** To a solution of hexyldimethylsilane (**4**), (8.1 g, 55.8 mmol) and 2-(undec-10-enyl)thiophene (**1**) (13.1 g, 55.8 mmol) in dry hexane (20 mL), Pt(dvtms) (362 μL, 36.2 μmol) was added at 0 °C. After 15 min, the mixture was heated to 55 °C and stirred for 24 h. The solvent then was evaporated and the brown crude product was purified by column chromatography (SiO<sub>2</sub>/hexane, *R*<sub>f</sub> = 0.62) to give **8** as a colorless liquid (16.6 g, 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ [ppm]: 7.08 (dd, <sup>3</sup>*J*(5,4) = 5.0 Hz, <sup>4</sup>*J*(5,3) = 1.0 Hz, 1 H, 5-H), 6.89 (dd, <sup>3</sup>*J*(4,5) = 5.0 Hz, <sup>3</sup>*J*(4,3) = 3.5 Hz, 1 H, 4-H), 6.76–6.75 (m, 1 H, 3-H), 2.80 (t, <sup>3</sup>*J*(α,β) = 7.7 Hz, 2 H, α-CH<sub>2</sub>), 1.70–1.62 (m, 2 H, β-CH<sub>2</sub>), 1.36–1.25 (m, 24 H, CH<sub>2</sub>), 0.87 (t, <sup>3</sup>*J*(H,H) = 6.8 Hz, 3 H, CH<sub>3</sub>), 0.48–0.44 (m, 4 H, CH<sub>2</sub>SiCH<sub>2</sub>), –0.07 (s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ [ppm]: 145.9, 126.6, 123.9, 122.7, 33.7, 33.4, 31.8, 31.6, 29.9, 29.7, 29.59, 29.55, 29.4, 29.1, 23.90, 23.88, 22.6, 15.3, 14.1, –3.3. MS (CI, 100 eV) *m/z* (%) 381 (98) [M+H]<sup>+</sup>, 365 (76) [M-CH<sub>3</sub>]<sup>+</sup>, 295 (100) [M-C<sub>6</sub>H<sub>13</sub>]<sup>+</sup>, 143 (15) [M-C<sub>15</sub>H<sub>25</sub>Si]<sup>+</sup>, 97 (3) [M-C<sub>18</sub>H<sub>39</sub>Si]<sup>+</sup>. Elemental analysis: Calcd. for C<sub>23</sub>H<sub>44</sub>SSi (380.75): C 72.55, H 11.65; Found: C 72.51, H 11.63.

**2-(11-((2-Ethylhexyl)dimethylsilyl)undec-1-yl)thiophene (9).** To a solution of (2-ethylhexyl)dimethylsilane (**5**) (4.3 g, 25.0 mmol) and 2-(undec-10-enyl)thiophene (**1**) (5.9 g, 25.0 mmol) in dry hexane (15 mL), Pt(dvtms) (150 μL, 15.0 μmol) was added at 0 °C. After 15 min, the reaction was heated to 55 °C and stirred for 18 h. The solvent then was evaporated and the crude product was purified by column chromatography (SiO<sub>2</sub>/hexane, *R*<sub>f</sub> = 0.65) to give **9** as a colorless liquid (8.0 g, 82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ [ppm]: 7.08 (dd, <sup>3</sup>*J*(5,4) = 5.1 Hz, <sup>4</sup>*J*(5,3) = 1.0 Hz, 1 H, 5-H), 6.90 (dd, <sup>3</sup>*J*(4,5) = 5.2 Hz, <sup>3</sup>*J*(4,3) = 3.4 Hz, 1 H, 4-H), 6.77–6.76 (m, 1 H, 3-H), 2.80 (t, <sup>3</sup>*J*(α,β) = 7.6 Hz, 2 H, α-CH<sub>2</sub>), 1.70–1.63 (m, 2 H, β-CH<sub>2</sub>), 1.36–1.22 (m, 25 H, CH and CH<sub>2</sub>), 0.88 (t, <sup>3</sup>*J*(H,H) = 7.0 Hz, 3 H, hexyl-CH<sub>3</sub>), 0.82 (t, <sup>3</sup>*J*(H,H) = 7.3 Hz, 3 H, ethyl-CH<sub>3</sub>), 0.49–0.44 (m, 4 H, CH<sub>2</sub>SiCH<sub>2</sub>), –0.04 (s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ [ppm]: 145.9, 126.6, 123.9, 122.7, 35.9, 35.4, 33.8, 31.9, 30.0, 29.7, 29.64, 29.60, 29.40, 29.2, 28.9, 24.0, 23.1, 20.0, 16.2, 14.3, 10.8, –2.3. MS (CI, 100 eV) *m/z* (%) 409 (42) [M+H]<sup>+</sup>, 393 (54) [M-CH<sub>3</sub>]<sup>+</sup>, 295 (100) [M-C<sub>8</sub>H<sub>17</sub>]<sup>+</sup>, 171 (50) [M-C<sub>15</sub>H<sub>25</sub>Si]<sup>+</sup>, 97 (5) [M-C<sub>20</sub>H<sub>43</sub>Si]<sup>+</sup>. Elemental analysis: Calcd. for C<sub>25</sub>H<sub>48</sub>SSi (408.80): C 73.45, H 11.83; Found: C 73.34, H 11.80.

**2-(6-(Dimethylundecylsilyl)hex-1-yl)thiophene (10).** To a solution of 2-(hex-5-enyl)thiophene (**2**) (7.2 g, 43.0 mmol) and

(39) Cheung, W.-H.; Zheng, S.-L.; Yu, W.-Y.; Zhou, G.-C.; Che, C.-M. *Org. Lett.* **2003**, *5*, 2535–2538.

(40) Hou, J.; Tan, Z.; Yan, Y.; He, Y.; Yang, C.; Li, Y. *J. Am. Chem. Soc.* **2006**, *128*, 4911–4916.

(41) Zhang, Y.; Wang, C.; Rothberg, L.; Ng, M.-K. *J. Mater. Chem.* **2006**, *16*, 3721–3725.

dimethylundecylsilane (**6**) (9.2 g, 43.0 mmol) in dry hexane (30 mL), Pt(dvtms) (280  $\mu$ L, 28.0  $\mu$ mol) was added at 0 °C. After 15 min, the reaction was heated up to 55 °C and stirred for 20 h. The solvent then was evaporated and the crude product was purified by column chromatography (SiO<sub>2</sub>/hexane,  $R_f$  = 0.73) to give **10** as a colorless liquid (12.7 g, 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 7.08 (dd, <sup>3</sup> $J$ (5,4) = 5.2 Hz, <sup>4</sup> $J$ (5,3) = 1.1 Hz, 1 H, 5-H), 6.89 (dd, <sup>3</sup> $J$ (4,5) = 5.1 Hz, <sup>3</sup> $J$ (4,3) = 3.5 Hz, 1 H, 4-H), 6.77–6.75 (m, 1 H, 3-H), 2.80 (t, <sup>3</sup> $J$ ( $\alpha,\beta$ ) = 7.7 Hz, 2 H,  $\alpha$ -CH<sub>2</sub>), 1.69–1.62 (m, 2 H,  $\beta$ -CH<sub>2</sub>), 1.35–1.25 (m, 24 H, CH<sub>2</sub>), 0.87 (t, <sup>3</sup> $J$ (H,H) = 6.8 Hz, 3 H, CH<sub>3</sub>), 0.48–0.44 (m, 4 H, CH<sub>2</sub>SiCH<sub>2</sub>), –0.07 (s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 145.9, 126.6, 123.9, 122.7, 33.7, 33.4, 31.9, 31.8, 30.0, 29.74, 29.66, 29.6, 29.40, 29.37, 28.9, 23.9, 23.8, 22.7, 15.3, 14.1, –3.3. MS (CI, 100 eV)  $m/z$  (%) 381 (40), [M+H]<sup>+</sup>, 365 (44) [M–CH<sub>3</sub>]<sup>+</sup>, 225 (100) [M–C<sub>11</sub>H<sub>23</sub>]<sup>+</sup>, 213 (33), [M–C<sub>10</sub>H<sub>15</sub>S]<sup>+</sup>, 97 (4) [M–C<sub>18</sub>H<sub>39</sub>Si]<sup>+</sup>. Elemental analysis: Calcd. for C<sub>23</sub>H<sub>44</sub>SSi (380.75): C 72.55, H 11.65; Found: C 72.65, H 11.58.

