Polymer-Supported Synthesis of Regioregular Head-to-Tail-Coupled Oligo(3-arylthiophene)s Utilizing a Traceless Silyl Linker

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The solid-phase synthesis of regioregular head-to-tail-coupled oligo(3-arylthiophene)s has been achieved in high yield and purity by using a traceless silyl ether linkage. In the first step, the solution-phase synthesis of this class of conjugated oligomers was investigated. Benzyl alcohol was chosen to serve as a mimic for the anchoring group of the hydroxymethyl-substituted polystyrene matrix. The development of a novel regioselective iodination process for silyl-protected thiophenes faciliates the successful application of the solution-phase protocol to the solid phase. Satisfactory loading was obtained by reaction of chlorosilyl-functionalized 3-arylthiophene with hydroxymethyl polystyrene in the presence of imidazole. The suitability of the following iterative halogenation and Suzuki cross-coupling sequence is illustrated by the preparation of a quater(3-arylthiophene), the first regioregular head-to-tail-coupled oligothiophene that is synthesized on solid support. Removal of the conjugated oligomers from the solid support could be effectively achieved by treatment with tetrabutylammonium fluoride.

Introduction

There is a considerable interest in the development of conjugated oligomers and polymers for applications in electronic devices, including all-organic field-effect transistors[1] and light emitting devices.[2] Polythiophene-based materials are particularly attractive, as these compounds are characterized by an excellent environmental and thermal stability.[3] Due to the statistical nature of polymerization processes, most synthetic reactions affording polymeric materials generate polydisperse compounds. As it became clear that regioregular head-to-tail-coupled poly(3-alkylthiophene)s show decidedly improved electronic properties in comparison to corresponding regiorandom polymers, several research groups started to selectively engineer this class of conducting polymers.[4] It is important to realize that the investigation of α-oligothiophenes as model compounds for the corresponding polymers provides specific information concerning their molecular and especially electronic properties.[5] Very recently, several synthetic routes to regioregular head-to-tail-coupled oligo(3-alkylthiophene)s were reported, but the synthesis of these model compounds generally faces some inherent problems.[6−8] Besides the moderate yields often reported for aryl/aryl cross-coupling steps in Stille or Suzuki reactions of longer oligomers, the appearance of homocoupling products impedes the purification processes.

To circumvent these time-consuming purification processes and to increase the yields for the transition metal-catalyzed cross-coupling reactions, a solid-phase strategy for the synthesis of these conjugated oligomers should perfectly overcome the problems of solution-phase synthesis. The possibility to use the coupling components in excess and to remove byproducts such as homocoupling products by washing should faciliate a fast and high-yielding synthesis. A few recent reports have demonstrated that synthesis of conjugated oligomers can successfully be performed on solid support.[9] Malenfant and Fréchet[9d] more recently reported the first polymer-supported synthesis of asymmetric oligothiophenes using an ester linkage to the Merrifield resin. Starting from an unsubstituted resin-bound bithiophene, alternating sequences of bromination and Stille cross-coupling reactions afforded an α-carboxy-substituted pentamer after cleavage from the polymer matrix.

Now, solid-phase synthesis has been established as a powerful methodology for preparing compound libraries by automated parallel and combinatorial synthesis, accelerating the search for new bioactive molecules.[10] Recently, it was shown that combinatorial strategies can be successfully applied to optimize lead structures in

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materials science. Mainly, inorganic materials libraries for new luminescent phosphors, high-temperature superconductors, and thin-film dielectric materials have been created by using combinatorial methods.[11]

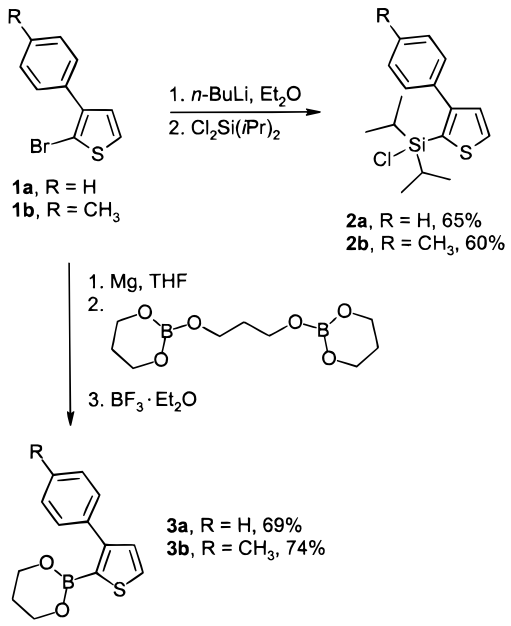
Our work is directed toward the development of a combinatorial methodology for the synthesis of conjugated oligomer libraries with special electronic properties. In this investigation, we focus our interest on the preparation of head-to-tail-coupled oligo(3-arylthiophene)s. So far, no synthetic studies have appeared in the literature concerning solution- or solid-phase synthesis of this type of oligomers. A systematic investigation including suitable screening methods could clearly elucidate the influence of different aryl substituents on molecular and especially electronic properties. Structure/property relationships obtained from this study will provide us with the possibility to develop new poly- and oligothiophene-based materials.

As a first step to a combinatorial approach, we developed an efficient synthetic route to this class of conjugated oligomers in solution in order to mimic the following polymer-supported synthesis. Transfer of this model to a solid-phase protocol will be an essential step toward the automated parallel synthesis and therefore to a combinatorial approach.

Herein, we report the synthesis of regioregular head-to-tail-coupled oligo(3-arylthiophene)s in solution and the application of the solution-phase protocol to solid support.

Several linker systems enable first the attachment of the core moieties to the solid support and second the cleavage of the generated oligomers after solid-phase synthesis. For example, carboxy and traceless triazene linkers were successfully applied to the solid-phase synthesis of conjugated oligomers.[9] Given that the presence of polar functionalities on the oligomeric backbone may bestow undesirable electrochemical and physicochemical properties, we aimed for nonfunctionalized oligothiophenes by using a traceless linker technology. The first and by far most widely explored of these traceless linkers is the silyl linker.[12] We chose a diisopropylsilyl ether linkage which was developed by Boehm and Showalter for the synthesis of 3-arylbenzofurans.[13] An attractive feature of this linker, besides the incorporation of two sterically demanding isopropyl groups, is the silyl ether functionality, which decidedly enhances the stability of the resin−linker−compound connection. Therefore, this traceless linkage is compatible with a wide range of reagents and various synthetic methodologies. Cleavage of the aryl−silicon bond and thus the release of the oligomer can be mildly affected by fluoride-mediated protiodesilylation leaving no residual functionality from linkage to the solid support. Moreover, the silyl linker provides a broad versatility to further functionalize the linear conjugated oligomers in the α-position by cleavage of the heteroaryl−silicon bond in the presence of electrophilic halogen or acyl sources.[14] Furthermore, fluoride-mediated transition metal-catalyzed cross-coupling reactions with aryl halides would result in unsymmetric aryl end-capped oligothiophenes.[15]

Scheme 1



Results and Discussion

Monomer Synthesis for the Solution- and Solid-Phase Approaches. The syntheses of the monomeric thiophene building blocks for the solution- and solid-phase approaches are depicted in Scheme 1. Terminal diisopropylsilyl groups were affixed to 3-arylthiophenes by lithium−halogen exchange of 2-bromo-3-arylthiophenes **1a**,**b**[16] with *n*-butyllithium and subsequent quenching with dichlorodiisopropylsilane. Chloro(diisopropyl)silylthiophenes **2a**,**b** were prepared in 65% and 60% yield, respectively. Furthermore, bromides **1a**,**b** were converted to the boronic esters **3a**,**b** in 69% and 74% yield, respectively, by adding 2,2′-propane-1,3-diyldioxyborinane to the Grignard reagent of **1a**,**b**, and treatment of the intermediates with boron trifluoride etherate.

