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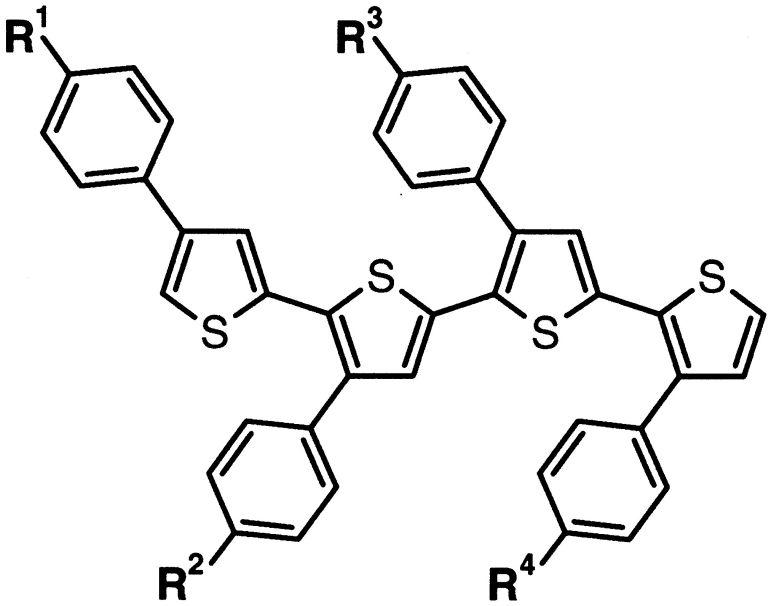


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# Design and Synthesis of a 256-Membered $\pi$-Conjugated Oligomer Library of Regioregular Head-to-Tail Coupled Quater(3-arylthiophene)s

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The rapid solid-phase synthesis of $\pi$-conjugated oligomers is demonstrated by utilizing the parallel and the "mix-and-split" methods for the preparation of a library of 256 regioregular head-to-tail coupled oligo(3-arylthiophene)s. Chemical diversity was introduced to the growing oligomer starting from four resin-bound 3-(*p*-X-phenyl)-2-silylthiophenes via an iterative sequence of iodinations and Suzuki cross-coupling reactions with four 3-(*p*-X-phenyl)thiophene boronic esters (X = $CF_3$, H, $CH_3$, $OCH_3$). Liberation from the solid support with TFA and subsequent chromatographic purification by normal-phase LC−MS provided all 256 regioregular head-to-tail coupled quater(3-arylthiophene)s.

## Introduction

The successful application of combinatorial strategies for lead structure identification and optimization of new materials has resulted in considerable enthusiasm for high-speed synthesis and high-throughput screening of material libraries.[1] Although numerous combinatorial strategies have been developed that enable the efficient generation of catalyst libraries and diverse solid-state material libraries, reports about the accelerated development of organic materials are scarce.[2,3] Very recently, Anderson developed a combinatorial approach toward phenylene ethynylene oligomers whose organic electroluminescent features are of interest for low-voltage multicolor displays.[4] A combinatorial strategy for the screening and optimization of organic electron transport materials and device configurations was reported that addresses the problem of parallel device preparation and evaluation.[5]

As one of the most versatile classes of organic materials, polythiophenes have attracted widespread interest and are the subject of intensive studies to develop structure−property relationships, which are essential for improvement of the material behavior.[6] Characterized by excellent environmental and thermal stability, these conjugated materials have found use in a variety of technical applications, including organic field effect transistors[7] and organic light-emitting devices.[8] It should be noted that this field of research has rapidly progressed because of the realization that well-defined $\pi$-conjugated oligomers can serve as excellent models for the parent polydisperse polymers.[9] Depending on the particular application, the use of these monodisperse oligomers offers significant advantages over the corresponding polymers. However, to date, a purely rational design of the electronic and optical properties of these compounds is still impossible. Moreover, the time-consuming process of the conventional "one-at-a-time" synthesis, purification, and screening impedes the rapid development of material applications. Accordingly, there is a need for both a rapid approach for synthesis and purification and powerful screening procedures.

Recently, several solid-phase approaches to linear $\pi$-conjugated oligomers have been reported that demonstrate the advantages of an oligomer growth on solid support.[10,11] Since a solid-phase synthesis is amenable to automation and combinatorial library generation, a reliable solid-phase protocol is the first step toward accelerated material development.

In accordance with these considerations, our work is directed toward the development of a rapid method for the synthesis, purification, and screening of a $\pi$-conjugated oligomer library. Using the information obtained from high-throughput screening and large-scale data analysis will promote a detailed understanding of structure−property relationships that are essential for a priori predictions of material properties. Recently, we developed an efficient solid-phase synthesis that granted access to regioregular head-to-tail coupled oligo(3-arylthiophene)s.[11e] Here, we demonstrate the utility of this synthetic strategy for the generation of a 256-membered oligomer library.

## Results and Discussion

**Library Design.** It was envisioned that the screening of a $\pi$-conjugated oligomer library could give rise to quantitative structure−property relationships concerning the electronic influence of backbone substituents on optical and electronic properties. Specifically, we were interested in the structural influence on the HOMO and LUMO levels and the energy gap of the frontier orbitals. To systematically study this influence, one has to reduce the possible structural variables to a limited set. Major factors that determine HOMO and LUMO levels and the associated energy gap

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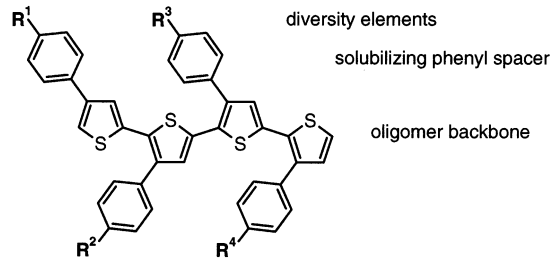


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**Figure 1.** Quater(3-arylthiophene) showing the four sites for introducing diversity.

include the bond length alternation, the aromatic resonance energy, the deviation from planarity, and inductive and mesomeric electronic effects.[12] In this work, we attempted to keep the former three factors constant in order to observe exclusively the influence of electronic effects on physical properties.

The most usual way to vary HOMO and LUMO levels of oligomers involves (besides the modification of the oligomer backbone) the introduction of electron-donating or electron-withdrawing substituents that increase the HOMO level and lower the LUMO level, respectively. In the case of oligothiophenes, substituents can be attached to α- and $\beta$-positions so that several substitution patterns become available. For the present target design, a regioregular head-to-tail junction of thiophene moieties appeared attractive because steric repulsions are minimized and each monomer unit can be modulated electronically by substitution in the $\beta$-position.

A further component of the target design is the incorporation of a phenyl spacer between substituents and the oligomer backbone. This structural feature of the target compound is fundamental for several reasons: (a) With a phenyl group as a spacer unit, undesired variations of the conformational geometry by different steric demands of the substituents can be minimized. Providing that the substituents are not too bulky, the geometry of the target molecule should remain almost constant while the $\beta$-substituents are varied. (b) The aryl side groups were expected to provide enhanced solubility as reported for similar $\pi$-conjugated systems.[13,14] (c) The spacer should promote molecular organization in the solid state.

It is worth mentioning that polar functionalities (e.g., amide, carboxylic acids, esters, etc.) on the oligomeric α- and $\omega$-termini may impart molecular properties that disguise the effects of functional variation in the $\beta$-positions. Thus, nonfunctionalized oligomers were sought that would enable a direct correlation between the functional modifications and the electronic properties. The structural features of the target compound **1** are summarized in Figure 1.

Factors that affected the design of the target compound include the results of preliminary studies on corresponding aryl-substituted oligomers and polymers. While numerous studies were reported on alkyl-substituted α-oligothiophenes and the corresponding polymers, studies on the aryl-substituted analogues are comparatively rare.[15,16] Interest in phenyl-substituted thiophene-based polymers arose when it became evident that $\beta$-phenyl substituents improved some characteristics of p- and n-doped polythiophenes (i.e., increased charge capacities and cycling stabilities).[17] Consequently, several studies on the potential application of poly(3-phenylthiophene) and its derivatives as active components in energy storage devices[18] and optoelectronic devices[16j−l] have been reported. Moreover, poly(3-arylthiophene)s were studied, since it was expected that (because of the introduction of the aromatic side groups and the subsequent extension of the $\pi$-system by the backbone substituents) the nonlinear optical effects would be enhanced.[16a]

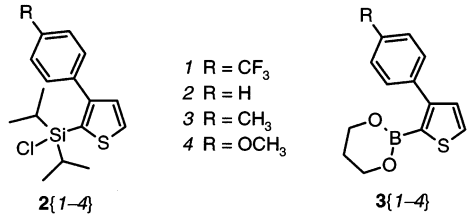


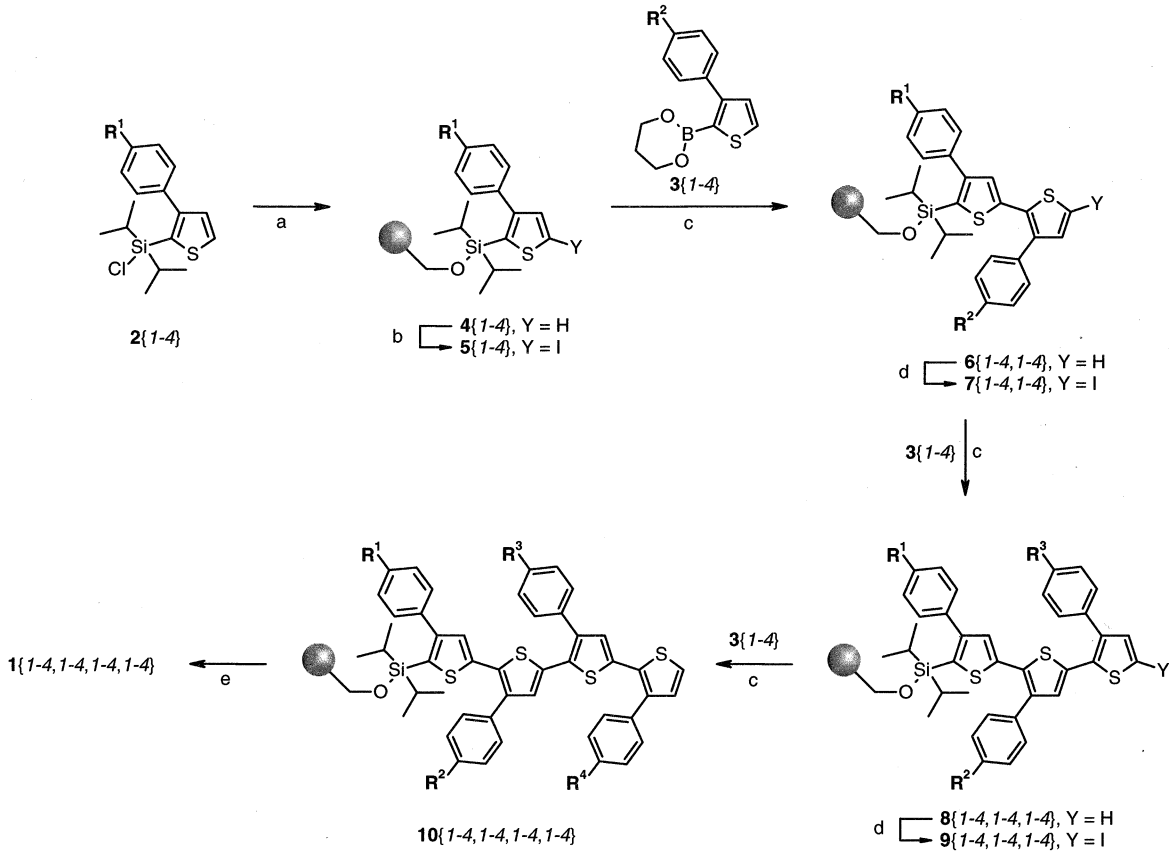

**Figure 2.** Diversity reagents **2**{*1*−*4*} and **3**{*1*−*4*}.

**Synthetic Strategy.** The oligomer elongation sequence that is based on the recently reported solid-phase synthesis of oligo(3-arylthiophene)s is shown in Scheme 1.[11e] A unidirectional stepwise addition approach on solid phase appears well-suited for the construction of a library of regioregular head-to-tail coupled oligothiophenes, since the oligomer growth involves a two-step iterative process of halogenations and cross-coupling reactions that can be easily translated into a combinatorial protocol.

