Synthesis and UV−Visible Properties of Soluble Regioregular Oligo(3-octylthiophenes), Monomer to Hexamer

G. Bidan, A. De Nicola, V. Enée, and S. Guillerez*

Département de Recherche Fondamentale sur la Matière Condensée, SI3M/EM, CEA Grenoble, 17, rue des Martyrs, 38054 Grenoble Cedex 09, France

Received September 22, 1997

A series of head to tail alkyl-substituted oligothiophenes was synthesized by a stepwise synthesis based on the repetitive use of the Suzuki coupling reaction between a stable thienyl boronic ester and the appropriate chloride-protected precursors catalyzed by $Pd[P(C_6H_5)_3]_4$, under mild conditions. By this method, a very high level of regiospecificity was achieved, as shown in the synthesis of the dimer 3,4′-dioctyl-5′-chloro-2,2′-bithiophene, where no regioisomers could be detected. From the thus obtained chlorinated oligomers, free-ends oligo(3-octylthiophenes) were synthesized by reductive dehalogenation. UV−visible properties were investigated in solution, and the absorption energy was found to depend linearly on the reciprocal of the number of thiophene units. A comparison with the properties of analogous regioregular poly(3-octylthiophenes) gave information on the structure of such polymers in solution.

Introduction

Oligothiophenes (OTs) are currently attracting increasing attention due to their potential applications in various electronic or optoelectronic devices.[1] In a more fundamental way, they are of interest as models for the parent polymer and can be chemically modified to act as a spacer in supramolecular assemblies. However, further development of these oligomers is greatly limited by their intrinsic insolubility, which makes purification difficult, as well as chemical modification and processability. To overcome this major inconvenience, efforts have been directed toward the synthesis of alkylated OTs, such as the grafting of lateral flexible side groups (such as alkyl groups) allowing the solubilization of such molecules in common organic solvents. However, as in the case of the analogous poly(3-alkylthiophenes) (PATs), introduction of long alkyl chains in the 3 position of each thiophene ring may cause a dramatic loss of the electronic properties if the substitution pattern is not strictly controlled. This was demonstrated unambiguously with the synthesis of purely head-to-tail (HT) coupled PATs, exhibiting enhanced photophysical properties and electrical conductivity[2−5] compared to the regiorandom analogues. On the basis of calculations, it was postulated that head-to-head (HH) couplings introduce a pronounced inter-ring twisting angle in order to minimize steric interactions between alkyl chains on the second neighboring rings.[2] This was later confirmed with the synthesis and solution spectroscopic studies of the four possible regioisomers of a ter(3-hexylthiophene),[6] at the same time proving the usefulness of the oligomers as models for the parent polymer.

On the basis of these works, it clearly appears that oligo(3-alkylthiophenes) having HT couplings only constitute ideal structures. However, these molecules have been studied very little and, to our knowledge, very few syntheses have been proposed to date.[6,7]

In most cases, to avoid the conformational problem outlined above, partially alkylated OTs were synthesized.[8−12] In this way, alkyl side groups may be placed far from each other and symmetrical structures (which are easier to synthesize) are accessible. For example, large OTs (up to 16 thiophene units) were produced in a fast convergent synthesis.[12] Despite the success of the later approach, we believe that extended purely HT coupled oligo(3-alkylthiophenes) present a great deal of interest from a fundamental point of view and also for application purposes.

Results and Discussion

We present here an efficient synthesis of such purely HT coupled oligo(3-alkylthiophenes) from the monomer

(1) See, for example: (a) Garnier, F.; Horowitz, G.; Peng, X. Z.; Fichou, D. *Synth. Met.* **1991**, *45*, 163. (b) Fichou, D.; Nunzi, J.-M.; Charra, F.; Pfeffer, N. *Adv. Mater.* **1994**, *6*, 64. (c) Horowitz, G.; Garnier, F.; Yassar, A.; Hajlaoui, R.; Kouki, F. *Adv. Mater.* **1996**, *8*, 52.

(2) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904.

(3) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.

(4) McCullough, R. D.; Tristam-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910.

(5) Bjornholm, T.; Greve, D. R.; Geisler, T.; Petersen, J. C.; Jayaraman, M.; McCullough, R. D. *Adv. Mater.* **1996**, *8*, 920.

(6) Barbarella, G.; Bongini, A.; Zambianchi, M. *Macromolecules* **1994**, *27*, 3039.

(7) Li, W.; Maddux, T.; Yu, L. *Macromolecules* **1996**, *29*, 7329.

(8) Delabouglise, D.; Hmyene, M.; Horowitz, G.; Yassar, A.; Garnier, F. *Adv. Mater.* **1992**, *4*, 107.

(9) Bäuerle, P.; Segelbacher, U.; Gaudl, K.-U.; Huttenlocher, D.; Mehring, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 76.

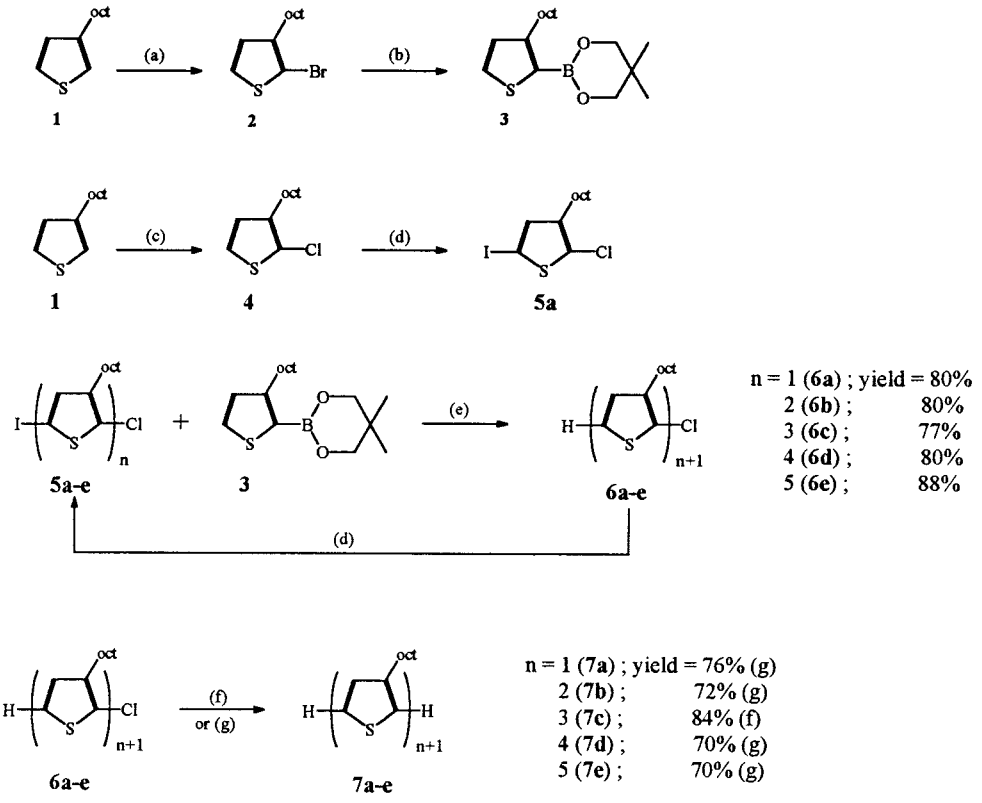
(10) Sato, M. A.; Hiroi, M. *Chem. Lett.* **1994**, 985.