Oligomer Synthesis in Solution. To implement our strategy for the solid-phase synthesis of oligo(3-arylthiophene)s, we investigated a model oligomer synthesis in a solution-phase study. Benzyl alcohol was chosen to serve as a mimic for the anchoring group of the polystyrene matrix. Regioregular head-to-tail-coupled oligo(3-

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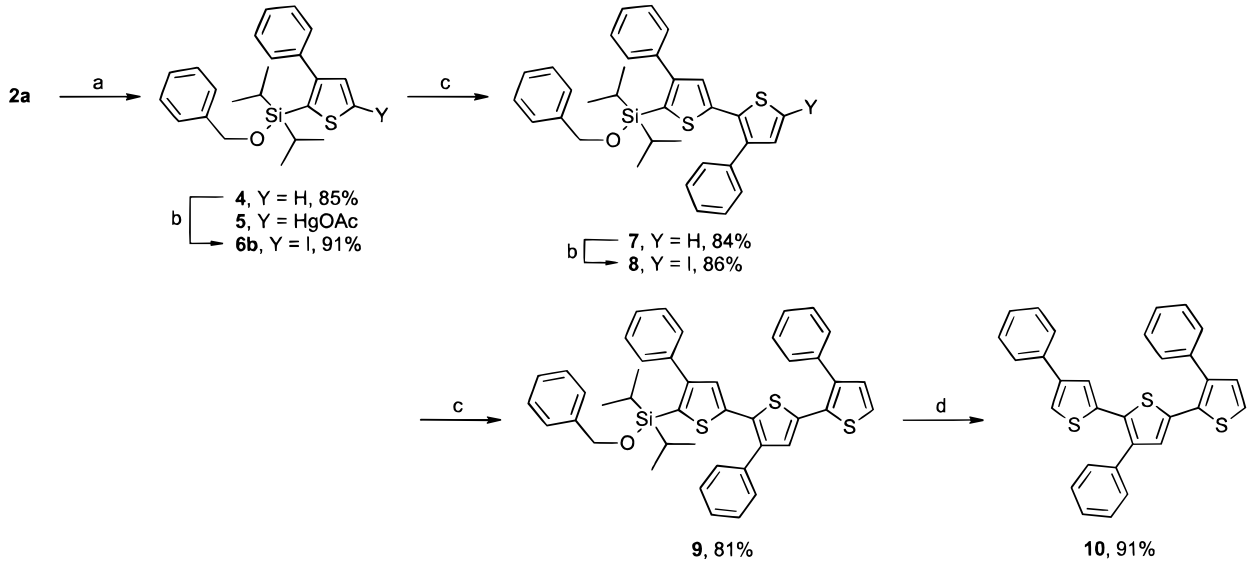
Scheme 2[a]



[a] Reagents: (a) $PhCH_2OH$, imidazole, DMF. (b) (1) $Hg(OAc)_2$, $CHCl_3$; (2) I_2. (c) **3a**, $Pd(PPh_3)_4$ (5 mol %), $NaHCO_3$, DME. (d) TBAF, THF.

arylthiophene)s should be available via a stepwise activation−elongation sequence as shown in Scheme 2. Silylated thiophene **2a** was treated with benzyl alcohol in the presence of imidazole at ambient temperature, yielding 85% of the desired benzyloxysilylthiophene **4**. As reported by Tour and Wu[17] for alkylated thiophenes bearing an α-trimethylsilyl group, the use of silica gel in chromatographic purifications partly resulted in the desilylation of the silylthiophene. To completely retain the silyl group on the monomer and oligomer termini, we used basic Al_2O_3 for purification processes.

Two different synthetic routes to halogenated silylthiophenes and oligothiophenes were investigated. Generally, iodination of the protected 3-phenylthiophene **4** should be possible, on one hand, by iodination of an in situ-generated lithiothiophene or by electrophilic aromatic substitution with elemental iodine. Treatment of **4** with *n*-butyllithium afforded the lithiated derivative, which subsequently reacted with iodine to afford iodosilylthiophene **6b** in 75% yield. On the other hand, we investigated the feasibility of an iodination by electrophilic aromatic substitution. As the silyl protecting group is not orthogonally stable to reactive electrophiles, it is obvious that both α-positions of the electronically activated 3-phenylthiophene **4** can be attacked by halogen electrophiles. The reaction of thiophene **4** with halogen electrophiles affords a mixture of 2-halo-3-phenylthiophene **1a** or **1c** and the desired substitution product **6a** or **6b**, as shown in Scheme 3. As indicated by the results summarized in Table 1, the product ratio is greatly dependent on the electrophile reactivity. As shown by entry 1, the substitution reaction with bromine as electrophile is not sensitive to the steric hindrance of the two diisopropyl groups in the vicinity of the site of electrophilic attack. The use of the mild electrophile NBS resulted in a preferred formation of **1a** (**1a**:**6a** = 89:11). Elemental iodine showed no conversion of the starting material **4** after 48 h (entry 2). Activation of elemental iodine with mercuric acetate led to a nearly 1:1 mixture

Scheme 3

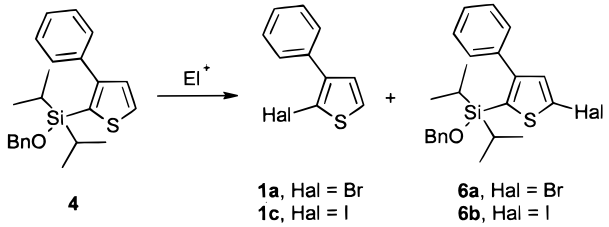


Table 1. Electrophilic Aromatic Halogenation of Silylthiophene 4

entry	reagent[a]	**1a,c** (%)	**6a,b** (%)
1	NBS	89	11
2	I_2	—[b]	—[b]
3	I_2, $Hg(OAc)_2$	48	52
4	(1) $Hg(OAc)_2$, (2) I_2	<1	>99

[a] Reaction conditions: solvent chloroform, equimolar ratio of **4** and reagent. [b] Starting compound remained unchanged after 48 h.

of **1c** and **6b** (entry 3). Interestingly, no trace of undesired mercuration/desilylation was observed when mercuric acetate was added in a first step. The addition of iodine afforded then, in a high selectivity, the desired 2-iodo-5-silylthiophene **6b** (entry 4). The reason for the selectivity of this halogenation reaction is the formation of an α′-mercurated silylthiophene **5** as an intermediate, which can be further iododemercurated to iodosilylthiophene **6b** in 91% yield. The reason for the high selectivity of the mercuration reaction seems to be preliminary coordination of a mercury atom to the thiophene sulfur atom.[18] As the mercuration/halodemercuration procedure results in nearly quantitative yield, we certainly prefer this halogenation method for the oligomer activation in solution.

