

Structure–property relationships in functional conjugated oligomers*

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Abstract: Relationships between the structure of defined α -conjugated oligothiophenes and their electronic properties were examined. Compared to the parent series of ‘end-capped’ oligothiophenes, the synthesis and characterization of mixed oligoheterocycles, oligothiophene metal complexes, and crown ether-functionalized oligothiophenes will elucidate the manifold possibilities to influence and extend their promising electronic properties, which are important with respect to technological applications in electronic devices, such as oligothiophene-based organic light-emitting diodes or sensors.

INTRODUCTION

Due to their defined structure, chain and conjugation length, α -conjugated oligothiophenes represent the most frequently investigated model compounds for conducting polymers [1]. Valuable information can be deduced from structure–property relationships, which are normally not obtainable from the corresponding polymers due to their polydisperse nature (Fig. 1). Various series of oligothiophenes, which were alkylated and therefore soluble, with controlled chain and conjugation length, have been synthesized by the stepwise assembly of defined units. In these series, the physical properties are well correlated to the (conjugated) chain length and thus ‘real’ structure–property relationships are available [1,2]. Very recently, oligomers with chain lengths exceeding the mean conjugation length of corresponding polymers were made available [3].

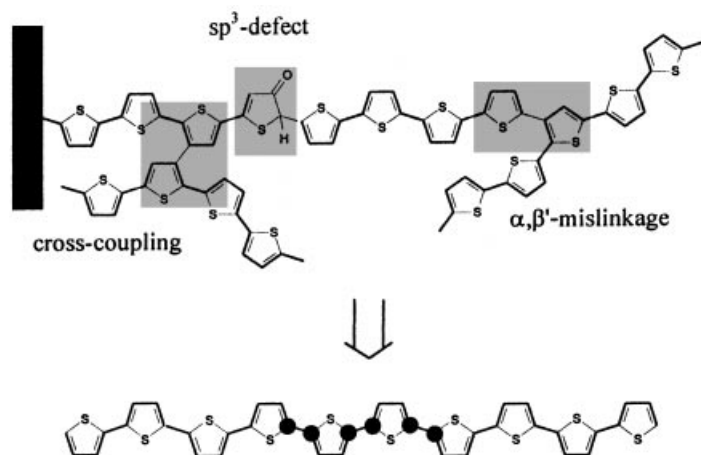


Fig. 1 Typical ‘real’ structure of polythiophene including mislinkages and defects in comparison to a defined and all- α -linked oligothiophene. Conjugation pathways are drawn with bold lines.

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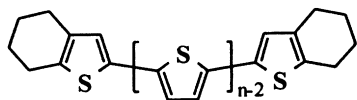


Fig. 2 Chemical structure of a series of monodisperse 'end-capped' oligothiophenes EC n T **1** ($n = 2-7$).

Moreover, studies of defined oligomers also provide information which may be used to improve strategies for the development of novel materials. For this reason, α -conjugated oligothiophenes have recently been advanced as very promising materials for technological applications in electro-optical devices. They have successfully been used as active components in all-organic field-effect transistors (FET) [4], light-emitting devices (OLED) [5], or photovoltaic solar cells [6]. For example, in an all- α -linked sexithiophene-based field-effect transistor, the mobility of the charge carriers and the transistor characteristics were found to be superior to those of an analogous poly(bithiophene) transistor and even to approach those of transistors based on amorphous silicon.

RESULTS AND DISCUSSION

'End-capped' oligothiophenes as an example of the 'oligomer approach'

At first glance, the performance of such materials is related to their electronic structure and, in particular, to the energy levels of their frontier orbitals. In this respect, the synthesis, characterization, and application of a whole series of 'end-capped' oligothiophenes EC n T **1** ($n = 2-7$) up to a heptamer clearly revealed the usefulness of the 'oligomer approach' (Fig. 2) [1,2,7].

The synthesis was mainly performed by nickel-catalysed cross-coupling reactions of metallated 'capped' thiophene building blocks and α,α' -dibromo(oligo)thiophenes in good yields (44%–75%). Importantly, purification of the oligomers was achieved by repeated chromatography, recrystallization, and finally by fractional sublimation. Due to the blocking of the reactive α - and β -positions with a cyclohexene 'cap' without perturbing the π -conjugation, a more precise characterization of the oligomers in various oxidation states was possible; and, due to the enhanced solubility, excellent correlations of the spectroscopic and electrochemical data in solution with the (inverse) chain length were obtained. These correlations now allow the estimation of the mean conjugation length of the corresponding polydisperse polymers, which typically corresponds to about 9–11 correctly α -linked thiophene units. Due to defects and mislinkages (Fig. 1) it dramatically differs from the mean chain length which is sometimes reaching 150–300 repeating units [1].