2-((3-Dimethyltetradecylsilyl)prop-1-yl)thiophene (**11**). To a solution of dimethyltetradecylsilane (**6**) (4.6 g, 17.9 mmol) and 2-allylthiophene (**3**) (2.2 g, 17.9 mmol) in dry toluene (25 mL), Pt(dvtms) (144  $\mu$ L, 14.4  $\mu$ mol) was added and the reaction was stirred for 16 h at 55 °C. The solvent then was evaporated and the crude product was purified by column chromatography (SiO<sub>2</sub>/hexane,  $R_f$  = 0.57) to give **11** as a colorless liquid (4.6 g, 67%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm]: 7.09 (dd, <sup>3</sup> $J$ (5,4) = 5.2 Hz, <sup>4</sup> $J$ (5,3) = 1.1 Hz, 1 H, 5-H), 6.91 (dd, <sup>3</sup> $J$ (4,5) = 5.0 Hz, <sup>3</sup> $J$ (4,3) = 3.3 Hz, 1 H, 4-H), 6.77 (tdd, <sup>3</sup> $J$ (3,4) = 3.3 Hz, <sup>4</sup> $J$ (3,5) = 1.0 Hz, <sup>4</sup> $J$ (3,a) = 1.0 Hz, 1 H, 3-H), 2.83 (dt, <sup>3</sup> $J$ ( $\alpha,\beta$ ) = 7.6 Hz, <sup>4</sup> $J$ ( $\alpha,3$ ) = 0.8 Hz, 2 H,  $\alpha$ -CH<sub>2</sub>), 1.71–1.63 (m, 2 H,  $\beta$ -CH<sub>2</sub>), 1.32–1.26 (m, 24 H, CH<sub>2</sub>), 0.88 (t, <sup>3</sup> $J$ (H,H) = 6.8 Hz, 3 H, CH<sub>3</sub>), 0.59–0.55 (m, 2 H,  $\beta$ -CH<sub>2</sub>CH<sub>2</sub>Si), 0.50–0.46 (m, 2 H, SiCH<sub>2</sub>), –0.04 (s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 145.7, 126.6, 124.0, 122.7, 33.8, 33.7, 31.9, 29.75, 29.72, 29.68, 29.6, 29.39, 29.38, 26.6, 23.9, 22.7, 15.2, 15.1, 14.1, –3.4. MS (CI, 100 eV),  $m/z$  (%): 381 (28) [M+H]<sup>+</sup>, 365 (27) [M–CH<sub>3</sub>]<sup>+</sup>, 255 (16) [M–C<sub>7</sub>H<sub>9</sub>S]<sup>+</sup>, 183 (100) [M–C<sub>14</sub>H<sub>29</sub>]<sup>+</sup>. Elemental analysis: Calcd for C<sub>23</sub>H<sub>44</sub>SSi, (380.75): C 72.55, H 11.65; Found: C 72.57, H 11.69.

2-Trimethylstannyl-5-(11-hexyldimethylsilyl)undec-1-yl)thiophene (**12**). To a solution of compound **8** (5.6 g, 14.7 mmol) in dry THF (20 mL) *n*-BuLi (13.8 mL, 22.1 mmol) was added dropwise at 0 °C. The mixture was allowed to warm to room temperature and stirred for 60 min. A solution of trimethyltin chloride (4.4 g, 22.1 mmol) in dry THF (5 mL) was then added. After stirring for 1 h, the solvent was evaporated to afford crude **12** as an orange oil in quantitative yield by <sup>1</sup>H NMR, which was used directly for the coupling step without further purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 6.99 (d, <sup>3</sup> $J$ (3,4) = 3.3 Hz, 1 H, 3-H), 6.88 (d, <sup>3</sup> $J$ (4,3) = 3.3 Hz, 1 H, 4-H), 2.83 (t, <sup>3</sup> $J$ ( $\alpha,\beta$ ) = 7.6 Hz, 2 H,  $\alpha$ -CH<sub>2</sub>), 1.70–1.62 (m, 2 H,  $\beta$ -CH<sub>2</sub>), 1.35–1.24 (m, 24 H, CH<sub>2</sub>), 0.87 (t, <sup>3</sup> $J$ (H,H) = 6.8 Hz, 3 H, CH<sub>3</sub>), 0.47–0.44 (m, 4 H, CH<sub>2</sub>SiCH<sub>2</sub>), 0.32 (s, 9 H, Sn(CH<sub>3</sub>)<sub>3</sub>), –0.07 (s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>).

2-Trimethylstannyl-5-(11-((2-ethylhexyl)dimethylsilyl)undec-1-yl)thiophene (**13**). To a solution of compound **9** (4.1 g, 10.0 mmol) in dry THF (25 mL) *n*-BuLi (8.8 mL, 14.0 mmol) was added dropwise at 0 °C. The mixture was allowed to warm to room temperature and stirred for 60 min. A solution of trimethyltin chloride (2.8 g, 14.0 mmol) in dry THF (5 mL) was then added. After stirring for 1 h, the solvent was evaporated to afford crude **13** as an orange oil in quantitative yield

determined by <sup>1</sup>H NMR, which was used directly for the coupling step without further purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 6.99 (d, <sup>3</sup> $J$ (3,4) = 3.3 Hz, 1 H, 3-H), 6.88 (d, <sup>3</sup> $J$ (4,3) = 3.3 Hz, 1 H, 4-H), 2.83 (t, <sup>3</sup> $J$ ( $\alpha,\beta$ ) = 7.6 Hz, 2 H,  $\alpha$ -CH<sub>2</sub>), 1.69–1.62 (m, 2 H,  $\beta$ -CH<sub>2</sub>), 1.38–1.16 (m, 25 H, CH and CH<sub>2</sub>), 0.87 (t, <sup>3</sup> $J$ (H,H) = 7.1 Hz, 3 H, hexyl-CH<sub>3</sub>), 0.80 (t, <sup>3</sup> $J$ (H,H) = 7.5 Hz, 3 H, ethyl-CH<sub>3</sub>), 0.47–0.43 (m, 4 H, CH<sub>2</sub>SiCH<sub>2</sub>), 0.32 (s, 9 H, Sn(CH<sub>3</sub>)<sub>3</sub>), –0.06 (s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>).

2-Trimethylstannyl-5-(6-(dimethylundecylsilyl)hex-1-yl)thiophene (**14**). To a solution of compound **10** (5.0 g, 13.1 mmol) in dry THF (25 mL) *n*-BuLi (12.3 mL, 19.7 mmol) was added dropwise at 0 °C. The mixture was allowed to warm to room temperature and stirred for 60 min. A solution of trimethyltin chloride (3.9 g, 19.7 mmol) in dry THF (5 mL) was then added. After stirring for 1 h, the solvent was evaporated to afford crude **14** as an orange oil in quantitative yield determined by <sup>1</sup>H NMR, which was used directly for the coupling step without further purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 6.99 (d, <sup>3</sup> $J$ (3,4) = 3.0 Hz, 1 H, 3-H), 6.88 (d, <sup>3</sup> $J$ (4,3) = 3.1 Hz, <sup>4</sup> $J$ (4, $\alpha$ ) = 0.8 Hz, 1 H, 4-H), 2.83 (t, <sup>3</sup> $J$ ( $\alpha,\beta$ ) = 7.4 Hz, 2 H,  $\alpha$ -CH<sub>2</sub>), 1.69–1.62 (m, 2 H,  $\beta$ -CH<sub>2</sub>), 1.34–1.24 (m, 24 H, CH<sub>2</sub>), 0.86 (t, <sup>3</sup> $J$ (H,H) = 6.8 Hz, 3 H, CH<sub>3</sub>), 0.47–0.43 (m, 4 H, CH<sub>2</sub>SiCH<sub>2</sub>), 0.32 (s, 9 H, Sn(CH<sub>3</sub>)<sub>3</sub>), –0.08 (s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>).

2-Trimethylstannyl-5-(3-dimethyltetradecylsilyl)prop-1-yl)thiophene (**15**). To a solution of compound **11** (3.5 g, 9.2 mmol) in dry THF (25 mL) *n*-BuLi (8.0 mL, 12.9 mmol) was added dropwise at 0 °C. The mixture was allowed to warm to room temperature and stirred for 60 min. A solution of trimethyltin chloride (2.6 g, 12.9 mmol) in dry THF (5 mL) was then added. After stirring for 1 h, the solvent was evaporated to afford crude product **15** as an orange oil in quantitative yield determined by <sup>1</sup>H NMR, which was used directly for the coupling step without further purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 6.99 (d, <sup>3</sup> $J$ (3,4) = 3.0 Hz, 1 H, 3-H), 6.88 (d, <sup>3</sup> $J$ (4,3) = 3.0 Hz, 1 H, 4-H), 2.85 (t, <sup>3</sup> $J$ ( $\alpha,\beta$ ) = 7.6 Hz, 2 H,  $\alpha$ -CH<sub>2</sub>), 1.70–1.62 (m, 2 H,  $\beta$ -CH<sub>2</sub>), 1.31–1.24 (m, 24 H, CH<sub>2</sub>), 0.86 (t, <sup>3</sup> $J$ (H,H) = 7.1 Hz, 3 H, CH<sub>3</sub>), 0.58–0.54 (m, 2 H,  $\beta$ -CH<sub>2</sub>CH<sub>2</sub>Si), 0.48–0.45 (m, 2 H, SiCH<sub>2</sub>), 0.32 (s, 9 H, Sn(CH<sub>3</sub>)<sub>3</sub>), –0.06 (s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>).