(11) Tour, J. M.; Wu, R. *Macromolecules* **1992**, *25*, 1901.

(12) Bäuerle, P.; Fischer, T.; Bidlingmeier, B.; Stabel, A.; Rabe, J. P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 303.

S0897-4756(97)00655-8 CCC: $15.00 © 1998 American Chemical Society
Published on Web 04/01/1998

Scheme 1[a]



[a] Reagents: (a) NBS; (b) Mg, $B(OMe)_3$, H^+, $HO\text{-}CH_2\text{-}C(CH_3)_2\text{-}CH_2\text{-}OH$; (c) SO_2Cl_2; (d) I_2, $Hg(OAc)_2$; (e) $Pd(PPh_3)_4$, aq. $NaHCO_3$; (f) H_2, Pd/C; (g) Bu_3SnH, AIBN.

to the hexamer. We have limited our study to the synthesis of 3-octylthiophene-based systems, but the general scheme developed here may be easily extended to other alkyl or alkoxy groups.

Due to the asymmetric structure and small size of the desired oligomers, an iterative synthesis appeared well suited to our needs. In an iterative route, a blocking group can be introduced at the first step to protect one of the two reactive positions α to the sulfur of the successive oligomers throughout the entire synthesis. Thus, the selective functionalization of the remaining active site is trivial, and only a single deprotection step is required during the synthesis of a determined oligomer.

Before describing further the synthetic scheme leading to chlorinated oligo(3-octylthiophenes) (Scheme 1), some general comments will be made on the choice of the protecting group and about the coupling reaction.

The reactive position α to the sulfur and to the alkyl substituent was protected by introducing a chloride group.[13] This offers the advantage of being stable to a large range of conditions; the more commonly used silyl groups are susceptible to protodesilylation.[11] However, the chloride can interfere in the subsequent catalyzed cross-coupling reaction with organometallic species, and particular care is needed to select appropriate conditions. The Suzuki coupling reaction seems to be particularly appropriate, since heteroaryl chlorides have been reported to be unreactive toward boronic acids when $Pd(PPh_3)_4$ was used as a catalyst.[14] Moreover, this coupling reaction was widely used by Gronowitz et al.[15] on the thiophene series, and suitable conditions have been determinated. According to these choices, we propose the synthesis outlined in Scheme 1.

3-octylthiophene, **1**, was brominated in the 2 position by *N*-bromosuccinimide (NBS) in a polar solvent to yield 65% of pure **2**.[16] During this reaction, 0.5−1% of the isomeric 2-bromo-4-octylthiophene was formed (determined by gas chromatography (GC)), and NBS in excess was added until complete disappearance (<0.1%) of this byproduct occurred; the resulting dibrominated compound was easily eliminated by distillation under vacuum.

2-bromo-3-octylthiophene, **2**, was converted to the boronic acid by quenching of its Grignard reagent with trimethyl borate and hydrolysis of the methoxy groups with aqueous acid. The boronic acid, being sensitive to protodeboronation, was not isolated but immediately allowed to react with 2,2-dimethyltrimethyleneglycol to yield 74% of the readily stable boronate **3**.[17] Chlorination of **1** with sulfuryl chloride under the same conditions used for the synthesis of **2** afforded isomerically pure **4** (>99.9% by GC) in 65% yield after distillation.[18]

(13) Mac Dowell, D. W. H.; Patrick. T. B.; Frame, B. K.; Ellison, D. L. *J. Org. Chem.* **1967**, *32*, 1226.

(14) Mitchell, M. B.; Wallbank, P. J. *Tetrahedron Lett.* **1991**, *32*, 2273.

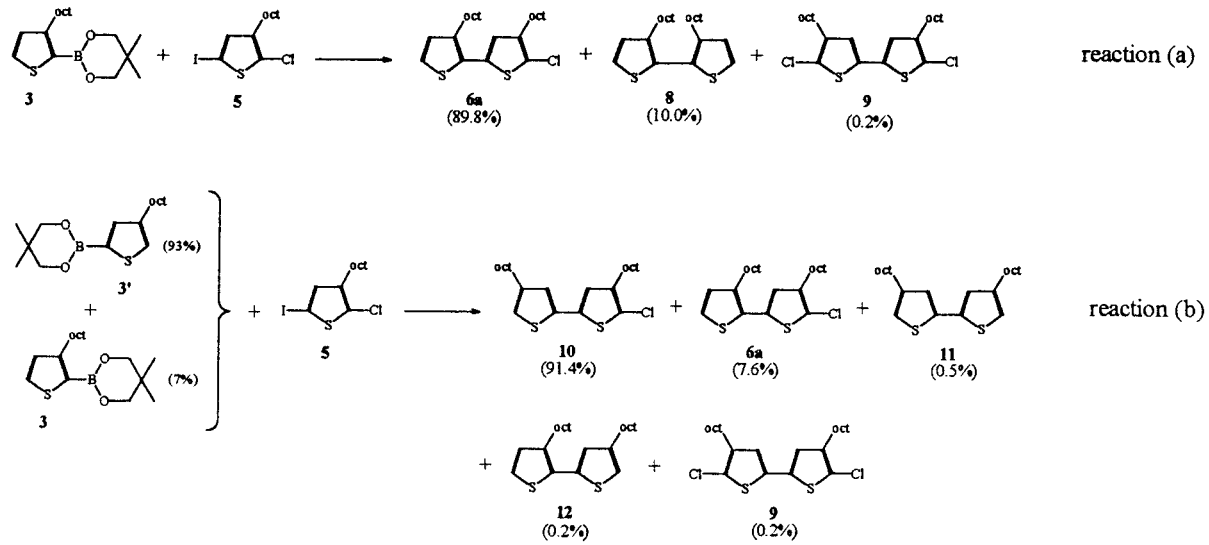
(15) Gronowitz, S.; Peters, D. *Heterocycles* **1990**, *30*, 645 and references therein.