Because of their excellent optical properties in solution as well as in the solid state, the photo- and electroluminescent properties of the EC n Ts **1** were studied in more detail, in particular in thin films. By controlled vacuum sublimation of the active organic material, EC4T to EC7T, single-layer OLEDs (Indium tin oxide (ITO)/EC n T/Ca), which emit yellow to orange light at relatively low voltages, moderate current densities, and at a quite appreciable external quantum yield of 0.01%, were prepared [5,8]. Structure–property relationships showed that, also in the solid state, the optical data, i.e. absorption, photo- and electroluminescence, correlate well with the (inverse) chain length of the oligomers. As oligothiophenes are generally electron-rich and therefore easy to oxidize, current–voltage curves are due to the injection and transport of holes. The mobility of electrons is diminished and light emission directly arises from a zone close to the cathode. Thus, the tailoring and modulation of the electronic properties of conjugated oligomers in general is an important tool for the development of improved organic materials and devices.

Modification of the electronic properties of 'end-capped' oligothiophenes by synthesis of mixed oligoheterocycles

The electronic properties of oligothiophenes can be 'tailored' by the attachment of either sterically and/or electronically active substituents at both the β - and the terminal α -positions of the conjugated π -system [1–3]. In order to investigate structure–property relationships, we systematically introduced five-membered heterocycles with more pronounced acceptor character into the parent EC n Ts **1**. Novel mixed oligoheterocycles **2–11** (Fig. 3) containing thiazole, 1,3,4-thiadiazole, furan, oxazole, and 1,3,4-oxadiazole units were synthesized and characterized [9]. On the other hand, incorporation of phenylated,

benzo[*c*]-anellated, and spirofluorenyl-substituted thiophene units led to the oligothiophenes **12–16** (Fig. 3) exhibiting excellent solubilities and film-forming properties. The synthesis of these oligomers was either achieved by transition metal-catalysed cross-coupling reactions or by the use of acyclic precursor molecules.

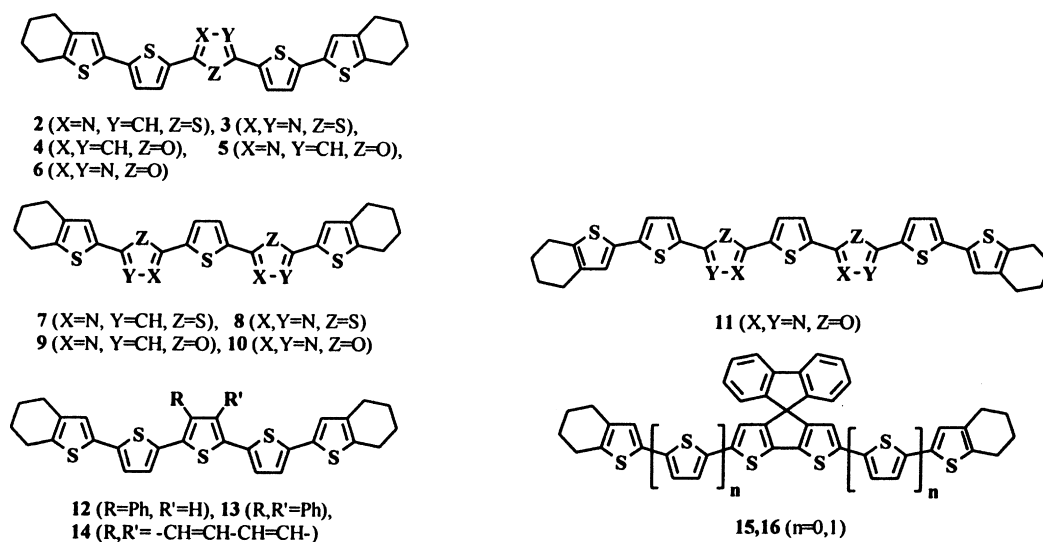


Fig. 3 Chemical structures of a series of mixed oligoheterocycles **2–11** and a series of substituted oligothiophenes **12–16**.

