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Solution-Phase Microwave-Assisted Synthesis of Unsubstituted and Modified α-Quinque- and Sexithiophenes

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The facile synthesis of poorly soluble unsubstituted and modified α-quinque- and sexithiophenes under microwave irradiation in the liquid phase is described. The use of microwave irradiation allowed these compounds to be prepared in a few minutes and at high yields by means of the Suzuki cross-coupling reaction. Unsubstituted sexithiophene was obtained in 10 min via the one-pot borylation/Suzuki reaction, purified according to a very simple procedure, and isolated in 84% yield. The efficient synthesis of two new methylated quinque- and sexithiophenes displaying liquid crystalline properties is reported. A new microwave-assisted methodology for the conversion of aldehyde-terminated quinque- and sexithiophenes into the corresponding cyano derivatives is also described. The use of microwaves was extended to the Sonogashira coupling reaction and found to be very effective in the preparation of a quinquethiophene containing acetylenic spacers. The electronic and optical characterization of this compound is reported and discussed in relation to that of unsubstituted quinquethiophene.

Due to their relevant electrical and optical features, oligothiophenes are among the most important and widely studied organic molecular materials.[1] Of main interest are oligomers bearing five and six thiophene rings that are important electroactive materials, capable of self-assembly in highly ordered structures in the solid state and giving high-performance organic thin film transistors (FET).[2] Despite the simplicity of their molecular structure, the preparation of quinque- and sexithiophenes with a degree of purity suitable for electrical applications requires many tedious purification steps to obtain them free of byproducts and contaminants, i.e. to obtain materials with reproducible electrical characteristics. To improve the solubility and processability, modifications of the structure by the grafting of substituents into the aromatic backbone or by the introduction of spacers between the thiophene rings are needed. However, the self-alignment properties, morphology, and, in the end, electrical performance of the oligomers are also modified by the presence of substituents or spacers, in a way that is difficult to predict. At present, understanding the property/structure relationship relies on testing as many modified molecular structures as possible, hence the preparation of families of variously modified quinque- and sexithiophenes. For this purpose, the development of rapid and efficient synthetic methodologies to prepare libraries of new materials, to test their optical and electrical properties as a function of the molecular structure, becomes a crucial task.

Currently, microwaves are applied in many fields of organic synthesis to shorten reaction times, improve reaction yields, and, more importantly, to provide environmentally more sustainable methodologies.[3] Studies are underway to investigate the scalability of microwave-assisted reactions from laboratory to industrial scale without changing the laboratory-optimized reaction conditions.[4] Nevertheless, so far, only a few papers have been published describing the improvements brought about by the use of microwaves in the synthesis of thiophene-based semiconductor materials.[5] Recently, we have developed a microwave-assisted, solvent-free methodology for the synthesis of thiophene oligomers via the Suzuki reaction,

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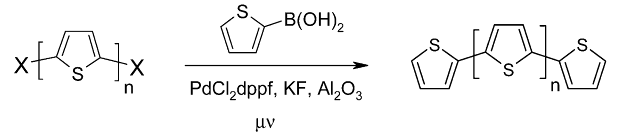
SCHEME 1



using PdCl$_2$dppf/KF as the catalytic system (Scheme 1).[5] This methodology is very effective in the preparation of soluble oligothiophenes, but it cannot be applied in the case of insoluble thiophene oligomers, such as unsubstituted sexithiophene, since the targeted products cannot be separated from the aluminum oxide used as the solid support in the solvent-free reaction.

In this paper we describe a novel, effective, microwave-assisted, solution-phase methodology for the preparation of poorly soluble unsubstituted and functionalized quinque- and sexithiophenes by means of Suzuki[6] and Sonogashira[7] cross-coupling reactions. We also show that the use of microwaves allows for the facile and very rapid transformation of aldehyde functionalized quinque- and sexithiophenes into the corresponding cyano derivatives without the use of expensive palladium catalysts or dangerous cyanide salts.

Results and Discussion

I. Synthesis of Unsubstituted α-Quinquethiophene (T5) and α-Sexithiophene (T6). To standardize the solution-phase, microwave-assisted, Suzuki reaction conditions, we tested the effectiveness of the PdCl$_2$dppf/KF catalytic system used in the solvent-free preparation of soluble oligothiophenes[5] in the synthesis of unsubstituted α-quinquethiophene (**T5**, **6**) from diiodoterthiophene **5** and thienyl boronic acid **3**, using a 1:1 (v/v) toluene/methanol mixture as the solvent (Scheme 2). The procedure depicted in Scheme 2 afforded **6** very rapidly (10 min) and in a higher yield (isolated yield 85%) than the solvent-free procedure (isolated yield 74%) previously described,[5] owing to the easier workup of the crude product. Indeed, methanol evaporation during microwave irradiation led to the formation of a fine suspension of **T5** in toluene, which could easily be isolated by centrifugation/filtration. Afterward the product was purified by washing first with warm water, then dissolving in warm dioxane and precipitating with a small volume of water.

A very good yield was also obtained in the preparation of unsubstituted sexithiophene **9** (**T6**, Scheme 2) by the one-pot borylation/Suzuki reaction of 5-bromoterthiophene **7** with commercial bis(pinacolato)diboron **8**. **T6** was obtained in 10 min and the crude product was easily purified, using a procedure similar to that described for **T5**, by first centrifuging the suspension formed in toluene, then washing the solid residue with warm water and then with CH$_2$Cl$_2$. Afterward, centrifugation and washing with warm dioxane afforded **9** in 84% isolated yield. Subsequent sublimation with a coldfinger gave a high-quality product. In the Supporting Information, micrographs of the nematic liquid-crystalline phase of **9** are reported.