Palladium-catalyzed cross-coupling reactions have been reported to proceed cleanly for substituted α-iodothio-

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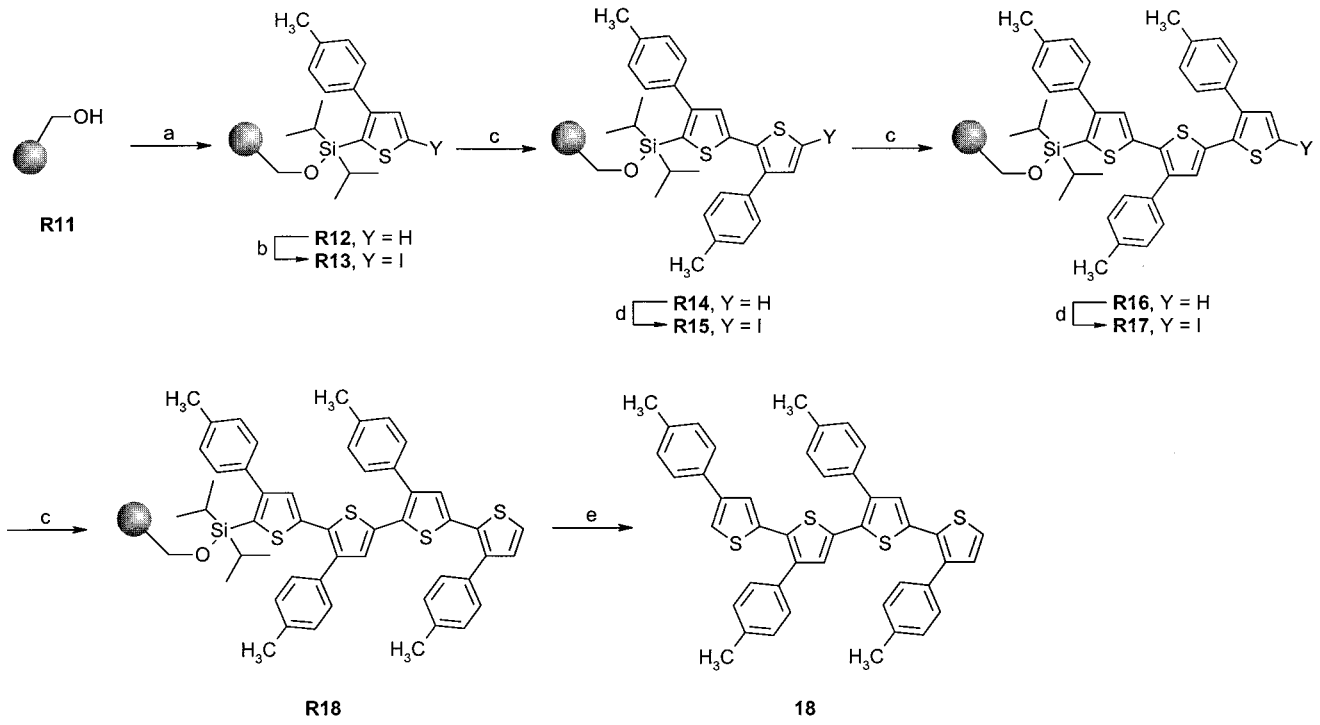
Scheme 4[a]



[a] Reagents: (a) **2b**, imidazole, DMF. (b) (1) LDA, THF; (2) I_2. (c) **3b**, $Pd(PPh_3)_4$ (5 mol %), $NaHCO_3$, THF. (d) (1) $Hg(OCOC_5H_{11})_2$, CH_2Cl_2; (2) I_2. (e) TBAF, THF.

phenes.[7,8b,19] The silyl-protected iodothiophene **6b** underwent facile Suzuki reaction with boronic ester **3a** to provide bithiophene **7** in 84% yield. Similarly to silylthiophene **4**, bithiophene **7** was iodinated after mercuration to afford iodide **8** in 86% yield. As in the case of iodothiophene **6b**, iodobithiophene **8** was treated with excess boronic ester **3a** and Pd catalyst to afford silylated head-to-tail-coupled triphenylterthiophene **9** in 81% yield.

Cleavage of the protecting group can be smoothly effected at any stage of the synthesis by using tetrabutylammonium fluoride (TBAF) in THF at ambient temperature. This fluoride-mediated desilylation proceeds nearly quantitatively, and, e.g., deprotection of silylterthiophene **9** afforded purely head-to-tail-coupled triphenylterthiophene **10** in 91% yield. Silanol and siloxane byproducts were observed in the crude mixtures by ^{1}H NMR and GC/MS which easily could be removed by filtration over silica.

Oligomer Synthesis on Solid Support. To successfully transfer the reported solution-phase protocol to solid support, we chose commercially available hydroxymethyl-substituted polystyrene **R11** (**R** = resin) as a matrix for the oligomer growth. Scheme 4 outlines the synthetic methodology for the solid-phase synthesis of regioregular aryl-substituted thiophene oligomers from the monomer to the tetramer. The resin-bound 3-(*p*-tolyl)thiophene **R12** was obtained by reaction of chloro(diisopropyl)-silylthiophene **2b** with hydroxymethylated polystyrene **R11** in the presence of imidazole. To maximize the loading, we used excessive chlorosilylated thiophene **2b** (2.5 equiv) for adaption to the solid-phase.

In the next step, halogenation of the resin-bound thiophene **R12** was investigated. In contrast to solution-phase synthesis, electrophilic aromatic substitution of substrates immobilized on polystyrene resins is inherently complicated by the reactivity of the solid support itself. Successful examples of electrophilic aromatic substitutions involving resin-bound compounds usually involve an activated aromatic system, or the functionality is achieved by methods avoiding this problematic reaction.[12b,20,21] In our approach, we were not able to attach or couple halogenated building blocks to the resin and the growing oligomer. Therefore, we were dependent on halogenation methods that selectively react with the thiophene moieties. Since thiophenes, in contrast to the polystyrene phenyl units, have in the α-position an extremely high reactivity to electrophiles and, moreover, the α-positions can be easily deprotonated by suitable bases, the mercuration/halodemercuration procedure and the lithiation/halodelithiation reaction should be selective methods for introducing halogen into a resin-bound thiophene.

Thiophene-derivatized resin **R12** was subjected to the novel mercuration/iododemercuration procedure. In contrast to the solution-phase chemistry, however, in this case a remarkably high portion of halodesilylation was observed. This discrepancy in reactivity between the resin-bound silylthiophene **R12** and the corresponding thiophene **4** in solution is so far not clearly understood. Alternatively, directed *ortho*-lithiation of the reactive α-position in **R12** and subsequent reaction with iodine afforded nearly quantitatively iodinated resin **R13**. Lithiation was performed using 3 equiv of LDA at room temperature. The following Suzuki reaction of thiophene boronic ester **3b** with the solid-phase attached 2-iodo-4-arylthiophene **R13** was carried out using typical solution-

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phase Suzuki conditions [excess of boronic ester, 5 mol % $Pd(PPh_3)_4$]. Although DME was the solvent of choice for the solution-phase reaction, presumably as a result of its superior resin-swelling ability, THF was preferred for solid-phase synthesis. Slightly more than 2 equiv of boronic ester **3b** was necessary to drive the reaction to completion. The typical use of fluoride salts as bases in nonaqueous Suzuki coupling reactions[7] would mediate the cleavage of the oligothiophene from the polymer matrix. Therefore, aqueous conditions with $NaHCO_3$ as an activating base were used and proved to be suitable. The resin-bound bithiophene **R14** was generated in high yield. Since in comparison to the iodination of the support-bound thiophene **R12** the yield of the iodination of polymer-bound bithiophene **R14** decreases considerably when LDA is used for metalation, we reacted the resin-bound bithiophene **R14** with mercuric caproate, which was used instead of the corresponding acetate taken in the solution synthesis. This reaction condition was elaborated for solid-phase synthesis because the caproate has markedly higher solubility in CH_2Cl_2. Since mercurated thiophene **5** could be unambiguously proven, it is very likely that, at the resin, an analogous species was also formed. The synthesis of the iodinated bithiophene **R15** was finally completed by addition of iodine to the resin-bound organometallic compound. To control whether desilylation occurred, the resin washings were concentrated but did not provide any UV-active material in the TLC. The fact that mercuration occurred along with a complete lack of electrophilic desilylation demonstrates the power of this halodemercuration reaction also on solid support. As in the case of iodothiophene **R13**, resin-bound iodobithiophene **R15** underwent an efficient Suzuki cross-coupling reaction and afforded terthiophene **R16** under the same reaction conditions. An additional iteration of the halogenation/Suzuki coupling sequence gave the resin-bound quaterthiophene **R18**.

