Practical One-step Synthesis of Symmetrical Liquid Crystalline Dialkyloligothiophenes for Molecular Electronic Applications

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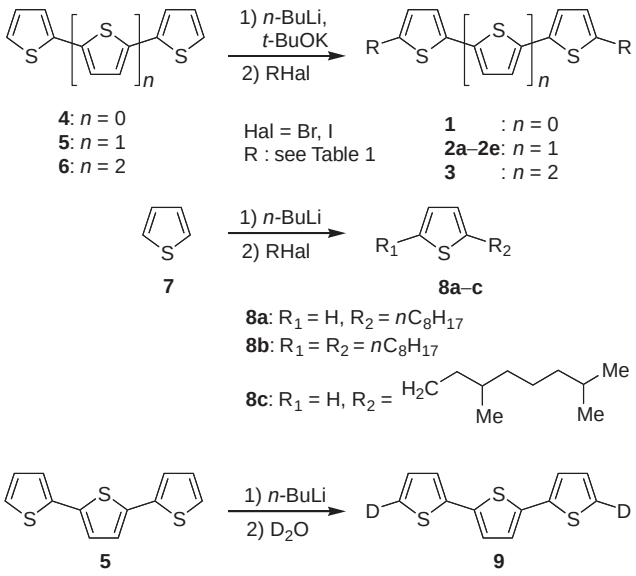
This communication describes extremely simple one-step synthesis of α,α'-dialkyloligothiophenes by the lithiation/alkylation of the corresponding commercially available oligothiophenes. Use of *t*-BuOK to enhance the reactivity of lithiated oligothiophene species towards alkyl halides is crucially important.

Oligothiophenes have received great deal of attention as realistic candidates for application in solution-processable electronic devices such as organic field effect transistors (OFETs).[1] Practical application of polycrystalline materials for OFET is, however, hampered by grain-boundary effects, which dramatically decrease the charge carrier mobility.[2] In contrast, liquid crystals has been recognized as a new type of self-organized organic semiconductor.[3] Indeed, some α,α'-disubstituted terthiophenes and quaterthiophenes demonstrated charge carrier mobility as high as 10^{-1} cm^2 V^{-1} s^{-1} in ordered smectic mesophases.[4] Here, we disclose a very simple synthesis of liquid crystalline α,α'-dialkyloligothiophenes **1**–**3** for OFET application.

Earlier, a four-step synthesis of symmetrical α,α'-dialkyloligothiophenes by repetitive Friedel–Crafts acylation followed by Wolff–Kishner reduction of terthiophene was reported by Byron et al.[5] More recently, Kirchmeyer and co-workers described a large scale synthesis of didecyloligothiophenes via Kumada cross-coupling or Cu-catalyzed oxidative homocoupling.[6] This approach provides fair-to-excellent yields but yet required relatively high number of synthetic steps. Thus, there is still a demand for a practical and simple route to the α,α'-dialkyloligothiophenes **1**–**3**. Commercial availability of bithiophene (**4**), terthiophene (**5**), and quaterthiophene (**6**) prompted us to examine their direct one-step functionalization to give **1**–**3**.

Mono- and bis-alkylation of thiophene via formation of the corresponding lithiated derivatives was described earlier, and reported yields are often moderate.[7] In our hands, lithiation of thiophene (**7**) with *n*-BuLi in THF followed by reaction with 1-bromooctane produced a mixture of 2-octylthiophene (**8a**) and 2,5-dioctylthiophene (**8b**) together with varied amounts of side products (Scheme 1). We also failed to reproduce the previously published procedure[8] for the synthesis of dihexylterthiophene (**2a**) by direct lithiation of **5** followed by alkylation with 1-bromo- or 1-iodohexane. In this case, only unchanged starting material (>85%) was recovered.

We quickly reckon that the crucial issue is a low reactivity of the bis-lithiated terthiophene towards 1-haloalkanes. Indeed, addition of *n*-BuLi to the solution of **5** in THF at −78 °C immediately produced an insoluble precipitate. When the reaction mixture was quenched by the addition of D_2O, the bisdeuterated terthiophene (**9**) was isolated in nearly quantitative yield. All attempts to increase the reactivity of the bis-lithiated intermediate towards 1-haloalkanes by addition of up to 10 equiv. of *N*,*N*,*N*′,*N*′-tetramethylethanediamine (TMEDA) and/or by variation



Scheme 1.

of reaction temperature between −80 and 25 °C remained unsuccessful.