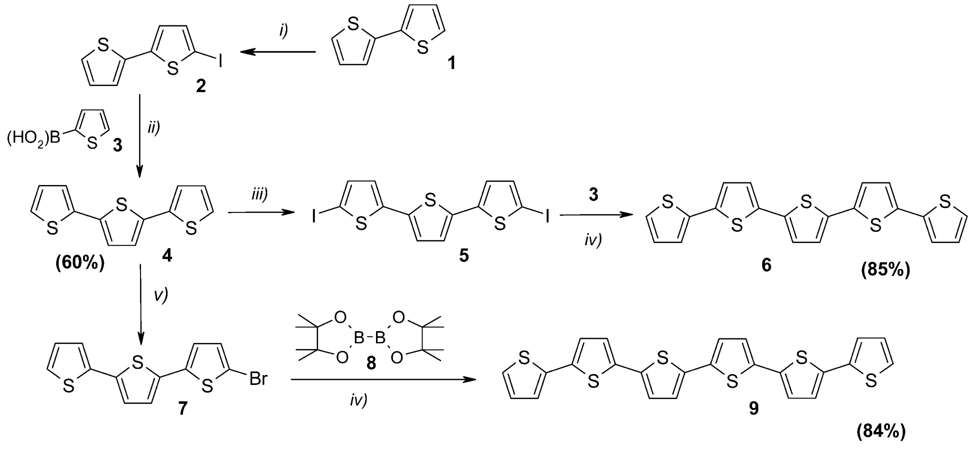
II. Synthesis and Characterization of Modified α-Quinque- and Sexithiophenes. The procedure described above was applied to the synthesis of scarcely soluble quinque- and sexithiophenes substituted at both terminal positions, α as well as *β* to sulfur.

Scheme 3 shows the preparation of the derivatives dimethylated at both *β*-terminal positions. Dimethylated quinquethiophene **11** was prepared from the reaction of diiodoterthiophene **5** and thienyl boronic ester **10** for 10 min under the action of microwaves. Compound **11** was slightly more soluble than **T5** and it was obtained in 90% isolated yield after recrystallization from toluene.

Scheme 3 also illustrates the preparation of dimethylated sexithiophene **13** from dibromoquatertiofene **12**[8] and thienyl boronic ester **10**. In this case, due to the low solubility of dibromoquaterthiophene **12**, the yield depended greatly on the solvent used in the cross-coupling reaction. By using a 1:1 (v/v) toluene:methanol mixture, **13** was obtained in only 20% isolated yield. However, the yield increased to nearly 70% with DMF as the solvent, in which **12** is more soluble, and increasing the temperature to about 100 °C.

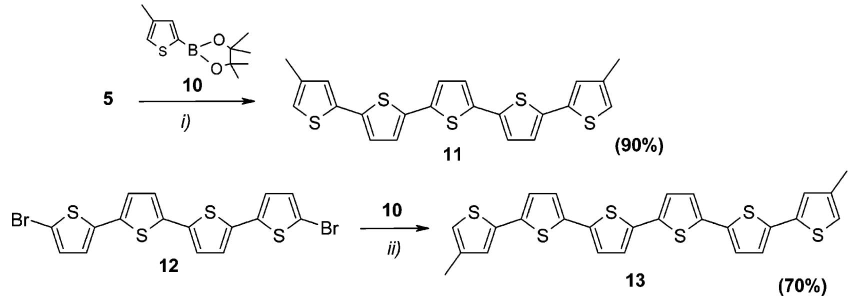
Both **11** and **13** displayed liquid-crystalline properties. As an example, Figure 1 shows the micrographs, taken under polarized light during the first cooling cycle, of

SCHEME 2. Synthesis of Quinquethiophene (T5, 6) and Sexithiophene (T6, 9) from Commercial Bithiophene (1)[a]



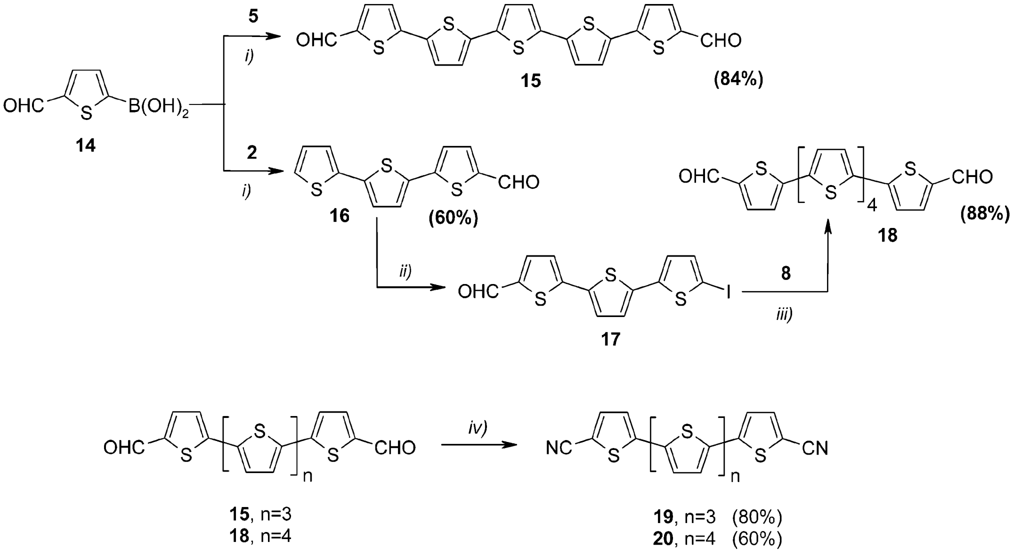
[a] Reagents and conditions: (i) NIS, DMF, overnight, −20 °C; (ii) PdCl$_2$dppf, basic alumina/KF, *μ*v 5 min, max temp 80 °C; (iii) NIS, CH$_2$Cl$_2$/AcOH, overnight, rt; (iv) PdCl$_2$dppf, toluene/methanol, *μ*v 10 min, max temp 70 °C; (v) NBS, DMF.