The first arylthiophene is anchored to the polymer matrix via a traceless silyl linker. This is achieved by reacting a (chlorosilyl)thiophene **2** with hydroxymethylated polystyrene. Oligomer growth is accomplished by an iterative sequence of iodination and Suzuki cross-coupling with the thiophene boronic ester **3**. Resin-bound thiophene **4** was halogenated by metalation with LDA and subsequent reaction with iodine. In contrast, a mercuration−iododemercuration reaction was required for selective access to the iodinated bi- and terthiophenes **7** and **9**. The Pd-catalyzed cross-couplings for the preparation of dimer **6**, trimer **8**, and tetramer **10** utilized a $Pd(PPh_3)_4$ catalyst. Finally, quaterthiophene **1** was liberated from the resin by treating the derivatized polymer support with 10% TFA in $CH_2Cl_2$.[19]

**Building Block Selection and Synthesis.** With an efficient synthetic protocol in hand, the next step toward the library construction was the selection of appropriate thiophene building blocks. Four $\beta$-substituents were chosen as representatives of electron-deficient and electron-rich arenes: *p*-(trifluoromethyl)phenyl, phenyl, *p*-tolyl, and *p*-anisyl. Synthetically, (chlorosilyl)thiophenes **2**{*1*−*4*} and thiophene boronic esters **3**{*1*−*4*} were utilized as building blocks and are shown in Figure 2. The building blocks were synthesized from 3-aryl-2-bromothiophenes **11a**−**d**.[11e] Compounds **2**{*2*}, **2**{*3*}, **3**{*2*}, and **3**{*3*} were synthesized according to literature procedures.[11e] Building blocks **2**{*1*} and **2**{*4*} were readily available in 73% and 79% yield, respectively, by reacting the lithiated thiophenes with dichloro(diisopropyl)silane. The methoxy-substituted boronic ester **3**{*4*} was synthesized by reacting the Grignard reagent of **11d** with triisopropyl borate. Hydrolysis to the boronic acid and the subsequent esterification with 1,3-propanediol afforded the desired boronic ester in 85% yield. The trifluoromethyl-substituted boronic ester

**Scheme 1.** Synthetic Route to the Oligo(3-arylthiophene) Library[a]




[a] Reagents and conditions: (a) hydroxymethylated polystyrene, imidazole, DMF; (b) (1) LDA, THF, −60 °C, (2) $I_2$; (c) [$Pd(PPh_3)_4$], THF/$H_2O$, $NaHCO_3$ or $Na_2HPO_4/NaH_2PO_4$, reflux or 75 °C (see text); (d) (1) $Hg(OCOC_5H_{11})_2$, $CH_2Cl_2$, (2) $I_2$, $CH_2Cl_2$; (e) 10% TFA, $CH_2Cl_2$.

**3**{*1*} was synthesized by reacting 2,2′-propane-1,3-diyldioxybis[1,3,2]dioxaborinane with the lithiated compound of **11a**. Subsequent treatment of the intermediate complex with boron trifluoride yielded the boronic ester **3**{*1*} in 71% yield.

**Optimization and Reaction Monitoring.** When *p*-anisyl- and *p*-(trifluormethyl)phenyl-substituted building blocks were employed for the oligomer growth, it became evident that further optimization studies were required to successfully translate the aforementioned synthesis into a combinatorial protocol. While both the immobilization of the silyl chlorides **2**{*1*−*4*} and the iodination of the resin-bound thiophenes **4**, **6**, and **8** proceeded in nearly quantitative conversions regardless of the electronic nature of the diversity substituent, the Suzuki cross-coupling reaction proved to be sensitive to the substituents. Boronic esters **3**{*2*−*3*} underwent smooth Suzuki cross-couplings with resin-bound iodothiophenes **5**, **7**, and **9** in high conversions under the standard reaction conditions: boronic ester (3 equiv), sodium hydrogencarbonate (12 equiv), $Pd(PPh_3)_4$ (5 mol %), THF/$H_2O$, heating to reflux for 8 h. Cross-coupling with the anisyl-substituted thiophene boronic ester **3**{*4*} was found to proceed more slowly than the reaction with **3**{*2*} and **3**{*3*}. In this case, quantitative conversion could be achieved with a prolonged reaction time of 12 h. In contrast, the trifluoromethyl-substituted arylthiophene boronic ester **3**{*1*} proved to be problematic in achieving complete conversions. A closer examination revealed that the incomplete conversion to the oligothiophenes was a result of the rapid deboronation of **3**{*1*}. Even an excess of 4 equiv of the boronic ester did not afford the coupling products in desired yields of greater than 85%. Consequently, effective suppression of the decomposition of **3**{*1*} under basic conditions was necessary to avoid extensive termination of the oligomer growth. To optimize the cross-coupling reactions, several conditions were explored including different solvents (THF/$H_2O$, toluene) and bases ($NaHCO_3$, $K_2CO_3$, $Na_2HPO_4/NaH_2PO_4$). Among them, the most efficient condition applicable for the Suzuki cross-coupling of building block **3**{*1*} was found to be a buffer system of sodium dihydrogenphosphate and hydrogenphosphate in THF/$H_2O$. When this aqueous buffer was used, the reaction of the iodinated thiophenes **5**, **7**, and **9** with boronic ester **3**{*1*} afforded the desired oligomers in good to excellent conversions.

For the combinatorial synthesis, the acidic cleavage of the traceless silyl linker with TFA instead of TBAF[19] proved to be advantageous because of the easier workup (evaporation of the cleavage reagent instead of extraction). In addition, the cleavage with TFA was advantageous for analytical reasons. The treatment of the resins with TFA/$CH_2Cl_2$ vapor results in the cleavage of the compounds, which remain physically adsorbed on the resin bead and can be used for subsequent mass spectrometric analysis.[20] However, for iodobithiophenes **7** and iodoterthiophene **9**, partial decomposition was observed when TFA was utilized as the cleavage reagent. Therefore, TBAF in THF was the reagent of choice for cleaving these intermediates from the polymer support.

**Library Synthesis.** By application of the improved protocols for synthesis, purification, and analytical quality

control, a library composed of 256 oligomers could be prepared according to Scheme 1. The library synthesis was initiated by loading the four (chlorosilyl)thiophenes **2**{*1*−*4*} in parallel onto the hydroxymethylated polystyrene (1% DVB, 100−200 mesh, 0.87 mmol/g). In all cases, treatment of the resin with a 2-fold excess of (chlorosilyl)thiophenes **2**{*1*−*4*} in the presence of imidazole proceeded with up to 98% completion. Formation of the resin-bound thiophenes **4**{*1*−*4*} was ascertained by using FT-IR spectroscopy[21] and the color test for resin-bound hydroxy groups.[22] The loading capacity was determined on the basis of the weight change of the vacuum-dried resin and mass recovery after cleaving a portion of the resin and was found to be between 0.64 and 0.68 mmol/g. Following the silylthiophene immobilization, the iodination of the resin-bound thiophenes was performed in parallel by metalating polymer-bound thiophenes **4**{*1*−*4*} with LDA (3 equiv) and subsequent reaction with iodine. Every iodothiophene **5**{*1*−*4*} was subjected to $^1$H NMR and GC analysis (after treating a portion of the resin with 10% TFA in $CH_2Cl_2$), and all iodothiophenes were found to be of high purity (>95%). Conversion of resin-bound iodothiophenes **5**{*1*−*4*} to bithiophenes **6**{*1*−*4,1*−*4*} was accomplished through a Suzuki cross-coupling reaction with diversity reagent **3**{*1*−*4*}. As a reaction control, a portion of all 16 resin-bound bithiophenes **6**{*1*−*4,1*−*4*} were treated with 10% TFA in $CH_2Cl_2$ and the resulting crude products were analyzed by $^1$H NMR and HPLC−MS. In all cases, the transition metal catalyzed cross-coupling reaction resulted in excellent conversions (90−95%), as estimated by $^1$H NMR analysis of the crude cleavage products. HPLC−MS analysis revealed that the constructed bithiophenes **6**{*1*−*4,1*−*4*} were greater than 72% pure. Chemset **6**{*1*−*4,1*−*4*} was then converted in parallel fashion to iodobithiophenes **7**{*1*−*4,1*−*4*} by a mercuration−iodination reaction. A portion of all members (50 mg) of chemset **7**{*1*−*4,1*−*4*} were subjected to $^1$H NMR analysis (after cleavage), which revealed >90% conversion for all compounds. Here, TBAF in THF was used for cleavage to avoid decomposition of the iodinated bithiophenes.

At this stage, the "mix-and-split" synthesis was employed to accelerate the following oligomer growth reactions. The 16 resin-bound iodobithiophenes **7**{*1*−*4,1*−*4*} were encapsulated in 256 MakroKans (IRORI) and sorted into four vessels each containing identical sets. For reaction monitoring, 32 additional microreactors (MicroKans, IRORI) filled with the 16 iodobithiophenes **7**{*1*−*4,1*−*4*} were distributed to the four pools. The Suzuki cross-coupling of encapsulated resin-bound iodobithiophenes **7**{*1*−*4,1*−*4*} with diversity reagents **3**{*1*−*4*} was performed in sealed round-bottom flasks and resulted in the formation of 64 terthiophenes **8**{*1*−*4,1*−*4,1*−*4*}.[23] Then, 16 of the 32 control microreactors were randomly selected and removed from the reaction pools to estimate the average reaction conversion and purity (after cleavage with TFA in $CH_2Cl_2$). According to the HPLC−MS analysis, the compound purity ranged from 67% to 87% and the reaction conversion was estimated by $^1$H NMR analysis to be greater than 90%. According to the stepwise mercuration−iodination sequence, terthiophenes **8**{*1*−*4,1*−*4,1*−*4*} were reacted to give iodoterthiophenes **9**{*1*−*4,1*−*4,1*−*4*} in the four sets that were pooled before the Suzuki coupling. The remaining 16 control microreactors were removed, and the polymer-bound iodoterthiophenes **9**{*1*−*4,1*−*4,1*−*4*} were cleaved from the resin with TBAF in THF. The reaction conversion was estimated by $^1$H NMR to be greater than 80%. Next, the 256 microreactors filled with 64 resin-bound iodoterthiophenes **9**{*1*−*4,1*−*4,1*−*4*} were recombined and subsequently sorted into four identical sets of 64 microreactors. To complete the library synthesis, the encapsulated **9**{*1*−*4,1*−*4,1*−*4*} was cross-coupled with boronic esters **3**{*1*−*4*}, providing resin-bound quaterthiophenes **10**{*1*−*4,1*−*4,1*−*4,1*−*4*}. In addition to the standard washing procedure, the resin was treated with a 1% solution of diethyl dithiocarbamate in DMF to remove the resin-trapped palladium. With the washing sequence complete, the 256 microreactors were distributed into 256 glass vials and treated with the cleavage solution (10% TFA in $CH_2Cl_2$). After agitating for 2 h at ambient temperature, the microreactors were rinsed with $CH_2Cl_2$ and removed. Finally, the cleavage solutions were concentrated in vacuo to provide the crude target compounds **1**{*1*−*4,1*−*4,1*−*4,1*−*4*} as yellow to red oils.