The characterization of the optical and electrochemical properties of the novel oligomers gave valuable information about their electronic structure and clearly revealed the influence of the heteroatoms in compounds **2–11** and the substituents in **12–16** on the electronic properties [10]. Corroborated by semi-empirical calculations, it became very evident that the introduction of nitrogen atoms rendered the oxidation of oligoheterocycles **2–11** more difficult, while reduction was facilitated stepwise. In particular, in the oxygen-containing systems, a hypsochromic shift of the longest wavelength absorption and emission was observed, along with a significant enhancement of the emission intensity both in solution and in the solid state. Within the series, the highest fluorescence quantum yield was measured for oxadiazole **6** exhibiting a value of 85% in solution, which is more than a factor of two greater than that of the parent compound EC5T **1**. The highest occupied–lowest unoccupied molecular orbital (HOMO–LUMO) energy differences determined from the optical and electrochemical measurements correspond qualitatively well with values obtained from semi-empirical calculations.

In the series of oligothiophenes **12–16**, phenyl substitution causes only insignificant changes of optical transitions and redox potentials. The incorporation of spiro-units, however, strengthens the effective conjugation by planarization of the central bithiophene unit, reflected in a bathochromic shift of its absorption and emission as well as lower oxidation potentials. Finally, benzo[*c*]-anellation strongly affects the electronic structure and causes a significant decrease of the energetic separation of the frontier orbitals.

Solubility studies on both series clearly revealed that, due to π – π interactions of the molecules in the solid state, oligoheterocycles **2–11** exhibit a rather low solubility, providing ideal candidates for vacuum evaporated thin film OLEDs. In contrast, oligothiophenes **12–16** and, in particular, spiro-substituted derivatives **15** and **16** are excellently soluble in common organic solvents and can be processed from solution by spin- or dip-coating techniques or incorporated in the polymeric matrices.

With respect to an application in OLEDs, the intensity and durability of the electroluminescence and the relative stability of the radical ions involved were examined for several oligomers by electrogenerated chemiluminescence. Spiro-compound **16** revealed the most durable and most intense electrochemiluminescence of all the systems investigated. First, experiments on multilayer composite

OLEDs incorporating oligomers **13**, **15**, or **16** in the active emission layer showed very promising device characteristics, including a yellow to blue electroluminescence, good brightness/current ratios and efficiencies at low threshold voltages (8 V), and luminances up to 3100 cd/m² (Fig. 4).

Since, for applications in electronic devices, the arrangement of the active molecules in the solid state is a very important issue, X-ray structure analysis provides valuable information about structural and intermolecular parameters. In this respect, single crystals of oligoheterocycles EC5T **1** and oxadiazoles **6** [9a] and **11** [9b], suitable for X-ray structure determination, could be grown by sublimation in a gradient-tube furnace. Oxadiazole oligomers **6** and **11** are packed in slipped π -stacks, whereas parent compound EC5T **1** shows a unique herringbone packing motif, not yet observed in oligothiophenes, with both edge-to-face as well as aromatic π - π interactions. All oligomers exhibited statistically distributed *syn*-conformations of the terminal thiophene rings. In oxadiazole **6**, the terminal rings are even preferentially *syn*-arranged. The molecular planes of oligomers **1** and **6** surprisingly show a very unusual u-type bending that was confirmed theoretically (Fig. 4).