SCHEME 3. Synthesis of Quinque- (11) and Sexithiophenes (13) Methylated at Both Terminal β-Positions[a]



[a] Reagents and conditions: (I) $PdCl_2dppf$, KF, toluene/methanol, $\mu\nu$ 10 min, max temp 70°C; (ii) $PdCl_2dppf$, KF, DMF, $\mu\nu$ 20 min, max temp 100 °C.

SCHEME 4. Synthesis of Aldehyde-Terminated Quinque- (15) and Sexithiophenes (18) and Their Transformation to the Corresponding Cyano Derivatives[a]



[a] Reagents and conditions: (i) $PdCl_2dppf$, KF, toluene/methanol, $\mu\nu$ 10 min, max temp 70°C; (ii) NIS, CH_2Cl_2/AcOH, 2 h, rt, 76%; (iii) $PdCl_2dppf$, toluene/methanol, $\mu\nu$ 20 min, max temp 70 °C; (iv) $NH_2OH\cdot HCl$, $MeSO_2Cl$, DMF, $\mu\nu$ 20 min, 100 °C.

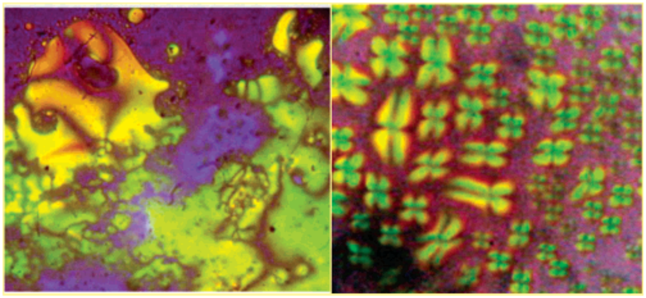
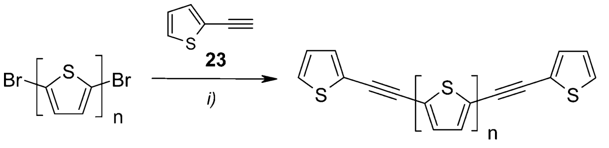


FIGURE 1. Optical micrographs under polarized light of dimethylated quinquethiophene **11** showing the birefringent Schlieren texture and maltese crosses typical of nematic phases.

pentamer **11**, showing the characteristic texture and maltese crosses of nematic mesophases. The first heating and cooling runs of the differential scanning calorimetry plots of **11** and **13** are reported in the Supporting Information. These plots display charateristics very similar to those reported for α,ω-dihexylquaterthiophene.[9] The first heating run of quinquethiophene **11** (mp 201 °C) showed the presence of a first endothermic peak centered at 188.33 °C ($\Delta H = 30.435$ J/g) followed by a second endothermic peak centered at 209.00 °C ($\Delta H = 64.021$ J/g). The subsequent cooling run showed an exothermic peak at 202.15 °C ($\Delta H = -60.695$ J/g) followed by a second exothermic peak at 162.48 °C ($\Delta H = -29.786$ J/g). The first heating run of sexithiophene **13** (mp 257 °C) showed the presence of a first endothermic peak at 205.67 °C ($\Delta H = 7.355$ J/g) followed by a second endothermic peak at 266.67 °C ($\Delta H = 65.517$ J/g). The subsequent cooling run showed an exothermic peak at 260.63 °C ($\Delta H = -62.215$ J/g) followed by a second exothermic peak at 155.30 °C ($\Delta H = -8.747$ J/g). However, while pentamer **11** could undergo several heating and cooling runs reversibly, the low-enthalpy transition of hexamer **13** became undetectable after the third heating−cooling run. In the Supporting Information we show a micrograph taken under polarized light of the nematic phase of this compound during the first cooling cycle.

Scheme 4 shows the preparation of aldehyde-terminated quinque- and sexithiophenes **15** and **18** starting from the commercially available 5-formyl-2-thiophene boronic acid **14** and their transformation into the corresponding cyano-terminated derivatives (**19** and **20**) under microwave action.

SCHEME 5. Sonogashira's Coupling of Dibromo Bi- and Terthiophene with 2-Ethynylthiophene[a]



21, n=2
22, n=3

24, n=2 (68%)
25, n=3 (71%)

[a] Reagents and conditions: (i) $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, (i-Pr)$_2$NH, $\mu\nu$ 5 min, 50 °C (**24**), and $\mu\nu$ 20 min, 100°C (**25**).

The diformyl quinquethiophene **15** was obtained in 10 min from diiodoterthiophene **5** in the presence of 4 mol % of $PdCl_2$dppf as the catalyst. After the usual work up (centrifugation, filtration, and precipitation with water from warm dioxane), the product was obtained in 84% isolated yield. The diformyl sexithiophene **18** was obtained in 88% isolated yield by the one-pot borylation-Suzuki coupling of 5″-bromo[2,2′;5′,2″]terthiophene-5-carbaldehyde **17**, using 5 mol % of $PdCl_2$dppf and irradiating with microwaves for 20 min.

