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Electrochemistry with alkyl-linked oligothiophenes

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ABSTRACT

Two pairs of β,β′-didodecyl substituted quinquethiophenes linked via a tri- (**3**) and tetramethylene spacer (**4**) at their α-positions have been synthesized and their electrochemical behavior investigated with cyclic voltammetry in solution and in solid films. Both compounds can be charged to a tetracation in two two-electron transfer steps, which are reversible at room temperature but become partially irreversible at low temperatures. Concentration and scan rate dependent measurements support an intramolecular coupling of the oligothiophene units preferentially next to their bridging site with σ-bond formation. In solution no electropolymerization can be observed. In the solid state upon oxidation intermolecular coupling of the oligothiophene segments takes place. Conductance measurements confirm the voltammetric findings. Obviously, the mechanism of conductance is based on hopping processes within mixed valence states.

1. Introduction

In contrast to alkyl substituted thiophenes, electrochemical studies of alkyl linked thiophenes are rare. For the first time, α,ω-bis(thienyl-)alkanes have been used only as pure linkers for polythiophene in order to improve the mechanical properties of this conducting polymer [1,2]. In stress–strain-experiments a behavior similar to vulcanized elastomers has been found and it has been concluded that the polythiophene chains are indeed cross-linked via alkyl groups. Four-probe resistance measurements with dry films, however, have shown decreasing conductivity with increasing cross linking. This has been explained with the argument that cross-linked thiophene chains are prevented from attaining a coplanar configuration which affects conductivity negatively. Further publications about this family of substances mainly describe the synthesis of monomers [3,4], their electropolymerization and the electrochemical properties of the resulting polymers [5,6]. As in all these experiments only simple α,ω-bis(thienyl-)alkanes with the coupling site at the 3-position of the thiophene units have been studied, their reactivity has been very high and electrochemical oxidation of the *monomers* has always resulted in the formation of typical polymers. Recently, a series of dimeric quinquethiophenes linked at the 2-position with a di- to a hexamethylene spacer were synthesized and examined as a π-dimer model of polythiophene [7]. The authors claim that these compounds upon chemical two-electron oxidation in methylene chloride readily form intramolecular π-dimer species, except for the dimethylene-linked dimer that cannot be bent into a π-stacked structure. In a subsequent paper, similar results are described for a cyclophane-type of dimeric quinquethiophenes [8].

In order to get further insights into the reactivity of alkyl linked thiophenes we have studied the electrochemistry of two newly synthesized bis(quinquethienyl-)alkanes. Surprisingly, in solution during anodic oxidation of the monomers intramolecular σ-coupling steps dominate in comparison to intermolecular coupling.

As model compounds oligothiophenes 1,3-bis(4′,3′′′′-didodecyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′-quinquethien-2-yl)propane **3** and 1,4-bis(4′,3′′′′-didodecyl-2,2′:5′,2′′:5′′,2′′′:5′′′’,2′′′′-quinquethien-2-yl) butane **4**, in which two quinquethiophene units were linked either by a propyl or a butyl bridge, were synthesized by nickel-catalyzed coupling of α-bromoquaterthiophene **1** and the Grignard reagent of 1,3-bis(5-bromothien-2-yl) propane **2a** or 1,4-bis(5-bromothien-2-yl) butane **2b**, respectively (Scheme 1) [9]. The oligothiophenes are forced to a certain proximity by the alkyl bridges, which should facilitate inter- and intramolecular bond formation. However, the alkyl groups are also spacers, which length has to be considered. The spacer acts as a barrier for mobile

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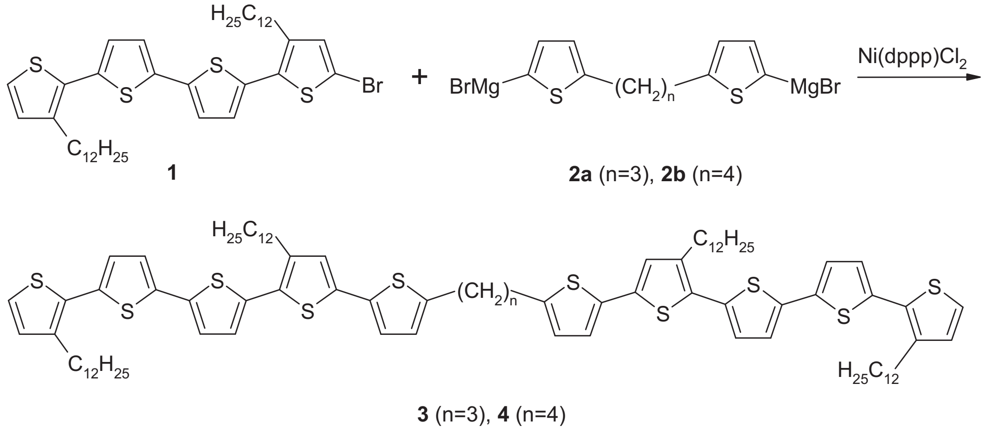

Scheme 1. Synthesis of 1,3-bis(4′,3′′′′-didodecyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′-quinquethien-2-yl)propan **3** and 1,4-bis(4′,3′′′′-didodecyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′-quinquethien-2-yl)butane **4**.

charge carriers and limits the size of the conjugated domain within the chain-like molecule. The longest possible conjugated length in the used model substances **3** and **4** comprises 10 thiophene units. The occurring conductivity has to derive from hopping processes between these conjugated domains, which are forced to a spatial proximity by covalent cross links between different chains.