**Table 1.** Validation of the Quater(3-arylthiophene) Library **1**{*1*−*4,1*−*4,1*−*4,1*−*4*}: Yields and Purity for 16 Randomly Selected Library Members

| entry | compound | $R^1$ | $R^2$ | $R^3$ | $R^4$ | purity,[a] % | yield,[b] % |
|---|---|---|---|---|---|---|---|
| 1 | **1**{*1,2,2,2*} | $CF_3$ | H | H | H | 80 | 16 |
| 2 | **1**{*1,2,2,3*} | $CF_3$ | H | H | $CH_3$ | 84 | 31 |
| 3 | **1**{*1,2,4,3*} | $CF_3$ | H | $OCH_3$ | $CH_3$ | 68 | 45 |
| 4 | **1**{*1,4,1,3*} | $CF_3$ | $OCH_3$ | $CF_3$ | $CH_3$ | 79 | 23 |
| 5 | **1**{*1,4,1,4*} | $CF_3$ | $OCH_3$ | $CF_3$ | $OCH_3$ | 81 | 25 |
| 6 | **1**{*1,4,2,3*} | $CF_3$ | $OCH_3$ | H | $CH_3$ | 76 | 36 |
| 7 | **1**{*1,4,3,2*} | $CF_3$ | $OCH_3$ | $CH_3$ | H | 74 | 26 |
| 8 | **1**{*2,2,2,2*} | H | H | H | H | 72 | 30 |
| 9 | **1**{*2,2,4,2*} | H | H | $OCH_3$ | H | 75 | 34 |
| 10 | **1**{*3,2,3,3*} | $CH_3$ | H | $CH_3$ | $CH_3$ | 85 | 24 |
| 11 | **1**{*3,4,2,2*} | $CH_3$ | $OCH_3$ | H | H | 83 | 12 |
| 12 | **1**{*3,4,2,4*} | $CH_3$ | $OCH_3$ | H | $OCH_3$ | 84 | 26 |
| 13 | **1**{*4,1,3,3*} | $OCH_3$ | $CF_3$ | $CH_3$ | $CH_3$ | 69 | 37 |
| 14 | **1**{*4,1,4,4*} | $OCH_3$ | $CF_3$ | $OCH_3$ | $OCH_3$ | 85 | 33 |
| 15 | **1**{*4,3,3,2*} | $OCH_3$ | $CH_3$ | $CH_3$ | H | 77 | 29 |
| 16 | **1**{*4,4,2,2*} | $OCH_3$ | $OCH_3$ | H | H | 82 | 19 |

[a] Purity of crude cleavage products as detected by analytical HPLC. UV detection at $\lambda = 250$ nm. [b] Overall isolated yields after preparative HPLC purification. Yields are based on initial polymer substitution of 0.87 mmol/g.

**Purification and Analytical Quality Control.** To confirm the diversity of the generated library, the purity and integrity of all 256 quaterthiophenes **1**{*1*−*4,1*−*4,1*−*4,1*−*4*} was assessed by analytical HPLC−MS. Analysis of the resin-cleaved compounds showed that all crude products contained the desired quaterthiophenes as main compounds free from major impurities. APCI-MS revealed confirmatory signals for all library members (vide infra). The principal impurities could be identified as unreacted oligomer precursors, namely, bithiophenes **6**{*1*−*4,1*−*4*} and terthiophenes **8**{*1*−*4,1*−*4,1*−*4*}. Summarized in Table 1 are the results of the HPLC evaluated purity analysis of the 16 randomly selected library members **1**. The purities of these crude products were in the range 68−85%.

Since the purity of the compound is a crucial prerequisite for a reliable and meaningful screening of material properties,

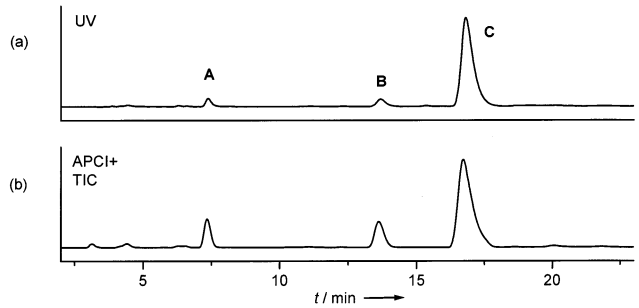



**Figure 3.** HPLC−MS analysis of the crude quaterthiophene **1**{*4,4,2,2*}: (a) UV absorbance trace (UV detection at $\lambda = 250$ nm); (b) total ion count (TIC) trace (APCI+).

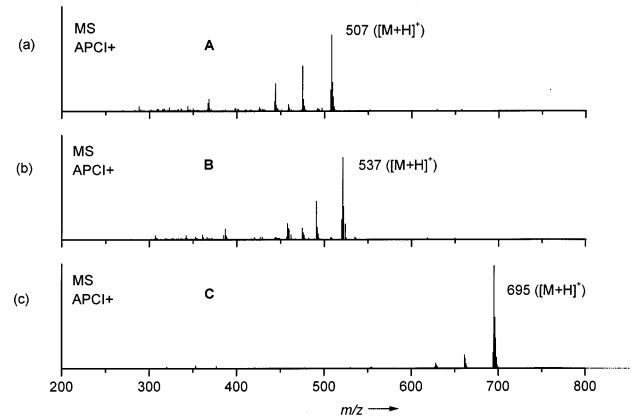



**Figure 4.** Mass spectra of the three major components **A**−**C** displayed in Figure 3. The molecular ions $[M + H]^+$ of these compounds are 507 amu (**A**), 537 amu (**B**) and 695 amu (**C**).

an efficient purification procedure was required. An automated HPLC−MS system was shown to provide both the purification and structure validation of the library members. Mixtures of $CH_2Cl_2$/*n*-hexane as eluents and normal-phase HPLC columns operating at flow rates of 1 mL/min (analytical) and 20 mL/min (preparative) were found to satisfy the separation requirements for the library compounds. Atmospheric-pressure chemical ionization (APCI) was employed as the ionization technique, which allowed the detection of the $[M + H]^+$ ions of the oligothiophenes as the base peaks of the mass spectra. A representative example of the HPLC−MS analysis before and after the preparative purification is illustrated in Figures 3−5.

Both the UV absorbance trace (Figure 3a) and the total ion count (TIC) trace (Figure 3b) reveal that the crude quaterthiophene **1**{*4,4,2,2*} contains two major byproducts **A** and **B** along with the desired oligomer **C**. As displayed by the mass spectra under the three peaks (Figure 4), impurity **A** can be assigned to terthiophene **8**{*4,2,2*} (507 amu) and byproduct **B** to terthiophene **8**{*4,4,2*} (537 amu). The molecular ion ($[M + H]^+$) of quaterthiophene **1**{*4,4,2,2*} (compound **C**) was determined to be 695 amu. The HPLC−MS analysis of the purified oligomer showed that byproducts of the synthesis could be completely removed, enabling the isolation of pure quaterthiophene **1**{*4,4,2,2*} (Figure 5).

The purification of all 256 library members **1**{*1*−*4,1*−*4,1*−*4,1*−*4*} by preparative HPLC furnished 243 compounds (corresponding to 95% of all library members) in HPLC purities of greater than 98%, 8 compounds (3%) in 95% purity, and 5 compounds (2%) in 90% purity as assessed by

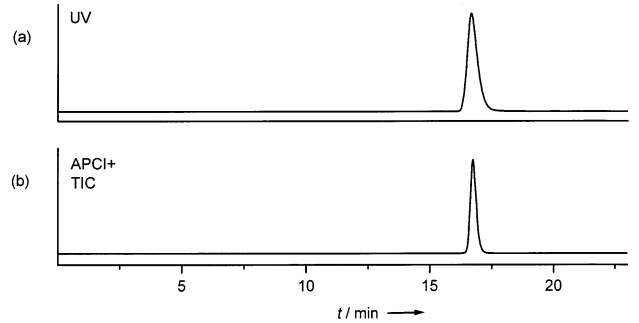



**Figure 5.** HPLC−MS analysis of the purified quaterthiophene **1**{*4,4,2,2*}: (a) UV absorbance trace (UV detection at $\lambda = 250$ nm); (b) total ion count (TIC) trace (APCI+). The mass spectrum under the peak is identical to the one displayed in Figure 4 for compound **C**.

HPLC−MS. Most members of the library were obtained in 5−15 mg quantities. The isolated overall yields of these compounds ranged from 2% to 51%, and the majority (71%) of library members were available in 11−35% yield. However, one has to recognize that the isolated yields do not generally reflect the overall conversion to the final product but are dependent on the respective purification problems. The isolated overall yields after purification are listed in Table 1 for a representative set of library members. $^1H$ and $^{13}C$ NMR spectra were obtained for selected library members to provide additional structural characterization. $^1H$ NMR spectra for some of these compounds along with the isolated overall yields of all library members are given in the Supporting Information.

## Conclusions

In summary, an efficient solid-phase protocol to a $\pi$-conjugated oligomer library of regioregular head-to-tail coupled quater(3-arylthiophene)s has been developed from readily accessible building blocks. Two sets of building blocks were necessary to grow the oligomers in a unidirectional stepwise addition approach utilizing a traceless silyloxy linkage. This general synthetic scheme was applied to the synthesis of 256 library members using a combination of parallel and "mix-and-split" synthesis. Purification of all library members was achieved through automated HPLC−MS on normal-phase columns. The purified compounds were screened for their electronic and optical properties,[3a] and detailed results will be reported in due course.