The yields in **15** and **18** are comparable to those obtained by Wei et al.[10] using the Stille coupling[11] (88% and 87% for **15** and **18**, respectively) but the reaction times are markedly reduced (from 4−6 h to 10−20 min). Moreover, the microwave-assisted reactions were carried out in air, while the Stille coupling needs an argon atmosphere.

We found that when the aldehydic quinque- and sexithiophene **15** and **18** were reacted with hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) and methanesulfonyl chloride ($MeSO_2Cl$) in DMF[12] under microwave irradiation, they were transformed into the corrisponding cyano derivatives **19** and **20** in high yields. After purification by repeated washing/centrifugation steps of the crude materials with warm water and CH_2Cl_2, we obtained **19** and **20** in 80% and 60% isolated yields, respectively. Since boronic acid **14** is a commercial product, the pattern of Scheme 4 is a useful alternative to the synthesis of cyano derivates based on Stille coupling or on the exchange reaction between a halogen atom and the nitrile group of copper cyanide.[13]

To prepare thiophene oligomers containing acetylenic spacers, we also tested the use of microwaves in the Sonogashira coupling reaction.[7,14]

The reaction conditions were optimized through the synthesis of quaterthiophene TATTAT (**24**, Scheme 5, a soluble compound) with the terminal thiophenes separated by the inner bithiophene subsystem through an acetylenic spacer. After several attempts, the synthesis of TATTAT was accomplished in 5 min simply by microwave irradiation of a solution of dibromobithiophene **21** and 2-ethynylthiophene **23** in (i-Pr)$_2$NH (isolated yield 68%). In the absence of microwaves, using THF as the solvent, the same reaction afforded **24** only in a 26% yield, the self-coupling of **23** being the main process taking place. The same reaction conditions proved to be effective also in the preparation of the targeted quinquethiophene TATTTAT, **25**, which was obtained in a 71% isolated yield. Contrary to quinque- and sexithiophenes **11** and **13**, the first heating run of the DSC plot of **25** showed only a single endothermic peak at 203.00 °C (ΔH = 99.213 J/g), while the subsequent cooling run displayed a single exothermic peak at T = 145.60 °C (ΔH = −86.295 J/g). Moreover, optical microscopy showed no birefringence under polarized light for this compound either on heating or cooling cycles. It is worth noting that, contrary to compound **25**, its dibutyl-terminated derivative displays liquid-crystalline properties.[15]

TABLE 1. Maximum Absorption (λ_{max}, nm) and Emission (λ_{PL}, nm) Wavelengths,[a] Molar Absorption Coefficients (ϵ, mol^{-1} cm^{-1}),[a] and Calculated[b] HOMO-LUMO Energies (E_{HOMO}, E_{LUMO}, eV) of TATTAT (24) and TATTTAT (25) Compared to Conventional Quater- (T4) and Quinquethiophene (T5)

compd	ϵ	λ_{max}	λ_{PL}	E_{HOMO}	E_{LUMO}
TATTAT (**24**)	41 500	395[a] (381)[b]	478	−6.91	−0.65
T4	31 500	391 (372)	480	−6.95	−0.50
TATTTAT (**25**)	63 500	422 (396)	516	−6.82	−0.70
T5	55 200	416 (390)	510	−6.84	−0.59

[a] In CH_2Cl_2. [b] ZINDO/S on optimized ab initio HF/6-31G* geometries.

To have an insight into the effects of the introduction of the acetylenic spacers into the aromatic backbone of quinquethiophene, we ran the absorption and photoluminescence spectra of compounds **24** and **25** and carried out theoretical calculations on their geometry and electronic and optical properties. All data were then compared to those obtained for unsubstituted quater- and quinquethiophene (**T4** and **T5**) in the same conditions. Table 1 shows the maximum absorption and emission wavelengths and molar absorption coefficients of **24** and **25** as well as **T4** and **T5**, together with the λ_{max} values obtained from ZINDO/S calculations on optimized ab initio HF/6-31G* geometries and the corresponding HOMO and LUMO energies. The normalized absorption and emission spectra of compounds **24** and **25** are reported in the Supporting Information. The absorption and emission spectra obtained for **T4** and **T5** were the same as those already reported for these compounds.[16] The overall picture resulting from the data of Table 1 and the absorption and photoluminescence spectra is that the presence of the acetylenic spacers in **24** and **25** has very little effect on the electronic and optical properties, which remain very close to those of **T4** and **T5**. It is worth