We observed facile and clean removal of compounds **12**−**18** from the resin in high isolated yields when TBAF in THF was used at 70 °C for 1 h. For example, mild protiodesilylation of quaterthiophene-derivatized resin **R18** afforded the corresponding regioregular head-to-tail-coupled tetraarylated quaterthiophene **18** in 48% overall yield. This corresponds to an average yield of 91% over eight reaction steps, including attachment, halogenation, coupling, and cleavage reactions. Contaminants observed were the corresponding bi- and terthiophenes, which could be easily removed by HPLC purification. Table 2 provides detailed information on product concentrations in final resins **R12**−**R18**, conversions, and isolated overall yields of thiophenes **12**−**18** after protiodesilylation.

Monitoring the progress of the solid-phase reactions by FTIR spectroscopy caused some problems since the compounds did not include typical functional groups with characteristic absorption bands. The attachment of chlorosilylthiophene **2b** to hydroxymethyl polystyrene **R11** could be quantitatively controlled by infrared analysis using KBr pellets. A sharp band at 3573 cm^{-1} and a broad band at 3449 cm^{-1}, which are attributed to the free and intraresin hydrogen-bonded hydroxy groups of resin **R11**, disappeared when anchoring of the chlorosilylthiophene **2b** was complete. Determined by this spectroscopic method, the product concentration in **R12** was greater than 98%. However, the on-bead analysis failed for monitoring the progress of the halogenation/cross-coupling reaction sequence. Therefore, we estimated the product concentration in the final resins by weight change. The concentration of **R12** calculated by weight change was confirmed by infrared analysis and thus used as a basis for further calculations. According to the literature,[9c] these calculated concentrations are only a rough estimation, as the results are often not reliable. Additionally, we estimated the conversion of the reactions by liberating the oligomers from the polymer-supports followed by ^1H NMR, GC, and HPLC analysis.

Table 2. Product Concentration in the Resins R12−R18 and Conversion and Isolated Yields of Thiophenes and Oligothiophenes 12−18

resin	conc[a] (mmol/g)	conv[b] (%)	isolated yield[c] (%)
R12	0.56	>99[d]	93 (of **12**)
R13	0.49	>98[e]	91 (of **13**)
R14	0.46	>98[e,f]	87 (of **14**)
R15	0.38	>90[e]	71 (of **15**)
R16	0.34	—[g]	68 (of **16**)
R17	0.27	—[h]	54 (of **17**)
R18	0.26	—[i]	48 (of **18**)

[a] Product concentration in the resin determined by resin weight difference (average of three experiments). [b] With respect to the resin. [c] Compounds **12**−**18** were purified after cleavage by silica gel chromatography or preparative HPLC. Yields based on 0.67 mmol/g hydroxymethyl substitution of polystyrene **R11** given by the manufacturer. [d] Determined by infrared analysis. [e] Determined from relative peak areas of ^1H NMR spectra in the crude product mixture after protiodesilylation. [f] Determined by GC integration. [g] Determination was problematic by HPLC because only bithiophene **14** as a product of Pd-mediated deiodination was detected besides product **16**. Ratio **16**:**14** = 81:19 (determination at 215 nm). [h] No determination possible. [i] Determination was problematic by HPLC because only terthiophene **16** as a product of Pd-mediated deiodination was detected besides product **18**. Ratio **18**:**16** = 69:31 (determination at 215 nm).

Summary

In conclusion, our work proves the suitability of a solid-phase approach to conjugated oligomers using a traceless silyl linkage. In particular, we have demonstrated the first two steps of a combinatorial approach to regioregular head-to-tail-coupled oligo(3-arylthiophene)s: the synthesis in solution and the consequent transfer to solid support. Our approach involves the first application of a traceless silyl linker for the preparation of conjugated oligomers, and this linkage proved to be compatible with the required activation and cross-coupling sequences. In solution-phase studies, we developed a novel halogenation method for silyl-protected thiophenes based on a mercuration/halodemercuration process. Taking advantage of the optimized reactions, this solution-phase synthesis has been successfully adapted to a solid-state protocol. Growing oligomers were attached to hydroxymethylated polystyrene by a traceless silyl linker. Iodination was effected by using either a mercuration/halodemercuration procedure or the reaction of the lithiated thiophene with elemental iodine. The Pd-catalyzed Suzuki cross-coupling reaction was carried out with excess of boronic ester and the iodinated resin-bound thiophenes. Removal of the conjugated oligomers from solid support could be effectively achieved by TBAF treatment.

Owing to the ease of the reactions carried out to build up the oligomeric backbone on solid support, a parallel preparation of these compounds incorporating *para*-substituted 3-arylthiophenes by automated synthesis

seems to be possible and is under active investigation. The diversity of an oligothiophene library generated by varying the 3-aryl substituents in the resulting oligomers together with rapid characterization methods will provide us a way to the accelerated investigation on structure/property relationships needed to design new oligo- and polythiophene-based materials.

Experimental Section

General Remarks. Solvents and reagents were purified and dried by usual methods prior to use. Preparative column chromatography was performed on silica gel 60 (0.020−0.200 nm) or aluminum oxide 90 (basic, activity stage II−III, 0.063−0.200). Melting points were determined with a Büchi B-545 melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer FTIR Spectrum 2000; absorptions are reported in cm^{-1}. The ^1H and ^{13}C NMR spectra were recorded at 500 and 200 MHz. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standard. Low- and high-resolution electron impact mass spectra were obtained operating at 70 eV. Assignments of corresponding fragments are appended in brackets. Elemental analyses were performed by the Ulm University Analytical Department. HPLC analysis was accomplished using an UV absorbance detector and a Nucleosil column (4 mm × 250 mm), 1.3 mL/min flow rate. Preparative HPLC was performed using a UV detector and a Nucleosil column (20 mm × 200 mm), 8 mL/min flow rate. All reactions were performed under argon. Polymer loading was determined by weighing the derivatized resins after extensive washing and drying in vacuo.

Benzyl alcohol (Merck), boron trifluoride etherate (Merck), *n*-butyllithium (Merck-Schuchardt), dichloro(diisopropyl)silane (Fluka), imidazole (Merck), iodine (Fluka), LDA (2 M in THF) (Fluka), magnesium turnings (Merck-Schuchardt), mercuric acetate (Merck), NBS (Merck-Schuchardt), and tetrabutylammonium fluoride (Fluka) were purchased and used without further purification. Tetrakis(triphenylphosphino)palladium-(0),[22] 2-bromo-3-phenylthiophene (**1b**),[16] 3-(*p*-tolyl)thiophene,[23] and 2,2′-propane-1,3-diyldioxybis[1,3,2]dioxaborinane[24] were prepared according to literature procedures. Hydroxymethyl polystyrene **R11** was purchased from Novabiochem with a loading capacity of 0.67 mmol/g (100−200 mesh, 1% DVB).

