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Synthesis and characterization of oligo- and crown ether-substituted polythiophenes—a comparative study

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The synthesis of two series of thiophenes substituted with crown and oligoether groups either *via* isolating oxaalkyl chains (**2**, **7–11**) or in direct π-conjugation (**4**, **12–15**) is described. Electrooxidative polymerization leads to the corresponding crown and oligoether-functionalized polythiophenes **P2**, **P7–P11**, and **P4**, **P12**, respectively. Their electrochemical and spectroscopic properties depend on the length of the spacer and the type of the ether unit. The polymers reveal a high mean conjugation. A specific and strong influence of alkali ions on the electrochemical behavior is found for several polymers. The selectivities correspond to the match of the cation size without solvent shell and the inner diameter of the crown ether units. Spectroelectrochemical experiments corroborate that the changes in redox properties are due to a hindered diffusion of the counter anions into the film when the polymer is oxidized. Due to the structural variation novel materials sensitive to different cations are obtained. Importantly, in these conjugated polymers *chemical information* which corresponds to a selective host–guest interaction of the alkali metal cations and the ether units is transduced into the change of an *electrical signal*.

Conducting polymers with various covalently attached functional groups have become more and more prominent in recent years. On the one hand, effective synthetic strategies are now available;[1] on the other hand, it is a challenge to address and influence the electronic properties of the conjugated backbone from the outside *via* specific interactions of covalently attached functional groups with external chemical or physical stimuli.[2] A very promising approach to this goal is to use conducting polymers bearing molecular recognizing groups in which very selective host–guest interactions modulate, switch, and amplify the electron transport properties of the conjugated chains. Very recently, several attempts to realize this concept have been demonstrated. These include various oligooxyethylene-substituted polythiophenes,[3] crown ether-substituted polythiophenes[4] and corresponding model oligothiophenes,[5] and aza-crown ether-substituted polypyrroles.[6] More complicated systems include calix[4]arene-substituted polythiophenes,[7] or metallorotaxane receptor sites attached to thiophene–pyridine copolymers.[8] Due to electrostatic and/or conformational perturbations of the conjugated backbone, in most cases, conductivity, electrochemical and optical responses may be influenced by the complexation of metal ions.

Approaches to exploit the unique but more complex recognizing properties of biomolecules in combination with conducting polymers have recently been described. Di- and tripeptides, known to be specifically recognized and bound by appropriate proteins, have been covalently linked to polypyrrole.[9] Single DNA-nucleobases linked to a polythiophene show that the specific recognition of a complementary base results in the modulation of the electronic properties of the polymeric backbone.[10] Even more intriguing, oligonucleotide-functionalized polypyrroles[11] or polythiophenes[12] respond specifically to complementary oligonucleotide sequences and represent very promising components for amperometric DNA-sensors.[13] The attachment of biotin at a water-soluble polyalkoxythiophene which specifically interacts with the protein avidin results in a color change in solution upon complexation.[14]

Selective host–guest interactions in combination with conducting polymers may be exploited in (iono-)electronic devices in which the complexation/decomplexation process allows an externally induced switching between the ON/OFF states, *i.e.* in field effect transistors.[15] Due to the stronger ion–dipole interactions with metal cations, crown ether-functionalized materials are particularly interesting for these applications, since it could be successfully demonstrated that it is possible to transduce *chemical information* into the change of an *electrical signal*.[3–7] In this respect, by systematic variation, we recently realized the synthesis of different thiophenes (**1–3**) with 12-crown-4-ether linked to the heterocycle *via* a non-conjugated oxaalkyl chain.[4a] Later on we synthesized a second series of thiophenes (**4–6**) in which the crown ether units are in direct π-conjugation (Scheme 1).[4f] Corresponding polythiophenes formed from derivatives of both classes (**P2**, **P4**, where P stands for polymer) showed selective and strong changes in their electrochemical behavior in the presence of alkali metal ions.

On the basis of these results we now present the synthesis of a series of crown ether- and oligo ether-substituted bithiophenes **7–11** which are directly comparable to compounds **1–3** and in which the oligoether or crown ether units are attached to the bithiophene unit *via* an oxaalkyl spacer. Additionally a series of related crown ether- and oligoether-substituted dialkoxythiophenes **12–15** were synthesized which are comparable to thiophenes **4–6** (Scheme 2). Furthermore, the electrochemical polymerization and the electrochemical behaviour of the corresponding polymers in various alkali ion electrolyte solutions are shown. (Monomer) structure–(polymer) property relationships are deduced and clearly show how the steric demand and/or the polarity of the side chain influences the polymerization, the electrochemical, and the spectroscopic properties of the polymer formed. On the basis of our results we discuss the observed alkali metal ion sensitivity and selectivity of the different polymers which support our earlier proposed model of a potential barrier.[4a,f]

Results and discussion

Syntheses of ether-substituted thiophenes 7–15

The synthesis of the bithiophene key building blocks 3-(ω-bromoalkyl)-2,2′-bithiophenes **20** ($n=5$)[4a] and **21** ($n=10$) started from the corresponding 3-(ω-bromoalkyl)thiophenes

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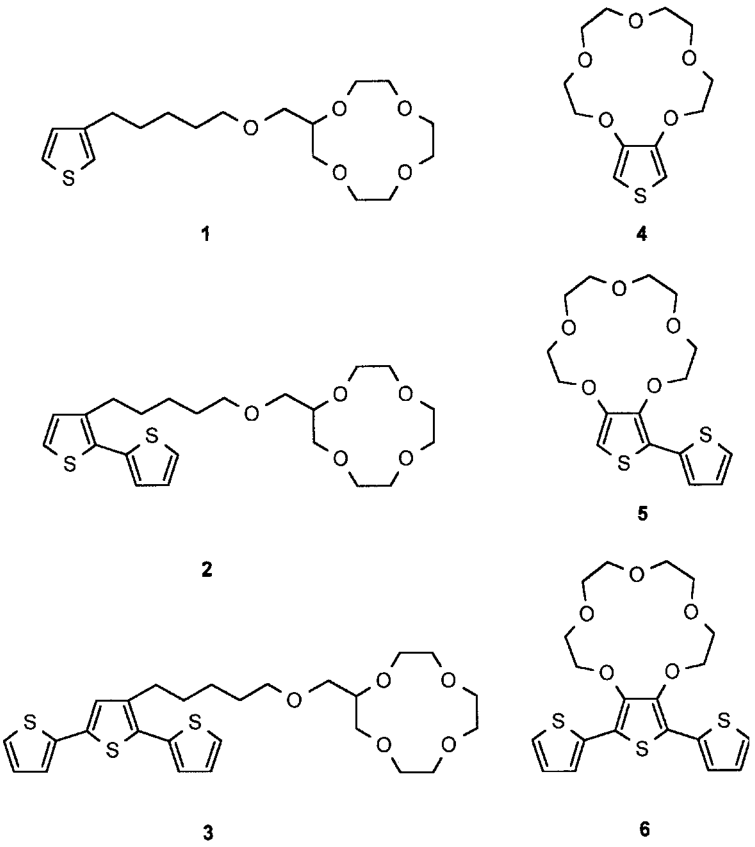
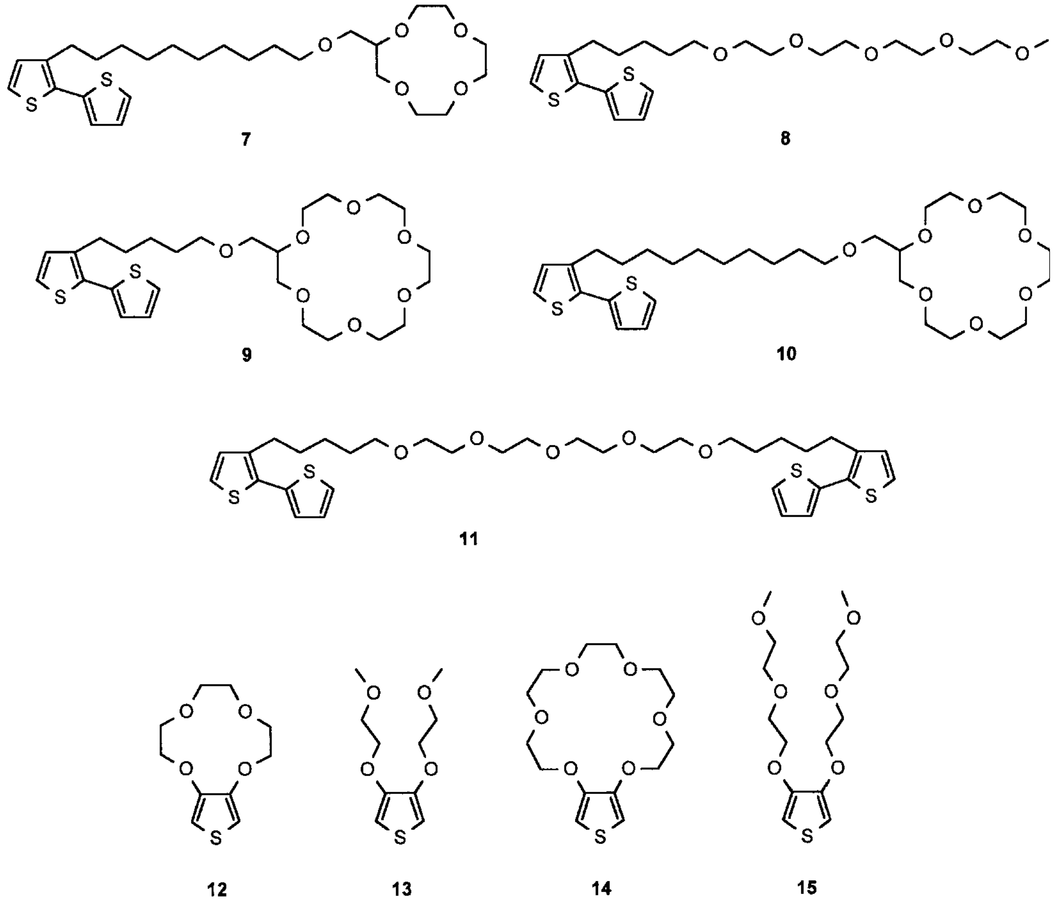