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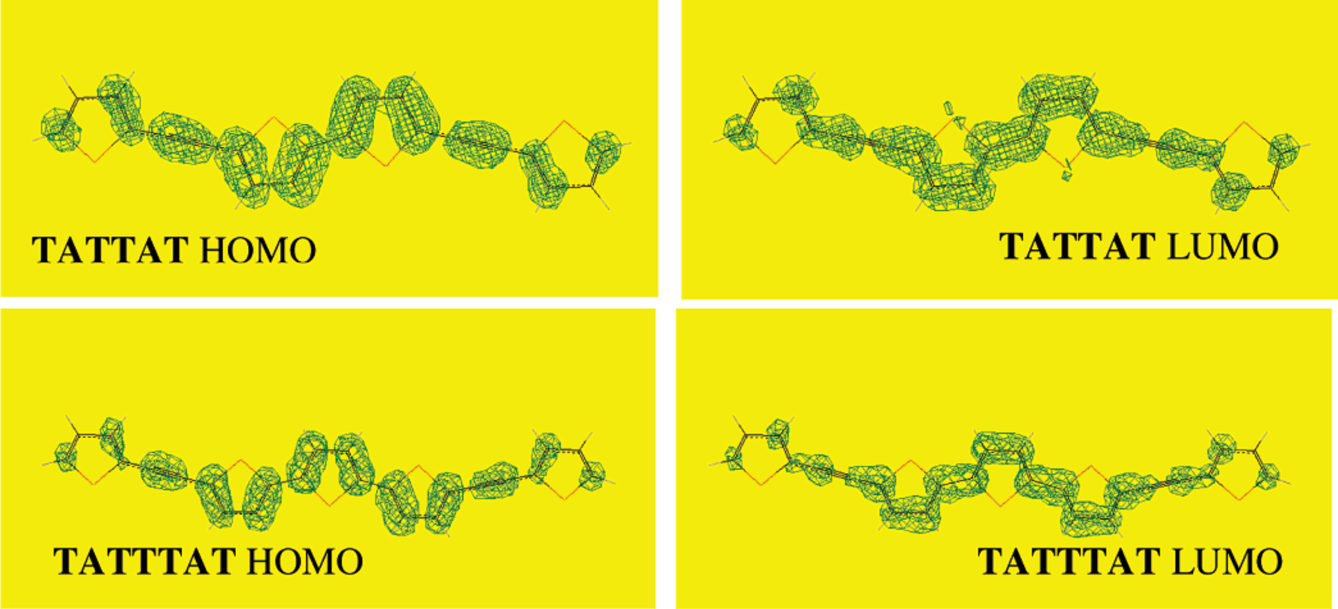

FIGURE 2. ZINDO/S calculated HOMO and LUMO frontier orbitals of compounds **24** (TATTAT) and **25** (TATTTAT), using optimized ab initio HF/6-31G* geometries.

noting that even the shape of the absorption and photoluminescence bands of the two compounds are very similar to those already reported for **T4** and **T5**, in particular with regard to the presence of vibronic bands in the PL spectra.[16] Nevertheless, as expected for compounds with larger molecular size, the molar absorption coefficients of **24** and **25** are markedly greater than those of **T4** and **T5**.

The calculated electronic densities of the frontier orbitals of **24** and **25** are shown in Figure 2. The calculations show that in both compounds the terminal TAT moieties, in which there are no steric interactions between adjacent rings, are planar, while in the central TT and TTT moieties the rings are tilted by 150° from each other. The electronic densities of both frontier orbitals, which are π in character, are extended over the entire molecule, in agreement with the large molar absorption coefficient values reported in Table 1. Moreover, ZINDO/S-C.I. calculations show that in both compounds the maximum UV absorption band is essentially due to a pure HOMO-LUMO transition, as in the case of **T4** and **T5**.

Discussion

Our data show that the solution-phase, microwave-assisted procedures described in this paper allow the preparation of poorly soluble, unsubstituted, and modified α-quinque- and sexithiophenes very rapidly, with great flexibility in experimental conditions, and in high yields.

Unsubstituted **T5** (**6**) and **T6** (**9**)—which are among the compounds with the highest field-effect charge mobilities,[2] also characterized by high self-affinity, i.e., the capability to display the same type of solid-state organization at different length scales[17]—could indeed be prepared in 60−90% isolated yields, with reaction times that were much shorter (minutes instead of hours) and using purification procedures that were far simpler.[18] This was the case, in particular, of the preparation of **T6** which, being insoluble, is difficult to purify to the degree that is useful for applications in thin film transistors.[19] The one-pot borylation/Suzuki reaction described in Scheme 2 is very rapid and the centrifugation/washing procedure for its purification is also rapid and expedient. A further vacuum sublimation with a coldfinger affords a high quality material for application in electronics, as already seen for **T5**.[17a]

Methyl-terminated quinque- and sexithiophenes **11** and **13** were prepared in the hope of obtaining organic semiconductors with charge transport properties as good as those of their unsubstituted counterparts[17,19] but more soluble, hence suitable for application in modern stamping procedures.[20] The rationale for grafting the methyls at the terminal β-positions was the fact that methyl groups in that position are expected to favor planar geometries, as inferred from single-crystal, X-ray analysis of a few methylated quaterthiophenes.[21]

Scheme 3 shows that, by means of microwave assistence, **11** and **13** could be prepared rapidly and in high yields. We found that both compounds possess liquid-crystalline properties. Although a detailed analysis of the liquid-crystalline properties of **11** and **13** is beyond the objective of this paper, the initial experimental evidence presented here (see Figure 1 and the Supporting Information) indicates that both compounds have a great tendency to self-organize in ordered structures, which is promising for their electrical properties (currently under

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investigation) and application in devices.[15d] It is worth noting that among unsubstituted oligothiophenes only **T6** is known to display liquid-crystalline properties,[22] while all the liquid-crystalline alkylated oligothiophenes reported so far bear long alkyl chains grafted at the terminal α positions.[9,15a−c]

As shown in Scheme 4, the poorly soluble aldehyde-terminated sexithiophene, **18**,[23] was rapidly prepared in a high yield by the one-pot borylation/Suzuki reaction, starting from commercial bithiophene. The scheme shows that the corresponding pentamer **15** was also prepared in a high yield taking advantage of microwave assistance. Moreover, by means of microwave assistance, both **15** and **18** were converted to the corresponding cyano-terminated derivatives, **19** and **20**, by using $NH_2OH{\cdot}HCl$ and $MeSO_2$-Cl in DMF as the solvent. As described by Sharghi et al.,[12] the reaction proceeds through the formation of an aldoxime, which is the key intermediate of the reaction, and the subsequent reaction with $MeSO_2Cl$ leads to the formation of the cyano-terminated oligomers through the elimination of $MeSO_3H$. α-Cyano-substituted quinque- and sexithiophenes are commonly prepared by cross-coupling halothienyls with metallothienyls containing cyano moieties or, alternatively, by transforming the CHO functionalities into the corresponding cyano groups by the use of cyanide salts in refluxing quinoline.[24] The procedure described in Scheme 4 is a rapid and convenient alternative to these methodologies.