(16) Kellog, R. M.; Shaap, A. P.; Harper, E. T.; Wynberg, H. *J. Org. Chem.* **1968**, *33*, 2902.

(17) Coutts, I. G. C.; Goldschmid, H. R.; Musgrave, O. C. *J. Chem. Soc. C* **1970**, 488.

(18) Campaigne, E.; Le Suer, W. M. *J. Am. Chem. Soc.* **1948**, *70*, 415.

Scheme 2[a]



[a] Yields of dimers were obtained by integration of the ion current in the GC-MS experiments.

4 was treated with iodine in the presence of mercuric acetate to form **5a** in 97% yield. The iodinated species **5a** was then reacted with a 20% excess of the boronate **3** in the presence of $Pd[P(C_6H_5)_3]_4$, following the experimental procedure of Gronowitz et al.,[15] to afford the chlorinated dimer **6a** in 80% yield. This was after purification by using either chromatography on silica gel or the more convenient semipreparative high-performance liquid chromatography (HPLC) reverse phase technique.

Higher chlorinated oligomers **6b**−**e** were obtained in a similar way, by a succession of iodination−coupling steps, with isolated yields up to 88%. However, contrary to observations from the synthesis of **5a**, the use of an excess of iodine for the iodination of chlorinated oligomers led to the formation of small amounts of bis-iodinated byproducts. This is probably due to the increased reactivity of the positions α to the coupling positions toward aromatic electrophilic substitution. To avoid the formation of these byproducts, whose separation by our chromatographic methods was unsuccessful, stochiometric amounts of iodine were allowed to react in small portions. By this way, the oligomers **5b**−**e** were synthesized in nearly quantitative yield and were determined to be free from poly-iodinated byproducts by mass spectrometry (MS).

From the chlorinated oligomers, free-ends oligomers (**7a**−**e**) can be easily obtained by reductive dehalogenation. Using H_2 over Pd/C in refluxing ethyl acetate in the presence of base, **7c** was obtained with 84% yield, but long reaction times were needed. A much more convenient procedure, using tributyltin hydride in the presence of azobisisobutyronitrile (AIBN), was preferred for the other oligomers, although lower yields (70−76%) were obtained.

The coupling reaction used throughout this synthesis seemed very efficient considering the overall yield and the regioselectivity, since after purification no isomers of **6a**−**e** could be detected by our techniques (GC and HPLC analyses). However, when analyses were performed on crude products of coupling reactions a and b (Scheme 2), different byproducts were detected by GC-MS techniques.

For these two test reactions, no higher oligomer nor iodinated byproducts were detected in the GC-MS experiments, demonstrating the efficiency of the chloride as a blocking group under these conditions. In the reaction **a**, only a single monochlorinated bis(3-octylthiophene) ($M = 424$) was detected and formally identified by ^{1}H NMR as **6a**. Besides this major product, a nonhalogenated bis(3-octylthiophene) ($M = 390$) was detected and further isolated by HPLC using reverse phase techniques and characterized by ^{1}H NMR to be the HH coupled isomer **8**. A dichlorinated byproduct ($M = 458$), present at about 0.2%, was detected but not characterized. It is postulated that this product is the symmetrical dichlorinated bis(3-octylthiophene) **9**, resulting from dehalogenative coupling of **5**. Therefore, apart from the cross-coupling reaction which leads to the desired dimer, two homocoupling side-reactions also producing dimers were identified. Due to the presence of the chloride on **5**, these byproducts are not regioisomers of **6a**, and this greatly facilitates their separation. Although seldom reported,[19] the homocoupling reaction of the boronic acid derivative **3** was unambiguously demonstrated to occur in our case, since **8** was identified by GC in a reaction mixture containing only **3** and the catalyst. In reaction b, a mixture containing 93% of the 5-boronate **3′** and 7% of the 2-boronate **3** (mixture synthesized by lithiation of **1** and subsequent treatment with $B(OMe)_3$) reacted with **5**. In this case, five different bis(3-octylthiophenes) derivatives were detected. According to the coupling reactions detected in reaction a and the analysis of the fragmentations observed in the GC-MS spectra, structures **9**−**12** and **6a** were proposed. **6a** and **10** were produced by the cross-coupling reaction between **5** and **3** or **3′** respectively. **11** and **12** were produced by the boronate homocoupling of **3′** with itself and of **3′** with **3** (the homocoupling of **3** was not detected), and **9** was produced by the dehalogenative homocoupling of **5**.

(19) Song, Z. Z.; Wong, H. N. C. *J. Org. Chem.* **1994**, *59*, 33.