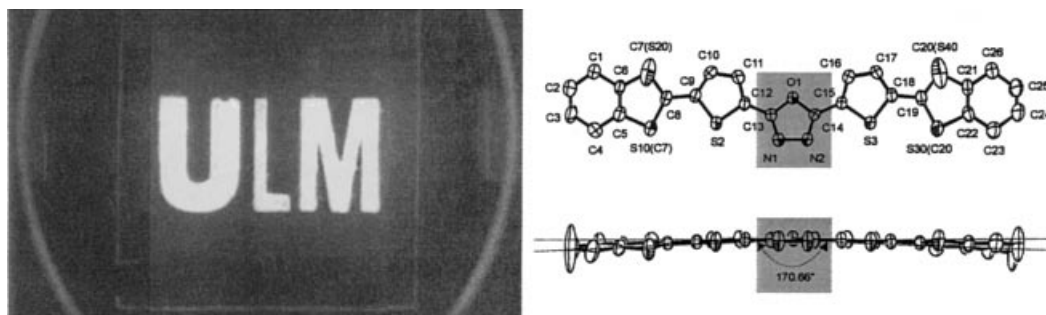


Fig. 4 Multilayer OLED [ITO/TPD(50 nm)/PBD(45.5%^{wt}):PMS(45.5%^{wt}):**13**(9%^{wt}) (60 nm)/Ca/Al] incorporating oligothiophene **13** as active emitting component (left). X-Ray structure analysis of oxadiazole oligoheterocycle **6** showing an ORTEP front (right, top) and side (right, bottom) view of the molecule. Interestingly, a rather unusual *syn*-orientation of the terminal thiophene units and a u-type bending of the molecule, exhibiting a curvature of about 5° at either end, are determined. TPD: *N,N'*-Diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine; PBD: 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole; PMS: poly(α -methylstyrene).

Modification of the electronic properties of 'end-capped' oligothiophenes by metal coordination

Recently, it was shown that the coordination of transition metals to an oligothiophene core leads to pronounced alterations of the (electronic) properties [11]. The metal centres have either been attached to an η^6 -fashion at terminal α - α' -phenyl substituents or were directly η^5 -bound to the terminal thiophene units. In analogy to the series of 'end-capped' oligothiophenes EC_{*n*}T **1**, we synthesized a homologous series of 'benzo-capped' derivatives Bu₄BC_{*n*}T **17** (*n* = 2–6) including butyl side chains due to solubility reasons (Fig. 5). They were used as conjugated ligands for novel oligothiophene metal π -complexes [12]. In contrast to other examples [11] the planar and stiff terminal benzo[*b*]thiophene unit should provide good stability and an optimal influence of the metal fragments on the electronic properties.

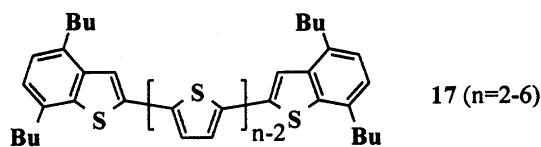


Fig. 5 Chemical structure of a series of 'benzo-capped' oligothiophenes Bu₄BC_{*n*}T **17** (*n* = 2–6).

The synthesis started with the Grignard reagent of 2-bromo-4,7-di-*n*-butylbenzo[*b*]thiophene, which was cross-coupled with α - α' -dibromo(oligo)thiophenes under nickel(0) catalysis to provide Bu₄BC_{*n*}T **17** in moderate to good yields (28–69%). Mono- and doubly metallated oligothiophenes were effectively formed by the reaction of the ligands with one or two equivalents of [CpRu(CH₃CN)₃]PF₆. The resulting

novel metal complexes $[(\text{CpRu})(\eta^6\text{-Bu}_4\text{BCnT})](\text{PF}_6)$ **18** and $[(\text{CpRu})_2(\eta^6, \eta^6\text{-Bu}_4\text{BCnT})](\text{PF}_6)_2$ **19** were purified by reprecipitation, and are typically stable in air as well as excellently soluble in polar solvents, such as dichloromethane and 1,2-dichloroethane, and coordinating solvents, such as acetone (Fig. 6).

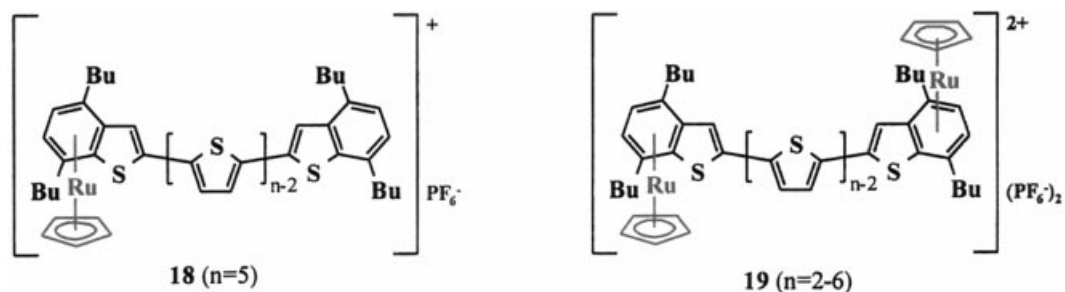


Fig. 6 Chemical structures of the monometallic ‘benzo-capped’ oligothiophene π -complex **18** ($n = 5$) and dimetallic π -complex **19** ($n = 2\text{--}6$).