For the preparation of pentamer TATTTAT (**25**) the microwave assistance in the Sonogashira coupling reaction[14] was tested. As shown in Scheme 5, by employing the reacting amine as the solvent, the use of microwaves not only allowed the targeted compound to be obtained very rapidly but also allowed the formation of the undesired homocoupling derivative of compound **23** to be markedly reduced. We found that in the absence of microwaves the formation of the homocoupling derivative of **23** was the major (62% vs <5%) reaction product. These results are of some interest in view of the fact that, recently, ethynyl units have been widely employed to build linear or dendritic π-conjugated nanostructures,[25] in which the triple bonds play the role of wires connecting the different aromatic moieties.

The data reported in Table 1 show that compound TATTTAT (**25**) and its shorter homologue TATTAT (**24**) have optical gaps which are very similar to those of quinque- (**T5**) and quaterthiophene (**T4**), respectively. This is in agreement with the fact that the presence of a triple bond between thiophene rings leads to an incomplete electron delocalization, owing to the mismatch of the electronic orbitals of the sp^2-hybridized carbon atoms in the thiophene rings and those of the sp-hybridized carbon atoms of the acetylenic linkage. This mismatch causes the increase of the energy gap, canceling out the effect that should be expected from the introduction of two π electrons in the conjugated system.[26] Nevertheless, as shown in Figure 2, the HOMO (as well as the LUMO) electronic densities of **24** and **25** are extended over the entire molecule and, in consequence, the molar absorption coefficients of these compounds are significantly larger than those measured for **T4** and **T5**. The molecular shape of **24** and **25** being different from that of **T4** and **T5**, it can be predicted that the thin film morphology of these compounds will be significantly different from that of **T4** and **T5**. Then these compounds are well suited for studies of the effects of thin film morphology on charge carrier mobility. Investigations in this direction are currently under way.

Concluding Remarks

The solution-phase, microwave-assisted methodology described here for poorly soluble unsubstituted and substituted quinque- and sexithiophenes, together with the previously reported solvent-free procedure for the preparation of soluble oligothiophenes,[5] provides access to a variety of new thiophene-based organic semiconductors and makes the preparation of the most performant of already known thiophene semiconductors more efficient and expedient.

Experimental Section

The characterization of compounds **2**,[27] **5**,[28] **6**,[18,5] **7**,[8] **9**,[8] **12**,[8] **15**−**18**,[10] **19** and **20**,[13,24] **21** and **22**,[8] and **23**[29] has already been reported.

2,2′;5′,2″-Terthiophene, 4. The microwave oven reactor was charged with 0.05 g (0.17 mmol) of **2**, 0.055 g (0.43 mmol) of **3**, 6 mg (0.0069 mmol) of Pd catalyst, 80 mg (1.36 mmol) of KF, and 240 mg of basic alumina. The mixture was stirred to homogenize the reagents. After 5 min of irradiation a TLC on silica gel with CH_2Cl_2/pentane 1:9 as eluent showed the absence of starting materials. The solid crude was directly charged on a cromatography column with the same conditions used for TLC. After cromatography 42 mg of **4** was isolated (60%). This reaction was repeated on a different scale, to obtain **4** in amounts of grams and with the same reaction yield.

2,2′:5″,2″:5″,2‴:5‴,2⁗-Quinquethiophene, 6. First 0.1 g (0.2 mmol) of **5** and 8 mg (0.01 mmol) of Pd catalyst were dissolved in 5 mL of toluene. Then a methanol solution (5 mL) of 0.132 g (1 mmol) of boronic acid **3** and 0.093 g (1.6 mmol) of KF was added. The mixture was irradiated for 10 min at 70 °C giving a suspension of orange powder. After centrifugation the crude product was washed twice with warm water, centrifuged again, and washed with CH_2Cl_2. The residue was first dissolved in warm dioxane and then precipitated with a small volume of water, affording 70 mg of **6** (85% of yield).

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This reaction was repeated on a different scale, to obtain **6** in amounts of 0.5 g and with same reaction yield.

2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′-Sexithiophene, 9. First 50 mg (0.15 mmol) of **7**, 19 mg (0.07 mmol) of bispinacolatodiboron **8**, and 4 mg (0.006 mmol) of $PdCl_2$dppf were introduced in the microwave oven reactor and dissolved in 2 mL of toluene, then 42 mg (0.73 mmol) of KF dissolved in 2 mL of MeOH was added. The mixture was irradiated for 10 min at 70 °C then the resulting suspension was centrifugated. The product obtained was washed twice with warm water to eliminate inorganic byproducts, then it was centrifuged again, washed with warm CH_2Cl_2, and finally washed with warm dioxane and 32 mg of **9** (84% yield) was obtained.