Scheme 1

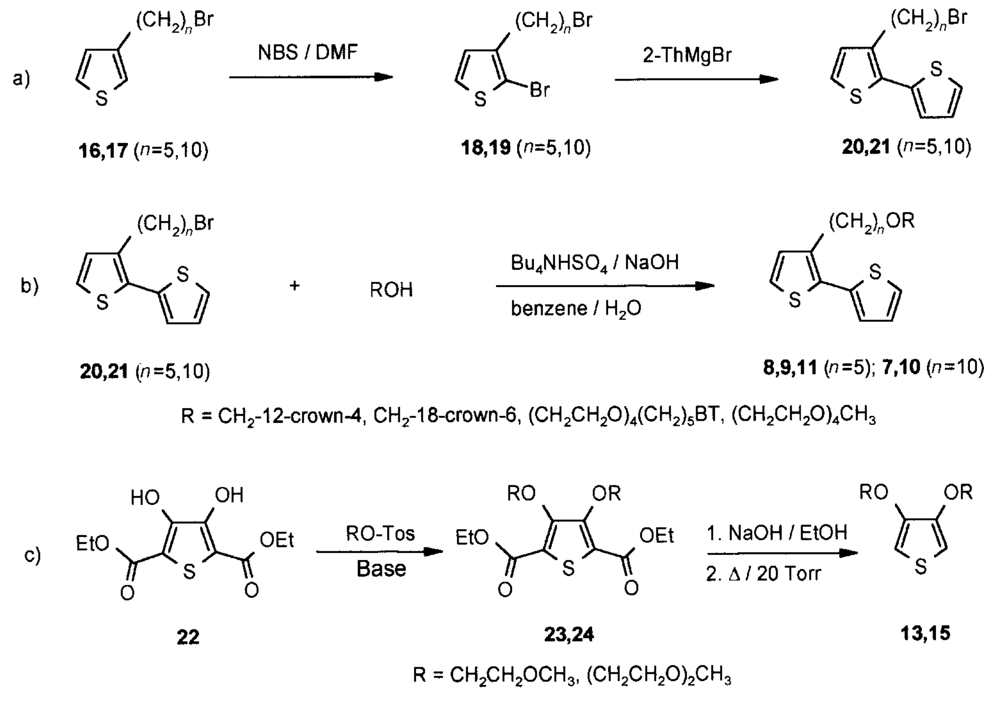


Scheme 2

16 ($n=5$)[16] or **17** ($n=10$)[16] which were selectively brominated in the 2-position with *N*-bromosuccinimide (NBS) in dimethylformamide (DMF)[17] forming the monobromo compounds **18** ($n=5$) and **19** ($n=10$) in 80 and 42% yield, respectively. *Via* nickel-catalyzed cross-coupling of thiophenes **18** and **19** with 2-thienylmagnesium bromide 3-alkyl-2,2′-bithiophenes **20** ($n=5$) and **21** ($n=10$) were obtained analytically pure after repeated distillation in 81 and 32% yield (Scheme 3a). The various novel ether-functionalized bithiophenes **7–11** were synthesized *via* phase-transfer reaction of bithiophenes **20** and **21** with the respective crown ether or oligoether alcohols. Chromatographic work-up of the raw material led in all cases to analytically pure compounds **7–11** as slightly yellow oils in 40–72% yield (Scheme 3b). Synthesis of the crown ether-substituted monothiophenes **4**, **12** and **14** was accomplished following the procedure of Sone *et al.*[18] Thus, 2,5-bis(ethoxycarbonyl)-3,4-dihydroxythiophene **22**,[19] one of the few stable dihydroxythiophenes, was alkylated with the ditosylates of tri-, tetra-, or pentaethylene glycol in dry acetonitrile with potassium fluoride as base in the case of thiophene **12** or cesium fluoride[20] for thiophenes **4** and **14**. The resulting crown ether-substituted bis(ethoxycarbonyl) thiophenes were saponified to the corresponding diacids which subsequently were heated under reduced pressure to eliminate carbon dioxide with formation of the monothiophenes **4**, **12** and **14** (45, 47, and 35% yield). The novel oligoether-substituted thiophenes **13** and **15** were prepared by similar procedures. Reaction of ethylene glycol monomethyl ether monotosylate with 2,5-bis(ethoxycarbonyl)-3,4-dihydroxythiophene **22** in dry DMF with potassium carbonate as base[21] led in 87% yield to the bis(ethoxycarbonyl)thiophene **23** which could be saponified and decarboxylated to the oligoether thiophene **13** in 38% yield. Bis(ethoxycarbonyl)thiophene **24** was prepared by the similar reaction of diethylene glycol monomethyl ether monotosylate and 2,5-bis(ethoxycarbonyl)-3,4-dihydroxythiophene **22** in dry acetonitrile with potassium fluoride as base in 31% yield after distillation. Saponification and decarboxylation led to oligoether thiophene **15** in 18% yield (Scheme 3c). 3-Dodecyl-2,2′-bithiophene **25** was synthesized separately[22] and is used here as an alkyl-substituted reference compound.

Electrochemistry of the crown ether- and oligoether-substituted bithiophenes 7–11

The electrochemical characterization of the bithiophenes **7–11** expectedly revealed an irreversible oxidation wave of the bithiophene unit in the cyclic voltammogram (CV). All peak potentials are essentially the same and are in a range of $E_{\mathrm{pa}}=$ 0.84–0.88 V *vs.* Fc/Fc$^+$ (Table 1). The ether and crown ether moieties are stable and electrochemically inactive in the potential range examined.[23] All electrochemical characterizations and polymerizations were carried out in dry acetonitrile (MeCN) with tetrabutylammonium hexafluorophosphate (TBAHFP) (0.1 M) as supporting electrolyte. All 3-substituted bithiophenes **2**, **7–11** and **25** could be polymerized to the corresponding poly(bithiophenes) **P2**, **P7–P11**, and **P25** by means of a potentiodynamic oxidation. Potentiostatic or galvanostatic polymerizations led to the same quality of films. The conditions employed for the potentiodynamic polymerizations were optimized and are given in Table 2. Although every monomer bears the same electroactive bithiophene unit, it was found in this series that the various functionalized bithiophenes have different tendencies to polymerize. Thus, oligoether **11** bearing two bithiophene units and reference compound **25** showed excellent film forming properties and growth rates. However, the 12-crown-4- and oligoether-substituted derivatives **2**, **7** and **8** polymerized somewhat more slowly and twice as many cycles were necessary to deposit about the same amount of polymer on the working electrode. The quantity of polymer deposited can be estimated from the CV taken in an electrolyte free of monomer by the charge which is reversibly exchanged in the oxidation/reduction cycle. However, there are evidently only small differences between the polymerization ability of bithiophenes **2** and **7** in which the spacer between the conjugated backbone and the crown ether unit is varied ($n=5$, 10) and between compounds **2** and **8** in which the pentamethylene spacer remains identical ($n=5$). Due to much more steric hindrance and in contrast to bithiophenes **2** and **7**, 18-crown-6-substituted bithiophenes **9** and **10** showed only moderate film forming behavior. During the polymerization of these compounds highly colored blueish–greenish oligomeric products were formed which did not



Scheme 3

Table 1 Electrochemical and spectroscopic data of the ether-substituted bithiophenes **2**, **7–11** and **25** and the corresponding polymers **P2**, **P7–P11**, **P25**

(**M**)/(**P**)	E_{pa} (**M**)/V^a	$E_{pa}{}^1$ (**P**)/V^a	$E_{pa}{}^2$ (**P**)/V^a	λ_{max} (**M**)/(**P**)/nm	E_g (**P**)/eV
2/P2	0.85	0.07	0.45	295/538	1.91
7/P7	0.86	0.19	0.48	294/524	1.90
8/P8	0.86	0.11	0.45	295/508	1.98
9/P9	0.88	0.14	0.42	295/477	2.04
10/P10	0.88	0.20	0.48	294/512	1.93
11/P11	0.84	0.10	0.26	295/482	1.98
25/P25	0.85	0.38^b	0.45	295/506	1.97

^{a}MeCN–TBAHFP, 0.1 M, 100 mV s^{-1}, all potentials *vs.* Fc/Fc$^+$. ^{b}Second scan of characterization.

Table 2 Polymerization conditions for the bithiophenes **2**, **7–11** and **25**

(**M**)	Concentration/mol L^{-1}	Potential range/V^a	Number of scans	Charge/µC^b	Polymerization tendency^c
2	$1.4 \cdot 10^{-2}$	−0.36–0.89	20	0.90	+ +
7	$6.1 \cdot 10^{-3}$	−0.36–0.89	10	0.58	+ +
8	$1.3 \cdot 10^{-2}$	−0.36–0.94	40	0.59	+ +
9	$5.5 \cdot 10^{-3}$	−0.36–0.99	80	0.60	+
10	$6.1 \cdot 10^{-3}$	−0.36–0.99	80	1.17	+
11	$1.0 \cdot 10^{-3}$	−0.36–0.89	10	1.04	+ + +
25	$5.1 \cdot 10^{-3}$	−0.36–0.81	10	1.00	+ + +

^{a}MeCN–TBAHFP, 0.1 M, 100 mV s^{-1}, all potentials *vs.* Fc/Fc$^+$. ^{b}Reversibly exchanged charge of the conducting polymer at 100 mV s^{-1} scan speed. This charge corresponds to the amount of electroactive polymer deposited on the working electrode. ^{c}+ + + very good; + + good; + moderate.

adhere to the electrode surface and diffused away into the solution. In the case of the other bithiophenes almost no coloring of the electrolyte was observed. Like bithiophene **2** all new ether-substituted bithiophenes **7–11** and the reference compound **25** form the corresponding polymers **P7–P11** and **P25**. Thus in general, the 3-substituted 2,2′-bithiophene unit allows the use of sterically very demanding side groups and therefore proved to be an ideal monomer for the formation of functionalized conducting polythiophenes which we could also confirm in other examples.[24]