Various two-dimensional nuclear magnetic resonance (2D NMR) spectroscopic experiments enabled the assignment of all ^1H and ^{13}C resonances in comparison to the non-complexed Bu_4BCnT **17**. The CpRu^+ fragments are exclusively η^6 -bound to the anellated benzene rings. Due to the influence of the metal, the proton resonances of the terminal benzo[b]thiophene units are strongly shifted upfield, whereas resonances of the central oligothiophene units are shifted downfield. Further structural elucidation was achieved by X-ray structure analysis of bismetallated π -complex **19** ($n = 5$) comprising a quinquethiophene core, which was obtained as small ruby crystals grown by recrystallization from dichloromethane-diethyl ether mixtures. Views of the molecule in Fig. 7 (left) verify the composition of the molecule. The oligothiophene core is nearly coplanar, exhibiting small interplanar angles (5.0° and 9.4°). As in the case of oxadiazole oligoheterocycle **6** rather unique *syn*-conformations of the terminal benzo[b]thiophene units with respect to the central all-*anti*-terthiophene moiety are found. In accordance with the NMR assignments, the CpRu^+ fragments are η^6 -coordinated to the terminal benzene rings and not η^5 to any thiophene ring. Interestingly, the two metal fragments are directed towards the opposite site with respect to the oligothiophene plane, representing one of two possible isomers. Simultaneously, the butyl side chains on each benzo[b]thiophene unit are directed in the opposite direction with respect to the coordinated metal. The distances $\text{Ru}\text{--}\text{C}5/\text{C}6$ are found to be shorter than $\text{Ru}\text{--}\text{C}8/\text{C}9$ indicating a transversal displacement of the metal atom by 0.07 \AA from the centre of the benzene ring to the ends of the molecule. As a consequence, bonds $\text{C}2\text{--}\text{C}3$, $\text{C}3\text{--}\text{C}8$, and $\text{S}1\text{--}\text{C}9$ are longer than expected; additionally, the corresponding bond angles are distorted.

In comparison to the non-complexed oligothiophenes Bu_4BCnT **17**, the electronic properties of π -metal complexes **19** were determined by optical measurements and by cyclic voltammetry. Metallation of the oligothiophene core typically causes, in the absorption spectrum, a displacement of the unstructured $\pi\text{--}\pi^*$ transition to lower energies. In comparison to the parent Bu_4BCnT **17**, in the emission spectra, the fluorescence of π -metal complexes **19** is strongly quenched due to a strong metal–ligand interaction. Electrochemical characterization of Bu_4BCnT **17** generally reveals two fully reversible oxidation waves corresponding to two one-electron transfer steps, whereas typically no reduction process can be observed in the negative potential regime ($E \geq -2 \text{ V vs. Fc/Fc}^+$) (Fig. 7, right). Due to the electron-withdrawing character of the metal fragments, oxidations of complexes **19** are shifted to more positive potentials. Additionally, in the cyclic voltammograms of **19** reversible two-electron reduction waves arise at potentials ranging from $E^\circ = -1.62 \text{ V}$ to $-1.80 \text{ V vs. Fc/Fc}^+$ which correspond well to values obtained for other $[\text{CpRu}(\text{arene})]\text{PF}_6$ salts [13]. From these results, one can clearly deduce that the oxidation processes are located on the oligothiophene core, whereas reductions occur at the metal fragments. Since no pronounced splitting of the reduction wave could be determined, the ruthenium centres evidently exhibit rather low interactions *via* the conjugated oligothiophene bridge.