2-Bromo-3-(*p*-tolyl)thiophene (1b).[16] In the absence of light, a solution of NBS (9.40 g, 52.8 mmol) in 100 mL of DMF was added dropwise to a solution of 3-(*p*-tolyl)thiophene (10.0 g, 57.4 mmol) in 80 mL of DMF, and the mixture was stirred for 20 h at ambient temperature, poured onto ice, and extracted with diethyl ether. The organic phases were combined, washed with water, and dried over sodium sulfate. Evaporation of the solvent and distillation under reduced pressure yielded 11.9 g (82%) of the title compound as a slightly yellow liquid, bp 104 °C/0.03 mbar. ^1H NMR (200 MHz, $CDCl_3$): δ 2.34 (s, 3H), 6.94 (d, J = 5.7 Hz, 1H), 7.18 (d, J = 5.7 Hz, 1H), 7.16−7.42 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.19, 108.13, 125.64, 128.41, 129.00, 129.02, 132.04, 137.30, 141.06. MS (EI): m/z 254 (M^+), 173 ($M^+ - {}^{81}Br$). IR (neat): 1503, 1403, 1346, 1248, 984, 870, 815 cm^{-1}. Anal. Calcd for $C_{11}H_9SBr$: C, 52.19; H, 3.58; S, 12.67. Found: C, 52.19; H, 3.61; S, 12.70.

General Procedure for the Synthesis of 2-[Chloro-(diisopropyl)silyl]-3-arylthiophenes 2a and 2b.[15b] To a solution of 2-bromo-3-arylthiophene **1a**,**b** (10.0 mmol) in 40 mL of diethyl ether was added *n*-butyllithium (11 mmol, 1.6 M, in hexane) at −70 °C. The mixture was warmed to room temperature and added via cannula to a solution of dichloro-(diisopropyl)silane (15 mmol) in 40 mL of diethyl ether at −30 °C. After the mixture was stirred at ambient temperature for 1 h, solvent and excessive dichlorodiisopropylsilane were evaporated. Distillation of the residue afforded **2a**,**b** as colorless solids.

2-[Chloro(diisopropyl)silyl]-3-phenylthiophene (2a). From **1a** (2.39 g, 10.0 mmol), 2.00 g (65%) of the title product was obtained, bp 153 °C/0.78 mbar. ^1H NMR (200 MHz, $CDCl_3$): δ 0.88 (d, J = 6.4 Hz, 6H), 0.99 (d, J = 6.4 Hz, 6H), 1.07 (sp, J = 6.4 Hz, 1H), 1.11 (sp, J = 6.4 Hz, 1H), 7.16 (d, J = 4.7 Hz, 1H), 7.35−7.38 (m, 5H), 7.66 (d, J = 4.7 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 15.82, 17.14, 17.28, 127.66, 128.00, 128.45, 128.98, 131.52, 131.72, 138.56, 151.19. MS (EI): m/z 308 (M^+), 265 ($M^+ - C_3H_7$), 229 ($M^+ - C_3H_7 - Cl$). IR (KBr): 1599, 1481, 1461, 1384, 1361, 1104, 1003, 880 cm^{-1}. Anal. Calcd for $C_{16}H_{21}ClSSi$: C, 62.20; H, 6.85; S, 10.38. Found: C, 62.38; H, 6.89; S, 10.27.

2-[Chloro(diisopropyl)silyl]-3-(*p*-tolyl)thiophene (2b). From **1b** (2.53 g, 10.0 mmol), 1.94 g (60%) of the title product was obtained, bp 146 °C/0.45 mbar. ^1H NMR (200 MHz, $CDCl_3$): δ 0.88 (d, J = 6.4 Hz, 6H), 1.00 (d, J = 6.4 Hz, 6H), 1.07 (sp, J = 6.4 Hz, 1H), 1.11 (sp, J = 6.4 Hz, 1H), 2.39 (s, 3H), 7.14 (d, J = 4.7 Hz, 1H), 7.12−7.26 (m, 4H), 7.64 (d, J = 4.7 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 15.84, 17.18, 17.34, 21.22, 128.24, 128.73, 128.87, 131.59, 131.69, 135.63, 137.38, 151.25. MS (EI): m/z = 322 (M^+), 279 ($M^+ - C_3H_7$), 243 ($M^+ - C_3H_7 - Cl$). IR (KBr): 1489, 1466, 1099, 990, 884 cm^{-1}. Anal. Calcd for $C_{17}H_{23}ClSSi$: C, 63.22; H, 7.18; S, 9.93. Found: C, 63.25; H, 7.21; S, 10.05.

General Procedure for the Synthesis of 2-Thienyl-1,3,2-dioxaborinanes 3a and 3b. To a Grignard reagent prepared of 2-bromo-3-arylthiophene **1a**,**b** (10.0 mmol) and magnesium turnings (10.0 mmol) in 40 mL of THF was added dropwise at −30 °C 2,2′-propane-1,3-diyldioxybis[1,3,2]dioxaborinane (5.00 mmol). After being stirred at −30 °C for 1 h, the mixture was allowed to come to room temperature. At −70 °C, boron trifluoride etherate (10.0 mmol) was added dropwise to the solution. The mixture was stirred for 1 h at −70 °C and heated to room temperature. After evaporation of the solvent, the residue was dissolved in petroleum ether and filtrated over Celite to afford **3a**,**b** as colorless solids in 88−92% purity which were used without further purification.

2-(3-Phenyl-2-thienyl)-1,3,2-dioxaborinane (3a). From **1a** (2.39 g, 10.0 mmol), 1.68 g (69%) of the title product was obtained. ^1H NMR (200 MHz, $CDCl_3$): δ 1.99 (qn, J = 5.5 Hz, 2H), 4.03 (t, J = 5.5 Hz, 4H), 7.18 (d, J = 4.7 Hz, 1H), 7.24−7.52 (m, 5H), 7.43 (d, J = 4.7 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 27.18, 61.88, 126.75, 127.47, 129.16, 130.02, 131.00, 137.66, 150.51. MS (EI): m/z 244 (M^+).

2-(3-*p*-Tolyl-2-thienyl)-1,3,2-dioxaborinane (3b). From **1b** (2.53 g, 10.0 mmol), 1.90 g (74%) of the title product was obtained. ^1H NMR (200 MHz, $CDCl_3$): δ 1.98 (qn, J = 5.5 Hz, 2H), 2.37 (s, 3H), 4.04 (t, J = 5.5 Hz, 4H), 7.14−7.41 (m, 4H), 7.16 (d, J = 4.8 Hz, 1H), 7.49 (d, J = 4.8 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.18, 27.32, 61.99, 126.28, 128.34, 129.11, 129.99, 131.14, 134.84, 136.46. MS (EI): m/z 258 (M^+).

2-[Benzyloxy(diisopropyl)silyl]-3-phenylthiophene (4). To a solution of **2a** (0.50 g, 1.62 mmol) in 0.5 mL of DMF were added benzyl alcohol (0.44 g, 4.05 mmol) and imidazole (0.28 g, 4.05 mmol). The reaction was stirred at ambient temperature for 18 h, poured into water, and extracted with cyclohexane. The organic extracts were combined, washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (Al_2O_3/pentane) to afford 0.52 g (85%) of the title compound as a colorless solid, mp 38 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 0.87 (d, J = 6.6 Hz, 6H), 0.96 (d, J = 6.6 Hz, 6H), 1.01 (sp, J = 6.6 Hz, 1H), 1.05 (sp, J = 6.6 Hz, 1H), 4.63 (s, 2H), 7.09 (d, J = 4.7 Hz, 1H), 7.15−7.33 (m, 10H), 7.50 (d, J = 4.7 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.02, 17.61, 17.71, 65.33, 125.96, 126.79, 127.19, 127.84, 128.08, 129.12, 129.85, 130.61, 131.50, 139.00, 140.99, 151.29. MS (EI): m/z 380 (M^+), 337 ($M^+ - C_3H_7$). IR (KBr): 1601, 1495, 1483, 1452, 1374, 1205, 1102, 1068, 880 cm^{-1}. Anal. Calcd for $C_{23}H_{28}OSSi$: C, 72.58; H, 7.41; S, 8.42. Found: C, 72.62; H, 7.43; S, 8.30.