5-(11-(Hexyldimethylsilyl)undec-1-yl)-2,2'-bithiophene (**16**). Crude compound **12** (14.7 mmol) and 2-bromothiophene (1.43 mL, 14.7 mmol) were dissolved in dry THF (35 mL). The solution was degassed for 1 h. Pd(PPh<sub>3</sub>)<sub>4</sub> (595 mg, 0.51 mmol) was then added and the mixture was refluxed for 16 h. After cooling to room temperature, water was added and the organic phase was separated. The aqueous phase was extracted with chloroform (2  $\times$  15 mL), and the combined organic phases were dried over anhydrous MgSO<sub>4</sub>. After evaporating the solvent, the crude product was purified by column chromatography (SiO<sub>2</sub>/hexane,  $R_f$  = 0.33) to give **16** as a greenish liquid (3.8 g, 58%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 7.14 (dd, <sup>3</sup> $J$ (5',4') = 5.1 Hz, <sup>4</sup> $J$ (5',3') = 1.0 Hz, 1 H, 5'-H), 7.07 (dd, <sup>3</sup> $J$ (3',4') = 3.5 Hz, <sup>4</sup> $J$ (3',5') = 1.0 Hz, 1 H, 3'-H), 6.97 (dd, <sup>3</sup> $J$ (4',5') = 5.3 Hz, <sup>3</sup> $J$ (4',3') = 3.5 Hz, 1 H, 4'-H), 6.96 (d, <sup>3</sup> $J$ (3,4) = 3.6 Hz, 1 H, 3-H), 6.65 (d, <sup>3</sup> $J$ (4,3) = 3.5 Hz, 1 H, 4-H), 2.77 (t, <sup>3</sup> $J$ ( $\alpha,\beta$ ) = 7.6 Hz, 2 H,  $\alpha$ -CH<sub>2</sub>), 1.70–1.62 (m, 2 H,  $\beta$ -CH<sub>2</sub>), 1.36–1.25 (m, 24 H, CH<sub>2</sub>), 0.87 (t, <sup>3</sup> $J$ (H,H) = 6.8 Hz, 3 H, CH<sub>3</sub>), 0.47–0.44 (m, 4 H, CH<sub>2</sub>SiCH<sub>2</sub>), –0.08 (s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 145.4, 138.0, 134.8, 127.6, 124.7, 123.7, 123.4, 123.0, 33.7, 33.4, 31.63, 31.61, 30.2, 29.7, 29.61, 29.56, 29.4, 29.1, 23.92, 23.89, 22.6, 15.3, 14.2, –3.3. MS (CI, 100 eV)  $m/z$  (%): 463 (100) [M+H]<sup>+</sup>, 447 (94) [M–CH<sub>3</sub>]<sup>+</sup>, 377 (66), [M–C<sub>6</sub>H<sub>13</sub>]<sup>+</sup>, 179 (6) [M–C<sub>18</sub>H<sub>39</sub>Si]<sup>+</sup>, 143 (8) [M–C<sub>19</sub>H<sub>27</sub>S]<sup>+</sup>. Elemental

analysis: Calcd. for  $C_{27}H_{46}S_2Si$  (462.87): C 70.06, H 10.02; Found: C 69.78, H 9.93.

2-(11-((2-Ethylhexyl)dimethylsilyl)undec-1-yl)-2,2'-bithiophene (**17**). Crude compound **13** (10 mmol) and 2-bromothiophene (0.97 mL, 10 mmol) were dissolved in dry THF (40 mL). The solution was degassed for 1 h.  $Pd(PPh_3)_4$  (404 mg, 0.35 mmol) was then added and the mixture was refluxed for 16 h. After cooling to room temperature, water was added and the organic phase was separated. The aqueous phase was extracted with dichloromethane ( $3 \times 10$  mL) and the combined organic phases were dried over  $MgSO_4$ . After the solvent was evaporated, the crude product was purified by column chromatography ( $SiO_2$ /hexane,  $R_f = 0.36$ ). **17** was obtained as a greenish liquid (2.1 g, 43%).  $^1H$  NMR (400 MHz,  $CDCl_3$ ),  $\delta$  [ppm]: 7.14 (dd,  $^3J(S',4') = 5.2$  Hz,  $^4J(S',3') = 1.1$  Hz, 1 H,  $5'-H$ ), 7.07 (dd,  $^3J(3',4') = 3.7$  Hz,  $^4J(3',5') = 1.1$  Hz, 1 H,  $3'-H$ ), 6.96 (dd,  $^3J(4',5') = 5.2$  Hz,  $^3J(4',3') = 3.7$  Hz, 1 H,  $4'-H$ ), 6.96 (d,  $^3J(3,4) = 3.6$  Hz, 1 H,  $3-H$ ), 6.65 (td,  $^3J(4,3) = 3.6$  Hz,  $^4J(4,\alpha) = 0.9$  Hz, 1 H,  $4-H$ ), 2.76 (dt,  $^3J(\alpha,\beta) = 7.3$  Hz, 2 H,  $\alpha-CH_2$ ), 1.69–1.62 (m, 2 H,  $\beta-CH_2$ ), 1.38–1.18 (m, 25 H, CH and  $CH_2$ ), 0.87 (t,  $^3J(H,H) = 7.1$  Hz, 3 H, hexyl- $CH_3$ ), 0.80 (t,  $^3J(H,H) = 7.5$  Hz, 3 H, ethyl- $CH_2$ ), 0.47–0.44 (m, 4 H,  $CH_2SiCH_2$ ), –0.06 (s, 6 H,  $Si(CH_3)_2$ ).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ),  $\delta$  [ppm]: 145.4, 138.0, 134.8, 127.6, 124.7, 123.7, 123.4, 123.0, 35.9, 35.5, 33.8, 31.6, 30.2, 29.7, 29.63, 29.58, 29.4, 29.1, 28.9, 24.0, 23.1, 20.1, 16.2, 14.2, 10.8, –2.3. MS (CI, 100 eV)  $m/z$  (%): 491 (100)  $[M+H]^+$ , 475 (65)  $[M-CH_3]^+$ , 377 (84),  $[M-C_8H_{17}]^+$ , 179 (3)  $[M-C_{20}H_{43}Si]^+$ . Elemental analysis: Calcd. for  $C_{29}H_{50}S_2Si$  (490.92): C 70.95, H 10.27; Found: C 71.31, H 10.23.

5-(6-(Dimethylundecylsilyl)hex-1-yl)-2,2'-bithiophene (**18**). Crude compound **14** (7.2 mmol) and 2-bromothiophene (0.68 mL, 7.0 mmol) were dissolved in dry THF (35 mL). The solution was degassed for 1 h.  $Pd(PPh_3)_4$  (404 mg, 0.35 mmol) was then added and the mixture was refluxed for 18 h. The solvent was evaporated and *n*-hexane was added to the remaining brown oil. The insoluble residue was filtered off and the solvent was removed from the filtrate. The crude product then was purified by column chromatography ( $SiO_2$ /hexane,  $R_f = 0.31$ ) to give **18** as a greenish liquid (2.2 g, 68%).  $^1H$  NMR (400 MHz,  $CDCl_3$ ),  $\delta$  [ppm]: 7.14 (dd,  $^3J(S',4') = 5.2$  Hz,  $^4J(S',3') = 1.1$  Hz, 1 H,  $5'-H$ ), 7.07 (dd,  $^3J(3',4') = 3.7$  Hz,  $^4J(3',5') = 1.1$  Hz, 1 H,  $3'-H$ ), 6.97 (dd,  $^3J(4',5') = 5.0$  Hz,  $^3J(4',3') = 3.6$  Hz, 1 H,  $4'-H$ ), 6.96 (d,  $^3J(3,4) = 3.6$  Hz, 1 H,  $3-H$ ), 6.65 (td,  $^3J(4,3) = 3.5$  Hz,  $^4J(4,\alpha) = 0.9$  Hz, 1 H,  $4-H$ ), 2.77 (dt,  $^3J(\alpha,\beta) = 7.6$  Hz,  $^4J(\alpha,4) = 0.8$  Hz, 2 H,  $\alpha-CH_2$ ), 1.69–1.62 (m, 2 H,  $\beta-CH_2$ ), 1.35–1.24 (m, 24 H,  $CH_2$ ), 0.86 (t,  $^3J(H,H) = 6.9$  Hz, 3 H,  $CH_3$ ), 0.48–0.44 (m, 4 H,  $CH_2SiCH_2$ ), –0.08 (s, 6 H,  $Si(CH_3)_2$ ).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ),  $\delta$  [ppm]: 145.4, 138.0, 134.8, 127.6, 124.7, 123.7, 123.4, 123.0, 33.7, 33.4, 31.9, 31.5, 30.2, 29.73, 29.66, 29.63, 29.40, 29.36, 28.8, 23.9, 23.8, 22.7, 15.31, 15.30, 14.1, –3.3. MS (CI, 100 eV)  $m/z$  (%): 463 (100)  $[M+H]^+$ , 447 (66)  $[M-CH_3]^+$ , 307 (84),  $[M-C_{11}H_{23}]^+$ , 213 (10)  $[M-C_{14}H_{17}S_2]^+$ , 179 (7)  $[M-C_{18}H_{39}Si]^+$ . Elemental analysis: Calcd. for  $C_{27}H_{46}S_2Si$  (462.87): C 70.06, H 10.02; Found: C 70.04, H 9.93.