The poly(bithiophenes) **P2**, **P7–P11** and **P25** were characterized electrochemically in an electrolyte free of monomer. The electrochemical properties of the polymers were determined from at least 10 polymer coated electrodes prepared under the same polymerization conditions. The resulting CVs for all polymers are depicted in Fig. 1. It should be pointed out that even under identical polymerization conditions the oxidation potentials of the same polymer can differ in a small potential range (Table 1). The shape of all reversible CVs is typical for polyheterocycles and includes two maxima in the oxidative part and less pronounced broad peaks in the reductive part. For poly(bithiophenes) **P2** and **P8** the first oxidation wave is sharp and well pronounced whereas the second one is very broad. For polymers **P7**, **P9–P11** the opposite behavior is observed. The lowest oxidation potential was obtained for poly(bithiophene) **P2** ($E_{pa}{}^1 = 0.07$ V *vs.* Fc/Fc$^+$) including the short pentamethylene spacer. Gradually increasing peak potentials are found for poly(bithiophenes) **P11** ($E_{pa}{}^1 = 0.10$ V *vs.* Fc/Fc$^+$), **P8** ($E_{pa}{}^1 = 0.11$ V *vs.* Fc/Fc$^+$), and **P9** ($E_{pa}{}^1 = 0.14$ V *vs.* Fc/Fc$^+$). Polymers **P7** ($E_{pa}{}^1 = 0.19$ V *vs.* Fc/Fc$^+$) and **P10** ($E_{pa}{}^1 = 0.20$ V *vs.* Fc/Fc$^+$) which include the longer decamethylene spacer show the most positive peak potentials in this series. Compared to the reference polymer **P25** ($E_{pa}{}^1 = 0.38$ V *vs.* Fc/Fc$^+$) these values are surprisingly low. Possibly a polar side chain including oxygen atoms (**P2**, **7–11**) lowers the oxidation potential due to the higher ionic conductivity of the polyether groups.[25] This allows easier diffusion of the counter ions into the film which are needed for the compensation of the positive charges in the oxidized polymer backbone.

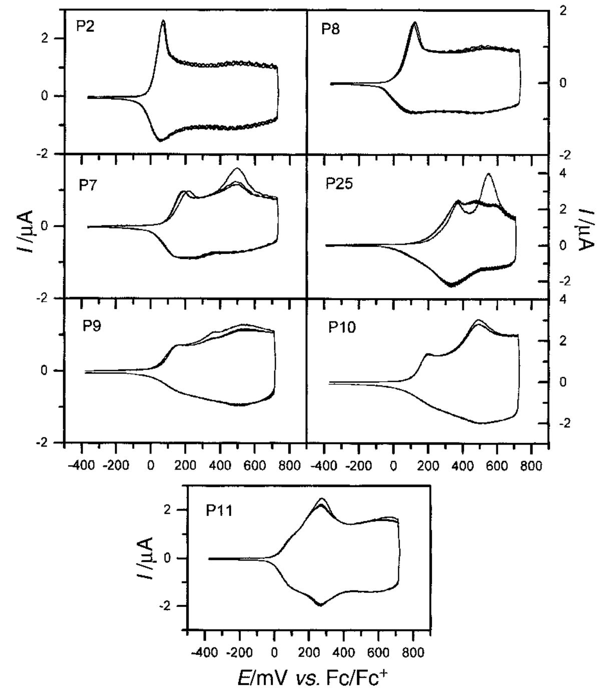


Fig. 1 Cyclic voltammograms of the polymers **P2**, **P7–P11**, and **P25** in MeCN–TBAHFP (0.1 M, 100 mV s^{-1}). The first successive three scans of the characterization are shown.

Spectroscopic characterization of the poly(bithiophenes) P2, P7–P11, and P25

Absorption data are sensitive parameters for structural and conformational effects in conjugated π-systems. Comparison of longest wavelength absorptions of the polymers allows determination of the influence of the side chain on the conformation of the conjugated backbone.[26] The spectroscopic characterization of the poly(bithiophenes) in different oxidation states was performed in a special spectroelectrochemical cell.[27] The monomers were directly polymerized *via* potentiodynamic polymerization onto a polished platinum electrode which afterwards was directly used as the working electrode in the spectroelectrochemical cell. The absorption spectra of the polymers were recorded through a thin layer of electrolyte with the aid of wave guides. By using this technique the polymers for both the electrochemical and the spectroscopic investigations were prepared in the same way and should therefore have the same characteristics. The absorption maximum of 12-crown-4-substituted bithiophenes **P2** (λ_{max} = 538 nm, E = 2.30 eV) is at lowest energy in this series which indicates in accordance with the electrochemical measurements that this polymer has the highest effective conjugation. According to the spectroscopic data of the other polymers under investigation, the degree of conjugation should decrease in the order **P2** > **P7** (λ_{max} = 524 nm) > **P10** (λ_{max} = 512 nm) > **P8** (λ_{max} = 508 nm) > **P25** (λ_{max} = 506 nm) > **P11** (λ_{max} = 482 nm) > **P9** (λ_{max} = 477 nm). In Table 1 additionally band gaps E_g are taken into account which were determined from the absorption spectra and which show the same tendency. Obviously, long and more flexible spacers as included in **P7**, **P10**, **P8**, and **P25** are more favorable for a planarized conjugated backbone than bulky 18-crown-6 units (**P9**) or the bridging of two bithiophene units (**P11**). The steric repulsion of the 18-crown-6 units in poly(bithiophene) **P9** induces conformational changes in the polymer and leads to distorsions of the thiophene rings.

So far only a few examples of 3-substituted poly(2,2′-bithiophenes) are known which were polymerized by electrochemical or chemical methods and cast into films on ITO electrodes from solution. Thus, the dodecyl (λ_{max} = 528 nm[28]) and the octyl derivative (λ_{max} = 525 nm[29]) exhibit absorptions in the same range as our oligoether-substituted polymers. Since the steric demand of the crown ether units is higher than that of an alkyl side chain, nevertheless in our cases functionalized poly(bithiophenes) with high conjugation are obtained. Evidently, low degrees of irregular couplings are included in the polymers which then result in relatively low steric interactions of the side chains.

Influence of alkali metal ions on the electrochemical behavior of poly(bithiophenes) P2, P7–P11, and P25

Complexation of cations in crown ether-substituted conducting polymers leads to strong changes of the electrochemical behaviour.[3–7] Especially in the case of poly(bithiophene) **P2** selective and strong changes in the CV were found upon complexation with alkali metal ions.[4a] The mechanism of how the host–guest-interaction is transformed into the change of the electrochemical signal is not well understood, since the complexing crown ether units in this material are separated by an isolating oxaalkyl chain from the electroactive conjugated backbone. Thus due to the structural variation, the electrochemical characterization of this series of crown ether- and oligoether-substituted poly(bithiophenes) **P2**, **P7–P11**, and reference polymer **P25** in the presence of alkali ions should give more insight into this subtle process. For polybithiophene **P2** we recently found that even very low concentrations ($c \leqslant 1 \times 10^{-4}$ mol L^{-1}) of especially lithium cations affect the electrochemical response of the polymer.[4a] In this investigation, the freshly prepared poly(bithiophenes) **P2**, **P7–P11**, and **P25** were characterized by multisweep CVs in MeCN containing either 0.1 M TBAHFP, $LiClO_4$, $NaClO_4$, or KPF_6. The presence of alkali metal ions in the latter electrolytes led for various polymers to changes in the CV. Besides the shift of the first oxidation peak to more positive potentials, a decrease in electroactivity was observed. By integrating the areas under the redox curves the change in electroactivity can be relatively evaluated. The value obtained for each polymer in the alkali ion-free electrolyte was set to 100%. For each polymer and each electrolyte solution at least five independent measurements were performed and the remaining average electroactivity is given after 50 scans (Table 3).

The experimental error of these data lies in between ±5% and therefore the results represent a general trend. Thus, the electrochemical behaviour of 12-crown-4-substituted poly(bithiophenes) **P2** and **P7** and oligoether-substituted poly(bithiophene) **P8** is strongly influenced in the presence of alkali metal ions. In the case of the other ether-substituted poly(bithiophenes) **P9**, **P10**, **P11**, and expectedly of the reference polymer **P25** only marginal or no changes were observed. The electrochemical behavior of the polymers **P2** and **P7** is most strongly influenced by lithium ions and less by sodium or potassium ions, whereas the electroactivity of the oligoether-substituted polymer **P8** is most changed by sodium ions. In polymer **P7** in which the crown ether unit is separated from the conjugated backbone by the longer decamethylene spacer the electroactivity drops to about one fifth of the original value in the presence of lithium ions. In polymer **P2** containing the shorter spacer 40% of the electroactivity rests. Comparison of the inner diameter of 12-crown-4 (1.2–1.5 Å)[30] with the diameter of lithium ions (1.36 Å in crystals)[30] shows the perfect match of the lithium ion with the cavity of 12-crown-4. Poly(bithiophene) **P8** comprising five oxyethylene units in the spacer is selective for sodium ions and the electroactivity is reduced to 35%. In the presence of lithium or potassium ions in either case the electroactivity is reduced to 58%. However, the selectivity of the non-cyclic oligoether polymer **P8** is expectedly smaller than that of the crown ether polymers **P2** and **P7**. Finally, 18-crown-6-polymer **P9** exhibits a small preference for the complexation of potassium ions, whereas lithium and sodium ions do not alter the electrochemical response of the polymer. Also in this case the size of the potassium ion (2.66 Å)[30] matches with the cavity of the crown ether unit (2.6–3.2 Å).[30] Despite comprising crown or oligoether units poly(bithiophenes) **P10** and **P11** are not sensitive to alkali ions. For each polymer the relative selectivity to either cation can be determined. In this respect, polymer **P7** ($Li^+ : Na^+ : K^+ = 4.5 : 1.0 : 1.5$) shows the highest discrimination and in comparison to the least recognized sodium ions (set to 1.0) lithium ions are better recognized by a factor of 4.5, potassium ions by a factor of 1.5. Thus, in comparison to the previously synthesized polymer **P2** ($Li^+ : Na^+ : K^+ = 2.0 : 1.0 : 1.1$), due to the elongation of the oxaalkyl chain in polymer **P7** a strong enhancement of the selectivity was found (Table 3).