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Mercurate 5. To a solution of **4** (0.19 g, 0.50 mmol) in 10 mL of chloroform was added mercuric acetate (0.16 g, 0.50 mmol) at 0 °C. The reaction was stirred at ambient temperature for 8 h. Evaporation of the solvent afforded **5** as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.93 (d, J = 7.0 Hz, 6H), 0.99 (d, J = 7.0 Hz, 6H), 1.07 (sp, J = 7.0 Hz, 1H), 1.10 (sp, J = 7.0 Hz, 1H), 2.05 (s, 3H), 4.71 (s, 2H), 7.18−7.38 (m, 11H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.07, 17.53, 17.62, 22.26, 65.39, 125.92, 126.84, 127.34, 127.90, 128.11, 129.05, 138.42, 138.47, 138.74, 140.83, 151.10, 177.09. MS (EI): *m*/*z* 640 (M^+), 597 ($M^+ - C_3H_7$).

General Procedure for the Iodination of Silylthiophenes 4 and 7. To a solution of **4** and **7** (2.00 mmol) in 40 mL of chloroform was added mercuric acetate (2.20 mmol) at 0 °C. The reaction was stirred at ambient temperature for 8 h. After addition of iodine (2.20 mmol) at 0 °C, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. The reaction mixture was poured into aqueous sodium hydrogencarbonate before being washed with aqueous sodium thiosulfate. The organic layer was dried over sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography on Al_2O_3 to afford **6b** and **8** as colorless oils.

5-[Benzyloxy(diisopropyl)silyl]-2-iodo-4-phenylthiophene (6b). From **4** (0.76 g, 2.00 mmol) was obtained 0.92 g (91%) of the title compound after flash chromatography on Al_2O_3 (cyclohexane). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.83 (d, J = 6.7 Hz, 6H), 0.87 (d, J = 6.6 Hz, 6H), 0.94 (sp, J = 6.7 Hz, 1H), 0.97 (sp, J = 6.6 Hz, 1H), 4.61 (s, 2H), 7.13 (s, 1H), 7.05−7.24 (m, 10H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 13.89, 17.47, 17.53, 65.35, 78.99, 125.85, 126.81, 127.51, 127.85, 128.04, 128.82, 137.53, 137.80, 140.56, 140.84, 152.65. MS (EI): *m*/*z* 506 (M^+), 463 ($M^+ - C_3H_7$), 379 ($M^+ - I$), 336 ($M^+ - C_3H_7 - I$). IR (neat): 1598, 1481, 1383, 1205, 1093, 1068, 939 cm^{-1}. Anal. Calcd for $C_{23}H_{27}IOSSi$: C, 54.54; H, 5.37; S, 6.33. Found: C, 54.51; H, 5.58; S, 6.13.

5-[Benzyloxy(diisopropyl)silyl]-5′-iodo-3′,4-diphenyl-2′,2-bithiophene (8). From **7** (1.08 g, 2.00 mmol) was obtained 1.14 g (86%) of the title compound after flash chromatography on Al_2O_3 (80:20, petroleum ether:CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.90 (d, J = 6.2 Hz, 6H), 0.92 (d, J = 6.0 Hz, 6H), 1.00 (sp, J = 6.2 Hz, 1H), 1.05 (sp, J = 6.0 Hz, 1H), 4.61 (s, 2H), 7.02 (s, 1H), 7.19−7.37 (m, 16H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 13.95, 17.52, 17.64, 65.34, 72.24, 126.00, 126.80, 127.36, 127.81, 127.88, 128.08, 128.37, 128.94, 129.23, 130.86, 130.93, 134.86, 137.36, 138.48, 139.61, 140.01, 140.06, 140.85, 151.11. MS (EI): *m*/*z* 664 (M^+), 621 ($M^+ - C_3H_7$). IR (neat): 1601, 1492, 1446, 1380, 1108, 1068, 950, 881 cm^{-1}. Anal. Calcd for $C_{33}H_{34}IOS_2Si$: C, 59.63; H, 5.00; S, 9.65. Found: C, 59.41; H, 5.10; S, 9.37.

General Procedure for the Suzuki Coupling of the Iodosilylthiophenes 6b and 8. To a degassed solution of **6b** and **8** (2.00 mmol) in 20 mL of DME was added $Pd(PPh_3)_4$ (5 mol %). The mixture was stirred for 10 min, and then boronic ester **3a** (3.00 mmol) and a solution of sodium hydrogencarbonate (20.0 mmol) in 1 mL of degassed water were added. The mixture was refluxed for 8 h under an argon atmosphere. The reaction was poured into water and the organic layer extracted with diethyl ether. The organic layer was dried over sodium sulfate, filtered, and concentrated in vacuo. The crude mixture was purified by flash chromatography on Al_2O_3 to afford **7** and **9**.

5-[Benzyloxy(diisopropyl)silyl]-3′,4-diphenyl-2′,2-bithiophene (7). From **6b** (1.01 g, 2.00 mmol) was obtained 0.91 g (84%) of the title product as a colorless oil after flash chromtography on Al_2O_3 (cyclohexane). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.83 (d, J = 6.3 Hz, 6H), 0.85 (d, J = 6.3 Hz, 6H), 0.91 (sp, J = 6.3 Hz, 1H), 0.93 (sp, J = 6.3 Hz, 1H), 4.54 (s, 2H), 6.98 (d, J = 5.2 Hz, 1H), 7.00 (s, 1H), 7.11−7.34 (m, 16H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 13.97, 17.54, 17.67, 65.30, 124.10, 126.01, 126.76, 127.24, 127.42, 127.83, 128.06, 128.27, 128.96, 129.34, 130.43, 130.49, 130.71, 131.44, 136.22, 138.67, 139.28, 140.90, 140.95, 151.15. MS (EI): *m*/*z* 538 (M^+), 495 ($M^+ - C_3H_7$). IR (neat): 1601, 1492, 1449, 1374, 1205, 1099, 1068, 1002, 878 cm^{-1}. Anal. Calcd for $C_{33}H_{34}OS_2Si$: C, 73.56; H, 6.36; S, 11.90. Found: C, 73.38; H, 6.49; S, 11.70.

5-[Benzyloxy(diisopropyl)silyl]-3′′,3′,4-triphenyl-2′′,5′:2′,2-terthiophene (9). From **8** (1.32 g, 2.00 mmol) was obtained 1.13 g (81%) of the title product as a yellow solid after flash chromtography on Al_2O_3 (95:5, cyclohexane:CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.89 (d, J = 6.1 Hz, 6H), 0.91 (d, J = 5.8 Hz, 6H), 0.98 (sp, J = 6.1 Hz, 1H), 1.02 (sp, J = 5.8 Hz, 1H), 4.60 (s, 2H), 6.95 (s, 1H), 6.99 (s, 1H), 7.07 (d, J = 5.1 Hz, 1H), 7.19−7.47 (m, 21H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 13.96, 17.52, 17.65, 65.30, 124.24, 126.00, 126.76, 127.27, 127.57, 127.61, 127.84, 128.06, 128.27, 128.51, 128.95, 129.32, 129.67, 129.74, 130.53, 130.57, 130.78, 131.21, 131.49, 134.31, 135.92, 136.09, 138.61, 139.26, 139.29, 140.56, 140.89, 151.05. MS (EI): *m*/*z* 696 (M^+), 653 ($M^+ - C_3H_7$). IR (KBr): 1598, 1492, 1096, 1068 cm^{-1}. Anal. Calcd for $C_{43}H_{40}OS_3Si$: C, 74.09; H, 5.78; S, 13.80. Found: C, 74.03; H, 5.87; S, 14.02.