5-(3-(Dimethyltetradecylsilyl)prop-1-yl)-2,2'-bithiophene (**19**). Crude compound **15** (9.2 mmol) and 2-bromothiophene (0.89 mL, 9.2 mmol) were dissolved in dry THF (35 mL). The solution was degassed for 1 h.  $Pd(PPh_3)_4$  (0.37 g, 0.32 mmol) was then added, and the mixture was refluxed for 18 h. After cooling to room temperature, water was added and the organic phase was separated. The aqueous phase was extracted with dichloromethane ( $3 \times 15$  mL) and the combined organic phases were dried over  $MgSO_4$ . The solvent then was evaporated and the

crude product was purified by column chromatography ( $SiO_2$ /hexane,  $R_f = 0.44$ ) to give **19** as a greenish liquid (2.4 g, 56%).  $^1H$  NMR (400 MHz,  $CDCl_3$ ),  $\delta$  [ppm]: 7.14 (dd,  $^3J(S',4') = 5.2$  Hz,  $^4J(S',3') = 1.1$  Hz, 1 H,  $5'-H$ ), 7.08 (dd,  $^3J(3',4') = 3.7$  Hz,  $^4J(3',5') = 1.1$  Hz, 1 H,  $3'-H$ ), 6.97 (dd,  $^3J(4',5') = 5.0$  Hz,  $^4J(4',3') = 3.6$  Hz, 1 H,  $4'-H$ ), 6.96 (d,  $^3J(3,4) = 3.6$  Hz, 1 H,  $3-H$ ), 6.65 (td,  $^3J(4,3) = 3.6$  Hz,  $^4J(4,\alpha) = 0.9$  Hz, 1 H,  $4-H$ ), 2.78 (t,  $^3J(\alpha,\beta) = 7.4$  Hz, 2 H,  $\alpha-CH_2$ ), 1.69–1.61 (m, 2 H,  $\beta-CH_2$ ), 1.30–1.24 (m, 24 H,  $CH_2$ ), 0.86 (t,  $^3J(H,H) = 6.9$  Hz, 3 H,  $CH_3$ ), 0.58–0.54 (m, 2 H,  $\beta-CH_2CH_2Si$ ), 0.49–0.45 (m, 2 H,  $SiCH_2$ ), –0.05 (s, 6 H,  $Si(CH_3)_2$ ).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ),  $\delta$  [ppm]: 145.2, 138.0, 134.8, 127.7, 124.8, 123.7, 123.4, 123.0, 34.1, 33.7, 32.0, 29.77, 29.70, 29.66, 29.42, 29.41, 26.4, 23.9, 22.7, 15.2, 15.0, 14.2, –3.4. MS (CI, 100 eV),  $m/z$  (%): 463 (82)  $[M+H]^+$ , 447 (36)  $[M-CH_3]^+$ , 265 (100),  $[M-C_{14}H_{29}]^+$ , 255 (8)  $[M-C_{11}H_{11}S_2]^+$ , 179 (7)  $[M-C_{184}H_{39}Si]^+$ . Elemental analysis: Calcd. for  $C_{27}H_{46}S_2Si$  (462.87): C 70.06, H 10.02; Found: C 70.17, H 10.05.

5-Trimethylstannyl-5'-(11-(hexyldimethylsilyl)undec-1-yl)-2,2'-bithiophene (**20**). To a solution of compound **16** (1.50 g, 3.2 mmol) in dry THF (20 mL), *n*-BuLi (3.0 mL, 4.8 mmol) was added dropwise at 0 °C. The mixture was allowed to warm to room temperature and stirred for 60 min. A solution of trimethyltin chloride (0.97 g, 4.8 mmol) in dry THF (3 mL) was then added. After stirring for 1 h, the solvent was evaporated to afford crude **20** as a brown solid in quantitative yield determined by  $^1H$  NMR, which was used directly for the coupling step without further purification.  $^1H$  NMR (400 MHz,  $CDCl_3$ ),  $\delta$  [ppm]: 7.18 (d,  $^3J(3,4) = 3.5$  Hz, 1 H,  $3-H$ ), 7.04 (d,  $^3J(4,3) = 3.3$  Hz, 1 H,  $4-H$ ), 6.94 (d,  $^3J(3',4') = 3.5$  Hz, 1 H,  $3'-H$ ), 6.64 (td,  $^3J(4',3') = 3.6$  Hz,  $^4J(4',\alpha) = 0.9$  Hz, 1 H,  $4'-H$ ), 2.76 (t,  $^3J(\alpha,\beta) = 7.6$  Hz, 2 H,  $\alpha-CH_2$ ), 1.69–1.62 (m, 2 H,  $\beta-CH_2$ ), 1.36–1.25 (m, 24 H,  $CH_2$ ), 0.87 (t,  $^3J(H,H) = 6.9$  Hz, 3 H,  $CH_3$ ), 0.47–0.43 (m, 4 H,  $CH_2SiCH_2$ ), 0.36 (s, 9 H,  $Sn(CH_3)_3$ ), –0.08 (s, 6 H,  $Si(CH_3)_2$ ).

5-Trimethylstannyl-5'-(11-((2-ethylhexyl)dimethylsilyl)undec-1-yl)-2,2'-bithiophene (**21**). To a solution of compound **17** (1.48 g, 3.0 mmol) in dry THF (15 mL), *n*-BuLi (2.6 mL, 4.2 mmol) was added dropwise at 0 °C. The reaction was allowed to warm to room temperature and stirred for 1 h. A solution of trimethyltin chloride (0.84 g, 4.2 mmol) in dry THF (3 mL) was then added. After stirring for 1 h, the solvent was evaporated to afford crude **21** as a brown solid in quantitative yield determined by  $^1H$  NMR, which was used directly for the coupling step without further purification.  $^1H$  NMR (400 MHz,  $CDCl_3$ ),  $\delta$  [ppm]: 7.18 (d,  $^3J(3,4) = 3.3$  Hz, 1 H,  $3-H$ ), 7.04 (d,  $^3J(4,3) = 3.3$  Hz, 1 H,  $4-H$ ), 6.94 (d,  $^3J(3',4') = 3.3$  Hz, 1 H,  $3'-H$ ), 6.64 (d,  $^3J(4',3') = 3.5$  Hz, 1 H,  $4'-H$ ), 2.76 (t,  $^3J(\alpha,\beta) = 7.5$  Hz, 2 H,  $\alpha-CH_2$ ), 1.69–1.62 (m, 2 H,  $\beta-CH_2$ ), 1.37–1.21 (m, 25 H,  $CH_2$ ), 0.87 (t,  $^3J(H,H) = 6.9$  Hz, 3 H, hexyl- $CH_3$ ), 0.81 (t,  $^3J(H,H) = 7.3$  Hz, 3 H, ethyl- $CH_3$ ), 0.48–0.46 (m, 4 H,  $CH_2SiCH_2$ ), 0.35 (s, 9 H,  $Sn(CH_3)_3$ ), –0.05 (s, 6 H,  $Si(CH_3)_2$ ).

5-Trimethylstannyl-5'-(6-(dimethylundecylsilyl)hex-1-yl)-2,2'-bithiophene (**22**). To a solution of compound **18** (1.82 g, 3.9 mmol) in dry THF (30 mL), *n*-BuLi (3.7 mL, 5.9 mmol) was added dropwise at 0 °C. The mixture was allowed to warm to room temperature and stirred for 1 h. A solution of trimethyltin chloride (1.18 g, 5.9 mmol) in dry THF (5 mL) was then added. After stirring for 1 h, the solvent was evaporated to afford crude **22** as a brown solid in quantitative yield determined by  $^1H$  NMR, which was used directly for the coupling step without further purification.  $^1H$  NMR (400 MHz,  $CDCl_3$ ),  $\delta$  [ppm]: 7.18 (d,  $^3J(3,4) = 3.3$  Hz, 1 H,  $3-H$ ), 7.04 (d,  $^3J(4,3) = 3.3$  Hz, 1 H,  $4-H$ ), 6.94 (d,  $^3J(3',4') = 3.5$  Hz, 1 H,  $3'-H$ ), 6.64 (td,  $^3J(4',3') = 3.5$  Hz,

$^4J(4',\alpha) = 0.9$  Hz, 1 H, 4'-H), 2.76 (t,  $^3J(\alpha,\beta) = 7.5$  Hz, 2 H,  $\alpha$ -CH<sub>2</sub>), 1.69–1.61 (m, 2 H,  $\beta$ -CH<sub>2</sub>), 1.36–1.28 (m, 24 H, CH<sub>2</sub>), 0.86 (t,  $^3J(\text{H,H}) = 6.9$  Hz, 3 H, CH<sub>3</sub>), 0.47–0.43 (m, 4 H, CH<sub>2</sub>SiCH<sub>2</sub>), 0.35 (s, 9 H, Sn(CH<sub>3</sub>)<sub>3</sub>), –0.08 (s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>).