Bithiophene monomers **2**, **8**, and **11** were also polymerized in electrolytes which already contained alkali ions. No difference in the polymerization tendency was found for bithiophenes **2** and **8** in MeCN–$LiClO_4$ (0.1 M). In comparison to the polymers obtained without alkali ions the resulting polymers **P2** and **P8**, however, reveal peak potentials shifted to positive values (ΔE_p = 50–160 mV) and longest wavelength absorptions shifted to higher energies ($\Delta\lambda_{max}$ = 17–30 nm). Further addition of alkali ions to the electrolyte does not lead to further changes of the electronic properties. These values approximately correspond to those which are obtained when the polymers are polymerized in MeCN–TBAHFP and alkali ions are added afterwards. In contrast, in the case of bis-bithiophene oligoether **11** which was polymerized in the presence of Li^+, Na^+, and K^+ polymers **P11** with increased conjugation are obtained. In the CVs peak potentials were found to be more negative (ΔE_p = 20–40 mV) and in optical measurements absorptions were red-shifted ($\Delta\lambda_{max}$ = 22–29 nm). We explain this with a preorganization of the bithiophene units which takes place in the presence of alkali ions. Evidently, due to this template effect polymers with a larger conjugated chain length were formed.

How does the remote host–guest-interaction influence the electronic properties of the conjugated backbone?

The electrochemical investigation of the oligo- and crown ether-functionalized poly(bithiophenes) unequivocally proved

Table 3 Remaining electroactivity (in percent) of poly(bithiophenes) **P2**, **P7–P11**, **P25** in different electrolyte solutions (MeCN–salt, 0.1 M, 100 mV s^{-1})

(**P**)	$LiClO_4$ (%)	$NaClO_4$ (%)	KPF_6 (%)	Influence	Selectivity ($Li^+ : Na^+ : K^+$)[a]
P2	41	83	77	$Li^+ \gg K^+ \geq Na^+$	2.0 : 1.0 : 1.1
P7	22	100[b]	66	$Li^+ \gg K^+ > Na^+$	4.5 : 1.0 : 1.5
P8	58	35	58	$Na^+ > Li^+, K^+$	1.0 : 1.8 : 1.0
P9	100[b]	100[b]	75	$K^+ > Li^+, Na^+$	1.0 : 1.0 : 1.3
P10	90	100	96	—	1.1 : 1.0 : 1.0
P11	100[b]	100[b]	100[b]	—	1.0 : 1.0 : 1.0
P25	100	100	88	—	1.0 : 1.0 : 1.1

[a] The selectivities were calculated by setting the least recognized ion to 1.0. [b] Values were little higher than this of the reference polymer.

that in the case of polymers **P2**, **P7–P9** a host–guest-interaction occurring at a remote molecular recognizing group affects changes in the electronic properties of the conjugated backbone. Thus, in these materials *chemical information* is transformed into the change of an *electrochemical response*. Secondly, depending on the structure of the (crown) ether side chain a selectivity and preference were found for those cations whose sizes match the diameter of the crown ether unit. In the following, we will discuss possible mechanisms. The general trend found in complexation studies of 12-crown-4 derivatives in solution is that sodium and potassium ions are more strongly bound than lithium ions. Usually these measurements are conducted in water or methanol in which the lithium ion has a large solvent shell. This behavior is distinctly different in MeCN in which the solvent shell consists only of nine atoms instead of 21 atoms when water is used as solvent.[3c,e] It was proposed earlier[4a,f] that if the complexation occurs in a polymer matrix, the ions strip off their solvent shell when entering the film and diffusing into the polymer matrix. Thus, in this case only the effective radii of the metal ions are important for complexation. This argument corresponds to the behavior of the ether-functionalized poly(bithiophenes) under investigation, and thus their selectivity might be governed by the match of crown ether radius and solvent-free size of the metal cation. It was also concluded from these experiments, that upon complexation of metal ions in ether units an electrostatic potential barrier in the polymer film is formed. This potential barrier then renders the diffusion of additional counter ions which are necessary for charge compensation to and into the positively charged oxidized polythiophene backbone more difficult. Thus, as the oxidation of the polymer is more and more shifted to positive potentials, the more metal cations are complexed in the film.[4a,f] Another explanation was recently introduced for the similar electrochemical behaviour of aza crown ether-functionalized polypyrroles. Complexation of cations in the crown ether units could lead to sterically forced twists of the thiophene units and therefore to a decrease in conjugation.[6] If this argument holds, in optical spectra the diminution of conjugation length should result in a hypsochromic shift of the longest wavelength absorption. In this respect, in a spectroelectrochemical experiment we coated electrodes with poly(bithiophenes) **P2** or **P8** which were cycled in alkali ion containing electrolytes. Surprisingly, no significant changes in the absorption spectra could be observed. For poly(bithiophene) **P2** only a slight hypsochromic shift of the longest wavelength absorption ($\Delta\lambda = 7$–9 nm) was found after 50 scans in MeCN–$LiClO_4$. For oligoether polymer **P8** exactly the same maximum was detected after cycling in an MeCN–$NaClO_4$-electrolyte. Although in these experiments thicker polymer films had to be used, these results clearly suggest that the change in electrochemical behavior of these polymers upon complexation is due rather to electrostatic and diffusional effects of the counter anions than to steric constraints which would reduce the mean conjugation of the backbone. However, thickness dependent electrochemical measurements showed that the amount of polymer deposited and the morphology of the film, which itself is strongly dependent on the film thickness, play a crucial role for the effects observed. Smaller changes in the electrochemical signals are observed for thicker films, which also indicates that diffusional processes play a crucial role.

However, the diffusion of ions in a polymer matrix is a complex overall process in which either anions are expelled or cations diffuse into the matrix. Additionally the diffusion of solvent molecules and ion contact pairs can occur so that the polymer shows complex ion exchange properties. The size of the ions and the interactions of the ions with the polymer influence the speed of diffusion. Taking into account that these processes are also important for the crown ether-functionalized poly(bithiophenes), the proposed model that an electrostatic potential barrier due to the complexed crown ether units hinders diffusion of the counter anions in the film is further supported.[4a,f] After immersion of a poly(bithiophene) coated electrode which was prepared in MeCN–TBAHFP into a solution of an alkali metal salt in MeCN, the alkali cations can spontaneously diffuse to a certain extent into the polymer matrix and become complexed by the crown ether units. Therefore, a Donnan potential[31] is built up that hinders further diffusion of anions into the film during the first oxidation/reduction cycle of the poly(bithiophene). The formation of the Donnan potential which is greater for cations with higher charge : radius ratios also explains the selectivity of poly(bithiophenes) for lithium ions due to their higher diffusion coefficients leading to a greater incorporation in a given time. The observed current in the first CV is significantly lower than the current observed in the CV measured in an alkali ion free electrolyte. During the reduction half cycle more cations diffuse into the polymer film and saturate most of the complexation sites available. The subsequent CVs show a further strongly reduced electroactivity (Fig. 2). The decrease in electroactivity

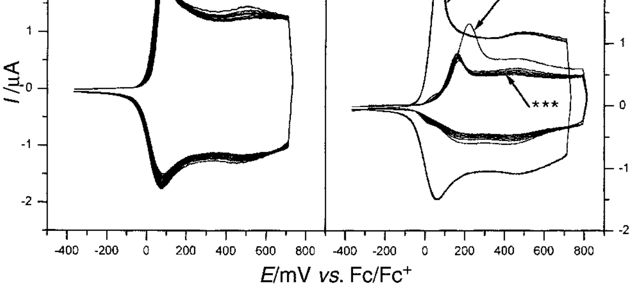


Fig. 2 Multisweep cyclic voltammogram (50 scans) of polymer **P2** in MeCN–TBAHFP (left). Multisweep cyclic voltammogram (3 scans) of polymer **P2** in MeCN–TBAHFP* (0.1 M, 100 mV s^{-1}), 1st scan in MeCN–$LiClO_4$**, and 2–50th scan in MeCN–$LiClO_4$*** (0.1 M, 100 mV s^{-1}, each fifth scan is shown) (right).

Table 4 Polymerization conditions of alkoxythiophenes **4** and **12–15**

(**M**)	Concentration/mol L^{-1}	Potential range/V[a]	Number of scans	Charge/μC	Polymerization tendency[b]
4	$2.0 \cdot 10^{-2}$	−0.36–1.14	20	4.03	+ +
12	$1.0 \cdot 10^{-3}$	−0.36–1.09	10	3.24	+ + +
13	0.1	−0.36–1.54	150	—	—
14	0.1	−0.36–1.54	20	—	—
15	0.1	−0.36–1.54	20	—	—

[a] MeCN–TBAHFP, 0.1 M, 100 mV s^{-1}, all potentials *vs.* Fc/Fc$^+$. [b] + + + very good; + + good;—no polymerisation.

is strongest for 12-crown-4 substituted poly(bithiophenes) **P2** and **P7** in lithium ion electrolyte solution. A change in electroactivity is observed when the diffusion of ions, which is crucial for the charge transport in a conducting polymer, is retarded or prevented by the complexed ether moieties.

Electrochemistry of the 3,4-dialkoxy-substituted thiophenes 4, 12–15

All 3,4-dialkoxy-substituted monothiophenes **4** and **12–15** showed the expected irreversible oxidation peaks in the same potential range (E_{pa} = 0.98–1.05 V *vs.* Fc/Fc$^+$, Table 4). Due to the strong electron-donating effect of the oxygen substituents these potentials are dramatically lower than for alkylthiophenes and comparable to those of 3,4-ethylenedioxythiophene[32] and other alkoxy-substituted thiophenes.[33] In potentiodynamic polymerization experiments, 12-crown-4 thiophene **12** and 15-crown-5 thiophene **4** formed stable polymers. All other monomers (**13–15**) did not lead to adhering films on the electrode even at high monomer concentrations (0.1 M) and relatively high applied oxidation potentials ($E \geqslant 1.54$ V). Since the smaller 12-crown-4 thiophene **12** polymerizes much faster than the bulkier 15-crown-5 thiophene **4**, the inhibition of the polymerization of the other monomers can be attributed to the steric influence of the ether moieties directly attached to the β-positions of the thiophene ring. This can clearly be seen in the multisweep CVs of the crown ether-substituted monothiophenes **4**, **12** and **14** which are depicted in Fig. 3. During the first scan in the polymerization of 12-crown-4 thiophene **12** a clear trace-crossing is observable which points to fast formation of oligomeric or polymeric material on the electrode or nearby. In the following scans new reversible redox waves at lower potentials are formed whose peak currents rapidly increase. This is a typical behavior indicating increasing amounts of polymer formed on the electrode. For 15-crown-5 monothiophene **4** the formation of polymer is observed as well but the increase of the waves in the CVs resulting in the formation of polymer on the electrode is lesser although a higher monomer concentration and a slightly extended potential range were applied for polymerization (Table 5). Probably due to steric reasons the 18-crown-6 monothiophene **14** showed no redox waves at more negative potentials and could not be polymerized. This is also true for the oligoether thiophenes **13** and **15** in which the acyclic substituents have a much higher conformational flexibility preventing the polymerization through steric repulsion of the radical cations.