## Experimental Section

Solvents and reagents were purified and dried by the usual methods prior to use. Unless otherwise stated, reactions were carried out in flame-dried glassware under an atmosphere of argon. Methylene chloride and THF were continuously distilled from calcium hydride and potassium, respectively. Melting points were determined with a Büchi B-545 melting point apparatus and are uncorrected. $^1H$ NMR spectra were recorded on a Bruker AMX 400 (400 MHz) spectrometer. Chemical shifts are expressed in parts per million ($\delta$) using residual solvent protons as internal standard. $^{13}C$ NMR spectra were recorded on a Bruker AMX 400 (101 MHz) spectrometer. Mass spectra were recorded on a Varian MAT 711. Ions were generated by electron impact at 70 eV. "On-bead" mass spectrometry was performed as follows. A

portion of the resin (50−100 beads) was filled into a glass vial of 1 mL capacity that was placed in a glass vial of 5 mL capacity. The 5 mL vial was filled with a 20% solution of TFA in $CH_2Cl_2$ (1 mL) and sealed, and the sample was exposed to TFA/$CH_2Cl_2$ vapor for 30 min. Cleavage of the compounds caused a slight coloration of the polymer support. The sample vial was then removed and mass spectra were recorded using EI-MS (70 eV). Elemental analyses were performed on an Elementar vario EL (limit of experimental error: ±0.3%). HPLC analysis and purification were accomplished using a Waters HPLC system (MassLynx, version 3.4; Waters 600E multisolvent delivery system; Waters 2700 sample manager; Waters fraction collector II; Waters reagent manager; Acurate Flowstream Splitting device ACM 10-50, LC Packings) equipped with a photodiode array detector (Waters 996 PDA detector) coupled to a Platform LC−MS detector (Micromass ZMD) operating with an APCI source. Conditions for analysis were the following. LC conditions: column, Nucleosil nitrophenyl column (Macherey-Nagel, 250 mm × 4 mm, 5 mm/100 Å); eluent, $CH_2Cl_2$/*n*-hexane mixtures (isocratic); flow rate, 1.0 mL/min; injection volume, 20 $\mu$L; photodiode array detection, scan range 250−500 nm. MS conditions: positive-ion APCI, source block temperature 130 °C; APCI probe temperature, 450 °C; cone voltage, 70 V; corona voltage, 3.5 kV; extractor, 5 V; RF lens, 0.0 V; LM resolution, 15.1; HM resolution, 15.0; ion energy, 0.5; multiplier, 650 desolvation gas flow, 443 L/h; cone gas flow, 86 L/h. Conditions for preparative purification were the following: column, Nucleosil nitrophenyl column (Macherey-Nagel, 250 mm × 16 mm, 5 mm/100 Å); eluent, $CH_2Cl_2$/*n*-hexane mixtures (isocratic); flow rate, 20.0 mL/min; injection volume, 1500 $\mu$L; photodiode array detection, scan range 250−500 nm. A stream-splitting device allowed the diversion of $^1/_{1000}$ of the eluant stream (0.02 mL/min) to the PDA inlet while the balance (19.98 mL/min) passed to the fraction collector. The reagent manager pump diluted the analytical eluant stream with an additional 0.8 mL/min of solvent ($CH_2Cl_2$/*n*-hexane, 50:50) before the combined stream passed the PDA. Fractionating was achieved using a predetermined UV threshold. Polymer loading of **4**{*1*−*4*} was determined by weighing the derivatized resins after extensive washing and drying in vacuo and by mass recovery of cleaved products. The following transformations to **10**{*1*−*4*,*1*−*4*,*1*−*4*,*1*−*4*} were based on this loading capacity, and quantitative conversions were anticipated for all reactions. For cross-coupling reactions, building block **3**{*4*} was used to calculate the theoretical product concentration in the resin. Chemicals were purchased from commercial suppliers: boron trifluoride etherate (Merck), *n*-butyllithium (1.6 M in *n*-hexane) (Merck-Schuchardt), Celite (Merck-Schuchardt), dichloro(diisopropyl)silane (Fluka), disodium hydrogenphosphate dodecahydrate (Fluka), imidazole (Merck), iodine (Fluka), lithium diisopropyl amide (2 M in THF, heptane, ethylbenzene) (Fluka), *N*-bromosuccinimide (Merck-Schuchardt), 1,3-propanediol (Merck-Schuchardt), sodium diethyldithiocarbamate trihydrate (Fluka), sodium dihydrogenphosphate dihydrate (Merck), sodium hydrogencarbonate (Merck), tetra-*n*-butylammonium fluoride trihydrate (TBAF) (Merck-Schuchardt), trifluoroacetic acid (TFA) (Merck-Schuchardt), tri(isopropyl)borate (Alfa). Hydroxymethyl polystyrene resin (100−200 mesh, 1% DVB, batch no. A22954) with a loading capacity of 0.87 mmol/g was purchased from Novabiochem. 3-[4-(Trifluoromethyl)phenyl]thiophene,[24] 3-(4-anisyl)thiophene,[24] 2-bromo-3-phenylthiophene **11b**,[11e] 2-bromo-3-(4-tolyl)thiophene **11c**,[11e] 2,2′-propane-1,3-diyldioxybis[1,3,2]dioxaborinane,[25] and tetrakis(triphenylphosphino)palladium(0)[26] were prepared according to literature procedures. The library was constructed using the IRORI Accutag 100 system. Employed MicroKans and MacroKans were filled with 30 and 200 mg of derivatized resin, respectively. All reactions involving microreactors were performed in heavy-walled, round-bottom flasks equipped with screw caps and a magnetic stirrer. For Suzuki cross-coupling reactions, the solvent volume was not more than $^3/_4$ of the reaction flask volume to allow headspace for pressure buildup during the reaction.[23] Cleavage of the library compounds was performed in a Labconco RAPID VAP evaporation system (model 79000) equipped with an aluminum rotor, which was also used for subsequent evaporation of the cleavage solutions.

**2-Bromo-3-[4-(trifluoromethyl)phenyl]thiophene (11a). 11a** was prepared according to the literature procedure (87%) starting from 3-[4-(trifluoromethyl)phenyl]thiophene.[11e,24] Colorless solid, mp 46 °C, bp 80 °C/0.008 mbar. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.03 (d, $J$ = 5.6 Hz, 1H), 7.34 (d, $J$ = 5.6 Hz, 1H), 7.62−7.72 (m, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 109.70, 124.70 (q, $J$ = 272.1 Hz), 125.34 (q, $J$ = 3.9 Hz), 126.43, 128.77, 128.92, 129.61 (q, $J$ = 32.5 Hz), 138.53, 139.74. EI-MS *m*/*z*: 308 [$M^+$], 289 [$M^+$ − F], 227 [$M^+$ − $^{81}$Br]. Anal. Calcd for $C_{11}H_6BrF_3S$: C, 43.02; H, 1.97; S, 10.44. Found: C, 43.01; H, 2.00; S, 10.65.

**3-(4-Anisyl)-2-bromothiophene (11d). 11d** was prepared according to the literature procedure (66%) starting from 3-(4-anisyl)thiophene.[11e,24] Colorless oil, bp 108 °C/0.013 mbar. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 3.86 (s, 3H), 6.94−7.02 (m, 2H), 7.03 (d, $J$ = 5.7 Hz, 1H), 7.28 (d, $J$ = 5.7 Hz, 1H), 7.49−7.58 (m, 2H). $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ 55.13, 107.69, 113.71, 125.59, 127.35, 128.95, 129.68, 140.70, 158.99. EI-MS *m*/*z*: 270 [$M^+$], 255 [$M^+$ − $CH_3$]. Anal. Calcd for $C_{11}H_9BrOS$: C, 49.09; H, 3.37; S, 11.91. Found: C, 49.19; H, 3.38; S, 11.80.

**Building Block Synthesis. 2-[Chloro(diisopropyl)silyl]-3-[4-(trifluoromethyl)phenyl]thiophene (2{*1*}). 2**{*1*} was prepared according to the literature procedure (73%) starting from 2-bromo-3-[4-(trifluoromethyl)phenyl]thiophene (**11a**).[11e] White solid, mp 69 °C, bp 110 °C/0.006 mbar. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.91 (d, $J$ = 7.3 Hz, 6H), 1.01 (d, $J$ = 6.8 Hz, 6H), 1.10 (sp, $J$ = 6.8 Hz, 1H), 1.12 (sp, $J$ = 7.3 Hz, 1H), 7.15 (d, $J$ = 4.8 Hz, 1H), 7.46−7.66 (m, 4H), 7.69 (d, $J$ = 4.8 Hz, 1H). $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ 15.89, 17.09, 17.24, 124.21 (q, $J$ = 272.1 Hz), 124.99 (q, $J$ = 3.9 Hz), 129.48, 129.89 (q, $J$ = 32.6 Hz), 131.47, 132.13, 142.30, 149.67. EI-MS *m*/*z*: 376 [$M^+$], 357 [$M^+$ − F], 333 [$M^+$ − $C_3H_7$]. Anal. Calcd for $C_{17}H_{20}ClF_3SSi$: C, 54.17; H, 5.35; S, 8.51. Found: C, 54.22; H, 5.39; S, 8.38.

**3-(4-Anisyl)-2-[chloro(diisopropyl)silyl]thiophene (2{*4*}). 2**{*4*} was prepared according to the literature procedure (79%) starting from 3-(4-anisyl)-2-bromothiophene (**11d**).[11e]

White solid, mp 52 °C, bp 120 °C/0.016 mbar. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.89 (d, $J$ = 7.5 Hz, 6H), 1.01 (d, $J$ = 7.2 Hz, 6H), 1.11 (sp, $J$ = 7.5 Hz, 1H), 1.12 (sp, $J$ = 7.2 Hz, 1H), 3.84 (s, 3H), 6.89−6.91 (m, 2H), 7.12 (d, $J$ = 4.7 Hz, 1H), 7.26−7.28 (m, 2H), 7.63 (d, $J$ = 4.7 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 15.79, 17.18, 17.33, 55.24, 113.42, 128.06, 130.09, 130.92, 131.58, 131.71, 150.95, 159.24. EI-MS *m*/*z*: 338 [$M^+$], 295 [$M^+ - C_3H_7$]. Anal. Calcd for $C_{17}H_{23}ClOSSi$: C, 60.24; H, 6.84; S, 9.46. Found: C, 60.25; H, 6.92; S, 9.19.

**2-{3-[4-(Trifluoromethyl)phenyl]-2-thienyl}-[1,3,2]dioxaborinane (3{*1*}).** To a solution of *n*-butyllithium (42.7 mL, 68.4 mmol, 1.6 M in *n*-hexane) in THF (150 mL) was added dropwise at −70 °C 2-bromo-3-[4-(trifluoromethyl)-phenyl]thiophene (**11a**) (20.0 g, 65.1 mmol). After stirring for 10 min, 2,2′-propane-1,3-diyldioxybis[1,3,2]dioxaborinane (7.93 g, 32.6 mmol) was added dropwise to the deep-green solution. The mixture was stirred at −70 °C for 1 h and allowed to warm to room temperature. The solution was recooled to −70 °C, and boron trifluoride etherate (8.40 mL, 65.1 mmol) was added dropwise. 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 filtered through a bed of Celite. Crystallization afforded 14.4 g (71%) of the title compound as a white solid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.00 (qn, $J$ = 5.5 Hz, 2H), 4.04 (t, $J$ = 5.5 Hz, 4H), 7.17 (d, $J$ = 5.0 Hz, 1H), 7.55 (d, $J$ = 5.0 Hz, 1H), 7.57−7.61 (m, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 27.25, 62.04, 124.44 (q, $J$ = 271.6 Hz), 124.45 (q, $J$ = 3.8 Hz), 128.83 (q, $J$ = 32.0 Hz), 129.56, 130.65, 130.85, 141.34, 148.99. EI-MS *m*/*z*: 312 [$M^+$].