**5-Trimethylstannyl-5'-(3-(dimethyltetradecylsilyl)prop-1-yl)-2,2'-bithiophene (23).** To a solution of compound **19** (1.80 g, 3.8 mmol) in dry THF (20 mL), *n*-BuLi (3.3 mL, 5.3 mmol) was added dropwise at 0 °C. The mixture was allowed to warm to room temperature and stirred for 1 h. A solution of trimethyltin chloride (1.06 g, 5.3 mmol) in dry THF (5 mL) was then added. After stirring for 1 h, the solvent was evaporated to afford crude **23** as a brown solid in quantitative yield determined by <sup>1</sup>H NMR, which was directly used for the coupling step without further purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 7.18 (d,  $^3J(3,4) = 3.3$  Hz, 1 H, 3-H), 7.04 (d,  $^3J(4,3) = 3.5$  Hz, 1 H, 4-H), 6.95 (d,  $^3J(3',4') = 3.6$  Hz, 1 H, 3'-H), 6.64 (td,  $^3J(4',3') = 3.5$  Hz,  $^4J(4',\alpha) = 0.9$  Hz, 1 H, 4'-H), 2.77 (t,  $^3J(\alpha,\beta) = 7.3$  Hz, 2 H,  $\alpha$ -CH<sub>2</sub>), 1.68–1.61 (m, 2 H,  $\beta$ -CH<sub>2</sub>), 1.30–1.24 (m, 24 H, CH<sub>2</sub>), 0.86 (t,  $^3J(\text{H,H}) = 6.8$  Hz, 3 H, CH<sub>3</sub>), 0.58–0.54 (m, 2 H,  $\beta$ -CH<sub>2</sub>CH<sub>2</sub>Si), 0.49–0.45 (m, 2 H, SiCH<sub>2</sub>), 0.35 (s, 9 H, Sn(CH<sub>3</sub>)<sub>3</sub>), –0.06 (s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>).

**1,2-Bis(2-(5-(11-(hexyldimethylsilyl)undec-1-yl)-2,2':5',2''-terthien-5''-yl)-1,3-dioxolan-2-yl)ethane (24).** Crude compound **20** (3.2 mmol) and brominated precursor **37** (794 mg, 1.6 mmol) were dissolved in dry THF (35 mL). The solution was degassed for 1 h. Pd(PPh<sub>3</sub>)<sub>4</sub> (130 mg, 0.1 mmol) then was added and the mixture was refluxed for 18 h. After cooling to room temperature, methanol was added and the resulting precipitate was filtered off. The orange crude product was recrystallized from acetone and **24** was obtained as a yellow powder (1.1 g, 55%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 6.97 (d,  $^3J(\text{H,H}) = 3.8$  Hz, 2 H, 3'-H, 4''''-H or 4'-H, 3''''-H), 6.96 (d,  $^3J(3'',4'') = ^3J(4''''',3''''') = 3.5$  Hz, 2 H, 3''-H, 4''''-H), 6.94 (d,  $^3J(\text{H,H}) = 3.8$  Hz, 2 H, 3'-H, 4''''-H or 4'-H, 3''''-H), 6.94 (d,  $^3J(3,4) = ^3J(3''''',4''''') = 3.6$  Hz, 2 H, 3-H, 3''''-H), 6.87 (d,  $^3J(4'',3'') = ^3J(3''''',4''''') = 3.5$  Hz, 2 H, 4''-H, 3''''-H), 6.65 (td,  $^3J(4,3) = 3.5$  Hz,  $^4J(4,\alpha) = ^4J(4''''',\alpha) = 1.0$  Hz, 2 H, 4-H, 4''''-H), 4.03–3.94 (m, 8 H, CH<sub>2</sub> protection groups), 2.76 (t,  $^3J(\alpha,\beta) = 7.4$  Hz, 4 H,  $\alpha$ -CH<sub>2</sub>), 2.16 (s, 4 H, CO<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>), 1.69–1.62 (m, 4 H,  $\beta$ -CH<sub>2</sub>), 1.38–1.25 (m, 48 H, CH<sub>2</sub>), 0.86 (t,  $^3J(\text{H,H}) = 6.9$  Hz, 6 H, CH<sub>3</sub>), 0.47–0.43 (m, 8 H, CH<sub>2</sub>SiCH<sub>2</sub>), –0.08 (s, 12 H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 145.9, 145.5, 136.9, 135.4, 134.3, 125.5, 125.1, 124.4, 123.7, 123.6, 123.4, 108.5, 65.3, 34.7, 33.9, 33.5, 31.7, 30.3, 29.83, 29.76, 29.7, 29.52, 29.51, 29.3, 24.03, 23.99, 22.8, 15.4, 14.4, –3.1. MS (MALDI-TOF)  $m/z$ : 1215.1 [M–C<sub>2</sub>H<sub>4</sub>O]<sup>+</sup>, 1170.1 [M–C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>]<sup>+</sup>, 671.6 [M–C<sub>33</sub>H<sub>51</sub>OS<sub>3</sub>Si]<sup>+</sup>, 615.6 [M–C<sub>36</sub>H<sub>55</sub>O<sub>2</sub>S<sub>3</sub>Si]<sup>+</sup>. Elemental analysis: Calcd. for C<sub>70</sub>H<sub>106</sub>O<sub>4</sub>S<sub>6</sub>Si<sub>2</sub> (1260.15): C 66.72, H 8.48; Found: C 66.61, H 8.56.

**1,2-Bis(2-(5-(11-(2-ethylhexyl)dimethylsilyl)undec-1-yl)-2,2':5',2''-terthien-5''-yl)-1,3-dioxolan-2-yl)ethane (25).** Crude compound **21** (3.0 mmol) and brominated precursor **37** (0.74 g, 1.5 mmol) were dissolved in dry THF (30 mL). The solution was degassed for 1 h. Pd(PPh<sub>3</sub>)<sub>4</sub> (0.12 g, 0.11 mmol) then was added and the mixture was refluxed for 20 h. After cooling to room temperature, methanol was added and the resulting precipitate was filtered off. The orange crude product was recrystallized from acetone and **25** was obtained as a yellow powder (0.86 g, 44%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 6.97 (d,  $^3J(\text{H,H}) = 3.8$  Hz, 2 H, 3'-H, 4''''-H or 4'-H, 3''''-H), 6.96 (d,  $^3J(3'',4'') = ^3J(4''''',3''''') = 3.5$  Hz, 2 H, 3''-H, 4''''-H), 6.94 (d,  $^3J(\text{H,H}) = 3.8$  Hz, 2 H, 3'-H, 4''''-H or 4'-H, 3''''-H), 6.94 (d,  $^3J(3,4) = ^3J(3''''',4''''') = 3.5$  Hz, 2 H, 3-H, 3''''-H), 6.87 (d,  $^3J(4'',3'') = ^3J(3''''',4''''') = 3.5$  Hz, 2 H, 4''-H, 3''''-H), 6.65 (d,  $^3J(4,3) = ^3J(4''''',3''''') = 3.5$  Hz, 2 H, 4-H, 4''''-H), 4.03–3.94 (m, 8 H, CH<sub>2</sub> protection groups), 2.78 (t,  $^3J(\alpha,\beta) = 7.3$  Hz, 4 H,  $\alpha$ -CH<sub>2</sub>), 2.17 (s, 4 H, CO<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>), 1.69–1.61 (m, 4 H,  $\beta$ -CH<sub>2</sub>), 1.28–1.24 (m, 48 H, CH<sub>2</sub>), 0.86 (t,  $^3J(\text{H,H}) = 7.0$  Hz, 6 H, CH<sub>3</sub>), 0.58–0.54 (m, 4 H,  $\beta$ -CH<sub>2</sub>CH<sub>2</sub>Si), 0.49–0.45 (m, 4 H, SiCH<sub>2</sub>), –0.05 (s, 12 H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 145.4, 137.0, 136.9, 135.5, 134.6, 125.2, 125.0, 124.1, 123.5, 123.4, 123.2, 108.5, 65.1, 34.7, 34.1, 33.7, 31.9, 29.74, 29.72, 29.70, 29.67, 29.6, 29.39, 29.37, 26.4, 23.9, 22.7,

(d,  $^3J(4'',3'') = ^3J(3''''',4''''') = 3.8$  Hz, 2 H, 4''-H, 3''''-H), 6.65 (d,  $^3J(4,3) = 3.5$  Hz, 2 H, 4-H, 4''''-H), 4.03–3.94 (m, 8 H, CH<sub>2</sub> protection groups), 2.76 (t,  $^3J(\alpha,\beta) = 7.6$  Hz, 4 H,  $\alpha$ -CH<sub>2</sub>), 2.16 (s, 4 H, CO<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>), 1.69–1.61 (m, 4 H,  $\beta$ -CH<sub>2</sub>), 1.38–1.17 (m, 50 H, CH and CH<sub>2</sub>), 0.87 (t,  $^3J(\text{H,H}) = 6.9$  Hz, 6 H, hexyl-CH<sub>3</sub>), 0.80 (t,  $^3J(\text{H,H}) = 7.3$  Hz, 6 H, ethyl-CH<sub>3</sub>), 0.47–0.43 (m, 8 H, CH<sub>2</sub>SiCH<sub>2</sub>), –0.06 (s, 12 H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 145.6, 145.3, 137.0, 136.8, 135.4, 134.5, 125.3, 124.8, 124.2, 123.5, 123.4, 123.2, 108.5, 35.9, 35.4, 34.7, 33.8, 31.7, 30.2, 29.7, 29.64, 29.60, 29.4, 29.1, 28.9, 24.0, 23.1, 20.1, 16.2, 14.3, 10.8, –2.3. MS (MALDI-TOF)  $m/z$ : 1316.3 [M+H]<sup>+</sup>, 643.5 [M–C<sub>38</sub>H<sub>59</sub>O<sub>2</sub>S<sub>3</sub>Si]<sup>+</sup>. Elemental analysis: Calcd. for C<sub>74</sub>H<sub>114</sub>O<sub>4</sub>S<sub>6</sub>Si<sub>2</sub> (1316.26): C 67.52, H 8.73; Found: C 67.31, H 8.65.