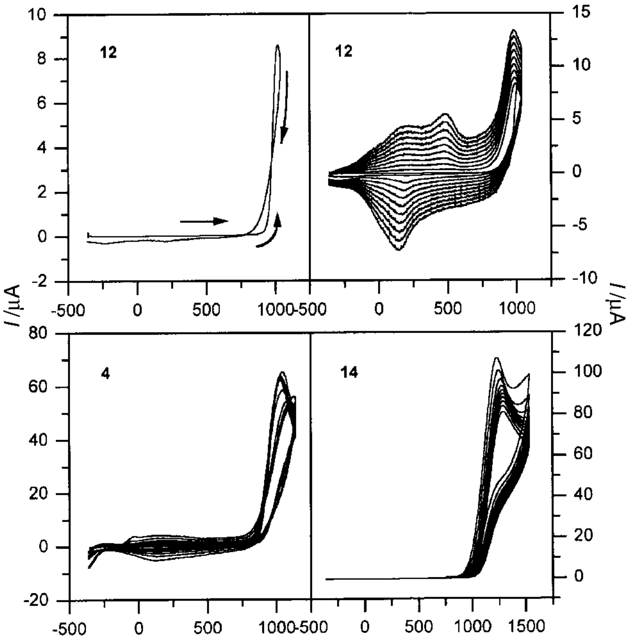


Fig. 3 Comparison of (multisweep) cyclic voltammograms (20 scans) during the polymerization of bithiophenes **4** (c = 1 mmol L^{-1}), **12** (c = 0.02 mol L^{-1}) (first scan top left; 20th scan top right), **14** (c = 0.1 mol L^{-1}) in MeCN–TBAHFP, 0.1 M, 100 mV s^{-1}; every 2nd scan shown.

The polythiophenes **P4** and **P12** were electrochemically characterized in an electrolyte free of monomer. The oxidation of the 12-crown-4 polythiophene **P12** starts indeed at a very low potential of $E_{pa} \approx -0.4$ V *vs.* Fc/Fc$^+$ and is followed by a wave with an oxidative peak at $E_{pa} \approx 0.44$–0.54 V *vs.* Fc/Fc$^+$. The CV of the 15-crown-5 polythiophene **P4** shows a sharp increase of the current also beginning at very negative potentials ($E_{pa} \approx -0.2$ V *vs.* Fc/Fc$^+$) with a sharp first oxidation peak at $E_{pa} = -0.05$ V *vs.* Fc/Fc$^+$ proceeding into a broad plateau (Fig. 4). Both polymers therefore should have a relatively long conjugated chain length. The absorption spectra of both polymers **P4** (λ_{max} = 601, 549, 520 nm) and **P12** (λ_{max} = 607, 556, 520 nm) in their neutral state are quite similar and the absorption maxima lie in the range of other 3,4-dialkoxy-substituted polythiophenes such as poly(3,4-ethylenedioxythiophene) (λ_{max} = 630 nm),[32] poly(3,4-propylenedioxythiophene) (λ_{max} = 613 nm),[32] and poly(3,4-dimethoxythiophene) (λ_{max} = 598 nm).[33b] The absorption maximum of 12-crown-4 polythiophene **P12** is slightly red-shifted ($\Delta\lambda$ = 7 nm) compared to that of 15-crown-5 polythiophene **P4** indicating that the thiophene rings are a little twisted in the latter case due to the sterically more demanding crown ether moieties. A band gap of about E_g = 1.85 eV was estimated for both polymers. Additionally, due to vibronic couplings both novel polymers exhibit an unusually pronounced fine structure of the π–π*-transition band. This indicates a rigid polymer,[34] with a high degree of a linear and regular structure. Spectroelectrochemical experiments on both polymers clearly reveal succesive interconversion of the reddish violet neutral form into the blue oxidized conducting form. A weak band at $\lambda_{max} \approx 950$–960 nm is at first formed upon oxidation which at a higher oxidation level changes into a very broad absorption band with a maximum in the NIR-regime at $\lambda_{max} > 1600$ nm, typical for metallic conduction.

In comparison to the monothiophenes **4**, **12–15**, electrochemical characterization of both polymers **P4** and **P12** in the presence of alkali metal ions was undertaken in an electrolyte containing 0.1 M of the alkali metal ion. For the monomers in solution an irreversible oxidation peak is found. For 12-crown-4 thiophene **12** (ΔE_{pa} = −6/18/18 mV; Li$^+$/Na$^+$/K$^+$)

Table 5 Electrochemical and spectroscopic data of the ether-substituted thiophenes **4**, **12–15** and the corresponding polymers **P4** and **P12**

(M)/(P)	E_{pa} **(M)**/V^a	E_{pa}^1 **(P)**/V^a	E_{pa}^2 **(P)**/V^a	λ_{max} **(M)/(P)**/nm	E_g **(P)**/eV
4/P4	0.98	−0.08	0.15–0.25^b	256/520, 549, 601	1.85
12/P12	1.00	−0.05–0.10	0.44–0.54^b	255/520, 556, 607	1.85
13	1.01	—	—		—
14	1.04	—	—	—	—
15	1.05	—	—	—	—

^{a}MeCN–TBAHFP, 0.1 M, 100 mV s^{-1}, all potentials *vs.* Fc/Fc$^+$. ^{b}Broad maximum.

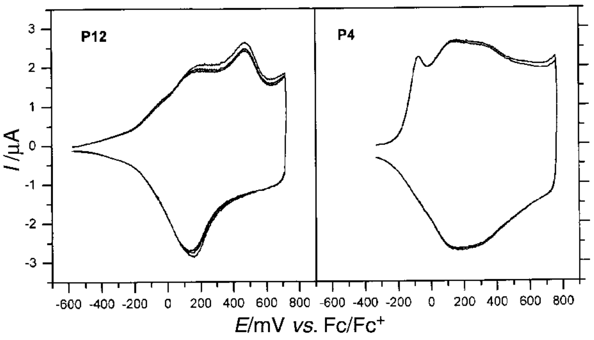


Fig. 4 Cyclic voltammograms of the poly(thiophenes) **P4** and **P12** (3 scans, MeCN–TBAHFP, 0.1 M, 100 mV s^{-1}).

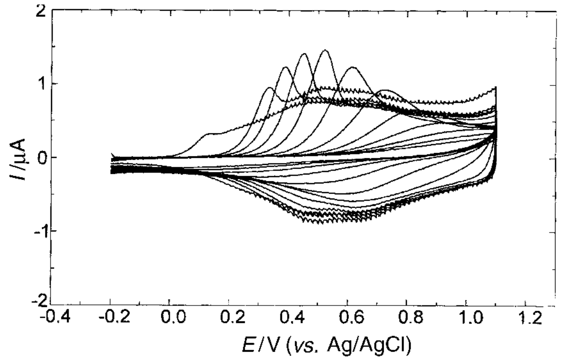


Fig. 5 Cyclic voltammograms of polythiophene **P4** (MeCN–NaClO$_4$, 0.1 M, 100 mV s^{-1}); first scan and each fifth successive scan are shown.

and the oligoether thiophenes **13** ($\Delta E_{pa} = -6/-8/12$ mV; Li$^+$/Na$^+$/K$^+$) and **15** ($\Delta E_{pa} = -39/-20/19$ mV; Li$^+$/Na$^+$/K$^+$), respectively, the peak potential and the shape of the CV are only slightly affected when an equivalent amount of alkali metal ions with respect to the monomer concentration is added. In contrast, 15-crown-5 thiophene **4** ($\Delta E_{pa} =$ 99/81/42 mV; Li$^+$/Na$^+$/K$^+$) and 18-crown-6 thiophene **14** ($\Delta E_{pa} = 7/159/187$ mV; Li$^+$/Na$^+$/K$^+$) exhibit relatively large positive shifts of the peak potential in the CVs. In the latter case not only a displacement of the peak is found, but a new oxidation peak including an isopotential point arises at more positive potentials upon addition of sodium or potassium ions (Table 6). This trend is also reflected in the corresponding polymers **P4** and **P12**. For 15-crown-5 polythiophene **P4** the oxidation peak successively shifts to more positive potentials and the electroactivity is decreased. After 50 scans, the polymer exhibited a selectivity for sodium ions ($\Delta E_{pa} = 600$ mV) whereas the effect is minor for lithium ($\Delta E_{pa} = 150$ mV) and potassium ions ($\Delta E_{pa} = 50$ mV) (Fig. 5).[4f] In good accordance with the corresponding monomers, the 12-crown-4 polythiophene **P12** showed only small effects in the presence of alkali metal ions. After 50 scans the peak potentials are only marginally shifted in the corresponding 0.1 M salt solution (Li$^+$: $\Delta E_{pa} = 20$ mV; Na$^+$: $\Delta E_{pa} = 40$ mV; K$^+$: $\Delta E_{pa} = 0$ mV). With respect to the selectivity, these experiments show that the behavior of both the monomers and the polymers is in agreement with extraction experiments.[18]

In order to get more insight into the mechanism, 15-crown-5 thiophene **4** was polymerized potentiodynamically in an electrolyte which already contained 0.1 M of sodium ions. Appreciable polymer films were only obtained when the monomer concentration was raised to 0.1 M. Depending on the number of successive scans polymers are formed whose oxidation potential is shifted by *ca.* $\Delta E_{pa} = 300$ mV to more positive values in comparison to films polymerized in alkali metal ion free electrolytes. Despite the electrochemical response being definitively altered, interestingly, the polymer films produced in the different electrolytes exhibit nearly the same absorption maxima ($\lambda_{max} = 607$ and 601 nm, respectively). This finding is in accordance with the results for the other series of polymers and again clearly indicates that under both conditions polymers with about the same mean conjugation length and morphology are obtained. Thus, the influence on the electrochemical response by complexation of alkali metal ions in the crown ether moieties is not caused by a reduction of the mean conjugation length *via* twisting of the thiophene units, but by a change of the diffusion behavior of counter ions into the polymer film. Due to electrostatic interactions with the complexed cations the penetration of counter anions into the film is rendered more difficult when the polythiophene backbone is oxidized. Thus, charge compensation occurs at more positive potentials and the functionalized polymer is more difficult to oxidize.