**2-[3-(4-Anisyl)-2-thienyl]-[1,3,2]dioxaborinane (3{*4*}).** To a Grignard reagent prepared from 2-bromo-3-(4-anisyl)-thiophene (**11d**) (20.0 g, 74.3 mmol) and magnesium turnings (1.99 g, 81.8 mmol) in THF (140 mL) was added dropwise at −70 °C tri(isopropyl)borate (18.2 g, 96.6 mmol). After being stirred at −70 °C for 1 h, the mixture was allowed to warm to room temperature and was stirred for 30 min. Water (100 mL) was added, and the aqueous layer was extracted with ether. The organic extracts were combined, washed with brine, and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was dissolved in THF (100 mL). Propane-1,3-diol (5.65 g, 74.3 mmol) and molecular sieves (20 g, 4 Å) were added to the solution, and the resulting mixture was stirred for 24 h at room temperature. Evaporation of the solvent afforded a brown solid containing the title product in 85% purity (calculated yield, 85%), which was used without further purification. For analytical purposes, the crude product was recrystallized from petroleum ether to give the title compound as a white crystalline solid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.99 (qn, $J$ = 5.5 Hz, 2H), 3.83 (s, 3H), 4.05 (t, $J$ = 5.5 Hz, 4H), 6.85−6.95 (m, 2H), 7.15 (d, $J$ = 4.8 Hz, 1H), 7.40−7.47 (m, 2H), 7.50 (d, $J$ = 4.8 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 27.30, 55.19, 62.00, 113.01, 127.50, 130.04, 130.34, 131.09, 150.29, 158.67. EI-MS *m*/*z*: 274 [$M^+$].

**Library Synthesis. Attachment of (Chlorosilyl)thiophenes 2{*1*−*4*} to the Hydroxymethylated Polystyrene Resin.**[11e] An oven-dried preweighed fritted column was charged with hydroxymethylpolystyrene resin (12.5 g, 0.87 mmol/g, 10.9 mmol, 1.0 equiv), imidazole (2.97 g, 43.6 mmol, 4.0 equiv), and DMF (80 mL). To the suspension was added (chlorosilyl)thiophene **2**{*1*−*4*} (21.8 mmol, 2.0 equiv). The resulting mixture was shaken periodically at room temperature for 52 h. The solvent was removed by filtration, and the polymer was washed successively with DMF (2 × 70 mL), THF (2 × 70 mL), and $CH_2Cl_2$ (2 × 70 mL) and then dried for 12 h in vacuo, providing **4**{*1*−*4*}. Loading capacities of 0.64 mmol/g (**4**{*1*}) and 0.68 mmol/g (**4**{*2*−*4*}) were determined by resin-weighing and by TFA-induced cleavage and subsequent mass recovery. FT-IR analysis revealed the disappearance of the hydroxy bands at 3449 and 3573 cm$^{-1}$.[11e] The negative color test for hydroxy groups verified the completeness of the loading reaction for all four resins **4**{*1*−*4*}.[22]

**Iodination of Resin-Bound Thiophenes 4{*1*−*4*}.** An oven-dried flask was charged with the polymer-bound thiophene **4**{*1*−*4*} (15.0 g, 0.68 mmol/g, 10.2 mmol, 1.0 equiv), and the resin was suspended in THF (120 mL). The reaction mixture was cooled to −60 °C, and LDA (15.3 mL, 30.6 mmol, 3.0 equiv, 2.0 M in THF/heptane/ethylbenzene) was added dropwise via cannula. After the addition was complete, the reaction mixture was warmed to room temperature over 30 min and stirred for an additional 1.5 h. The resulting suspension of orange beads was treated with iodine (7.77 g, 30.6 mmol, 3.0 equiv) at −60 °C and stirred at room temperature for 2 h. The polymer was collected by filtration in a fritted filter, washed successively with MeOH (2 × 70 mL), THF (2 × 70 mL), $CH_2Cl_2$ (2 × 70 mL), and $Et_2O$ (2 × 70 mL), and dried in vacuo, providing **5**{*1*−*4*}. For reaction control, a small portion (50 mg) of the bead-bound iodothiophene was cleaved according to the general test cleavage procedure given below and analyzed by $^1$H NMR and GC−MS.

**Suzuki Cross-Couplings with Resin-Bound Iodothiophenes 5{*1*−*4*}.** An oven-dried flask was charged with the resin-bound thiophene iodide **5**{*1*−*4*} (3.75 g, 0.63 mmol/g, 2.36 mmol, 1.0 equiv), and the resin was suspended in degassed THF (60 mL). Tetrakis(triphenylphoshino)-palladium (136 mg, 0.12 mmol, 5 mol %), boronic ester **3**{*1*−*4*} (7.08 mmol, 3.0 equiv), and a degassed solution of base (see *method A* and *B*) were added sequentially, and the mixture was refluxed for 12 h. For workup, the reaction mixture was drained, and deboronated 3-arylthiophene was recovered from the solution. After being washed with THF (2 × 50 mL), MeOH (2 × 50 mL), $H_2O$ (2 × 50 mL), MeOH (2 × 50 mL), THF (2 × 50 mL), $CH_2Cl_2$ (2 × 50 mL), and $Et_2O$ (2 × 50 mL), the resin was dried overnight in vacuo, providing **6**{*1*−*4*,*1*−*4*}.

**Method A. Suzuki Coupling with Boronic Ester 3{*1*}.** A buffer solution of sodium dihydrogenphosphate (1.47 g, 9.44 mmol, 4.0 equiv) and disodium hydrogenphosphate (6.77 g, 18.9 mmol, 8.0 equiv) in degassed water (15 mL) was used as base.

**Method B. Suzuki Coupling with Boronic Esters 3{*2*−*4*}.** A solution of sodium hydrogencarbonate (2.37 g, 28.3 mmol, 12 equiv) in degassed water (15 mL) was used as base.

For reaction control, a small portion (50 mg) of bead-bound bithiophene **6**{*1*−*4,1*−*4*} was cleaved according to the general test cleavage procedure given below and was analyzed by $^1$H NMR and HPLC−MS.

**Iodination of Bithiophenes 6{*1*−*4,1*−*4*}.** *Due caution should be exercised. Mercuric caproate and iodide are toxic. Waste containing mercuric salts should be disposed of properly.* Resin-bound bithiophene **6**{*1*−*4,1*−*4*} (3.75 g, 0.59 mmol/g, 2.21 mmol, 1.0 equiv) was suspended in $CH_2Cl_2$ (60 mL) in a preweighed fritted column, and mercuric caproate (1.24 g, 2.88 mmol, 1.3 equiv) was added. The resulting mixture was shaken periodically for 24 h at room temperature, drained, washed with $CH_2Cl_2$ (2 × 50 mL), and reacted with iodine (0.73 g, 2.88 mmol, 1.3 equiv) in $CH_2Cl_2$ (60 mL). After 1 h, the solvent was removed by filtration and the polymer was washed successively with $CH_2Cl_2$ (2 × 50 mL), MeOH (2 × 50 mL), THF (2 × 50 mL), MeOH (2 × 50 mL), and $CH_2Cl_2$ (2 × 50 mL) and then dried overnight in vacuo, providing **7**{*1*−*4,1*−*4*}. For reaction control, a small portion (50 mg) of bead-bound iodobithiophene **7**{*1*−*4,1*−*4*} was cleaved according to the general test cleavage procedure given below and analyzed by $^1$H NMR and HPLC−MS.

**Suzuki Cross-Couplings with Resin-Bound Iodobithiophenes 7{*1*−*4,1*−*4*}.** *Caution must be exercised when performing reactions in closed reaction flasks because of the risk of explosion! Appropriate precautions should be taken.* For each of the four thiophene boronic esters **3**{*1*−*4*}, 64 MacroKans filled with resin-bound bithiophene iodides **7**{*1*−*4,1*−*4*} (each MacroKan contained 200 mg of approximately 0.55 mmol/g loaded bithiophene iodide, 7.04 mmol per 64 microreactors, 1.0 equiv) were placed in a 1 L heavy-walled round-bottom flask equipped with a magnetic stirrer. To control the subsequent transformations in the microreactors, 32 additional MicroKans were filled with 30 mg of derivatized resin and randomly sorted into the four reaction vessels. The resin in the MacroKans was swollen in degassed THF (700 mL). Tetrakis(triphenylphoshino)-palladium (407 mg, 0.35 mmol, 5 mol %), boronic ester **3**{*1*−*4*} (28.2 mmol, 4.0 equiv), and a degassed solution of base (see methods A and B) were added sequentially. The reaction mixture was purged with argon for 15 min, and then the flask was sealed and the resulting suspension stirred at 75 °C for 24 h. For workup, each reaction was individually drained and washed with THF (2 × 500 mL), MeOH (2 × 500 mL), $H_2O$ (2 × 500 mL), MeOH (2 × 500 mL), THF (2 × 500 mL), $CH_2Cl_2$ (2 × 500 mL), and $Et_2O$ (2 × 500 mL). The first THF wash was used to recover deboronated 3-arylthiophenes. The MacroKans were then dried overnight in vacuo, providing **8**{*1*−*4,1*−*4,1*−*4*}.

**Method A. Suzuki Coupling with Boronic Ester 3{*1*}.** A buffer solution of sodium dihydrogenphosphate (4.39 g, 28.2 mmol, 4.0 equiv) and disodium hydrogenphosphate (20.2 g, 56.3 mmol, 8.0 equiv) in degassed water (50 mL) was used as base.

**Method B. Suzuki Coupling with Boronic Esters 3{*2*−*4*}.** A solution of sodium hydrogencarbonate (9.40 g, 112 mmol, 16 equiv) in degassed water (50 mL) was used as base.

For reaction control, 16 of the 32 control MicroKan microreactors were randomly selected and removed. Bead-bound terthiophenes **8**{*1*−*4,1*−*4,1*−*4*} were cleaved according to the general test cleavage procedure given below and analyzed by $^1$H NMR and HPLC−MS.

**Iodination of Terthiophenes 8{*1*−*4,1*−*4,1*−*4*}.** *Due caution should be exercised. Mercuric caproate and iodide are toxic. Waste containing mercuric salts should be disposed of properly.* The MacroKans (and 16 MicroKan control microreactors) were reacted in four batches of 64 microreactors containing resin-bound terthiophenes **8**{*1*−*4,1*−*4,1*−*4*} (7.04 mmol per 64 microreactors, 1.0 equiv). For each batch, the microreactors were suspended in $CH_2Cl_2$ (800 mL) and mercuric caproate (3.94 g, 9.15 mmol, 1.3 equiv) was added. The mixture was stirred for 48 h at room temperature, drained, washed with $CH_2Cl_2$ (2 × 600 mL), and reacted with iodine (2.32 g, 9.15 mmol, 1.3 equiv) in $CH_2Cl_2$ (800 mL). After 2 h, each reaction mixture was individually drained and washed with $CH_2Cl_2$ (2 × 600 mL), MeOH (2 × 600 mL), THF (2 × 600 mL), MeOH (2 × 600 mL), and $CH_2Cl_2$ (2 × 600 mL). The MacroKans were then dried overnight in vacuo, providing **9**{*1*−*4,1*−*4,1*−*4*}. For reaction control, the remaining 16 control MicroKan microreactors were removed and bead-bound iodoterthiophenes **9**{*1*−*4,1*−*4,1*−*4*} were cleaved according to the general test cleavage procedure given below and analyzed by $^1$H NMR and HPLC−MS.