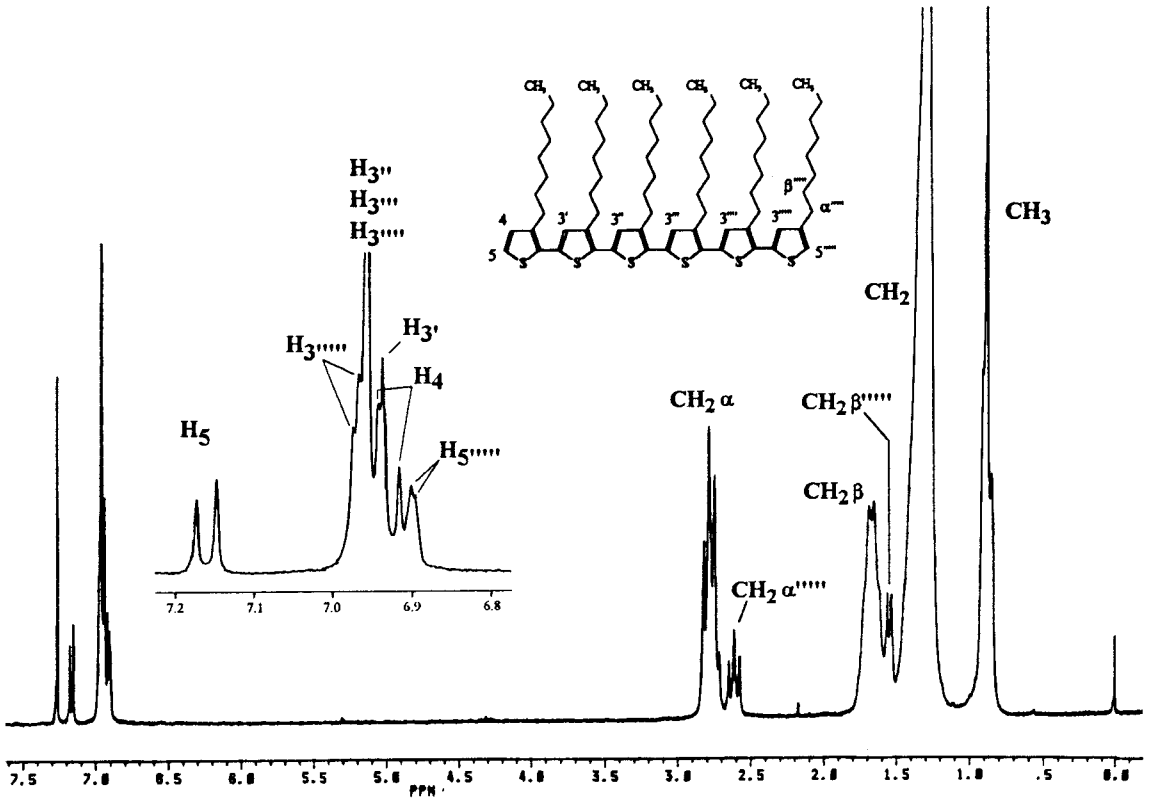


Figure 1. ^{1}H NMR spectrum (200 MHz) of the free-ends hexamer **7e** in $CDCl_3$. The inset shows the expanded aromatic region.

Despite our best efforts, these side-reactions could not be eliminated and the byproducts have to be separated. However, as outlined above, the presence of the chloride on the starting material **5** led to a mixture of dimers which are not regio-isomers. Thus, their separation by standard chromatography is easier (the presence of the chloride α to sulfur decreasing the polarity).

Structural Characterization. The structures of the oligothiophenes were characterized by ^{1}H NMR spectroscopy. The overall integration ratio between the aliphatic protons and the aromatic protons is consistent with the composition of the different oligomers. In the aliphatic region, a set of two triplet-like multiplets at 2.5−2.9 ppm is assigned to the methylene protons in the α position. The multiplet at higher field is assigned to the α protons of the more external chain; the integration ratio between these two signals is dependent on the length of the oligomer. The same characteristics are observed for the multiplets at 1.5−1.8 ppm, which are assigned to the methylene protons in the β position. In the aromatic region, except for the more acidic proton H5, which gives a doublet at 7.16 ppm, all the protons give signals between 7.0 and 6.8 ppm. A tentative assignment of the spectrum of the free-ends hexamer **7e** is given in Figure 1, where the four protons of the terminal thiophene units give doublets with characteristic $^3J_{AB}$ and $^4J_{AB}$ values (about 5.5 and 1.3 Hz respectively). The other protons belonging to the internal thiophene units give singlets at 6.93 and 6.96 ppm. For the chlorinated oligomers **6a**−**e**, the H3 proton of the chlorine-substituted ring gave a characteristic singlet at 6.78−6.83 ppm.

The UV−visible data for the oligomers **6a**−**e**, **7a**−**e**, and **8** are summarized in Table 1.

Table 1. UV−Vis Data of Oligothiophene Compounds in Solution in Chloroform

compd	no. of thiophenes	λ_{max} (nm)	ϵ_{max}, $\times 10^{-4}$ (M^{-1} cm^{-1})
4	1	240	0.65
6a	2	308	0.96
7a	2	302	0.89
8	2	275	sh
6b	3	344	1.67
7b	3	344	1.61
6c	4	372	2.35
7c	4	372	2.25
6d	5	393	2.93
7d	5	393	3.21
6e	6	405	3.68
7e	6	405	3.81

The general trend is that, in a homogeneous series, the energy of the absorption maximum of the $\pi-\pi^*$ transition continuously decreases with increasing chain length and that at the same time the probability of the transition increases linearly with the number of thiophene rings, n. This is exemplified by the spectra of chlorinated oligomers **6a**−**e** in Figure 2. However, according to previous work of Arbizzani et al.,[20] a large difference of λ_{max} between dimers **6a** and **8** was recorded, which demonstrates that HH junctions have a dramatic effect on the electronic coupling of neighboring rings.

As previously theoretically described for linear polyenes[21] and experimentally observed for thiophene oli-

(20) Arbizzani, C.; Barbarella, G.; Bongini, A.; Mastragostino, M.; Zambianchi, M. *Synth. Met.* **1992**, *52*, 329.

(21) See, for examples: (a) Yarkony, D. R.; Silbey, R. *Chem. Phys.* **1977**, *20*, 183. (b) Wenz, G.; Müller, M. A.; Schmidt, M.; Wegner, G. *Macromolecules* **1984**, *17*, 837. (c) Horowitz, G.; Yassar, A.; von Bardeleben, H. J.; *Synth. Met.* **1994**, *62*, 245.