Summary

We have described the syntheses, the electrochemical and optical properties of two series of crown and oligoether-functionalized poly(bithiophenes) in which several structural

Table 6 Influence of alkali cations on the electrochemical response of monothiophenes **4**, **12–15** and poly(bithiophenes) **P4**, **P12**

(M),(P)	ΔE_{pa}/mV LiClO$_4$^{a}	ΔE_{pa}/mV NaClO$_4$^{a}	ΔE_{pa}/mV KPF$_6$^{a}	Influence
12 (12-C-4)	−6	18	18	
4 (15-C-5)	99	81	42	Li$^+$, Na$^+$ ≫K$^+$
14 (18-C-6)	7	159	187	Na$^+$, K$^+$ ≫Li$^+$
13 (OE-4)	−6	−8	12	
15 (OE-6)	−39	−20	19	
P12 (12-C-4)	20	40	0	
P4 (15-C-5)	150	600	50	Na$^+$ ≫Li$^+$ ≫K$^+$

^{a}Concentration of the monomer/alkali cation is 1 : 1.

parameters were varied. We observe that the electrochemical behavior of polymers **P2**, **P7–P9** in which the crown ether units are separated from the conjugated backbone *via* insulating oxaalkyl spacers and of polymer **P4** from the other series is strongly influenced in the presence of alkali ions. Selectivities corresponding to the match of the cation size without solvent shell and the inner diameter of the crown ether units are found. Supporting optical and spectroelectrochemical experiments on these novel polymers clearly reveal that the changes in electronic properties are due to a hindered diffusion of the counter anions into the film which is necessary for charge compensation when the conjugated polymer is oxidized. Finally, our investigation gives a detailed insight into the structural prerequisites necessary for materials which transduce a *host–guest interaction* and therefore *chemical information* into the *change of an electrical signal.*

Experimental

General procedures

Melting points are not corrected. ^{1}H- and ^{13}C-NMR spectroscopic data were obtained with a Bruker ACF 250 or AC 250 instrument with $CDCl_3$ as solvent using TMS as standard. J values are given in Hz. All solvents were distilled prior to use. Diethyl ether was distilled from sodium–benzophenone ketyl, acetonitrile from phosphorous pentoxide. DMF was distilled from CaH_2 under reduced pressure. The following compounds were prepared according to literature procedures: 3-(10-bromodecyl)thiophene (**17**),[4a] 3-(5-bromopentyl)-2,2′-bithiophene (**20**),[4a] 2-hydroxymethyl-1,4,7,10-tetraoxacyclododecane (12-crown-4-methanol),[35] 2-hydroxymethyl-1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6-methanol),[35] 2,5-bis(ethoxycarbonyl)-3,4-dihydroxythiophene,[18,20,36] 2,5,8,11-tetraoxa-14-thiabicyclo[10.3.0]pentadeca-1(15),12-diene,[18] 2,5,8,11,14-pentaoxa-17-thiabicyclo[13.3.0]octadeca-1(18),15-diene,[18] 2,5,8,11,14,17-hexaoxa-20-thiabicyclo[16.3.0]heneicosa-1(21),18-diene,[18] ethylene glycol monomethyl ether monotosylate,[38] diethylene glycol monomethyl ether monotosylate,[37] tetraethylene glycol monomethyl ether.[38] All spectroscopic and analytical data are in agreement with the structures and the data reported. *N*-Bromosuccinimide (Fluka), Ni(dppp)Cl_2 (Aldrich), tetraethylene glycol (Merck), tetrabutylammonium hydrogen sulfate (TBAHS, Aldrich) were used as received.

2-Bromo-3-(10-bromodecyl)thiophene 19

Under nitrogen atmosphere 13.5 g (75.9 mmol) *N*-bromosuccinimide, dissolved in 60 ml DMF, are added to a solution of 23.0 g (75.8 mmol) 3-(10-bromodecyl)thiophene **17** in 60 ml DMF and stirred for five hours at ambient temperature. The reaction mixture is poured on water and extracted with dichloromethane. The organic phase is washed with saturated sodium bicarbonate solution and dried over sodium sulfate. After evaporation of the solvent the resulting oil is distilled twice but the starting material could not be completely removed (*ca.* 7%, GC-analysis). Yield: 12.3 g (32.2 mmol, 42%) of a clear colorless oil; bp 148–153 °C ($5{\cdot}10^{-3}$ Torr); ^{1}H NMR ($CDCl_3$): δ (ppm) 7.16 (d, $^{3}J_{(5,4)}=5.8$ Hz, 1 H, 5-H), 6.77 (d, $^{3}J_{(4,5)}=5.5$ Hz, 1 H, 4-H), 3.39 (t, $^{3}J_{(a,b)}=6.9$ Hz, 2 H, H_a), 2.54 (t, $^{3}J_{(j,i)}=7.6$ Hz, 2 H, H_j), 1.89–1.78 (m, 2 H, H_b), 1.58–1.28 (m, 14 H, H_c to H_i). ^{13}C NMR ($CDCl_3$): δ (ppm) 141.9 (C-3), 128.2 (C-4), 125.1 (C-5), 108.8 (C-2) 34.0, 32.8, 29.7, 29.4, 29.3, 29.1, 28.7, 28.1 (C_a to C_j).

3-(10-Bromodecyl)-2,2′-bithiophene 21

Under an inert gas atmosphere 6.55 g (40.2 mmol) 2-bromothiophene in 40 ml dry diethyl ether are added dropwise to 0.98 g (40.2 mmol) magnesium turnings in 10 ml diethyl ether. After formation of the Grignard reagent this solution is transferred *via* Teflon tube connected needles to another apparatus and added dropwise to an ice cooled suspension of 12.3 g (32.2 mmol) 2-bromo-3-(10-bromodecyl)thiophene **19** and 64.0 mg (0.12 mmol, 0.37 mol%) Ni(dppp)Cl_2 in 50 ml diethyl ether. After 37 h under reflux the reaction mixture is hydrolyzed with 1 M hydrochloric acid and extracted with diethyl ether. After drying with sodium sulfate the solvent is evaporated and the resulting oil is distilled twice under reduced pressure to yield 4.01 g (10.4 mmol, 32%) of a clear yellowish oil: bp 141–156 °C ($5{\cdot}10^{-3}$ Torr). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.30 (dd, $^{3}J_{(5',4')}=5.0$ Hz, $^{4}J_{(5',3')}=1.3$ Hz, 1 H, 5′-H), 7.17 (d, $^{3}J_{(5,4)}=5.2$ Hz, 1 H, 5-H), 7.10 (dd, $^{3}J_{(3',4')}=3.6$ Hz, $^{4}J_{(3',5')}=1.3$ Hz, 1 H, 3′-H), 7.06 (dd, $^{3}J_{(5',4')}=5.0$ Hz, $^{3}J_{(4',3')}=3.6$ Hz, 1 H, 4′-H), 6.92 (d, $^{3}J_{(4,5)}=5.2$ Hz, 1 H, 4-H), 3.40 (t, $^{3}J_{(a,b)}=6.9$ Hz, 2 H, H_a), 2.74 (t, $^{3}J_{(i,j)}=7.6$ Hz, 2 H, H_j), 1.90–1.78 (m, 2 H, H_b), 1.68–1.56 (m, 2 H, H_i), 1.53–1.27 (m, 12 H, H_c to H_h). ^{13}C NMR ($CDCl_3$): δ (ppm) 139.6 (C-3′), 136.2 (C-2″), 130.5 (C-2′), 129.8 (C-4′), 127.3 (C-4″), 125.9 (C-3″), 125.2 (C-5″), 123.7 (C-5′), 34.0, 32.8, 30.7, 29.4, 29.1, 28.7, 28.1 (C_a to C_j). Anal. calcd. for $C_{18}H_{25}BrS_2$: C 56.09, H 6.54, S 16.64, Br 20.73. Found: C 56.32, H 6.52, S 16.43, Br 20.75%. UV (CH_2Cl_2): λ_{max} (log ε) = 295 nm (3.97), 248 nm (3.87).