**1,2-Bis(2-(5-(6-(dimethylundecylsilyl)hex-1-yl)-2,2':5',2''-terthien-5''-yl)-1,3-dioxolan-2-yl)ethane (26).** Crude compound **22** (3.9 mmol) and brominated precursor **37** (0.97 g, 1.95 mmol) were dissolved in dry THF (50 mL). The solution was degassed for 1 h. Pd(PPh<sub>3</sub>)<sub>4</sub> (0.16 g, 0.14 mmol) then was added and the mixture was stirred under reflux for 20 h. After cooling to room temperature, methanol (60 mL) was added and the resulting precipitate was filtered. The orange crude product was recrystallized from acetone and **26** was obtained as a yellow powder (0.80 g, 33%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 6.97 (d,  $^3J(\text{H,H}) = 3.8$  Hz, 2 H, 3'-H, 4''''-H or 4'-H, 3''''-H), 6.96 (d,  $^3J(3'',4'') = ^3J(4''''',3''''') = 3.8$  Hz, 2 H, 3''-H, 4''''-H), 6.94 (d,  $^3J(\text{H,H}) = 3.8$  Hz, 2 H, 3'-H, 4''''-H or 4'-H, 3''''-H), 6.94 (d,  $^3J(3,4) = ^3J(3''''',4''''') = 3.6$  Hz, 2 H, 3-H, 3''''-H), 6.87 (d,  $^3J(4'',3'') = ^3J(3''''',4''''') = 3.8$  Hz, 2 H, 4''-H, 3''''-H), 6.65 (d,  $^3J(4,3) = 3.8$  Hz, 2 H, 4-H, 4''''-H), 4.03–3.94 (m, 8 H, CH<sub>2</sub> protection group), 2.76 (t,  $^3J(\alpha,\beta) = 7.6$  Hz, 4 H,  $\alpha$ -CH<sub>2</sub>), 2.16 (s, 4 H, CO<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>), 1.69–1.61 (m, 4 H,  $\beta$ -CH<sub>2</sub>), 1.35–1.24 (m, 48 H, CH<sub>2</sub>), 0.86 (t,  $^3J(\text{H,H}) = 6.9$  Hz, 6 H, CH<sub>3</sub>), 0.48–0.44 (m, 8 H, CH<sub>2</sub>SiCH<sub>2</sub>), –0.08 (s, 12 H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 145.6, 145.3, 137.0, 136.8, 135.4, 134.5, 125.3, 124.8, 124.1, 123.5, 123.4, 123.2, 108.5, 65.1, 34.7, 33.8, 33.4, 32.0, 31.6, 30.2, 29.8, 29.68, 29.66, 29.42, 29.40, 28.8, 23.9, 23.8, 22.7, 15.31, 15.29, 14.2, –3.3. MS (MALDI-TOF)  $m/z$  (%): 1259.8 [M+H]<sup>+</sup>, 715.4 [M–C<sub>31</sub>H<sub>47</sub>S<sub>3</sub>Si]<sup>+</sup>, 615.4 [M–C<sub>36</sub>H<sub>55</sub>OS<sub>3</sub>Si]<sup>+</sup>. Elemental analysis: Calcd. for C<sub>70</sub>H<sub>106</sub>O<sub>4</sub>S<sub>6</sub>Si<sub>2</sub> (1260.15): C 66.72, H 8.48; Found: C 66.34, H 8.48.

**1,2-Bis(2-(5-(3-(dimethyltetradecylsilyl)prop-1-yl)-2,2':5',2''-terthien-5''-yl)-1,3-dioxolan-2-yl)ethane (27).** Crude product **(23)** (3.6 mmol) and brominated precursor **37** (0.89 g, 1.79 mmol) were dissolved in dry THF (30 mL). The solution was degassed for 1 h. Pd(PPh<sub>3</sub>)<sub>4</sub> (0.15 g, 0.13 mmol) then was added and the mixture was stirred under reflux for 18 h. After cooling to room temperature, methanol was added and the resulting precipitate was filtered. The crude product then was dissolved in THF, charcoal was added, and the mixture was refluxed for 30 min. After filtration, the product was precipitated by the addition of methanol. **27** was obtained as a yellow solid (0.72 g, 32%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 6.98–6.94 (m, 8 H, 3-H, 3'-H, 4'-H, 3''-H, 4''''-H, 3''''-H, 4''''-H, 3''''-H), 6.87 (d,  $^3J(4'',3'') = ^3J(3''''',4''''') = 3.5$  Hz, 2 H, 4''-H, 3''''-H), 6.65 (d,  $^3J(4,3) = ^3J(4''''',3''''') = 3.5$  Hz, 2 H, 4-H, 4''''-H), 4.03–3.94 (m, 8 H, CH<sub>2</sub> protection group), 2.78 (t,  $^3J(\alpha,\beta) = 7.3$  Hz, 4 H,  $\alpha$ -CH<sub>2</sub>), 2.17 (s, 4 H, CO<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>), 1.69–1.61 (m, 4 H,  $\beta$ -CH<sub>2</sub>), 1.28–1.24 (m, 48 H, CH<sub>2</sub>), 0.86 (t,  $^3J(\text{H,H}) = 7.0$  Hz, 6 H, CH<sub>3</sub>), 0.58–0.54 (m, 4 H,  $\beta$ -CH<sub>2</sub>CH<sub>2</sub>Si), 0.49–0.45 (m, 4 H, SiCH<sub>2</sub>), –0.05 (s, 12 H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 145.4, 137.0, 136.9, 135.5, 134.6, 125.2, 125.0, 124.1, 123.5, 123.4, 123.2, 108.5, 65.1, 34.7, 34.1, 33.7, 31.9, 29.74, 29.72, 29.70, 29.67, 29.6, 29.39, 29.37, 26.4, 23.9, 22.7,

15.2, 15.1, 14.1, -3.4. MS (MALDI-TOF),  $m/z$  (%): 1259.0  $[M+H]^+$ . Elemental analysis: Calcd for  $C_{70}H_{106}O_4S_6Si_2$ , (1260.15): C 66.72, H 8.48; Found: C 66.52, H 8.48.

*1,4-Bis(5-(11-(Hexyldimethylsilyl)undec-1-yl)-2,2':5',2''-terthien-5''-yl)-butane-1,4-dione (28)*. Compound **24** (0.86 g, 0.68 mmol) was dissolved in THF (40 mL). Then conc. HCl (2 mL) was added. The mixture was stirred at 50 °C for 3 h. After cooling to room temperature, the resulting precipitate was filtered, washed with acetone, and dried in vacuo to give **28** as a yellow solid (0.74 g, 93%). Melting point (mp): 242 °C.  $^1H$  NMR (400 MHz,  $C_2D_2Cl_4$ ),  $\delta$  [ppm]: 7.72 (d,  $^3J(4'',3'') = ^3J(3''''',4''''') = 4.0$  Hz, 2 H, 4''-H, 3''''-H), 7.24 (d,  $^3J(H,H) = 3.8$  Hz, 2 H, 3'-H, 4''''-H or 4'-H, 3''''-H), 7.20 (d,  $^3J(3'',4'') = ^3J(4''''',3''''') = 4.0$  Hz, 2 H, 3''-H, 4''''-H), 7.06-7.05 (m, 4 H, 3-H, 3''''-H and 3'-H, 4''''-H or 4'-H, 3''''-H), 6.73 (d,  $^3J(4,3) = ^3J(4''''',3''''') = 3.3$  Hz, 2 H, 4-H, 4''''-H), 3.36 (s, 4 H,  $CO(CH_2)_2CO$ ), 2.81 (t,  $^3J(\alpha,\beta) = 7.6$  Hz, 4 H,  $\alpha-CH_2$ ), 1.73-1.65 (m, 4 H,  $\beta-CH_2$ ), 1.39-1.28 (m, 48 H,  $CH_2$ ), 0.89 (t,  $^3J(H,H) = 6.8$  Hz, 6 H,  $CH_3$ ), 0.50-0.46 (m, 8 H,  $CH_2SiCH_2$ ), -0.04 (s, 12 H,  $Si(CH_3)_2$ ). MS (MALDI-TOF)  $m/z$ : 1171.6  $[M+H]^+$ , 627.3  $[M-C_{31}H_{47}S_3Si]^+$ . Elemental analysis: Calcd. for  $C_{66}H_{98}O_2S_6Si_2$  (1172.04): C 67.63, H 8.43; Found: C 67.51, H 8.33.