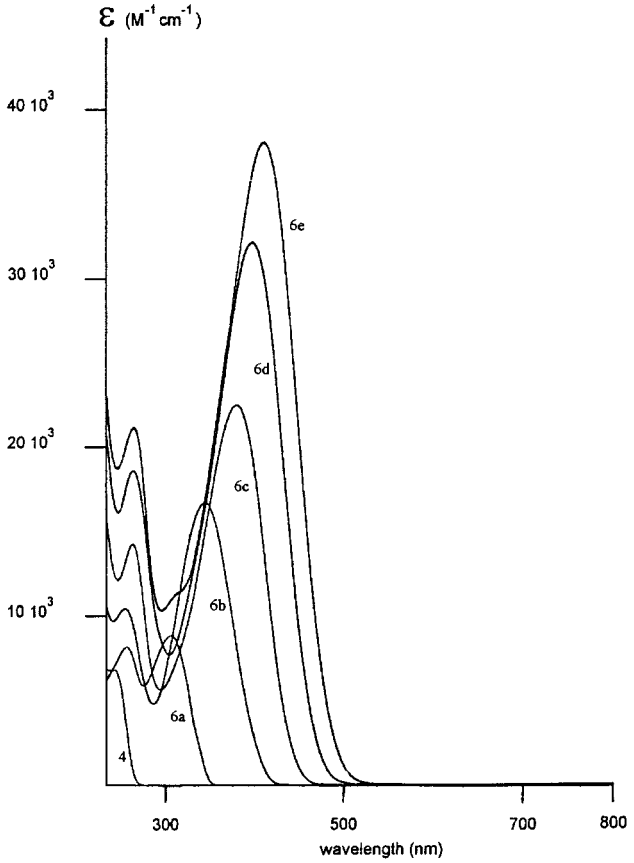


Figure 2. UV−vis spectra of chlorinated oligo(3-octylthiophenes) in solution in chloroform.

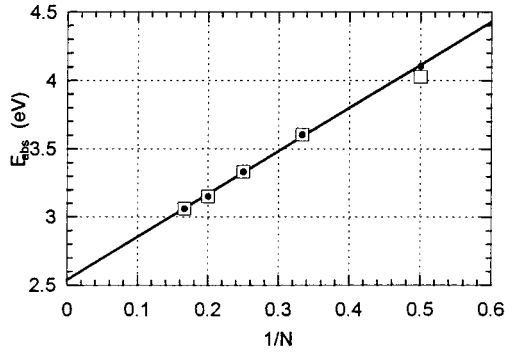


Figure 3. Dependence of the absorption energies E_{abs} of oligothiophenes **6a**−**e** (□), **7a**−**e** (●) on the reciprocal of the number of units.

gomers,[22] the absorption energy for regioregular HT coupled oligo(3-octylthiophenes) depends linearly on the reciprocal of the number of thiophene rings (Figure 3). Experimental data were fitted by eq 1. Compared to

$$E_{(eV)} = 2.54 + 3.15/n \quad (1)$$

$$E_{(eV)} = 2.26 + 3.73/n \quad (2)$$

the data previously obtained for thiophene oligomers[22] (fitted by eq 2[5]), our results (higher value of $E_{(1/n=0)}$ and lower value of the slope) suggest that regioregular oligo(3-octylthiophenes) adopt a less planar mean conformation in solution, which decreases the effective conjugation length.

From our data, extrapolation to $1/n = 0$ (infinite length) leads to an absorption energy of 2.54 eV, corresponding to $\lambda_{max} = 488$ nm. Such a low value of E_{abs} has never been reported for a poly(3-octylthiophene) in solution in chloroform, even in cases where very high values of regioregularity were attained.[2,3] In these examples, the difference between the extrapolated and experimental values of E_{abs} may not be due to structural defects but probably originates in intrinsic properties of this class of molecules. The influence of the length of the conjugated backbone on its structure has to be considered with particular attention and more precisely the energetic cost of an interruption of conjugation, which diminishes when the number of double bonds is increased.[23] As a consequence of this, on one hand, short oligomers behave as rigid rods in which the molecular disorder affecting the conjugated skeleton (inter-ring twisting angles, for example) is limited. This structural information determines the extent of π conjugation and then the slope of $E_{abs} = f(1/n)$. On the other hand, in longer molecules, kinks delimiting rigid segments, structurally analogous to short oligomers, can be introduced, and conjugated polymers can be simply described as semirigid chains (Kratky and Porod model), where the persistence length (lp) is the statistical length of the successive rigid segments.[24] This provides a possible explanation to the abnormally high value of E_{abs} experimentally measured for regioregular poly(3-octylthiophenes) and to the discrepancy toward linearity reported for longer oligomers ($n > 8$).[12] Moreover, if the kinks totally interrupt the conjugation between adjacent rigid segments, the polymer will be spectroscopically equivalent to oligomers of length lp, and the simple measure of E_{abs} for a polymer will allow us to determine its length of persistence, usually attained by neutron scattering techniques. As an example, the E_{abs} value of regioregular poly(3-octylthiophenes) in solution in chloroform was determined by McCullough[2] and Rieke[3] to be 2.78 and 2.75 eV, respectively. On the basis of our data, the length of persistence can be estimated to 13 and 15 thiophene units, respectively. These values, consistent with those measured by neutron scattering by Aimé et al. for a poly(3-butylthiophene) in nitrobenzene at 65 °C (14 units),[25] confirm that the poly(alkylthiophenes) are fairly flexible molecules in solution.

In summary, the preparation of soluble regioregularly coupled 3-octylthiophene oligomers has been described. By analysis of their UV−visible properties, information concerning the structure of the analogous polymeric system has been accessed in a very convenient way, demonstrating the usefulness of these compounds as models for the corresponding polymers. Moreover, these soluble compounds may find interest in electronics and photonics and can also be used as conjugated and electroactive spacers in supramolecular assemblies.

(22) Zhao, M.-T.; Singh, B. P.; Prasad, P. N. *J. Chem. Phys.* **1988**, *89*, 5535.

(23) Surjàn, P. R.; Kuzmany, H. *Phys. Rev. B* **1986**, *33*, 2615.

(24) For a description of structural properties of conjugated polymers, see: Brédas, J. L., Silbey, R., Eds. *Conjugated Polymers*; Kluwer Academic Publishers: Dordrecht, The Netherlands 1991; pp 229−314.

(25) Aimé, J. P. Bargain, F.; Schott, M.; Eckhardt, H.; Miller, G. G.; Elsenbaumer, R. L. *Phys. Rev. Lett.* **1989**, *62*, 55.