**Suzuki Cross-Couplings with Resin-Bound Iodoterthiophenes 9{*1*−*4,1*−*4,1*−*4*}.** *Caution must be exercised when performing reactions in closed reaction flasks because of the risk of explosion! Appropriate precautions should be taken.* For each of the four thiophene boronic esters **3**{*1*−*4*}, 64 MacroKans filled with resin-bound terthiophene iodides **9**{*1*−*4,1*−*4,1*−*4*} (7.04 mmol per 64 microreactors, 1.0 equiv) were placed in a 1 L heavy-walled round-bottom flask equipped with a magnetic stirrer. The resin in the MacroKans was swollen in THF (700 mL). Tetrakis-(triphenylphoshino)palladium (407 mg, 0.35 mmol, 5 mol %), boronic ester **3**{*1*−*4*} (28.2 mmol, 4.0 equiv), and a solution of base (see methods A and B) were added sequentially. The reaction mixture was purged with argon for 15 min, and then the flask was sealed and the resulting suspension stirred at 75 °C for 24 h. For workup, each reaction mixture was individually drained and washed with THF (2 × 500 mL), MeOH (2 × 500 mL), $H_2O$ (2 × 500 mL), MeOH (2 × 500 mL), THF (2 × 500 mL), 1% solution of sodium diethyldithiocarbamate in DMF (2 × 500 mL), $CH_2Cl_2$ (2 × 500 mL), and $Et_2O$ (2 × 500 mL). The first THF wash was used to recover deboronated 3-arylthiophenes. The MacroKans were then dried overnight in vacuo, providing **10**{*1*−*4,1*−*4,1*−*4,1*−*4*}.

**Method A. Suzuki Coupling with Boronic Ester 3{*1*}.** A buffer solution of sodium dihydrogenphosphate (4.39 g, 28.2 mmol, 4.0 equiv) and disodium hydrogenphosphate

(20.2 g, 56.3 mmol, 8.0 equiv) in degassed water (50 mL) was used as base.

**Method B. Suzuki Coupling with Boronic Esters 3{*2*−*4*}.** A solution of sodium hydrogencarbonate (9.40 g, 112 mmol, 16 equiv) in degassed water (50 mL) was used as base.

**Standard Procedures for Cleavage, Purification, and Analysis. Test Cleavage of Compounds 4{*1*−*4*}, 5{*1*−*4*}, and 6{*1*−*4*,*1*−*4*}.** A portion of the derivatized resin (50 mg) was treated with a solution of 10% TFA in $CH_2Cl_2$ (1.5 mL) and agitated at ambient temperature for 2 h. The suspension was filtered, and the solvent was evaporated, affording the cleaved product as white to yellow solids.

**Test Cleavage of Compounds 7{*1*−*4*,*1*−*4*}.** A portion of the derivatized resin (50 mg) was treated with a solution of TBAF (30 mg) in THF (1.5 mL) and agitated at 70 °C for 2 h. The suspension was filtered, and the solvent was evaporated. The residue was dissolved in diethyl ether, washed with water and brine, and dried, and the residue was dissolved in $CH_2Cl_2$. After filtration through a silica bed (0.5 g in a Pasteur pipet) into a glass vial (7.4 mL capacity), the resulting solution was concentrated under reduced pressure to afford the cleaved product.

**Test Cleavage of Compounds 8{*1*−*4*,*1*−*4*,*1*−*4*}.** The microreactors were distributed into glass vials (10 mL capacity for MicroKans, 25 mL capacity for MacroKans). The Rf code was read, and the vials were labeled with the compound code. A solution of 10% TFA in $CH_2Cl_2$ (MicroKans, 2 mL; MacroKans, 10 mL) was added to each vial. The mixture was shaken for 2 h at ambient temperature and drained, and the microreactor was rinsed with $CH_2Cl_2$ and removed. The solvent was evaporated under reduced pressure, and the residue was dissolved in $CH_2Cl_2$. After filtration through a silica bed (0.5 g in a Pasteur pipet) into a glass vial (7.4 mL capacity), the resulting solution was concentrated under reduced pressure to afford the cleaved product.

**Test Cleavage of Compounds 9{*1*−*4*,*1*−*4*,*1*−*4*}.** The microreactors were distributed into glass vials (10 mL capacity for MicroKans, 25 mL capacity for MacroKans). The Rf code was read, and the vials were labeled with the compound code. A solution of TBAF in THF (MicroKans, 30 mg TBAF in 2 mL of THF; MacroKans, 200 mg of TBAF in 10 mL of THF) was added to each vial. The mixture was shaken for 2 h at 70 °C and drained, and the microreactor was rinsed with THF and removed. After evaporation of the solvent, the residue was dissolved in diethyl ether, washed with water and brine, and then dried. After filtration through a silica bed (0.5 g in a Pasteur pipet) into a glass vial (7.4 mL capacity), the resulting solution was concentrated to afford the cleaved product.

**Parallel Cleavage of the Quaterthiophene Library 10{*1*−*4*,*1*−*4*,*1*−*4*,*1*−*4*}.** The MacroKans were distributed into 256 glass vials (25 mL capacity). The Rf code was read, and the vials were labeled with the compound code. A solution of 10% TFA in $CH_2Cl_2$ (10 mL) was added to each vial. The mixtures were shaken for 2 h and drained; the microreactors were rinsed with $CH_2Cl_2$ and then removed. The resulting solutions were concentrated under reduced pressure to afford the cleaved products **1**{*1*−*4*,*1*−*4*,*1*−*4*,*1*−*4*}. Dissolved in $CH_2Cl_2$ (1 mL), the crude products were filtered into glass vials (7.4 mL capacity) through 0.5 g of $SiO_2$ in Pasteur pipets, which were rinsed with additional $CH_2Cl_2$ (3 mL), and the solvent was evaporated.

**Compound Purification.** All 256 quaterthiophenes **1**{*1*−*4*,*1*−*4*,*1*−*4*,*1*−*4*}, some cleaved bithiophenes (**6**{*1*,*1*}, **6**{*1*,*4*}, **6**{*2*,*2*}, **6**{*3*,*3*}, **6**{*4*,*1*}, **6**{*4*,*4*}), and terthiophenes (**8**{*1*,*1*,*1*}, **8**{*1*,*4*,*1*}, **8**{*2*,*2*,*2*}, **8**{*3*,*3*,*3*}, **8**{*4*,*1*,*4*}, **8**{*4*,*4*,*4*}) were purified by automated normal-phase HPLC. Samples were dissolved in $CH_2Cl_2$/*n*-hexane (30:70, 3.0 mL), and an aliquot (1.5 mL) was injected at various $CH_2Cl_2$/*n*-hexane mixtures (mixtures between 25:75 and 10:90, depending on the compound structure).

**Compound Analysis.** The HPLC purity of 16 randomly selected crude quaterthiophenes **1**{*1*−*4*,*1*−*4*,*1*−*4*,*1*−*4*}, 16 bithiophenes **6**{*1*−*4*,*1*−*4*}, and 16 terthiophenes (**8**{*1*,*1*,*1*}, **8**{*1*,*3*,*3*}, **8**{*1*,*4*,*1*}, **8**{*1*,*4*,*2*}, **8**{*1*,*4*,*4*}, **8**{*2*,*1*,*2*}, **8**{*2*,*1*,*3*}, **8**{*2*,*2*,*3*}, **8**{*3*,*4*,*1*}, **8**{*3*,*4*,*3*}, **8**{*3*,*4*,*4*}, **8**{*4*,*2*,*1*}, **8**{*4*,*2*,*3*}, **8**{*4*,*3*,*1*}, **8**{*4*,*3*,*2*}, **8**{*4*,*4*,*4*}) was assessed by HPLC−MS. In addition, HPLC−MS analysis was accomplished for the HPLC-purified compounds mentioned above, providing molecular weight information and UV absorbance. Samples were injected as solutions in $CH_2Cl_2$/*n*-hexane (30:70) at various $CH_2Cl_2$/*n*-hexane mixtures (mixtures between 25:75 and 10:90, depending on the compound structure). For 16 randomly selected pure quaterthiophenes **1**{*1*−*4*,*1*−*4*,*1*−*4*,*1*−*4*}, iodothiophenes **5**{*1*−*4*}, purified bithiophenes **6**{*1*−*4*,*1*−*4*}, and terthiophenes **8**{*1*−*4*,*1*−*4*,*1*−*4*}, $^1$H and $^{13}$C NMR spectra were recorded.

**Representative Spectral Data of Purified Library Members. Bithiophenes 6{*1*−*4*,*1*−*4*}. 6{*1*,*1*}.** $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.11 (d, $J$ = 5.2 Hz, 1H), 7.26 (d, $J$ = 1.5 Hz, 1H), 7.35 (d, $J$ = 5.2 Hz, 1H), 7.40 (d, $J$ = 1.5 Hz, 1H), 7.49−7.64 (m, 8H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 122.53, 124.16 (q, $J$ = 271.8 Hz), 124.17 (q, $J$ = 271.8 Hz), 125.15, 125.43 (q, $J$ = 3.8 Hz), 125.8 (q, $J$ = 3.8 Hz), 126.4, 129.3 (q, $J$ = 32.7 Hz), 129.6, 129.7 (q, $J$ = 32.6 Hz), 130.2, 132.04, 136.67, 137.98, 138.66, 139.67, 139.68, 140.90. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 455 $[M + H]^+$.

**6{*1*,*4*}.** $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.83 (s, 3H), 6.89−6.92 (m, 2H), 7.07 (d, $J$ = 5.2 Hz, 1H), 7.28 (d, $J$ = 5.2 Hz, 1H), 7.29 (d, $J$ = 1.5 Hz, 1H), 7.30−7.34 (m, 2H), 7.35 (d, $J$ = 1.5 Hz, 1H), 7.58−7.63 (m, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 55.26, 113.93, 121.95, 124.20 (q, $J$ = 271.8 Hz), 124.21, 125.14, 125.77 (q, $J$ = 3.8 Hz), 126.38, 128.33, 129.11 (q, $J$ = 32.3 Hz), 130.47, 130.68, 137.68, 138.90, 139.23, 140.57, 159.21. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 417 $[M + H]^+$.