4,4,5,5-Tetramethyl-2-(4-methylthiophen-2-yl)[1,3,2]-dioxaborolane, 10. To a stirred solution of 2-bromo-4-methylthiophene (1.0 g, 5.6 mmol) in fresh distilled THF (43 mL) was added 2.76 mL of 2.5 M *n*-BuLi in hexane (6.7 mmol) dropwise at −78 °C under nitrogen atmosphere. After 10 min the flask was warmed to 0 °C and left at this temperature for 30 min. Then, after cooling the solution to −78 °C, 2.5 mL (12 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added by syringe and the reaction allowed to warm to room temperature. After 12 h of stirring the gray cloudy mixture was poured into water and extracted with ether. The organic phase was washed with brine and dried over $MgSO_4$. After flash chromatography on silica gel with petroleum ether/Et_2O (9:1) 1.13 g of **10** was obtained as a yellow oil (yield 90%). MS *m*/*e* 224 $[M^{\bullet+}]$. ^1H NMR ($CDCl_3$) δ 1.34 (s, 12H), 2.29 (s, 3H), 7.20 (s, 1H), 7.46 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 15.03, 24.70, 29.67, 83.94, 128.12, 138.94, 139.43 ppm.

4,4⁗-Dimethyl-2,2′:5″,2″:5″,2‴:5‴,2⁗-quinquethiophene, 11. The microwave oven reactor was charged with 10 mL of toluene, 50 mg (0.1 mmol) of 2,2‴-diiodoterthiophene (**5**), and 3 mg (0.004 mmol) of $PdCl_2$(dppf). Then a solution of KF (46 mg, 0.8 mmol) in MeOH (10 mL) was added at room temperature. Finally, 112 mg (0.5 mmol) of boronic ester **10** was added at once. After 10 min of irradiation at 70 °C, the solvent was evaporated under reduced pressure and the crude product was purified by repeated washing steps with warm H_2O and then crystallized from toluene yielding **11** in 90% yield as an orange solid. Mp 231 °C. MS (*m*/*e*) 440 $[M^{\bullet+}]$; λ_{max} (CH_2Cl_2) 421.10 nm. ^1H NMR ($CS_2/CDCl_3$) δ 2.62 (s, 3H), 6.80 (m, 1H), 6.99 (m, 1H), 7.06 (m, 3H). ^{13}C NMR ($CS_2/CDCl_3$) δ 138.2, 136.7, 136.6, 135.9, 135.5, 125.9, 124.2, 124.1, 124.0, 120.0, 15.7. Anal. Calcd for $C_{22}H_{16}S_5$: C, 59.96; H, 3.66. Found: C, 60.04; H, 3.67.

4,4′′′′′-Dimethyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′-sexithiophene, 13. The microwave oven reactor was charged with 0.125 g (0.26 mmol) of dibromoquaterthiophene[8] **12** and 11 mg (0.013 mmol) of $PdCl_2$(dppf) dissolved in 4 mL of DMF. Then 0.286 g (1.3 mmol) of **10** and 0.075 g (1.3 mmol) of KF were added and the mixture was irradiated for 20 min at 100 °C. The red suspension obtained was centrifuged and the precipitate washed twice with warm water and centrifuged again. Then the red precipitate was washed with warm CH_2Cl_2, centrifuged, and washed twice with warm toluene. Sexithiophene **13** was obtained as an intense red powder (95 mg, 70% yield). Mp 257 °C MS (*m*/*e*) 522 $[M^{\bullet+}]$; λ_{max} (CH_2Cl_2) 430.94 nm. ^1H NMR ($CS_2/CDCl_3$) δ 2.18 (s, 6H), 7.05 (m, 8), 6.80 (br s, 4H). Anal. Calcd for $C_{26}H_{18}S_6$: C, 59.73; H, 3.47. Found: C, 59.61; H, 3.46.

5′,5⁗-Diformyl-2,2′:5″,2″:5″,2‴:5‴,2⁗-quinquethiophene, 15. To a solution of 0.1 g (0.25 mmol) of **5** and 5 mg (0.006 mmol) of $PdCl_2$(dppf) in 8 mL of toluene was added a solution of 0.156 g (1 mmol) of thiophene boronic acid **14** and 0.093 g (1.6 mmol) of KF on 8 mL of methanol. The mixture was irradiated at 70 °C for 10 min then the dark-red suspension obtained was centrifuged and the precipitate washed twice with warm water, centrifuged again, and finally washed twice with CH_2Cl_2. The solid was then crystallized from dioxane−water to give 80 mg (85% yield) of a bright red powder corresponding to the characteristics reported in the literature for compound **15**.

5″-Iodo-[2,2′;5′,2″]terthiophene-5-carbaldehyde, 17. To a solution of 0.1 g (0.36 mmol) of **16** dissolved in 3.5 mL of CH_2Cl_2 was added 3.5 mL of CH_3COOH. The mixture was shielded from light and cooled in an ice bath and 0.1 g (0.398 mmol) of NIS was added stepwise. After 2 h the solvent was evaporated and the crude was washed twice with MeOH. Compound **17** was isolated as an orange powder (0.11 g, 76%). Mp 182 °C; MS *m*/*e* 402 $[M^{\bullet+}]$; λ_{max} (CH_2Cl_2) 405.11 nm; ^1H NMR ($CDCl_3$, TMS/ppm) δ 9.86, (s, 1H), 7.67 (d, $J = 4$ Hz, 1H), 7.24 (d, $J = 4$, 1H), 7.13 (d, $J = 4.0$ Hz, 1H), 7.07 (d, $J = 3.6$ Hz, 1H), 6.89, (d, $J = 3.6$ Hz, 1H); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 182.5, 146.5, 142.3, 141.8, 137.9, 137.7, 137.3, 126.9, 125.8, 125.1, 124.2. Anal. Calcd for $C_{13}H_7S_3OI$: C, 38.81; H, 1.75. Found: C, 38.75; H, 1.76.