Experimental Section

General Procedures. All operations were carried out under a dry oxygen-free argon atmosphere unless otherwise specified. Proton NMR spectra were recorded at 200 MHz on a Brücker AM-200 spectrometer, using solvents as internal references. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. UV−vis spectra were recorded on a Perkin-Elmer Lambda 9 spectrometer. Capillary GC analyses were obtained using a Varian Vista 6000 gas chromatograph equipped with a Chrompack capillary column (CPsil5CB, 25 m × 0.32 mm, df = 0.11 μm) and a flame ionization detector. HPLC experiments were conducted on a Waters Delta Prep 4000 chromatograph equipped with an absorbance detector tuned at 254 nm. Analyses were performed using 2 cartridges (Delta-Pak C18, 15 μm, 15 Å, 8 × 100 mm or Nova-Pak C18, 6 μm, 60 Å, 8 × 100 mm). Preparative runs were performed using 3 PrepPak cartridges (Delta-Pak C18, 15 μm, 100 Å, 40 × 100 mm). GC-MS experiments were conducted on a Hewlett-Packard 5972 mass detector. Fast atom bombardment (FAB) mass spectra and accurate-mass spectra were determined on a VG Analytical ZAB-SEQ mass spectrometer. Elemental analyses were carried out by the Service Central d'Analyses, CNRS, B.P. 22, 69390 Vernaison, France. For liquid samples, the slightly higher experimental value found for chloride was matched by introducing a small amount of chloroform, which was a solvent used in the chromatographic purifications and was difficult to totally remove from our viscous samples. Chemicals were purchased from Aldrich and used without purification, except 3-octylthiophene which was purchased from LCSO/ESCIL, Université LYON 1, F-69622 Villeurbanne Cedex. Dry tetrahydrofuran (THF) was distilled under argon from sodium benzophenone ketyl.

2-Bromo-3-octylthiophene (2). Solid NBS (27.2 g, 153 mmol) was added in small portions to a solution of 3-octylthiophene (**1**) (30.0 g, 153 mmol) in 200 mL of a chloroform/acetic acid mixture (1/1).The reaction, monitored by GC, was pursued for 30 min, and an additional amount of NBS (0.85 g, 5 mmol) was added to consume the undesired isomer. After being stirred for 1 h, the reaction mixture was poured into 200 mL of water. The organic layer was separated, and thoroughly washed with water, aqueous sodium bicarbonate, aqueous sodium thiosulfate, and again with water. After the solution was dried over sodium sulfate, the solvent was evaporated, yielding an orange liquid, which was distilled under reduced pressure to give 27.4 g (65%) of a colorless liquid, bp = 95−96 °C/0.2 mmHg, purity (GC) > 99%.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.18 (d, J = 5.6 Hz, 1H), 6.79 (d, J = 5.6 Hz, 1H), 2.56 (m, 2H),1.57 (m, 2H), 1.27 (bs, 10H), 0.88 (m, 3H).

[1′,3′-(2′,2′-Dimethylpropylene)]-3-octyl-2-thienylboronate (3). To magnesium (1.34 g, 55 mmol) in anhydrous THF (50 mL) heated to maintain a mild reflux was added dropwise **2** (10.00 g, 36.3 mmol). At the end of the addition, the reaction mixture was refluxed for 1 h and then transferred via cannula to a solution of trimethylborate (16.0 mL, 143 mmol) in THF (50 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 30 min before being poured into hydrochloric acid (10 %, 50 mL). The aqueous layer was extracted with diethyl ether. The combined organic extracts were successively dried over sodium sulfate and molecular sieves in the presence of 2,2-dimethyl-1,3-propanediol (3.78 g, 36.3 mmol). The solvent was removed by rotary evaporation to provide 10.86 g of a slightly yellow liquid contaminated by white crystals. This crude product was dissolved in hexanes, filtered on Celite, and heated for 1 day at 100 °C under vacuum to produce 8.32 g (74%) of the title product as a thick slightly yellow liquid, purity (GC) > 99%.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.42 (d, J = 4.7 Hz, 1H), 6.99 (d, J = 4.7 Hz, 1H), 3.75 (s, 4H), 2.86 (m, 2H), 1.55 (m, 2H), 1.27 (bs, 10H), 1.02 (s, 6H), 0.88 (m, 3H).

2-Chloro-3-octylthiophene (4). A mixture of 3-octylthiophene (**1**) (25.0 g, 127 mmol) and sulfuryl chloride (10.4 mL, 130 mmol) was stirred overnight at room temperature. The reaction was monitored by GC, and an additional amount of sulfuryl chloride (1.0 mL, 12 mmol) was added to ensure disappearance of the undesired isomer. At completion of the reaction, the green reactant mixture was poured onto water and extracted with diethyl ether. The organic layer was carefully washed with water, aqueous sodium hydrogenocarbonate, and again with water. After the solution was dried over sodium sulfate, the solvent was removed under vacuum, yielding a slightly orange liquid, which was distilled under reduced pressure to produce 19.0 g (65%) of a colorless liquid, bp = 72−73 °C/0.1 mmHg, purity (GC) = 98.5%.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.02 (d, J = 5.6 Hz, 1H), 6.79 (d, J = 5.6 Hz, 1H), 2.57 (m, 2H), 1.57 (m, 2H), 1.28 (bs, 10H), 0.88 (m, 3H). FAB/MS (NBA) m/z = 231.0; calcd for $C_{12}H_{19}SCl$: 231.1.

General Procedure for Iodination Reactions. To a solution of the appropriate chlorinated compound (1 equiv) in a mixture chloroform:acetic acid (1:1) was added mercuric acetate (0.6 equiv). After 10 min of stirring at room temperature, powdered iodine (1 equiv) was added by small portions over a period of 20 min, and stirring was continued for 2 h. The red precipitate was filtered off, and the filtrate was poured onto water before being extracted with pentane. The combined extracts were washed successively with water, saturated aqueous sodium hydrogenocarbonate, and aqueous sodium thiosulfate and dried over sodium sulfate. The solvent was removed by rotary evaporation to provide virtually pure iodinated compounds which were used without purification.

2-Chloro-3-octyl-5-iodothiophene (5a). From **4** (5.00 g, 21.7 mmol), 7.50 g (97%) of the title product were obtained.

^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.97 (s, 1H), 2.52 (m, 2H), 1.53 (m, 2H), 1.27 (bs, 10H), 0.88 (m, 3H). FAB/MS (NBA) m/z = 357.0 (M + 1); calcd for $C_{12}H_{19}SClI$: 357.0.