**6{*2*,*2*}.** Analytical data were in conformity with literature data.[15c]

**6{*3*,*3*}.** Analytical data were in conformity with literature data.[15c]

**6{*4*,*1*}.** $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.81 (s, 3H), 6.89−6.91 (m, 2H), 7.09 (d, $J$ = 5.3 Hz, 1H), 7.19−7.22 (m, 2H), 7.32 (d, $J$ = 5.3 Hz, 1H), 7.39−7.44 (m, 2H), 7.49−7.54 (m, 2H), 7.58−7.62 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 55.31, 114.22, 119.78, 124.21 (q, $J$ = 272.1 Hz), 124.82, 125.36 (q, 3.8 Hz), 126.13, 127.35, 128.19, 129.28, 129.44 (q, $J$ = 32.3 Hz), 129.58, 130.06, 132.63, 135.75,

137.56, 139.82, 142.08, 159.06. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 417 $[M + H]^+$.

**6**{***4,4***}. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 3.81 (s, 3H), 3.82 (s, 3H), 6.88−6.92 (m, 4H), 7.05 (d, $J = 5.2$ Hz, 1H), 7.16 (d, $J = 1.5$ Hz, 1H), 7.24 (d, $J = 1.5$ Hz, 1H), 7.25 (d, $J = 5.2$ Hz, 1H), 7.30−7.35 (m, 2H), 7.41−7.46 (m, 2H). $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 55.24, 55.30, 113.85, 114.16, 119.23, 123.90, 125.47, 127.35, 128.45, 128.51, 130.45, 130.58, 131.01, 136.76, 138.81, 141.74, 158.93, 159.08. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 379 $[M + H]^+$.

**Terthiophenes 8**{***1*−*4,1*−*4,1*−*4***}. **8**{***1,1,1***}. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 6.96 (s, 1H), 7.12 (d, $J = 5.2$ Hz, 1H), 7.19 (d, $J = 1.3$ Hz, 1H), 7.38 (d, $J = 5.2$ Hz, 1H), 7.39 (d, $J = 1.3$ Hz, 1H), 7.44−7.68 (m, 12H). $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 122.69, 124.10 (q, $J = 272.2$ Hz), 124.14 (q, $J = 272.5$ Hz), 124.18 (q, $J = 272.4$ Hz), 125.35, 125.47 (q, $J = 3.8$ Hz), 125.49 (q, $J = 3.8$ Hz), 125.84, 125.86 (q, $J = 3.8$ Hz), 126.41, 129.42 (q, $J = 32.4$ Hz), 129.61, 129.83 (q, $J = 32.6$ Hz), 129.93 (q, $J = 32.4$ Hz), 130.44, 131.55, 132.43, 134.68, 136.05, 137.97, 138.12, 138.52, 139.15, 139.66, 140.98. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 681 $[M + H]^+$.

**8**{***1,4,1***}. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 3.82 (s, 3H), 6.87−6.89 (m, 2H), 6.91 (s, 1H), 7.09 (d, $J = 5.2$ Hz, 1H), 7.21 (d, $J = 1.5$ Hz, 1H), 7.23−7.27 (m, 2H), 7.33 (d, $J = 1.5$ Hz, 1H), 7.33 (d, $J = 5.2$ Hz, 1H), 7.55−7.66 (m, 8H). $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 55.26, 113.98, 122.12, 124.17 (q, $J = 272.8$ Hz), 124.18 (q, $J = 272.8$ Hz), 125.05, 125.11, 125.49 (q, $J = 3.8$ Hz), 125.78 (q, $J = 3.8$ Hz), 126.37, 127.77, 129.20 (q, $J = 32.2$ Hz), 129.65 (q, $J = 32.3$ Hz), 130.28, 130.36, 130.41, 131.09, 132.04, 133.60, 137.01, 137.73, 138.72, 139.30, 139.76, 140.61, 159.40. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 643 ($[M + H]^+$).

**8**{***2,2,2***}. Analytical data were in conformity with literature data.[11e]

**8**{***3,3,3***}. Analytical data were in conformity with literature data.[11e]

**8**{***4,1,4***}. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 3.81 (s, 3H), 3.83 (s, 3H), 6.87−6.95 (m, 4H), 6.99 (s, 1H), 7.05 (d, $J = 5.2$ Hz, 1H), 7.12 (d, $J = 1.5$ Hz, 1H), 7.17 (d, $J = 1.5$ Hz, 1H), 7.27 (d, $J = 5.2$ Hz, 1H), 7.34−7.41 (m, 4H), 7.44−7.49 (m, 2H), 7.56−7.60 (m, 2H). $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 55.29, 55.31, 114.03, 114.21, 119.77, 124.17 (q, $J = 272.2$ Hz), 124.28, 125.35 (q, $J = 3.8$ Hz), 125.98, 127.34, 128.11, 128.25, 128.86, 129.54 (q, $J = 32.7$ Hz), 129.55, 130.18, 130.48, 130.94, 132.27, 135.39, 135.47, 137.36, 139.25, 139.53, 139.54, 142.05, 159.06, 159.29. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 605 $[M + H]^+$.

**8**{***4,4,4***}. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 3.81 (s, 3H), 3.82 (s, 3H), 3.84 (s, 3H), 6.85−6.95 (m, 6H), 6.96 (s, 1H), 7.04 (d, $J = 5.3$ Hz, 1H), 7.13 (d, $J = 1.5$ Hz, 1H), 7.16 (d, $J = 1.5$ Hz, 1H), 7.24−7.29 (m, 3H), 7.36−7.43 (m, 4H). $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 55.25, 55.29, 55.32, 113.85, 113.99, 114.16, 119.25, 124.01, 125.32, 127.36, 128.24, 128.38, 128.42, 129.61, 130.45, 130.47, 130.66, 130.86, 130.95, 134.33, 136.46, 138.68, 138.90, 141.73, 158.94, 159.18, 159.19. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 567 ($[M + H]^+$).

**Quaterthiophenes 1**{***1*−*4,1*−*4,1*−*4,1*−*4***}. **1**{***1,2,2,2***}. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 6.87 (s, 1H), 6.96 (s, 1H), 7.08 (d, $J = 5.2$ Hz, 1H), 7.12 (d, $J = 1.4$ Hz, 1H), 7.26−7.48 (m, 17H), 7.50−7.61 (m, 4H). $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 122.01, 124.17 (q, $J = 271.8$ Hz), 124.33, 125.10, 125.74 (q, $J = 3.8$ Hz), 126.34, 127.72, 127.82, 128.46, 128.54, 129.27, 129.28, 129.29 (q, $J = 32.6$ Hz), 129.35, 129.50, 129.88, 130.85, 130.90, 130.98, 131.05, 134.32, 134.65, 135.66, 135.73, 136.03, 137.01, 138.74, 139.32, 139.37, 139.42, 140.58. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 703 $[M + H]^+$.

**1**{***1,2,2,3***}. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.38 (s, 3H), 6.88 (s, 1H), 6.98 (s, 1H), 7.05 (d, $J = 5.2$ Hz, 1H), 7.12 (d, $J = 1.5$ Hz, 1H), 7.17−7.21 (m, 2H), 7.26 (d, $J = 5.2$ Hz, 1H), 7.28 (d, $J = 1.5$ Hz, 1H), 7.25−7.42 (m, 12H), 7.49−7.61 (m, 4H). $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 21.30, 122.00, 124.17 (q, $J = 271.8$ Hz), 124.24, 125.09, 125.74 (q, $J = 3.8$ Hz), 126.34, 127.72, 127.80, 128.46, 128.53, 129.12 (q, $J = 32.5$ Hz), 129.16, 129.27, 129.28, 129.32, 129.52, 129.83, 130.65, 130.82, 130.97, 133.03, 134.39, 134.83, 135.67, 135.78, 137.02, 137.44, 138.73, 138.74, 139.32, 139.34, 139.44, 140.58. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 717 $[M + H]^+$.

**1**{***1,2,4,3***}. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.38 (s, 3H), 3.82 (s, 3H), 6.89−6.94 (m, 2H), 6.91 (s, 1H), 6.96 (s, 1H), 7.05 (d, $J = 5.2$ Hz, 1H), 7.13 (d, $J = 1.5$ Hz, 1H), 7.17−7.22 (m, 2H), 7.26 (d, $J = 5.2$ Hz, 1H), 7.29 (d, $J = 1.5$ Hz, 1H), 7.30−7.36 (m, 9H), 7.51−7.61 (m, 4H). $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 21.30, 55.28, 113.99, 121.98, 124.17 (q, $J = 271.8$ Hz), 124.18, 125.10, 125.74 (q, $J = 3.8$ Hz), 126.34, 127.71, 128.07, 128.46, 129.12 (q, $J = 32.6$ Hz), 129.16, 129.26, 129.29, 129.37, 129.94, 130.31, 130.46, 130.73, 130.83, 130.96, 133.05, 134.60, 134.62, 135.72, 137.07, 137.41, 138.74, 138.75, 139.02, 139.31, 139.36, 140.58, 159.32. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 747 $[M + H]^+$.

**1**{***1,4,1,3***}. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.38 (s, 3H), 3.81 (s, 3H), 6.83 (s, 1H), 6.84−6.90 (m, 2H), 6.98 (s, 1H), 7.01 (d, $J = 5.2$ Hz, 1H), 7.17 (d, $J = 1.5$ Hz, 1H), 7.18−7.24 (m, 4H), 7.28 (d, $J = 5.2$ Hz, 1H), 7.30 (d, $J = 1.5$ Hz, 1H), 7.31−7.36 (m, 2H), 7.50−7.63 (m, 8H). $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 21.31, 55.25, 113.97, 122.12, 123.12 (q, $J = 272.2$ Hz), 123.13 (q, $J = 272.2$ Hz), 124.43, 125.07, 125.48 (q, $J = 3.8$ Hz), 125.77 (q, $J = 3.8$ Hz), 126.35, 127.70, 129.16, 129.17 (q, $J = 32.3$ Hz), 129.18, 129.32, 129.72 (q, $J = 32.3$ Hz), 130.13, 130.28, 130.39, 131.03, 131.06, 131.66, 132.92, 133.30, 135.57, 136.96, 137.57, 138.68, 139.23, 139.47, 139.69, 140.60, 159.40. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 815 $[M + H]^+$.

**1**{***1,4,1,4***}. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 3.81 (s, 3H), 3.84 (s, 3H), 6.83 (s, 1H), 6.85−6.96 (m, 4H), 6.99 (s, 1H), 7.05 (d, $J = 5.2$ Hz, 1H), 7.18 (d, $J = 1.5$ Hz, 1H), 7.19−7.23 (m, 2H), 7.28 (d, $J = 5.2$ Hz, 1H), 7.31 (d, $J = 1.5$ Hz, 1H), 7.34−7.39 (m, 2H), 7.51−7.64 (m, 8H). $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 55.26, 55.30, 113.97, 114.06, 122.12, 124.17 (q, $J = 272.2$ Hz), 124.18 (q, $J = 272.2$ Hz), 124.36, 125.08, 125.49 (q, $J = 3.1$ Hz), 125.77 (q, $J = 3.8$ Hz), 126.36, 127.70, 128.21, 129.09, 129.17 (q, $J = 32.6$ Hz), 129.60, 129.72 (q, $J = 32.6$ Hz), 130.12, 130.44, 130.49, 131.00, 131.06, 131.63, 133.29, 135.64, 136.97, 137.53,

138.69, 139.25, 139.36, 139.47, 140.60, 159.40. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 831 $[M + H]^+$.