Earlier, it was reported that simple addition of *t*-BuOK considerably enhances the reactivity of various lithiated species, including 2-lithiated derivatives of furan and N-substituted pyrroles, toward alkylating agents such as haloalkanes and epoxides.[9] The observed effect was attributed to formation of organopotassium compound, possibly in an equilibrium with a lithium derivative. The higher reactivity of the former towards alkyl halide may be due to lower aggregation, as organolithium compounds are well known to form associates in solution.[10]

We were pleased to find that reaction of dilithiated terthiophene with 1-haloalkanes also benefits greatly from the addition of *t*-BuOK. After addition of 2.4 equiv. of *n*-BuLi to solution of terthiophene (**5**) in THF at −80 °C, excess of *t*-BuOK was added followed by the alkylating agent.[11] After quenching with water and usual extractive work up, symmetrical α,α'-dialkylterthiophenes **2a**–**2e** were isolated in 80–85% yield (Table 1, Entries 2–6). NMR spectra of crude product indicated only traces of starting material and no monoalkylterthiophenes or other side products. Generally, 1-bromoalkanes gave lower yields than 1-iodoalkanes. After some experimenting, we have found that addition of twofold excess of *t*-BuOK gave the best results. Equimolar amount of *t*-BuOK resulted in incomplete conversion of starting material, while larger excess did not improve the yield of major product any further. After extractive aqueous work-up, products of alkylation were purified by column chromatography or by crystallization from methanol–toluene. Eliminating a need

Table 1. Yields of symmetrical α,α'-dialkyloligothiophenes[11]

Entry	Oligo-thiophene	R (Scheme 1)	Yield/%
1	**1**	n-C_8H_{17}	93
2	**2a**	n-C_6H_{13}	85
3	**2b**	n-C_7H_{15}	80
4	**2c**	n-C_8H_{17}	85
5	**2d**	n-C_9H_{19}	85
6	**2e**	$Me_2CH(CH_2)_3CH(Me)CH_2CH_2$	88
7	**3**	n-C_8H_{17}	82
8	**8c**	$Me_2CH(CH_2)_3CH(Me)CH_2CH_2$	95

for chromatography is particularly beneficial for larger scale synthesis. Thus, synthesis of **2c** from **5** was scaled up to ca. 10 mmoles without notable decrease in yield.

The optimized procedure was also used for the alkylation of thiophene, bithiophene (**4**), and quaterthiophene (**6**) (Table 1). As expected, lower analogs gave almost quantitative yield of alkylated products. When only 1 equiv. of *n*-BuLi was used in reaction with thiophene, 2-alkylthiophenes **8**, valuable intermediates for the synthesis of higher nonsymmetrically substituted oligothiophenes via metal-catalyzed cross-coupling reactions,[12] were prepared in excellent yield (Entry 8).

Table 2. Transition temperatures for oligothiophenes **1**–**3**

Entry	Oligo-thiophene	Transition temperatures[a,b,c]/°C
1	**1**	K 43 I
2	**2a**	K 51 (51) SmG 80 (82) I
3	**2b**	K 52 (52) SmG 79 (78) SmF 84 (83) SmC 90 (89) I
4	**2c**	K 64 (65) SmG 70 (72) SmF 85 (87) SmC 90 (91) I
5	**2d**	K 68 (64) SmF 92 (91) SmC 99 (95) I
6	**2e**	K 37 I
7	**3**	K 82 SmX 158 I

[a]Determined from the onset of the DSC heating curve. [b]K: crystalline phase; SmC: smectic C phase; SmF: smectic F phase; SmG: smectic G phase; SmX: undefined smectic phase; I: isotropic liquid. [c]Previously published values[5] are given in parenthesis for comparison.

Thermotropic properties of terthiophene derivatives with linear alkyl substituents **2a**–**2d** are in good agreement with previously published data (Table 2, Entries 2–5).[5] Branched 3,7-dimethyloctyl substituent remarkably changes organization of terthiophene **2e**, and no liquid crystalline phase was observed (Entry 6). Quaterthiophene **3** forms smectic mesophase in relatively wide temperature range (Entry 7), while bithiophene **1** is not liquid crystalline (Entry 1). More detailed studies on properties and performance of **1**–**3** in organic compositions for electronic devices are in progress.

In conclusion, we have developed an extremely simple one-step synthesis of liquid crystalline α,α'-dialkyloligothiophenes from commercially available materials. Use of *t*-BuOK to enhance the reactivity of bis-lithiated oligothiophene species towards alkylating agents is crucially important.

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11 **Alkylation of terthiophene (general procedure)**: A solution of 2,2′:5′,2″-terthiophene (**5**) (500 mg, 2.12 mmol) in 10 mL of dry THF was cooled to −78 °C, and a solution of *n*-BuLi (ca. 1.6 M in hexane, 6.04 mmol) was added dropwise via cannula. The reaction mixture was stirred for 10 min at −78 °C, then a solution of *t*-BuOK (1.0 M in THF, 8.05 mmol) in THF was added. The stirring was continued for 15 min at −78 °C, then the 1-iodoalkane (4.24 mmol) was added. The reaction mixture was allowed to slowly reach room temperature and stirred overnight, quenched by slow addition of water (10 mL) and extracted with hexane (3 × 10 mL). After evaporation of solvent the residue was purified by column chromatography or crystallized from methanol/toluene to give pure **2a**–**2e**. Supporting Information contains analytical data of synthesized compounds.
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