2. Experimental

2.1. Chemicals

3,3′′′-Didodecyl-2,2′:5′,2′′:5′′,2′′′-quaterthiophene, 1,3-Di(2-thienyl)-propane and 1,4-Di(2-thienyl)-butane were synthesized according to literature [3,4,9]. Acetonitrile was bought from Fisher Scientific in *HPLC/FarUV* quality and used without further purification. The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAPF$_6$) was used as bought from Fluka in *electrochemical grade* quality and stored in an oven at 80 °C. All experiments were carried out under an argon atmosphere.

2.2. Characterization

NMR spectra were recorded on a *Bruker* ACF 250 spectrometer and AC 250, resp. at 25 °C [^{1}H NMR: 250 MHz, ^{13}C NMR: 63 MHz]. (Further details: see Supporting Information) Mass spectra were measured on a *Kratos Kompact* MALDI 3 V4.0.0 (ETH Zürich). UV/VIS spectra were recorded at a *PerkinElmer* Lambda 19 spectrometer. Melting points were determined at an *Electrothermal* Model 9100 and are not corrected.

2.3. Synthesis

2.3.1. General procedure for the synthesis of the bromo-oligothiophenes *1* and *2*

In an inert atmosphere and under exclusion of light a solution of *N*-bromosuccinimide in DMF was added slowly to a solution of the oligothiophene in the same solvent. The mixture was stirred at room temperature for 15 h. Water, twice the volume of DMF in total, was added and the organic layer extracted three times with dichloromethane. The combined organic phases were washed with saturated NaHSO$_4$ and water and dried over MgSO$_4$. After evaporation of the solvent the crude product was purified by column chromatography.

*2.3.1.1. 5-Bromo-3,3′′′-didodecyl-2,2′:5′,2′′:5′′,2′′′-quaterthiophene (**1**).* According to the general bromination procedure starting from 17.0 g (25.5 mmol) 3,3′′′-didodecyl-2,2′:5′,2′′:5′′,2′′′-quaterthiophene dissolved in 1 L DMF at 40 °C and 4.6 g (25.9 mmol) *N*-bromosuccinimide in 50 mL DMF. Purification on a column of silica (32–63 μm) with n-hexane followed by recrystallization from the same solvent yielded a yellow solid in 11.0 g (58%). M.p. 56–57 °C; elemental analysis: $C_{40}H_{57}BrS_4$ (M_w 746.03), calc.(%) C 64.40, H 7.70, S 17.19, found C 64.68, H 7.87, S 17.22.

*2.3.1.2. 1,3-Di(5-brom-2-thienyl)-propane (**2a′**).* According to the general bromination procedure starting from 7.0 g (33.6 mmol) 1,3-di(2-thienyl)-propane in 7 mL and 12.1 g (68 mmol) *N*-bromosuccinimide in 60 mL DMF. The crude product was filtered over silica with n-hexane and afforded 12.0 g (98%) of colourless oil. elemental analysis: $C_{11}H_{10}Br_2S_2$ (M_w 366.13), calc.(%) C 36.09, H 2.75, S 17.51, found C 36.36, H 2.50, S 17.39.

*2.3.1.3. 1,4-Di(5-brom-2-thienyl)-butane (**2b′**).* According to the general bromination procedure starting from 7.0 g (31.5 mmol) 1,4-di(2-thienyl)-butane in 7 mL and 11.4 g (64 mmol) *N*-bromosuccinimide in 60 mL DMF. The crude product was filtered over silica with n-hexane and afforded 11.4 g (95%) of colourless, waxy product. M.p. 28 °C; elemental analysis: $C_{12}H_{12}Br_2S_2$ (M_w 380.15), calc.(%) C 37.91, H 3.18, Br 42.04, S 16.87, found: decomposition.

2.3.2. General procedure for the Ni-catalyzed cross-coupling to the oligothiophenes to *3* and *4*

In a dried apparatus purged with argon the magnesium, α,ω-bis(5-bromo-2-thienyl)alkane and diethyl ether were mixed and the reaction started with 2–5 droplets of 1,2-dibromoethane. After 2 h of ultrasonication a brown oil has formed, which was heated under reflux for further 2 h. The reagent was cooled to room temperature. 10 mg of NidpppCl$_2$ was added followed by a solution of bromoquaterthiophene **1** in ether in one portion under reflux conditions. Reflux conditions were maintained for 6 days while the residual catalyst was added after 3 days. The reaction mixture was hydrolyzed with 2 mL 2N HCl under cooling and extracted with dichloromethane. Combined organic layers were washed with saturated NaHSO$_4$ and water and dried over MgSO$_4$. The residue after evaporation of the solvent was purified by column chromatography on silica with a cyclohexane–dichloromethane gradient. A second chromatography on a preparative HPLC-column filled with nitrophenyl modified silica (5 μm, ID = 20 mm, *L* = 200 mm) and n-hexane-dichloromethane as eluent furnished a pure product, which was recrystallized from n-hexane.