3′′,3′,4-Triphenyl-2′′,5′:2′,2-terthiophene (10). To a solution of **9** (55 mg, 0.07 mmol) in 5 mL of THF was added TBAF (0.11 g, 0.35 mmol). The mixture was stirred for 3 h at ambient temperature. The solvent was evaporated in vacuo and the residue dissolved in cyclohexane. Washing with water and brine afforded, after extraction with cyclohexane and drying over sodium sulfate, a yellow solid. The crude product was purified by flash chromatography (SiO_2, 90:10, cyclohexane:CH_2Cl_2) to yield 34 mg (91%) of the title compound as a yellow oil. HPLC (85:15, *n*-hexane:CH_2Cl_2): t_R = 13.3 min. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.96 (s, 1H), 7.08 (d, J = 5.2 Hz, 1H), 7.17−7.48 (m, 18H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 120.64, 124.25, 125.54, 126.21, 127.22, 127.60, 127.66, 128.41, 128.52, 128.75, 129.29, 129.35, 129.64, 129.66, 130.80, 131.49, 134.42, 135.47, 135.85, 136.09, 136.35, 139.12, 139.33, 142.14. MS (EI): *m*/*z* 476 (M^+). IR (KBr): 1598, 1492, 1070, 841 cm^{-1}. HRMS (EI): calcd for $C_{30}H_{20}S_3$, 476.0727; found, 476.0729.

Resin-Bound Thiophene R12. To a suspension of hydroxymethyl polystyrene resin **R11** (15.00 g, 0.67 mmol/g, 10.1 mmol), imidazole (1.71 g, 25.2 mmol), and DMF (80 mL) in a preweighed fritted column was added **2b** (6.52 g, 20.2 mmol). The resulting mixture was shaken periodically at room temperature for 52 h. The solvent was removed by filtration and the polymer washed successively with DMF (2 × 60 mL), THF (3 × 60 mL), and CH_2Cl_2 (3 × 60 mL), and dried to constant mass in vacuo to afford the derivatized resin **R12** (17.88 g, Δw = 2.88 g, 0.56 mmol/g) as a colorless solid. IR (KBr): 3082, 3025, 2923, 2852, 1941, 1870, 1802, 1742, 1601, 1492, 1452, 1272, 1208, 1091, 1068, 1028, 880, 818, 756, 697 cm^{-1}. Characteristic absorptions for the attached silylthiophene were observed at 1097 (strong), 881 (weak), and 818 cm^{-1} (weak).

Resin-Bound Iodothiophene R13. An oven-dried flask was charged with polymer-supported thiophene **12** (10.00 g, 0.56 mmol/g, 5.60 mmol) and suspended in THF (80 mL). The reaction mixture was cooled to −60 °C, and LDA (8.40 mL, 16.8 mmol, 2.0 M in hexane) was added dropwise via cannula. After the addition was complete, the reaction mixture was warmed to room temperature over 30 min and stirred for additional 2 h. The resulting suspension of orange-colored beads was treated, via cannula, with a premade THF solution of iodine (4.26 g, 16.8 mmol) and stirred at room temperature for 2 h. The polymer was collected by filtration in a preweighed fritted filter, washed successively with CH_2Cl_2 (3 × 60 mL), Et_2O (2 × 60 mL), MeOH (2 × 60 mL), CH_2Cl_2 (2 × 60 mL), and Et_2O (2 × 60 mL), and dried to constant mass in vacuo to afford the derivatized resin **R13** (10.66 g, Δw = 0.66 g, 0.49 mmol/g) as a yellow solid. IR (KBr): 3080, 3022, 2919, 2850, 1942, 1868, 1802, 1740, 1598, 1489, 1449, 1377, 1108, 1088, 939, 815, 755, 695 cm^{-1}. Characteristic bands are located in the fingerprint region and overlap with resin absorbance. However, weak infrared absorption at 939 cm^{-1} was characteristic for the carbon−iodine bond.

General Procedure for the Suzuki Coupling of Resin-Bound Iodothiophenes with Boronic Ester 3b. An oven-dried flask was charged with resin-bound monomeric or oligomeric thiophene iodide (1.0 equiv) and catalytic tetrakis(triphenylphoshino)palladium(0) (5 mol %) and suspended in degassed THF (10 mL/g of polymer). The reaction mixture was

stirred for 10 min, and then boronic ester **3b** (2.5 equiv) and a solution of sodium hydrogencarbonate (10 equiv) in degassed water (1 mL/g of polymer) were added. The mixture was refluxed for 8 h under an argon atmosphere. The supension was then cooled to room temperature and diluted with water. The polymer was collected by filtration in a preweighed fritted filter, washed successively (40 mL/g of polymer) with water, CH_2Cl_2, Et_2O, MeOH, CH_2Cl_2, and Et_2O, and dried to constant mass in vacuo.

Resin-Bound Bithiophene R14. Resin-bound thiophene iodide **R13** (5.00 g, 0.49 mmol/g, 2.45 mmol), THF (50 mL), boronic ester **3b** (1.58 g, 6.13 mmol), sodium hydrogen carbonate (2.10 g, 24.5 mmol), and water (5 mL) afforded **R14** (5.11 g, Δw = 0.11 g, 0.46 mmol/g) as slightly yellow beads. IR (KBr): 3080, 3022, 2925, 2850, 1942, 1868, 1799, 1741, 1598, 1489, 1449, 1374, 1179, 1093, 1016, 878, 749, 695 cm^{-1}.

Resin-Bound Terthiophene R16. Resin-bound bithiophene iodide **R15** (3.50 g, 0.38 mmol/g, 1.33 mmol), THF (35 mL), boronic ester **3b** (0.86 g, 3.33 mmol), sodium hydrogen carbonate (1.11 g, 13.3 mmol), and water (3.5 mL) afforded **R16** (3.56 g, Δw = 0.06 g, 0.34 mmol/g) as deep yellow beads. IR (KBr): 3080, 3022, 2919, 2850, 1939, 1868, 1799, 1741, 1601, 1489, 1452, 1372, 1179, 1093, 1019, 878, 755, 698 cm^{-1}.

Resin-Bound Quaterthiophene R18. Resin-bound terthiophene iodide **R17** (2.50 g, 0.27 mmol/g, 0.68 mmol), THF (25 mL), boronic ester **3b** (0.44 g, 1.70 mmol), sodium hydrogen carbonate (0.57 g, 6.80 mmol), and water (2.5 mL) afforded **R18** (2.53 g, Δw = 0.03 g, 0.24 mmol/g) as brown beads. IR (KBr): 3080, 3022, 2919, 2850, 1942, 1868, 1799, 1741, 1598, 1489, 1449, 1374, 1179, 1113, 1016, 878, 812, 755, 695 cm^{-1}.

General Procedure for Iodination of the Resin-Bound Oligothiophenes. To a suspension of resin-bound oligothiophene (1.0 equiv) and CH_2Cl_2 (15 mL/g of polymer) in a preweighed fritted column was added mercuric caproate (1.1 equiv). The resulting mixture was shaken periodically at room temperature for 24 h. To the resulting suspension was added dropwise a premade THF solution of iodine (1.1 equiv), and the reaction mixture was shaken for an additional 2 h. The solvent was removed by filtration and the polymer washed (40 mL/g of polymer) successively with CH_2Cl_2, MeOH, Et_2O, CH_2Cl_2, and Et_2O, and dried to constant mass in vacuo.

Resin-Bound Bithiophene Iodide R15. Resin-bound bithiophene **R14** (4.00 g, 0.46 mmol/g, 1.84 mmol), CH_2Cl_2 (60 mL), mercuric caproate (0.87 g, 2.02 mmol), and iodine (0.51 g, 2.02 mmol) afforded **R15** (4.20 g, Δw = 0.20 g, 0.38 mmol/g) as yellow beads. IR (KBr): 3080, 3022, 2919, 2850, 1939, 1868, 1796, 1748, 1598, 1489, 1449, 1374, 1179, 1093, 1025, 881, 812, 752, 695 cm^{-1}.