*1,4-Bis(5-(11-(2-ethylhexyl)dimethylsilyl)undec-1-yl)-2,2':5',2''-terthien-5''-yl)-butane-1,4-dione (29)*. Compound **25** (0.73 g, 0.55 mmol) was dissolved in THF (40 mL). Then conc. HCl (2 mL) was added. The mixture was stirred at 60 °C for 20 h. After cooling to room temperature, the resulting precipitate was filtered, washed with acetone, and dried in vacuo to give **29** as a yellow solid (0.63 g, 92%). Melting point (mp): 235 °C.  $^1H$  NMR (400 MHz,  $C_2D_2Cl_4$ ),  $\delta$  [ppm]: 7.72 (d,  $^3J(4'',3'') = ^3J(3''''',4''''') = 4.0$  Hz, 2 H, 4''-H, 3''''-H), 7.24 (d,  $^3J(H,H) = 3.8$  Hz, 2 H, 3'-H, 4''''-H or 4'-H, 3''''-H), 7.20 (d,  $^3J(3'',4'') = ^3J(4''''',3''''') = 4.0$  Hz, 2 H, 3''-H, 4''''-H), 7.06-7.05 (m, 4 H, 3-H, 3''''-H and 3'-H, 4''''-H or 4'-H, 3''''-H), 6.73 (d,  $^3J(4,3) = ^3J(4''''',3''''') = 3.6$  Hz, 2 H, 4-H, 4''''-H), 3.35 (s, 4 H,  $CO(CH_2)_2CO$ ), 2.80 (t,  $^3J(\alpha,\beta) = 7.5$  Hz, 4 H,  $\alpha-CH_2$ ), 1.73-1.65 (m, 4 H,  $\beta-CH_2$ ), 1.39-1.22 (m, 50 H, CH and  $CH_2$ ), 0.90 (t,  $^3J(H,H) = 7.0$  Hz, 6 H, hexyl- $CH_3$ ), 0.83 (t,  $^3J(H,H) = 7.3$  Hz, 6 H, ethyl- $CH_3$ ), 0.50-0.46 (m, 8 H,  $CH_2SiCH_2$ ), -0.02 (s, 12 H,  $Si(CH_3)_2$ ). MS (MALDI-TOF)  $m/z$ : 1227.2,  $[M+H]^+$ , 655.5  $[M-C_{33}H_{51}S_3Si]^+$ . Elemental analysis: Calcd. for  $C_{70}H_{106}O_2S_6Si_2$  (1228.15): C 68.46, H 8.70; Found: C 68.25, H 8.56.

*1,4-Bis(5-(6-(dimethylundecylsilyl)hex-1-yl)-2,2':5',2''-terthien-5''-yl)-butane-1,4-dione (30)*. Compound **26** (0.70 g, 0.56 mmol) was dissolved in THF (30 mL). Then conc. HCl (3 mL) was added. The mixture was stirred at 60 °C for 18 h. After cooling to room temperature, the resulting precipitate was filtered and washed with acetone. The orange crude product was recrystallized from acetone/THF (2:1) to give **30** as a yellow solid (0.50 g, 77%). Melting point (mp): 214 °C.  $^1H$  NMR (400 MHz,  $C_2D_2Cl_4$ )  $\delta$  [ppm]: 7.72 (d,  $^3J(4'',3'') = ^3J(3''''',4''''') = 3.8$  Hz, 2 H, 4''-H, 3''''-H), 7.24 (d,  $^3J(H,H) = 3.8$  Hz, 2 H, 3'-H, 4''''-H or 4'-H, 3''''-H), 7.20 (d,  $^3J(3'',4'') = ^3J(4''''',3''''') = 3.8$  Hz, 2 H, 3''-H, 4''''-H), 7.06-7.05 (m, 4 H, 3-H, 3''''-H and 3'-H, 4''''-H or 4'-H, 3''''-H), 6.74 (d,  $^3J(4,3) = ^3J(4''''',3''''') = 3.8$  Hz, 2 H, 4-H, 4''''-H), 3.36 (s, 4 H,  $CO(CH_2)_2CO$ ), 2.81 (t,  $^3J(\alpha,\beta) = 7.4$  Hz, 4 H,  $\alpha-CH_2$ ), 1.73-1.65 (m, 4 H,  $\beta-CH_2$ ), 1.38-1.27 (m, 48 H,  $CH_2$ ), 0.89 (t,  $^3J(H,H) = 6.8$  Hz, 6 H,  $CH_3$ ), 0.51-0.47 (m, 8 H,  $CH_2SiCH_2$ ), -0.04 (s, 12 H,  $Si(CH_3)_2$ ). MS (MALDI-TOF)  $m/z$ : 1171.7  $[M+H]^+$ , 627.4  $[M-C_{31}H_{47}S_3Si]^+$ . Elemental analysis: Calcd. for  $C_{66}H_{98}O_2S_6Si_2$  (1172.04): C 67.63, H 8.43; Found: C 68.22, H 8.64.

*1,4-Bis(5-(3-(dimethyltetradecylsilyl)prop-1-yl)-2,2':5',2''-terthien-5''-yl)-butane-1,4-dione (31)*. Compound **27** (0.65 g, 0.52 mmol) was dissolved in THF (20 mL). Then conc. HCl (2 mL) was added and the mixture was stirred for 16 h at 50 °C. After cooling to room temperature, acetone (10 mL) was added and the resulting precipitate was filtered and washed with acetone. The crude product was recrystallized from acetone/THF (1:1) and **31** was obtained as a yellow solid (0.57 g, 94%). Melting point (mp): 189 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  [ppm]: 7.69 (d,  $^3J(4'',3'') = ^3J(3''''',4''''') = 3.8$  Hz, 2 H, 4''-H, 3''''-H), 7.19 (d,  $^3J(H,H) = 4.0$  Hz, 2 H, 3'-H, 4''''-H or 4'-H, 3''''-H), 7.14 (d,  $^3J(3'',4'') = ^3J(4''''',3''''') = 4.0$  Hz, 2 H, 3''-H, 4''''-H), 7.01 (d,  $^3J(H,H) = 4.0$  Hz, 2 H, 3'-H, 4''''-H or 4'-H, 3''''-H), 7.01 (d, 2 H,  $^3J(3,4) = ^3J(3''''',4''''') = 3.6$  Hz, 3-H, 3''''-H), 6.68 (d,  $^3J(4,3) = ^3J(4''''',3''''') = 3.6$  Hz, 2 H, 4-H, 4''''-H), 3.35 (s, 4 H,  $CO(CH_2)_2CO$ ), 2.79 (t,  $^3J(\alpha,\beta) = 7.2$  Hz, 4 H,  $\alpha-CH_2$ ), 1.68-1.62 (m, 4 H,  $\beta-CH_2$ ), 1.25-1.24 (m, 48 H,  $CH_2$ ), 0.86 (t,  $^3J(H,H) = 6.8$  Hz, 6 H,  $CH_3$ ), 0.59-0.55 (m, 4 H,  $\beta-CH_2CH_2$ ), 0.49-0.46 (m, 4 H,  $SiCH_2$ ), -0.05 (s, 12 H,  $Si(CH_3)_2$ ). MS (MALDI-TOF)  $m/z$ : 1170.2  $[M]^+$ . Elemental analysis: Calcd. for  $C_{66}H_{98}O_2S_6Si_2$  (1172.04): C 67.63, H 8.43; Found: C 67.46, H 8.38.

*5,5''''''-Bis(11-(hexyldimethylsilyl)undec-1-yl)-2,2':5',2''':5''',2''''':5''''',2''''''-septithiophene (32)*. To a solution of diketone precursor **28** (460 mg, 0.39 mmol) in dry THF (50 mL), Lawesson's reagent (470 mg, 1.16 mmol) was added. The reaction was stirred under reflux for 22 h. After cooling to room temperature, the resulting precipitate was separated by centrifugation and washed several times with THF. The crude product was recrystallized from THF to give **32** as a red solid (390 mg, 85%). Melting point (mp): 290 °C.  $^1H$  NMR (500 MHz,  $C_2D_2Cl_4$ , 100 °C)  $\delta$  [ppm]: 7.15 (s, 2 H, 3''-H, 4''-H), 7.15 (d,  $^3J(H,H) = 3.7$  Hz, 2 H, 3''-H, 4''''-H or 4''-H, 3''''-H), 7.13 (d,  $^3J(H,H) = 3.9$  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), 7.07 (d,  $^3J(H,H) = 3.7$  Hz, 2 H, 3'-H, 4''''-H or 4'-H, 3''''-H), 7.05 (d,  $^3J(3,4) = ^3J(3''''',4''''') = 3.5$  Hz, 2 H, 3-H, 3''''-H), 6.75 (d,  $^3J(4,3) = ^3J(4''''',3''''') = 3.5$  Hz, 2 H, 4-H, 4''''-H), 2.86 (t,  $^3J(\alpha,\beta) = 7.5$  Hz, 4 H,  $\alpha-CH_2$ ), 1.80-1.74 (m, 4 H,  $\beta-CH_2$ ), 1.42-1.36 (m, 48 H,  $CH_2$ ), 0.96 (t,  $^3J(H,H) = 7.0$  Hz, 6 H,  $CH_3$ ), 0.58-0.55 (m, 8 H,  $CH_2SiCH_2$ ), 0.03 (s, 12 H,  $Si(CH_3)_2$ ). MS (MALDI-TOF)  $m/z$ : 1168.6  $[M]^+$ . Elemental analysis: Calcd. for  $C_{66}H_{96}S_7Si_2$  (1170.09): C 67.75, H 8.27; Found: C 67.55, H 8.18.