5-Iodo-3,4′-dioctyl-5′-chloro-2,2′-bithiophene (5b). Iodination of **6a** (1.36 g, 3.20 mmol) following the general procedure provided 1.726 g (98%) of **5b**.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.11 (s, 1H), 7.04 (s, 1H), 2.64 (m, 2H), 2.55 (m, 2H), 1.55 (m, 4H), 1.27 (bs, 20H), 0.88 (m, 6H). FAB/MS (NBA) m/z = 549.9 (M); calcd for $C_{24}H_{36}ClIS_2$: 550.1.

5-Iodo-3,4′,4″-trioctyl-5″-chloro-2,2′:5′,2″-terthiophene (5c). Iodination of **6b** (1.29 g, 2.08 mmol) following the general procedure provided 1.49 g (96%) of **5c**.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.06 (s, 1H), 6.85 (s, 1H), 6.80 (s, 1H), 2.68 (m, 4H), 2.56 (m, 2H), 1.59 (m, 6H), 1.27 (bs, 30H), 0.87 (m, 9H). FAB/MS (NBA) m/z = 744.3 (M); calcd for $C_{36}H_{54}ClIS_3$: 744.2.

5-Iodo-3,4′,4″,4‴-tetraoctyl-5‴-chloro-2,2′:5′,2″:5″,2‴-quaterthiophene (5d). Iodination of **6c** (1.26 g, 1.55 mmol) following the general procedure provided 1.42 g (98%) of **5d**.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.06 (s, 1H), 6.92 (s, 1H), 6.87 (s, 1H), 6.81 (s, 1H), 2.70 (m, 6H), 2.57 (m, 2H), 1.58 (m, 8H), 1.27 (bs, 40H), 0.87 (m, 12H).

5-Iodo-3,4′,4″,4‴,4⁗-pentaoctyl-5⁗-chloro-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (5e). Iodination of **6d** (0.51 g, 0.51 mmol), following the general procedure provided 0.52 g (91%) of **5e**.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.06 (s, 1H), 6.94 (s, 1H), 6.94 (s, 1H), 6.87 (s, 1H), 6.82 (s, 1H), 2.73 (m, 8H), 2.57 (m, 2H), 1.65 (m, 10H), 1.28 (bs, 50H), 0.88 (m, 15H).

General Procedure for the Coupling Reactions. A solution of the appropriate iodinated precursor (**5a**−**e**) (1 equiv) in 1,2-dimethoxyethane (5−7 mL/mmol of iodinated compound) was carefully degassed, and tetrakis(triphenylphosphine)palladium(0) (0.03 equiv) was added. After the mixture was stirred for 10 min at room temperature, the boronate **3** (1.1−1.2 equiv) and a molar aqueous solution of sodium hydrogenocarbonate (3 equiv) were successively added. The reaction mixture was then refluxed under vigorous stirring until complete consumption of the iodinated species (4 h were generally required) before being poured into water. The organic phase was separated, and the aqueous phase was extracted ether. The combined extracts were washed with water, with brine, and dried over sodium sulfate. The solvent was removed by rotary evaporation, and the residue was heated overnight at 100 °C under vacuum. The crude product

was then purified by gravity chromatography, using silicagel 60 and hexane as eluent, or by semipreparative HPLC on reverse phase, using chloroform:acetonitrile mixtures as eluents.

3,4′-Dioctyl-5′-chloro-2,2′-bithiophene (6a). Following the general procedure, 3.00 g of **5a** (8.4 mmol) were reacted with **3** (3.05 g, 9.9 mmol) to produce 2.85 g (80%) of **6a** as a slightly yellow liquid, purity (GC) > 99%.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.16 (d, J = 5.2 Hz, 1H), 6.91 (d, J = 5.2 Hz, 1H), 6.78 (s, 1H), 2.70 (m, 2H), 2.57 (m, 2H), 1.61 (m, 4H), 1.28 (bs, 20H), 0.88 (m, 6H). HRMS Calcd for $C_{24}H_{37}ClS_2$: 424.2025. Found: 424.2049. Anal. Calcd for $C_{24}H_{37}ClS_2$, 0.011 $CHCl_3$: C, 67.63; H, 8.75; Cl, 8.59. Found: C, 67.49; H, 8.72; Cl, 8.59.

3,4′,4″-Trioctyl-5″-chloro-2,2′:5′,2″-terthiophene (6b). Following the general procedure, 1.73 g (3.14 mmol) of **5b** were reacted with **3** (1.06 g, 3.45 mmol) to produce 1.55 g (80%) of **6b**, as a thick yellow liquid, purity (HPLC) > 99%.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.16 (d, J = 5.3 Hz, 1H), 6.92 (m, 2H), 6.81 (s, 1H), 2.73 (m, 4H), 2.57 (m, 2H), 1.62 (m, 6H), 1.28 (bs, 30H), 0.88 (m, 9H). GC analysis (iso 300 °C): purity = 99.9%. HRMS Calcd for $C_{36}H_{55}ClS_3$: 618.3155. Found: 618.3211. Anal. Calcd for $C_{36}H_{55}ClS_3$, 0.041 $CHCl_3$: C, 69.33; H, 8.89; Cl, 6.38. Found: C, 69.27; H, 8.91; Cl, 6.38.

3,4′,4″,4‴-Tetraoctyl-5‴-chloro-2,2′:5′,2″:5″,2‴-quaterthiophene (6c). Following the general procedure, 1.49 g (2.01 mmol) of **5c** were reacted with **3** (0.68 g, 2.21 mmol) to produce 1.26 g (77%) of **6c**, as a yellow viscous liquid, purity (HPLC) > 99%.

^{1}H NMR (CD_2Cl_2, 200 MHz): δ 7.16 (d, J = 5.2 Hz, 1H), 6.93 (m, 3H), 6.83 (s, 1H), 2.72 (m, 6H), 2.56 (m, 2H), 1.63 (m, 8H), 1.26 (bs, 40H), 0.85 (m, 12H). HRMS Calcd for $C_{48}H_{73}ClS_4$: 812.4284. Found: 812.4537. Anal. Calcd for $C_{48}H_{73}ClS_4$, 0.020 $CHCl_3$: C, 70.67; H, 9.02; Cl, 4.60. Found: C, 70.74; H, 9.08; Cl, 4.60.

