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Non-symmetrical oligothiophenes with 'incompatible' substituents

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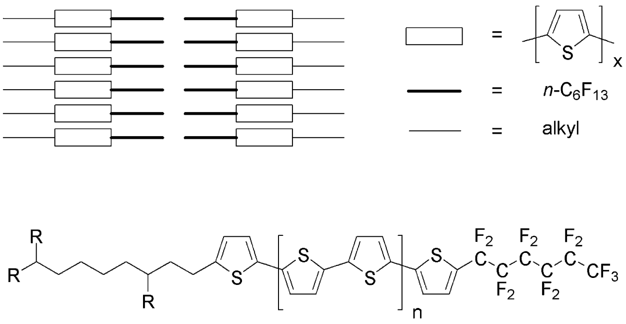
Abstract—The syntheses of oligothiophenes **1** and **2** comprising two different types of peripheral substituents, namely alkyl and perfluoroalkyl, is reported. The key synthetic step is the Pd-catalyzed cross-coupling of perfluoroalkylated bromide **3** with an appropriate boronate. This molecular design is expected to promote unusual two-layer packing, which is of interest for application in electronic devices. Quaterthiophene **1** forms smectic mesophase, though in the narrow temperature range, and is suitable for the fabrication of thin films by solution processing methods.

1. Introduction

Oligothiophenes have been receiving increasing attention in the field of organic electronics due to their interesting semiconducting properties. In particular, α,ω-dialkylthiophenes demonstrate high charge carrier mobility in liquid crystalline mesophases combined with the excellent chemical and electrochemical stability.[1,2] However, all such systems behave as p-type (hole transporting) semiconductors, presumably because of the electron-richness of the thiophene rings.

On the other hand, development of n-type (electron transporting) semiconducting materials would promote new applications such as ambipolar transistors or p–n junction diodes and contribute to a better fundamental understanding of charge transport in organic molecular semiconductors.[3] Recently, the synthesis of a series of α,ω-diperfluorohexyloligothiophene was reported.[4] Notably, α,ω-diperfluorohexylsexithiophene shows n-type semiconductivity in thin film transistors.[3] Apparently, electron transport in this molecule bearing polyfluoroalkyl substituents is facilitated by the stabilization of anion-radicals.



1 n = 1, R = H
2 n = 2, R = Me

Figure 1. Molecular structure of oligothiophenes **1** and **2** (bottom) and their two-layer packing (top).

Here, we report the syntheses and characterization of the non-symmetric quaterthiophene **1** and sexithiophene **2**, comprising three 'incompatible' parts: a rigid aromatic core, a perfluoroalkyl chain and an alkyl chain. Several new features are anticipated from these rod-like molecules depicted in Figure 1: (i) the self-organization into a large variety of lyotropic mesophases as a function of concentration and the nature of solvent (alkanes, perfluoroalkanes, aromatics); (ii) formation of thin films with different morphologies depending on deposition conditions; and (iii) the packing into highly ordered smectic mesophases promoting fast ambipolar charge transport.

2. Results and discussion

The convergent syntheses of oligothiophenes **1** and **2** comprising alkyl and perfluoroalkyl substituents rely on Suzuki–Miyaura coupling[5] as a key step (Schemes 1 and 2). It should be noted here that only few examples of oligothiophenes with different substituents in one molecule are known to date. Thus, Funahashi and Hanna recently reported high charge

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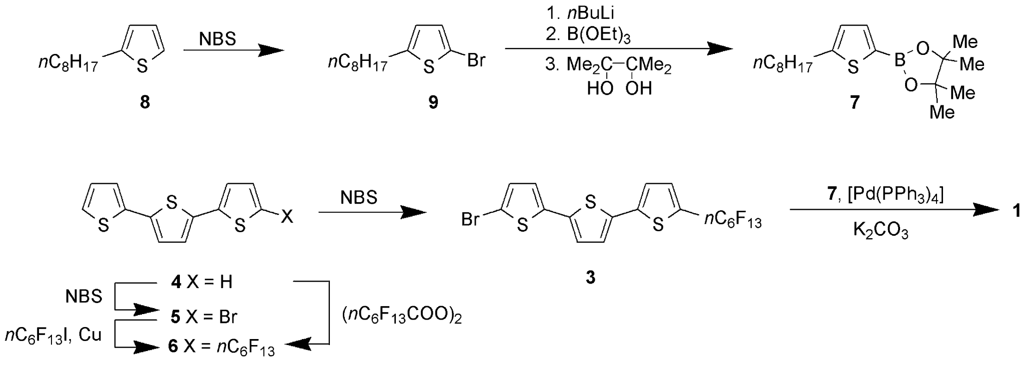