2-[2-Oxa-12-(2,2′-bithienyl-3-yl)dodecyl]-1,4,7,10-tetraoxacyclododecane 7

1.10 g (5.33 mmol) 12-Crown-4-methanol are added dropwise to a suspension of 2.00 g (5.92 mmol) 3-(10-bromodecyl)-2,2′-bithiophene **21**, 100 mg (0.29 mmol, 5 mol%) TBAHS and 3 ml 50% sodium hydroxide solution in 7 ml benzene. After 68 h at 75 °C the reaction mixture is poured on water, extracted with dichloromethane and the organic layer washed with sodium bicarbonate and dried over sodium sulfate. After evaporation of the solvent the resulting oil is chromatographed on silica gel with ethyl acetate followed by chromatography with dichloromethane yielding 1.49 g (2.92 mmol, 55%) of a slightly yellow clear oil. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.29 (dd, $^{3}J_{(5'',4'')}=5.1$ Hz, $^{4}J_{(5'',3'')}=1.2$ Hz, 1 H, 5″ H), 7.16 (d, $^{3}J_{(5',4')}=5.2$ Hz, 1 H, 5′-H), 7.10 (dd, $^{3}J_{(3'',4'')}=3.6$ Hz, $^{4}J_{(3'',5'')}=1.2$ Hz, 1 H, 3″-H), 7.05 (dd, $^{3}J_{(4'',3'')}=3.6$ Hz, $^{3}J_{(4'',5'')}=5.0$ Hz, 1 H, 4′-H), 6.92 (d, $^{3}J_{(4',5')}=5.2$ Hz, 1 H, 4′-H), 3.89–3.59 (m, 14 H, 3-H to 12-H), 3.51–3.36 (m, 5 H, H_a, H_c, 2-H), 2.74 (t, $^{3}J_{(l,k)}=7.8$ Hz, 2 H, H_l), 1.65–1.49 (m, 4 H, H_d, H_k), 1.27 (s, 12 H, H_e to H_j). ^{13}C NMR ($CDCl_3$): δ (ppm) 139.6 (C-3′), 136.2 (C-2″), 130.5 (C-2′), 129.9 (C-4′), 127.3 (C-4″), 126.0 (C-3″), 125.3 (C-5″), 123.7 (C-5′), 78.6, 71.8, 70.9, 70.8, 70.7, 70.4, 70.2 (C-2 to C-12, C_a, C_c), 30.7, 29.5, 29.4, 29.1, 26.1 (C_d to C_l). Anal. calcd. for $C_{27}H_{42}O_5S_2$: C 63.49, H 8.29, S 12.56. Found: C 63.36, H 8.40, S 12.62%. UV (CH_2Cl_2): λ_{max} (log ε) = 294 nm (3.95), 249 nm (3.84).

19-(2,2′-Bithienyl-3-yl)-2,5,8,11,14-pentaoxanonadecane 8

1.00 g (4.80 mmol) Tetraethylene glycol monomethyl ether are added dropwise to a suspension of 1.66 g (5.26 mmol) 3-(5-bromopentyl)-2,2′-bithiophene **20**, 80.6 mg (0.24 mmol, 4.5 mol%) TBAHS and 2.4 ml 50% aqueous sodium hydroxide solution in 5 ml benzene. After 30 h at 70 °C the reaction mixture is poured on water, extracted with dichloromethane and the organic layer washed with sodium bicarbonate and dried over sodium sulfate. After evaporation of the solvent the resulting oil is chromatographed on silica gel with ethyl acetate–hexane yielding 1.07 g (2.41 mmol, 50%) of a slightly yellow clear oil. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.29 (dd, $^{3}J_{(5'',4'')}=4.9$ Hz, $^{4}J_{(5'',3'')}=1.2$ Hz, 1 H, 5″-H), 7.16 (d, $^{3}J_{(5',4')}=5.2$ Hz, 1 H, 5′-H), 7.09 (dd, $^{3}J_{(3'',4'')}=3.7$ Hz, $^{4}J_{(3'',5'')}=1.2$ Hz, 1 H, 3″-H), 7.04 (dd, $^{3}J_{(5'',4'')}=5.0$ Hz, $^{3}J_{(4'',3'')}=3.5$ Hz, 1 H, 4″-H), 6.92 (d, $^{3}J_{(4',5')}=5.2$ Hz, 1 H, 4′-H), 3.53–3.66 (m, 16 H, 3-H to 13-H), 3.44 (t, $^{3}J_{(15,14)}=6.4$ Hz, 2 H, 15-H), 3.37 (s, 3 H, 1-H), 2.75 (t, $^{3}J_{(19,18)}=7.6$ Hz, 2 H, 19-H), 1.71–1.55 (m, 4 H, 18-H, 16-H), 1.46–1.35 (m, 2 H, 17-H). ^{13}C NMR ($CDCl_3$):

δ (ppm) 139.3 (C-3′), 136.1 (C-2″), 130.5 (C-2′), 129.8 (C-4′), 127.3 (C-4″), 125.9 (C-3″), 125.2 (C-5″), 123.7 (C-5′), 71.9, 71.3, 70.5, 70.4, 70.0 (C-3 to C-15), 59.0 (C-1), 30.5, 29.4, 29.0, 25.9 (C-16 to C-19). Anal. calcd. for $C_{22}H_{34}O_5S_2$: C 59.70, H 7.74, S 14.49. Found: C 59.73, H 7.63, S 14.33%. UV (CH_2Cl_2): λ_{max} (log ε) = 295 nm (3.96), 248 nm (3.87).

2-[2-Oxa-7-(2,2′-bithienyl-3-yl)heptyl]-1,4,7,10,13,16-hexaoxacyclooctadecane 9

0.52 g (1.76 mmol) 18-Crown-6-methanol are added dropwise to a suspension of 0.64 g (2.03 mmol) 3-(5-bromopentyl)-2,2′-bithiophene **20**, 34.0 mg (0.1 mmol) TBAHS and 1 ml 50% aqueous sodium hydroxide solution in 3 ml benzene. After 26 h at 65 °C the reaction mixture is poured on water, extracted with dichloromethane and the organic layer washed with sodium bicarbonate and dried over sodium sulfate. After evaporation of the solvent the resulting oil is chromatographed on aluminium oxide with dichloromethane–acetone (7:3) yielding 0.67 g (1.27 mmol, 72%) of yellow–brown clear oil. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.30 (dd, $^{3}J_{(5'',4'')} = 5.0$ Hz, $^{4}J_{(5'',3'')} = 1.3$ Hz, 1 H, 5″-H), 7.16 (d, $^{3}J_{(5',4')} = 5.2$ Hz, 1 H, 5′-H), 7.10 (dd, $^{3}J_{(3'',4'')} = 3.5$, $^{4}J_{(3'',5'')} = 1.2$ Hz, 1 H, 3″-H), 7.05 (dd, $^{3}J_{(4'',5'')} = 5.0$ Hz, $^{3}J_{(4'',3'')} = 3.6$ Hz, 1 H, 4″-H), 6.92 (d, $^{3}J_{(4',5')} = 5.2$ Hz, 1 H, 4′-H), 3.82–3.39 (m, 27 H, H_a, H_c, 1-H to 18-H), 2.74 (t, $^{3}J_{(g,f)} = 7.7$ Hz, 2 H, H_g), 1.70–1.53 (m, 4 H, H_f, H_d), 1.45–1.33 (m, 2 H, H_e). ^{13}C NMR ($CDCl_3$): δ (ppm) 139.4 (C-3′), 136.2 (C-2″), 130.6 (C-2′), 129.8 (C-4′), 127.3 (C-4″), 126.0 (C-3″), 125.3 (C-5″), 123.8 (C-5′), 78.4, 71.5, 70.9, 70.8, 70.7, 67.0 (C-2 to C-18, C_a, C_c), 26.0, 29.0, 29.5, 30.5 (C_d to C_g). Anal. calcd. for $C_{26}H_{40}O_7S_2$: C 59.06, H 7.63, S 12.13. Found: C 59.00, H 7.75, S 12.22%. UV (CH_2Cl_2): λ_{max} (log ε) = 295 nm (3.97), 248 nm (3.87).

2-[2-Oxa-12-(2,2′-bithienyl-3-yl)dodecyl]-1,4,7,10,13,16-hexaoxacyclooctadecane 10

1.75 g (5.93 mmol) 18-Crown-6-methanol are added dropwise to a suspension of 1.82 g (5.39 mmol) 3-(10-bromodecyl)-2,2′-bithiophene **21**, 100 mg (0.29 mmol) TBAHS and 3 ml 50% aqueous sodium hydroxide solution in 7 ml benzene. After 43 h at 70 °C the reaction mixture is poured on water, extracted with dichloromethane and the organic layer washed with sodium bicarbonate and dried over sodium sulfate. After evaporation of the solvent the resulting oil is chromatographed on aluminium oxide with ethyl acetate followed by a second chromatography on aluminium oxide with diethyl ether yielding 1.72 g (2.88 mmol, 53%) of a slighlty brown clear oil. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.29 (dd, $^{3}J_{(5'',4'')} = 5.0$ Hz, $^{4}J_{(5'',3'')} = 1.3$ Hz, 1 H, 5″-H), 7.16 (d, $^{3}J_{(5',4')} = 5.2$ Hz, 1 H, 5′-H), 7.10 (dd, $^{3}J_{(3'',4'')} = 3.6$ Hz, $^{4}J_{(3'',5'')} = 1.3$ Hz, 1 H, 3″-H), 7.06 (dd, $^{3}J_{(4'',5'')} = 5.0$ Hz, $^{3}J_{(4'',3'')} = 3.6$ Hz, 1 H, 4″-H), 6.92 (d, $^{3}J_{(4',5')} = 5.2$ Hz, 1 H, 4′-H), 3.83–3.39 (m, 27 H, 2-H to 18-H, H_a, H_c), 2.73 (t, $^{3}J_{(l,k)} = 7.8$ Hz, 2 H, H_l), 1.65–1.52 (m, 4 H, H_k, H_d), 1.26 (s, 12 H, H_j to H_e). ^{13}C NMR ($CDCl_3$): δ (ppm) 139.6 (C-3′), 136.2 (C-2″), 130.5 (C-2′), 129.9 (C-4′), 127.3 (C-4″), 125.9 (C-3″), 125.3 (C-5″), 123.7 (C-5′), 78.4, 71.8, 71.6, 70.9, 70.7, 70.6, 69.9 (C-2 to C-12, C_a, C_c), 30.7, 29.5, 29.1, 26.1 (C_d to C_l). Anal. calcd. for $C_{31}H_{50}O_7S_2$: C 62.17, H 8.42, S 10.71. Found: C 62.23, H 8.29, S 10.64%. UV (CH_2Cl_2): λ_{max} (log ε) = 294 nm (3.95), 248 nm (3.85).