3,4′,4″,4‴,4⁗-Pentaoctyl-5⁗-chloro-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (6d). Following the general procedure, 1.42 g (1.51 mmol) of **5d** were reacted with **3** (0.56 g, 1.82 mmol) to produce 1.22 g (80%) of **6d** as orange wax-like solid, purity (HPLC) = 98.3%.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.16 (d, J = 5.2 Hz, 1H), 6.93 (m, 4H), 6.82 (s, 1H), 2.74 (m, 8H), 2.57 (m, 2H), 1.65 (m, 10H), 1.28 (bs, 50H), 0.87 (m, 15H). HRMS Calcd for $C_{60}H_{91}ClS_5$: 1006.5413. Found: 1006.5474. Anal. Calcd for $C_{60}H_{91}ClS_5$: C, 71.48; H, 9.10; Cl, 3.52. Found: C, 70.96; H, 9.16; Cl, 3.48.

3,4′,4″,4‴,4⁗,4⁗′-Sexioctyl-5⁗′-chloro-2,2′:5′,2″:5″-2‴:5‴-2⁗:5⁗-2⁗′-sexithiophene (6e). Following the general procedure, 0.52 g (0.46 mmol) of **5e** were reacted with **3** (0.17 g, 0.55 mmol) to produce 0.48 g (88%) of **6e** as a reddish powder, purity (HPLC) = 99%.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.16 (d, J = 5.2 Hz, 1H), 6.93 (m, 5H), 6.82 (s, 1H), 2.74 (m, 10H), 2.57 (m, 2H), 1.61 (m, 12H), 1.28 (bs, 60H), 0.87 (m, 18H). FAB/MS (NBA) m/z = 1200.6 (M); calcd for $C_{72}H_{109}ClS_6$: 1200.6. Anal. Calcd for $C_{72}H_{109}ClS_6$: C, 71.92; H, 9.14; Cl, 2.95. Found: C, 71.90; H, 9.19; Cl, 2.95.

General Procedure for the Dechlorination Reactions. A mixture containing the chlorinated oligomer (0.15−0.30 mmol), excess tributyltin hydride, and 5 mg of AIBN in 2 mL of anhydrous THF was refluxed overnight before being poured onto water. The aqueous phase was extracted with hexane, and the organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by semipreparative HPLC on reverse phase, using chloroform:acetonitrile mixtures as eluents.

3,4′-Dioctyl-2,2′-bithiophene (7a). Following the general procedure, **6a** (0.115 g, 0.27 mmol) reacted with tributyltin hydride (100 μL, 0.37 mmol) and AIBN to produce 0.080 g (76%) of **7a**.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.14 (d, J = 5.1 Hz, 1H), 6.90-(m, 3H), 2.72 (m, 2H), 2.58 (m, 2H), 1.61 (m, 4H), 1.26 (bs, 20H), 0.85 (m, 6H). HRMS Calcd for $C_{24}H_{38}S_2$: 390.2415. Found: 390.2423.

3,4′,4″-Trioctyl-2,2′:5′,2″-terthiophene (7b). Following the general procedure, **6b** (0.150 g, 0.24 mmol) reacted with tributyltin hydride (200 μL, 0.74 mmol) and AIBN to produce 0.102 g (72%) of **7b**, as a yellow viscous liquid.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.16 (d, J = 5.2 Hz, 1H), 6.91-(m, 4H), 2.73 (m, 4H), 2.58 (m, 2H), 1.61 (m, 6H), 1.27 (bs, 30H), 0.87 (m, 9H).

3,4′,4″,4‴-Tetraoctyl-2,2′:5′,2″:5″,2‴-quaterthiophene (7c). General Procedure. Following the general procedure, **6c** (0.26 g, 0.32 mmol) reacted with tributyltin hydride (351 μL, 1.32 mmol) and AIBN to produce 0.18 g (70%) of **7c**.

Hydrogenolysis. A mixture containing 2.50 g (3.07 mmol) of **6c**, 0.66 g of 10% Pd/C (0.62 mmol of Pd), and 1.0 mL (7.2 mmol) of triethylamine was refluxed under hydrogen atmosphere for 2 days. The catalyst was filtered off and washed with ether. The combined filtrates were successively washed with dilute hydrochloric acid, water, and brine and dried over sodium sulfate. The solvent was removed by rotary evaporation and the residue was purified by gravity chromatography to give 2.00 g (84%) of the title product as a greenish orange wax-like solid, purity (HPLC) > 99%.

^{1}H NMR (CD_2Cl_2, 200 MHz): δ 7.16 (d, J = 5.2 Hz, 1H), 6.95 (m, 5H), 2.74 (m, 6H), 2.60 (m, 2H), 1.59 (m, 8H), 1.26 (bs, 40H), 0.85 (m, 12H). HRMS Calcd for $C_{48}H_{74}ClS_4$: 778.4675. Found: 778.4693. Anal. Calcd for $C_{48}H_{74}S_4$: C, 73.97; H, 9.57. Found: C,73.98; H, 9.57.

3,4′,4″,4‴,4⁗-Pentaoctyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (7d). Following the general procedure, **6d** (0.15 g, 0.15 mmol) reacted with tributyltin hydride (200 μL, 0.74 mmol) and AIBN to produce 0.102 g (70%) of **7d** as an orange powder, purity (HPLC) = 98.5%.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.16 (d, J = 5.4 Hz, 1H), 6.93 (m, 6H), 2.76 (m, 8H), 2.61 (m, 2H), 1.65 (m, 10H), 1.28 (bs, 50H), 0.87 (m, 15H). HRMS Calcd for $C_{60}H_{92}S_5$: 972.5803. Found: 972.5992.

3,4′,4″,4‴,4⁗,4⁗′-Sexioctyl-2,2′:5′,2″:5″-2‴:5‴-2⁗:5⁗-2⁗′-sexithiophene (7e). Following the general procedure, **6e** (0.18 g, 0.15 mmol) reacted with tributyltin hydride (200 μL, 0.74 mmol) and AIBN to produce 0.121 g (70%) of **7e** as a reddish powder, purity (HPLC) = 99%.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.16 (d, J = 5.1 Hz, 1H), 6.94 (m, 7H), 2.77 (m, 10H), 2.61 (m, 2H), 1.65 (m, 12H), 1.28 (bs, 60H), 0.87 (m, 18H). FAB/MS (NBA) m/z = 1166.6 (M); calcd for $C_{72}H_{110}S_6$: 1166.7.

Acknowledgment. The authors thank T. Douki (DRFMC/SCIB/LAN, CEA Grenoble) for GC-MS experiments.

CM9706558