*5,5''''''-Bis(11-(2-(ethylhexyl)dimethylsilyl)undec-1-yl)-2,2':5',2''':5''',2''''':5''''',2''''''-septithiophene (33)*. To a solution of diketone precursor **29** (0.25 g, 0.2 mmol) in dry THF (30 mL), Lawesson's reagent (0.24 g, 0.6 mmol) was added. The reaction was stirred under reflux for 18 h. After cooling to room temperature the resulting precipitate was filtered. The crude product was suspended in hot THF (40 mL) for 1 h, filtered and dried in vacuo. **33** was obtained as a red solid (0.21 g, 82%). Melting point (mp): 285 °C.  $^1H$  NMR (500 MHz,  $C_2D_2Cl_4$ , 100 °C),  $\delta$  [ppm]: 7.15-7.12 (m, 8 H, 3''-H, 4''-H, 3''''-H, 4''''-H, 3''''-H, 4''''-H and 3'-H, 4''''-H or 4'-H, 3''''-H), 7.07 (d,  $^3J(H,H) = 3.8$  Hz, 2 H, 3'-H, 4''''-H or 4'-H, 3''''-H), 7.05 (d,  $^3J(3,4) = ^3J(3''''',4''''') = 3.6$  Hz, 2 H, 3-H, 3''''-H), 6.75 (d,  $^3J(4,3) = ^3J(4''''',3''''') = 3.6$  Hz, 2 H, 4-H, 4''''-H), 2.86 (t,  $^3J(\alpha,\beta) = 7.6$  Hz, 4 H,  $\alpha-CH_2$ ), 1.79-1.74 (m, 4 H,  $\beta-CH_2$ ), 1.42-1.30 (m, 50 H, CH and  $CH_2$ ), 0.96 (t,  $^3J(H,H) = 7.0$  Hz, 6 H, hexyl- $CH_3$ ), 0.91 (t,  $^3J(H,H) = 7.4$  Hz, 6 H, ethyl- $CH_3$ ), 0.58-0.56 (m, 8 H,  $CH_2SiCH_2$ ), 0.05 (s, 12 H,  $Si(CH_3)_2$ ). MS (MALDI-TOF)  $m/z$ : 1225.2  $[M+H]^+$ . Elemental analysis: Calcd. for  $C_{70}H_{104}S_7Si_2$  (1126.2): C 68.57, H 8.55; Found: C 68.18, H 8.18.

5,5''''''-Bis(6-(dimethylundecylsilyl)hex-1-yl)-2,2':5',2'':5'',2''':5''',2''''':5''''''-septithiophene (**34**). A solution of diketone precursor **30** (455 mg, 0.39 mmol) and Lawesson's reagent (470 mg, 1.16 mmol) in dry THF (40 mL) was stirred under reflux for 18 h. After cooling to room temperature, the resulting precipitate was separated by centrifugation and washed several times with THF. The crude product was recrystallized from THF to give **34** as a red solid (400 mg, 83%). Melting point (mp): 260 °C. <sup>1</sup>H NMR (500 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 100 °C), δ [ppm]: 7.15 (s, 2 H, 3'''-H, 4'''-H), 7.15 (d, <sup>3</sup>J(H,H) = 3.7 Hz, 2 H, 3''-H, 4''''-H or 4''-H, 3''''''-H), 7.13 (d, <sup>3</sup>J(H,H) = 3.8 Hz, 2 H, 3''-H, 4''''-H or 4''-H, 3''''''-H), 7.12 (d, <sup>3</sup>J(H,H) = 3.7 Hz, 2 H, 3'-H, 4''''''-H or 4'-H, 3''''''-H), 7.07 (d, <sup>3</sup>J(H,H) = 3.7 Hz, 2 H, 3'-H, 4''''''-H or 4'-H, 3''''''-H), 7.05 (d, <sup>3</sup>J(3,4) = <sup>3</sup>J(3''''''', 4''''''') = 3.5 Hz, 2 H, 3-H, 3''''''-H), 6.75 (d, <sup>3</sup>J(4,3) = <sup>3</sup>J(4''''''', 3''''''') = 3.5 Hz, 2 H, 4-H, 4''''''-H), 2.86 (t, <sup>3</sup>J(α,β) = 7.5 Hz, 4 H, α-CH<sub>2</sub>), 1.80–1.74 (m, 4 H, β-CH<sub>2</sub>), 1.42–1.35 (m, 48 H, CH<sub>2</sub>), 0.95 (t, <sup>3</sup>J(H,H) = 7.0 Hz, 6 H, CH<sub>3</sub>), 0.60–0.56 (m, 8 H, CH<sub>2</sub>SiCH<sub>2</sub>), 0.04 (s, 12 H, Si(CH<sub>3</sub>)<sub>2</sub>). MS (MALDI-TOF) *m/z*: 1168.6 [M]<sup>+</sup>. Elemental analysis: Calcd. for C<sub>66</sub>H<sub>96</sub>S<sub>7</sub>Si<sub>2</sub> (1170.09): C 67.75, H 8.27; Found: C 67.71, H 8.32.

5,5''''''-Bis(3-(dimethyltetradecylsilyl)prop-1-yl)-2,2':5',2'':5'',2''':5''',2''''':5''''''-septithiophene (**35**). A solution of diketone precursor **31** (0.40 g, 0.34 mmol) and Lawesson's reagent (0.41 g, 1.02 mmol) in dry THF (35 mL) was stirred under reflux for 18 h. After cooling to room temperature, acetone

(10 mL) was added and the resulting precipitate was filtered. The crude product was then recrystallized from THF/acetone (4:1). **35** was obtained as a red powder (0.37 g, 92%). Melting point (mp): 241 °C. <sup>1</sup>H NMR (500 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 100 °C), δ [ppm]: 7.15–7.12 (m, 8 H, 3''-H, 4''-H, 3''''-H, 4''''-H, 3''''''-H, 4''''''-H and 3''''''-H, 4''-H or 4''''''-H, 3'-H), 7.07 (d, <sup>3</sup>J(H,H) = 3.8 Hz, 2 H, 3'-H, 4''''''-H or 4'-H, 3''''''-H), 7.06 (d, <sup>3</sup>J(3,4) = <sup>3</sup>J(3''''''', 4''''''') = 3.7 Hz, 2 H, 3-H, 3''''''-H), 6.75 (d, <sup>3</sup>J(4,3) = <sup>3</sup>J(4''''''', 3''''''') = 3.7 Hz, 2 H, 4-H, 4''''''-H), 2.88 (t, <sup>3</sup>J(α,β) = 7.4 Hz, 4 H, α-CH<sub>2</sub>), 1.81–1.75 (m, 4 H, β-CH<sub>2</sub>), 1.38–1.35 (m, 48 H, CH<sub>2</sub>), 0.95 (t, <sup>3</sup>J(H,H) = 6.9 Hz, 6 H, CH<sub>3</sub>), 0.69–0.67 (m, 4 H, β-CH<sub>2</sub>CH<sub>2</sub>), 0.61–0.58 (m, 4 H, SiCH<sub>2</sub>), 0.06 (s, 12 H, Si(CH<sub>3</sub>)<sub>2</sub>). MS (MALDI-TOF), *m/z*: 1168.5 [M]<sup>+</sup>. Elemental analysis: Calcd. for C<sub>58</sub>H<sub>80</sub>S<sub>7</sub>Si<sub>2</sub> (1170.09): C 67.75, H 8.27; Found: C 67.91, H 8.39.

**Acknowledgment.** The authors acknowledge the European Synchrotron Radiation Facility for providing the excellent environment for X-ray measurements. We are grateful to W. Bras and G. Portale (BM26, ESRF) and T. Narayanan (ID02, ESRF) for assistance in the experiments. The authors are grateful to D. Anokhin and M. Rosenthal for fruitful discussions. M.D. gratefully acknowledges financial support from the CNRS and Region of Alsace (BDI bursary). We gratefully acknowledge financial support of the present work by the *Deutsche Forschungsgemeinschaft* (ZI567/4-1).