1,23-Bis(2,2′-bithienyl-3-yl)-6,9,12,15,18-pentaoxatricosane 11

0.78 g (4.02 mmol) Tetraethylene glycol are added dropwise to a suspension of 3.00 g (9.50 mmol) 3-(5-bromopentyl)-2,2′-bithiophene **20**, 161 mg (0.48 mmol) TBAHS and 4 ml 50% aqueous sodium hydroxide solution in 10 ml benzene. After 47 h at 70 °C the reaction mixture is poured on water, extracted with dichloromethane and the organic layer washed with sodium bicarbonate and dried over sodium sulfate. After evaporation of the solvent the resulting oil is chromatographed twice on aluminium oxide with diethyl ether yielding 1.07 g (1.61 mmol, 40%) of a green–yellow oil. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.29 (dd, $^{3}J_{(5'',4'')} = 5.1$ Hz, $^{4}J_{(5'',3'')} = 1.4$ Hz, 2 H, 5″-H), 7.16 (d, $^{3}J_{(5',4')} = 5.5$ Hz, 2 H, 5′-H), 7.10 (dd, $^{3}J_{(3'',4'')} = 3.7$ Hz, $^{4}J_{(3'',5'')} = 1.2$ Hz, 2 H, 3″-H), 7.05 (dd, $^{3}J_{(4'',5'')} = 5.1$ Hz, $^{3}J_{(4'',3'')} = 3.7$ Hz, 2 H, 4″-H), 6.92 (d, $^{3}J_{(4',5')} = 5.5$ Hz, 2 H, 4′-H), 3.65–3.52 (m, 16 H, 7-H to 17-H), 3.43 (t, $^{3}J_{(5,4;19,20)} = 6.6$ Hz, 4 H, 5-H, 19-H), 2.75 (t, $^{3}J_{(1,2;23,22)} = 7.8$ Hz, 4 H, 1-H, 23-H), 1.71–1.55 (m, 8 H, 2-H, 4-H, 20-H, 22-H), 1.46–1.36 (m, 4 H, 3-H, 21-H). ^{13}C NMR ($CDCl_3$): δ (ppm) 139.3 (C-3′), 136.1 (C-2″), 130.5 (C-2′), 129.8 (C-4′), 127.3 (C-4″), 126.0 (C-3″), 125.3 (C-5″), 123.7 (C-5′), 71.3, 70.5, 70.0, 65.8 (C-5 to C-19), 30.5, 29.4, 29.0, 26.0 (C-1 to C-4, C-18 to C-23). Anal. calcd. for $C_{34}H_{46}O_5S_2$: C 61.60, H 6.99, S 19.35. Found: C 61.40, H 6.98, S 19.15%. UV (CH_2Cl_2): λ_{max} (log ε) = 295 nm (4.25), 248 nm (4.15).

3,4-Bis(2-methoxyethoxy)-2,5-bis(ethoxycarbonyl)thiophene 23

Under inert gas atmosphere 20.8 g (79.9 mmol) 2,5-bis(ethoxycarbonyl)-3,4-dihydroxythiophene, 40.5 g (176 mmol) ethylene glycol monomethyl ether monotosylate, 12.2 g (88.3 mmol) potassium carbonate and 50 ml dry DMF are mixed together and heated for 26 h to 100 °C. The hot solution is filtered and the solvent evaporated under reduced pressure. The resulting oil is distilled three times with a Kugelrohr yielding 26.3 g (69.8 mmol, 87%) of a yellow oil: bp 170–180 °C ($5\cdot10^{-3}$ Torr). ^{1}H NMR ($CDCl_3$): δ (ppm) 4.34–4.26 (m, 8 H, 1′-H, 3′-H), 3.70–3.67 (m, 4 H, 2′-H), 3.37 (s, 6 H, 4′-H), 1.33 (t, $^{3}J_{(4'',3'')} = 7.2$ Hz, 6 H, 4′-H). ^{13}C NMR ($CDCl_3$): δ (ppm) 160.6 (C-1″), 153.0, 119.9 (C-2 to C-5), 73.5, 71.5, 61.3, 58.9 (C-1′ to C-4′, C-3″), 14.2 (C-4″). Anal. calcd. for $C_{16}H_{24}O_8S$: C 51.05, H 6.43, S 8.52. Found: C 50.96, H 6.41, S 8.66%. UV (CH_2Cl_2): λ_{max} (log ε) = 283 nm (4.15).

3,4-Bis[2-(2-methoxyethoxy)ethoxy]-2,5-bis(ethoxycarbonyl)thiophene 24

Under an inert gas atmosphere a mixture of 13.1 g (0.05 mol) 2,5-bis(ethoxycarbonyl)-3,4-dihydroxythiophene and 9.88 g (0.17 mol) potassium fluoride in 350 ml dry acetonitrile is stirred for one hour at room temperature. The yellow suspension is heated under reflux and a solution of 30.7 g (0.11 mol) diethylene glycol monomethyl ether monotosylate in 100 ml dry acetonitrile is slowly added *via* a dropping funnel. After 24 h under reflux the solution is filtered and the solvent evaporated. The resulting brown oil is extracted with chloroform. After concentration of the solution the resulting oil is chromatographed twice on silica gel (first ethyl acetate, second diethyl ether) yielding 7.11 g (15.3 mmol, 31%) of a yellow oil. ^{1}H NMR ($CDCl_3$). δ (ppm) 4.35–4.25 (m, 8 H, 1′-H, 3″-H), 3.80–3.77 (m, 4 H, 2′-H), 3.66–3.62 (m, 4 H, 4′-H), 3.51–3.47 (m, 4 H, 5′-H), 3.33 (s, 6 H, 7′-H), 1.33 (t, $^{3}J_{(4'',3'')} = 7.2$ Hz, 6 H, 4″-H). ^{13}C NMR ($CDCl_3$): δ (ppm) 160.6 (C-1″), 153.1, 119.6 (C-2 to C-5), 73.6, 71.9, 70.5, 70.3, 61.3, 59.0 (C-1′ to C-7′, C-3″), 14.2 (C-4″). Anal. calcd. for $C_{20}H_{32}O_{10}S$: C 51.71, H 6.94, S 6.90. Found: C 51.79, H 7.06, S 6.98%. UV (CH_2Cl_2): λ_{max} (log ε) = 283 nm (4.14).

3,4-Bis(2-methoxyethoxy)thiophene 13

7.53 g (20.0 mmol) 3,4-Bis(2-methoxyethoxy)-2,5-bis(ethoxycarbonyl)thiophene are dissolved in 100 ml ethanol and 100 ml 5% aqueous sodium hydroxide solution are added. The mixture is heated for two hours at 60 °C. After that time the solution is acidified under ice cooling with concentrated hydrochloric acid. The formed solid is filtered off, dried and decarboxylated under reduced pressure (15 Torr) at 250 °C. The formed black mixture is extracted with dichloromethane, filtered through silica gel and the solvent evaporated. The resulting oil is distilled twice in a Kugelrohr yielding 1.78 g (7.66 mmol, 38%) of a clear colorless oil: bp 105 °C ($5{\cdot}10^{-3}$ Torr). ^{1}H NMR ($CDCl_3$): δ (ppm) 6.20 (s, 2 H, 2-H, 5-H), 4.11–4.08 (m, 4 H, 1′-H), 3.73–3.69 (m, 4 H, 2′-H), 3.39 (s, 6 H, 4′-H). ^{13}C NMR ($CDCl_3$): δ (ppm) 147.1, 97.9 (C-2 to C-5), 70.7, 69.6, 59.0 (C-1′ to C-4′). Anal. calcd. for $C_{10}H_{16}O_4S$: C 51.71, H 6.94, S 13.80. Found: C 51.93, H 7.01, S 13.70%. UV (CH_2Cl_2): λ_{max} (log ε) = 255 nm (3.86).

3,4-Bis[2-(2-methoxyethoxy)ethoxy]thiophene 15

7.11 g (15.3 mmol) 3,4-Bis[2-(2-methoxyethoxy)ethoxy]-2,5-bis(ethoxycarbonyl)thiophene are dissolved in 80 ml ethanol and 80 ml 5% aqueous sodium hydroxide solution are added. After 5 h at 60 °C the solution is cooled with an ice bath and acidified with concentrated hydrochloric acid. It is then extracted with diethyl ether and the solvent evaporated under reduced pressure. The remaining solid is decarboxylated at 210–220 °C for 1.5 h. The resulting black mixture is extracted with dichloromethane and filtered through silica gel. After evaporation of the solvent the resulting oil is distilled twice with a Kugelrohr apparatus yielding 0.90 g (2.79 mmol, 18%) of a slightly brownish clear oil. Bp 140 °C ($5{\cdot}10^{-3}$ Torr). ^{1}H NMR ($CDCl_3$): δ (ppm) 6.17 (s, 2 H, 2-H, 5-H), 4.10 (t, $^3J_{(1',2')} = 5.0$ Hz, 4 H, 1′-H), 3.81 (t, $^3J_{(2',1')} = 5.0$ Hz, 4 H, 2′-H), 3.68–3.64 (m, 4 H, 4′-H), 3.53–3.49 (m, 4 H, 5′-H), 3.34 (s, 6 H, 7′-H). ^{13}C NMR ($CDCl_3$): δ (ppm) 147.0, 97.8 (C-2 to C-5), 71.8, 70.6, 69.7, 69.4, 58.9 (C-1′ to C-7′). Anal. calcd. for $C_{14}H_{24}O_6S$: C 52.48, H 7.55, S 10.01. Found: C 52.14, H 7.56, S 10.08%. UV (CH_2Cl_2): λ_{max} (log ε) = 255 nm (3.88).

Electrochemical methods

Tetrabutylammonium hexafluorophosphate, lithium perchlorate, sodium perchlorate and potassium hexafluorophosphate were recrystallized and dried *in vacuo* prior to use. Acetonitrile (Chromasolv, Merck) was filtered through activated basic alumina and saturated with oxygen-free argon. All electrochemical measurements were performed with a computer-controlled EG&G PAR 273 potentiostat or a computer-controlled EG&G PAR363 potentiostat. The platinum working electrode was a platinum wire sealed in a soft glass tube with a surface of $A = 0.785$ mm^2 and polished down to 0.5 µm (Buehler polishing paste) prior to use in order to get reproducible surfaces. The counter electrode consisted of a platinum wire, the reference was an Ag/AgCl secondary electrode. General procedure for the electrosynthesis of polythiophenes: acetonitrile–tetrabutylammonium hexafluorophosphate (0.1 M) was deoxygenated with dry argon for 15 min. The corresponding monomers were characterized at a concentration of 1.10^{-3} mol l^{-1}. Then the concentration was increased to the given values and the monomers were electropolymerized by successive scanning in the given potential range. The modified working electrodes were subsequently rinsed with dry acetonitrile, dried in air, and characterized in electrolyte free of monomer.

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