Scheme 1. Synthesis of quaterthiophene **1**.

carrier mobility in smectic phases of α-alkyl-α′-alkynyloligothiophenes, prepared by multi-step synthesis involving sequential Kumada couplings as key steps to assemble the oligothiophene core.[2] Although it appears clear that non-symmetrical oligothiophenes should be easily accessible by the Suzuki coupling of the correspondent building blocks, no successful attempt is mentioned in the literature. In addition, the synthetic approach based on Suzuki coupling is particularly attractive since a great number of arylboronate building blocks is either available commercially or can be easily prepared from commercial precursors.

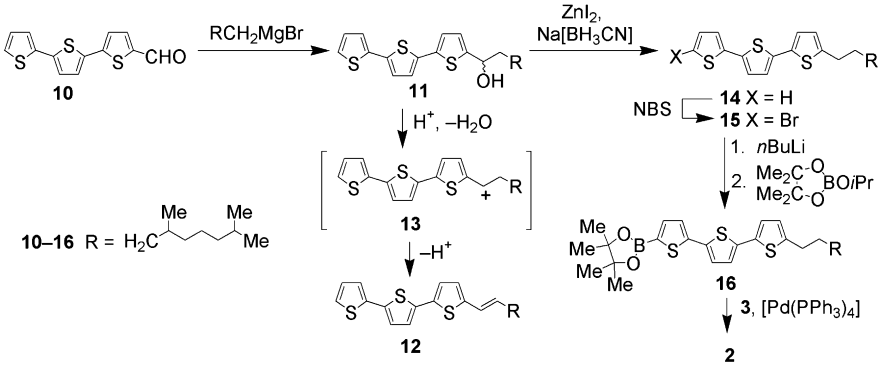
They key intermediate in the syntheses of **1** and **2** is the perfluorohexyl terthiophene **3**. Among known methods of perfluoroalkylation of aromatic molecules, a Cu-promoted cross-coupling between aryl bromides or iodides and perfluoroalkyl iodides in polar solvent (typically DMSO) is frequently used. This method was reported to give satisfactory results for a variety of aromatic substrates[6] including thiophenes and oligothiophenes.[4] The use of the Cu-promoted cross-coupling method requires the synthesis of the intermediate monobromide **5**, which was prepared from the commercial terthiophene (**4**) by slightly modified known methods.[4,7] We have found that the bromination with *N*-bromosuccinimide (NBS) in *N*,*N*-dimethylformamide (DMF) at the ambient temperature gives the best results (69% yield of **5** after crystallization) while reaction in CCl_4 produced considerable amounts of the corresponding dibromide.

The subsequent reaction of bromide **5** with *n*–$C_6F_{13}I$ and copper in DMSO at 125 °C furnished perfluoroalkylterthiophene **6** (Scheme 1). However, we found this reaction to be poorly reproducible: the yield of **6** varied between 14 and 68% while 53% was reported by Facchetti et al.[4] In addition, further unidentified side products were detected (TLC and ^{1}H NMR).

Due to encountered reproducibility problem, we decided to test an alternative synthesis of **6** by the mild radical perfluoroalkylation of terthiophene (**4**) with perfluorohexanoyl peroxide. This method was successfully employed in the synthesis of various perfluoroalkyl thiophenes and furans and demonstrated excellent regioselectivity and high yields.[8] However, its use for the perfluoroalkylation of oligothiophenes was not reported. Perfluorohexyl peroxide was generated in situ from the corresponding acyl chloride and H_2O_2/NaOH in water[9] and its concentration in solution was determined by the iodometric titration.[10] When terthiophene (**4**) was allowed to react with solution of perfluorohexanoyl peroxide at 40 °C, the product **6** with the perfluorohexyl substituent in the α-position of the terminal thiophene ring was isolated. No detectable amounts of regioisomeric side products or products resulting from the multiple substitution of hydrogen atoms by the C_6F_{13} radical were observed. On the other hand, the yield of **6** remained rather moderate (31%). In addition, the polyfluorinated diacyl peroxides are unstable at ambient conditions even in diluted solutions and require quick manipulations at low temperatures.

Finally, perfluorohexyl terthiophene **6** was brominated (NBS and DMF) to give bromide **3** in 68% yield.

Another intermediate in the synthesis of quaterthiophene **1** is boronate **7**. It was synthesized from the bromo thiophene **9**,



Scheme 2. Synthesis of sexithiophene **2**.