5′,5′′′′′-Diformyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′-sexithiophene, 18. The procedure was the same as used for the preparation of **15**, starting from 0.1 g (0.25 mmol) of **17** and 30 mg (0.18 mmol) of **8**. After 10 min of irradiation at 70 °C a further 0.5 equiv of **8** and 2 mol % of $PdCl_2$dppf were added and the mixture was irradiated for an additional 10 min. The precipitate obtained was centrifuged and washed twice with warm MeOH, centrifuged again, and washed twice with toluene and then twice with CH_2Cl_2 yielding 60 mg (88%) corresponding to the characteristics reported in the literature for compound **18**.[10]

General Procedures for Microwave-Assisted Trasformation of Aldehyde End-Capped Oligomers into the Corresponding Cyano End-Capped Ones (19, 20). Aldehyde end-capped oligomers **15** and **18** (1 equiv), $NH_2OH{\cdot}HCl$ (8 equiv), $MeSO_2Cl$ (2.4 equiv), and DMF (0.5 mL) were introduced into the microwave oven reactor and irradiated for 20 min at 100 °C. The crude obtained was washed with warm water, centrifuged, and then washed with CH_2Cl_2 to give cyano end-capped oligomers **19** and **20**[13,24] in 80% and 60% yields, respectively.

5,5′-Bis(2-thienylethynyl)-2,2′-bithiophene, 24 (TATTAT). The microwave oven reactor was charged with 165 mg (0.50 mmol) of **21**,[8] 130 mg (1.20 mmol) of 2-ethynylthiophene **23**,[28] 28 mg (0.04 mmol) of $Pd(PPh_3)_2Cl_2$, 31 mg (0.12 mmol) of triphenylphosphine, 30 mg (0.16 mmol) of copper(I) iodide, and 2.02 g (2.80 mL, 20 mmol) of diisopropylamine. The mixture was irradiated for 5 min at 50 °C. After cooling, the crude product was poured into water (15 mL) and extracted with dichloromethane (3 × 15 mL). The combined extracts were centrifuged for 3 min at 3000 rpm and the isolated solid recrystallized from toluene to afford 128 mg (68% yield) of **24** as a deep chrome yellow solid. Mp 165 °C; MS *m*/*e* 378 $[M^{\bullet+}]$; λ_{max} (CH_2Cl_2) 395 nm; λ_{PL} (CH_2Cl_2) 478 nm. ^1H NMR ($CDCl_3$, TMS/ppm) δ 7.33 (dd, $^3J = 5.2$ Hz, $^4J = 1.2$ Hz, 2H), 7.29 (dd, $^3J = 3.6$ Hz, $^4J = 1.2$ Hz, 2H), 7.17 (d, $^3J = 4.0$ Hz, 2H), 7.08 (d, $^3J = 4.0$ Hz, 2H), 7.02, (dd, $^3J = 5.2$ Hz, $^3J = 3.6$ Hz, 2H); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 138.1, 132.8, 132.2, 127.8, 127.1, 124.0, 122.5, 122.1, 87.7, 86.0. Anal. Calcd for $C_{20}H_{10}S_4$: C, 63.46; H, 2.66. Found: C, 63.37; H, 2.68.

5,5″-Bis(2-thienylethynyl)-2,2′:5′,2″-terthiophene, 25 (TATTTAT). Compound **25** was synthesized by using the same method as was used for the synthesis of compound **24**. The starting material in this case was 5,5″-bisbromo-2,2′:5′,2″-terthiophene **22**.[8] The reaction took 20 min of microwave irradiation at 100 °C to be completed. Pure title compound **25** was obtained in 71% yield as a bright orange solid. Mp 200 °C; MS *m*/*e* 460 $[M^{\bullet+}]$; λ_{max} (CH_2Cl_2) 421 nm; λ_{PL}(CH_2Cl_2) 517 nm; ^1H NMR ($CDCl_3$, TMS/ppm) δ 7.33, (dd, $^3J = 5.2$ Hz, $^4J = 1.2$ Hz, 2H), 7.29 (dd, $^3J = 4.0$ Hz, $^4J = 1.2$ Hz, 2H), 7.18 (d, $^3J = 4.0$ Hz, 2H), 7.11 (s, 2H), 7.08 (d, $^3J = 4.0$ Hz, 2H), 7.02, (dd, $^3J = 5.2$ Hz, $^3J = 4.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 138.6, 136.1, 133.0, 132.3, 127.86, 127.2, 125.0, 123.7, 122.8, 121.9, 87.7, 86.1. Anal. Calcd for $C_{24}H_{12}S_5$: C, 62.57; H, 2.63. Found: C, 62.72; H, 2.64.

Theoretical Calculations. Ab initio calculations were performed with the Gaussian98 series of programs.[30] The geometries were fully optimized by standard gradient techniques and the critical points checked by frequency analysis. Optimized coordinates are reported as Supporting Information. Frontier orbitals and UV transitions were calculated by ZINDO/S-C.I. (8 × 8) single-point calculations on ab initio geometries with the HyperChem integrated package.[31]

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Supporting Information Available: Micrographs of the nematic mesophase of compound **9**, ^{1}H and ^{13}C NMR spectra of compound **10**, DSC plots of compound **11**, DSC plots and micrographs of the nematic phase of compound **13**, normalized absorption and photoluminescence spectra of compounds **24** and **25**, and optimized Cartesian coordinates of compounds **24** and **25**. This material is available free of charge via the Internet at http://pubs.acs.org.

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