**1**{***1,4,2,3***}. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.38 (s, 3H), 3.80 (s, 3H), 6.84−6.88 (m, 2H), 6.84 (s, 1H), 6.98 (s, 1H), 7.05 (d, $J$ = 5.2 Hz, 1H), 7.15 (d, $J$ = 1.4 Hz, 1H), 7.18−7.23 (m, 4H), 7.26 (d, $J$ = 5.18 Hz, 1H), 7.28 (d, $J$ = 1.4 Hz, 1H), 7.32−7.42 (m, 7H), 7.52−7.62 (m, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 21.30, 55.25, 113.91, 121.94, 124.18 (q, $J$ = 271.8 Hz), 124.21, 124.93, 125.74 (q, $J$ = 3.8 Hz), 126.35, 127.77, 127.93, 128.51, 128.78 (q, $J$ = 32.6 Hz), 129.16, 129.27, 129.31, 129.62, 129.83, 130.41, 130.44, 130.67, 130.92, 130.97, 133.03, 134.15, 134.75, 135.81, 137.25, 137.43, 138.77, 139.06, 139.24, 139.41, 140.52, 159.29. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 747 $[M + H]^+$.

**1**{***1,4,3,2***}. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.36 (s, 3H), 3.81 (s, 3H), 6.84−6.88 (m, 2H), 6.86 (s, 1H), 6.94 (s, 1H), 7.07 (d, $J$ = 5.2 Hz, 1H), 7.15−7.19 (m, 3H), 7.20−7.24 (m, 2H), 7.26−7.30 (m, 4H), 7.31−7.47 (m, 5H), 7.54−7.60 (m, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 21.30, 55.25, 113.89, 121.93, 124.18 (q, $J$ = 272.2 Hz), 124.26, 124.95, 125.75 (q, $J$ = 3.8 Hz), 126.36, 127.69, 127.97, 128.53, 129.09, 129.11 (q, $J$ = 32.6 Hz), 129.24, 129.35, 129.54, 130.02, 130.39, 130.44, 130.65, 130.84, 131.15, 132.76, 134.25, 134.44, 136.06, 137.30, 137.56, 138.79, 139.08, 139.27, 139.34, 140.50, 159.28. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 747 $[M + H]^+$.

**1**{***2,2,2,2***}. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.86 (s, 1H), 6.96 (s, 1H), 7.07 (d, $J$ = 5.2 Hz, 1H), 7.13 (d, $J$ = 1.4 Hz, 1H), 7.21 (d, $J$ = 1.4 Hz, 1H), 7.23−7.46 (m, 20H), 7.28 (d, $J$ = 5.2 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 120.66, 124.28, 125.51, 126.19, 127.22, 127.60, 127.71, 127.79, 128.40, 128.52, 128.54, 128.74, 129.28, 129.35, 129.48, 129.86, 130.83, 131.07, 131.11, 131.49, 134.02, 134.51, 135.43, 135.75, 135.77, 136.04, 136.28, 139.06, 139.21, 139.38, 142.13. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 635 $[M + H]^+$.

**1**{***2,2,4,2***}. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.82 (s, 3H), 6.88−6.93 (m, 2H), 6.90 (s, 1H), 6.93 (s, 1H), 7.07 (d, $J$ = 5.2 Hz, 1H), 7.14 (d, $J$ = 1.5 Hz, 1H), 7.22 (d, $J$ = 1.5 Hz, 1H), 7.23−7.47 (m, 17H), 7.27 (d, $J$ = 5.2 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 55.27, 113.99, 120.64, 124.23, 125.51, 126.20, 127.22, 127.60, 127.68, 128.05, 128.40, 128.52, 128.75, 129.30, 129.35, 129.98, 130.43, 130.54, 130.83, 131.20, 131.38, 134.25, 134.29, 135.44, 135.81, 136.07, 136.34, 138.91, 139.04, 139.30, 142.12, 159.30. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 665 $[M + H]^+$.

**1**{***3,2,3,3***}. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.33 (s, 3H), 2.37 (s, 3H), 2.38 (s, 3H), 6.89 (s, 1H), 6.96 (s, 1H), 7.04 (d, $J$ = 5.2 Hz, 1H), 7.12 (d, $J$ = 1.5 Hz, 1H), 7.13−7.20 (m, 6H), 7.17 (d, $J$ = 1.5 Hz, 1H), 7.25 (d, $J$ = 5.2 Hz, 1H), 7.27−7.36 (m, 11H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 21.11, 21.27, 21.30, 120.04, 124.11, 125.54, 126.07, 127.56, 128.38, 129.13, 129.16, 129.24, 129.26, 129.31, 129.42, 129.94, 130.69, 130.80, 130.94, 131.49, 132.67, 121.82, 133.06, 134.18, 134.50, 135.86, 136.19, 136.98, 137.39, 137.52, 138.95, 139.21, 139.32, 142.09. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 677 $[M + H]^+$.

**1**{***3,4,2,2***}. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.33 (s, 3H), 3.80 (s, 3H), 6.82 (s, 1H), 6.82−6.86 (m, 2H), 6.95 (s, 1H), 7.07 (d, $J$ = 5.2 Hz, 1H), 7.14 (d, $J$ = 1.5 Hz, 1H), 7.14−7.16 (m, 2H), 7.17 (d, $J$ = 1.5 Hz, 1H), 7.19−7.24 (m, 2H), 7.27 (d, $J$ = 5.2 Hz, 1H), 7.31−7.47 (m, 12H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 21.10, 55.22, 113.83, 119.99, 124.25, 125.37, 126.08, 127.70, 127.75, 128.09, 128.50, 128.53, 129.28, 129.35, 129.42, 129.58, 129.86, 130.40, 130.82, 131.08, 131.15, 131.20, 132.69, 133.71, 134.41, 135.79, 136.05, 136.33, 136.96, 138.70, 139.10, 139.34, 142.04. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 679 $[M + H]^+$.

**1**{***3,4,2,4***}. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.33 (s, 3H), 3.80 (s, 3H), 3.83 (s, 3H), 6.83 (s, 1H), 6.83−6.87 (m, 2H), 6.91−6.95 (m, 2H), 6.99 (s, 1H), 7.04 (d, $J$ = 5.2 Hz, 1H), 7.12−7.16 (m, 2H), 7.15 (d, $J$ = 1.5 Hz, 1H), 7.17 (d, $J$ = 1.5 Hz, 1H), 7.20−7.24 (m, 2H), 7.25 (d, $J$ = 5.2 Hz, 1H), 7.30−7.42 (m, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 21.10, 55.22, 55.28, 113.84, 114.01, 119.98, 124.08, 125.36, 126.08, 127.74, 128.09, 128.34, 128.50, 129.30, 129.42, 129.59, 129.72, 130.41, 130.47, 130.54, 130.91, 131.05, 131.08, 132.68, 133.77, 134.65, 135.83, 136.35, 136.96, 138.69, 139.02, 139.08, 142.04, 159.18, 159.22. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 709 $[M + H]^+$.

**1**{***4,1,3,3***}. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.37 (s, 3H), 2.38 (s, 3H), 3.80 (s, 3H), 6.85−6.90 (m, 2H), 6.89 (s, 1H), 6.97 (s, 1H), 7.05 (d, $J$ = 5.2 Hz, 1H), 7.08 (d, $J$ = 1.5 Hz, 1H), 7.15 (d, $J$ = 1.5 Hz, 1H), 7.16−7.21 (m, 4H), 7.26 (d, $J$ = 5.2 Hz, 1H), 7.26−7.30 (m, 2H), 7.32−7.44 (m, 6H), 7.54−7.57 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 21.30, 55.30, 114.20, 119.77, 124.16 (q, $J$ = 272.2), 124.23, 125.32 (q, $J$ = 3.8 Hz), 125.96, 127.32, 128.09, 128.77, 129.11, 129.15, 129.26, 129.28, 129.52 (q, $J$ = 32.6 Hz), 129.54, 129.97, 130.23, 130.65, 130.96, 132.26, 132.71, 133.03, 134.78, 134.99, 135.43, 137.32, 137.42, 137.64, 139.42, 139.48, 142.03, 159.05. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 761 $[M + H]^+$.

**1**{***4,1,4,4***}. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.81 (s, 3H), 3.83 (s, 3H), 3.84 (s, 3H), 6.86−6.95 (m, 6H), 6.89 (s, 1H), 6.97 (s, 1H), 7.04 (d, $J$ = 5.2 Hz, 1H), 7.09 (d, $J$ = 1.3 Hz, 1H), 7.16 (d, $J$ = 1.3 Hz, 1H), 7.26 (d, $J$ = 5.2 Hz, 1H), 7.29−7.59 (m, 10H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 55.29, 55.30, 55.31, 114.01, 114.03, 114.20, 119.77, 124.16, 124.17 (q, $J$ = 272.2 Hz), 125.34 (q, $J$ = 3.8 Hz), 125.95, 127.34, 127.98, 128.09, 128.35, 128.71, 129.54 (q, $J$ = 32.6 Hz), 129.55, 129.86, 130.02, 130.45, 130.48, 130.94, 132.23, 134.77, 135.04, 135.44, 137.32, 139.08, 139.14, 139.48, 142.05, 159.05, 159.23, 159.37. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 793 $[M + H]^+$.

**1**{***4,3,3,2***}. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.35 (s, 3H), 2.36 (s, 3H), 3.80 (s, 3H), 6.86 (s, 1H), 6.86−6.90 (m, 2H), 6.93 (s, 1H), 7.06 (d, $J$ = 5.2 Hz, 1H), 7.09−7.45 (m, 18H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 21.26, 21.29, 55.29, 114.13, 119.29, 124.19, 125.40, 127.33, 127.68, 128.36, 128.51, 129.09, 129.13, 129.22, 129.34, 129.52, 129.99, 130.81, 130.84, 131.21, 131.22, 132.78, 132.86, 133.95, 134.27, 136.06, 136.30, 137.34, 137.50, 138.99, 139.13, 139.27, 141.69, 158.92. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 693 $[M + H]^+$.

**1**{***4,4,2,2***}. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.80 (s, 3H), 3.81 (s, 3H), 6.83 (s, 1H), 6.83−6.90 (m, 4H), 6.95 (s, 1H), 7.07 (d, $J$ = 5.2 Hz, 1H), 7.10−7.12 (m, 2H), 7.19−7.24

(m, 2H), 7.27 (d, $J$ = 5.2 Hz, 1H), 7.30−7.47 (m, 12 H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 55.23, 55.30, 113.83, 114.14, 119.29, 124.25, 125.29, 127.33, 127.70, 127.75, 128.10, 128.33, 128.50, 128.53, 129.28, 129.35, 129.58, 129.86, 130.41, 130.83, 131.10, 131.15, 131.20, 133.70, 134.41, 135.79, 136.05, 136.33, 138.68, 139.10, 139.34, 141.71, 158.94, 159.18. APCI-MS ($CH_2Cl_2$/*n*-hexane) *m*/*z*: 695 $[M + H]^+$.

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**Supporting Information Available.** $^1$H NMR spectra of a representative set of library members and isolated overall yields of all library compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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