Resin-Bound Terthiophene Iodide R17. Resin-bound terthiophene **R16** (3.00 g, 0.34 mmol/g, 1.02 mmol), CH_2Cl_2 (45 mL), mercuric caproate (0.48 g, 1.12 mmol), and iodine (0.28 g, 1.12 mmol) afforded **R17** (3.10 g, Δw = 0.10 g, 0.27 mmol/g) as brown beads. IR (KBr): 3080, 3022, 2919, 2850, 1942, 1868, 1799, 1736, 1653, 1598, 1489, 1449, 1260, 1091, 1019, 812, 752, 695 cm^{-1}.

Procedure for Monomer and Oligomer Removal by Protiodesilylation. To a suspension of polymer-supported monomer or oligomer (1.0 equiv) and THF (5 mL/g of polymer) in a flask was added TBAF (5 equiv). The reaction mixture was heated for 1 h to 70 °C, cooled to room temperature, and filtrated to remove the polymer. After evaporation of the solvent, the residue was dissolved in diethyl ether, washed with water and brine, dried, and concentrated. Flash chromatography on SiO_2 or preparative HPLC afforded the monomer or oligomer thiophenes as pure compounds.

3-(*p*-Tolyl)thiophene (12). Resin **R12** (1.00 g, 0.56 mmol/g, 0.56 mmol), THF (5 mL), and TBAF (0.88 g, 2.80 mmol) afforded after flash chromatography on SiO_2 (cyclohexane) **12** (91 mg, 93%) as a colorless solid. Analytical data are in conformity with literature data.[23]

2-Iodo-4-(*p*-tolyl)thiophene (13). Resin **R13** (1.00 g, 0.49 mmol/g, 0.49 mmol), THF (5 mL), and TBAF (0.77 g, 2.45 mmol) afforded after flash chromatography on SiO_2 (cyclohexane) **13** (142 mg, 91%) as a colorless solid. ^1H NMR (200 MHz, $CDCl_3$): δ 2.35 (s, 3H), 7.17−7.43 (m, 4H), 7.38 (d, J = 1.7 Hz, 1H), 7.48 (d, J = 1.7 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.13, 73.85, 125.40, 126.11, 129.52, 131.83, 136.02, 137.32, 144.10. MS (EI): m/z 300 (M^+), 173 ($M^+ - I$).

3′,4-Di(*p*-tolyl)-2′,2-bithiophene (14). Resin **R14** (0.50 g, 0.46 mmol/g, 0.23 mmol), THF (2.5 mL), and TBAF (0.36 g, 1.15 mmol) afforded after flash chromatography on SiO_2 (cyclohexane) **14** (77 mg, 87%) as a colorless solid. Analytical data are in conformity with literature data.[8a]

5′-Iodo-3′,4-di(*p*-tolyl)-2′,2-bithiophene (15). Resin **R15** (0.50 g, 0.38 mmol/g, 0.19 mmol), THF (2.5 mL), and TBAF (0.30 g, 0.95 mmol) afforded after preparative HPLC **15** (31 mg, 71%) as a yellow oil. HPLC (85:15, *n*-hexane:CH_2Cl_2): t_R = 8.22 min. ^1H NMR (200 MHz, $CDCl_3$): δ 2.34 (s, 3H), 2.35 (s, 3H), 7.11−7.39 (m, 11H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.12, 21.27, 72.03, 120.43, 125.93, 126.09, 129.05, 129.20, 129.47, 131.80, 132.60, 135.38, 137.09, 137.67, 140.13, 140.80, 142.16. MS (EI): m/z 472 (M^+).

3″,3′,4-Tri(*p*-tolyl)-2″,5′:2′,2-terthiophene (16). Resin **R16** (0.50 g, 0.34 mmol/g, 0.17 mmol), THF (2.5 mL), and TBAF (0.27 g, 0.85 mmol) afforded after preparative HPLC **16** (29 mg, 68%) as a yellow oil. HPLC (85:15, *n*-hexane:CH_2Cl_2): t_R = 13.0 min. ^1H NMR (200 MHz, $CDCl_3$): δ 2.33 (s, 3H), 2.35 (s, 3H), 2.37 (s, 3H), 6.95 (s, 1H), 7.04 (d, J = 5.2 Hz, 1H), 7.25 (d, J = 5.2 Hz, 1H), 7.10−7.35 (m, 14H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.11, 21.26, 21.29, 119.98, 124.06, 125.52, 126.11, 129.11, 129.16, 129.25, 129.43, 129.70, 130.89, 131.19, 132.76, 132.97, 133.12, 134.37, 136.40, 136.97, 137.35, 137.36, 139.07, 139.27, 142.05. MS (EI): m/z 518 (M^+). IR (KBr): 1509, 1492, 1185, 1111, 875, 812 cm^{-1}. HRMS (EI): calcd for $C_{33}H_{26}S_3$, 518.1196; found, 518.1196.

5″-Iodo-3″,3′,4-tri(*p*-tolyl)-2″,5′:2′,2-terthiophene (17). Resin **R17** (0.50 g, 0.27 mmol/g, 0.14 mmol), THF (2.5 mL), and TBAF (0.22 g, 0.70 mmol) afforded after preparative HPLC **17** (22 mg, 54%) as a yellow oil. HPLC (85:15, *n*-hexane:CH_2Cl_2): t_R = 11.9 min. ^1H NMR (200 MHz, $CDCl_3$): δ 2.34 (s, 3H), 2.36 (s, 3H), 2.38 (s, 3H), 6.91 (s, 1H), 7.12−7.38 (m, 15H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.12, 21.27, 21.31, 72.16, 120.17, 125.65, 126.09, 129.04, 129.11, 129.12, 129.15, 129.32, 129.44, 129.94, 131.71, 132.67, 132.72, 132.96, 136.10, 136.70, 137.02, 137.47, 137.81, 139.05, 140.41, 140.84, 142.08. MS (EI): m/z 644 (M^+).

3‴,3″,3′,4-Tetra(*p*-tolyl)-2‴,5″:2″,5′:2′,2-quaterthiophene (18). Resin **R18** (0.50 g, 0.24 mmol/g, 0.12 mmol), THF (2.5 mL), and TBAF (0.19 g, 0.60 mmol) afforded after preparative HPLC **18** (17 mg, 48%) as a yellow oil. HPLC (80:20, *n*-hexane:CH_2Cl_2): t_R = 13.8 min. ^1H NMR (500 MHz, $CDCl_3$): δ 2.27 (s, 3H), 2.28 (s, 3H), 2.30 (s, 3H), 2.31 (s, 3H), 6.80 (s, 1H), 6.88 (s, 1H), 6.98 (d, J = 5.1 Hz, 1H), 7.03−7.29 (m, 19H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.11, 21.26, 21.31, 120.00, 124.09, 125.49, 126.09, 129.11, 129.13, 129.16, 129.23, 129.26, 129.42, 129.54, 129.94, 130.78, 130.84, 130.93, 131.16, 132.72, 132.84, 132.88, 133.06, 134.03, 134.44, 136.33, 136.98, 137.36, 137.39, 137.50, 138.98, 139.13, 139.30, 142.03. MS (EI): m/z 690 (M^+). IR (KBr): 1506, 1495, 1260, 1179, 1102, 1019, 873, 810 cm^{-1}. HRMS (EI): calcd for $C_{44}H_{34}S_4$, 690.1543; found, 690.1544.

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Supporting Information Available: ^1H NMR and ^{13}C NMR spectra and mass spectra for **10**, **16**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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