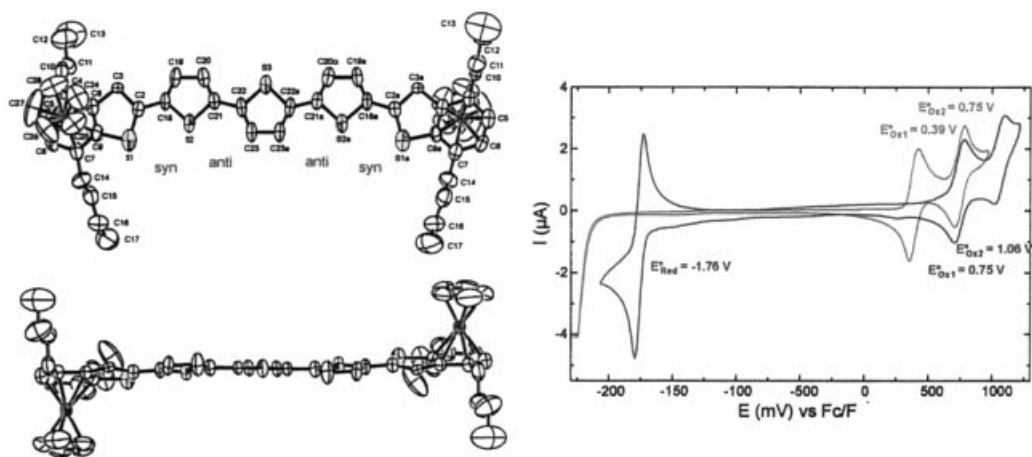


Fig. 7 ORTEP front view of dimetallic oligothiophene π -complex **19** ($n = 5$) showing atomic labeling, 50% thermal ellipsoids (left, top). Side view of **19** (left, bottom). The PF_6^- counter ions have been omitted for clarity. Cyclic voltammograms of dimetallic π -complex **19** ($n = 5$) (black line) in comparison to the non-metallated ligand **17** ($n = 5$) (grey line) ($c = 10^{-3}$ mol/l substrate in $\text{CH}_2\text{Cl}_2/\text{TBAHFP}$ (0.1 M), $\nu = 100$ mV/s; Pt disc working electrode, Pt wire counter electrode, Ag/AgCl reference electrode internally calibrated with the Fc/Fc⁺ couple). (TBAHFP: tetra-*n*-butylammoniumhexafluorophosphate or Bu_4NPF_6 .)

End-capped oligothiophenes functionalized with molecular recognizing groups

Recent attention in host–guest chemistry has been focused on the combination of molecular receptors with redox active moieties. On the one hand the complexation ability of the host could be electrostatically affected by the oxidation state of the electrophore and, on the other hand, the molecular recognition process could lead to a change in the electronic properties of the functional group, i.e. a shift in redox potentials or optical transitions [14]. In this respect, it was recently demonstrated that the selective complexation of alkali ions strongly influences the electrochemical response of crown ether-functionalized polythiophenes [15] or polypyrroles [16] proving that a chemical information can be transduced into an electrical signal. As the mechanism of how the host–guest interaction influences the electronic properties of the conjugated polymers and *vice versa* is not well understood, defined and soluble oligomeric model compounds excluding any bulk effects of the polymers would be highly desirable.

In this context, we synthesized a series of novel ‘end-capped’ oligothiophenes **20** comprising molecular recognizing crown ether units of different ring sizes directly linked to the electroactive π -system [17]. Stannylated ‘capped’ thiophenes were cross-coupled with dibrominated crown ether thiophenes under palladium catalysis to provide the crown ether-functionalized oligothiophenes **20** in moderate yields (18–26%). Unfortunately, homocoupling products **EC_nT 1** are formed as major products (Fig. 8).

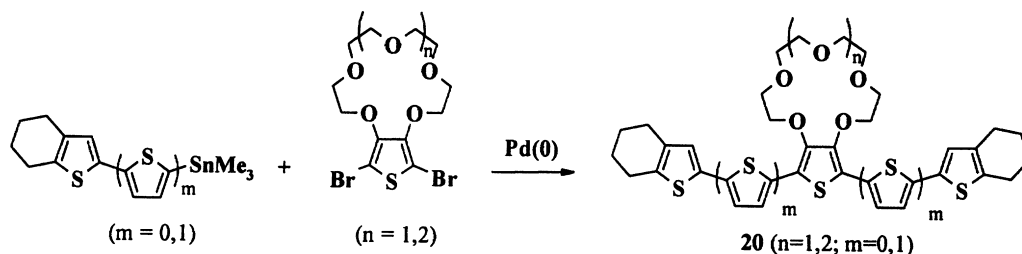


Fig. 8 Synthesis of crown ether-functionalized ‘end-capped’ oligothiophenes **20**.

In comparison to the parent oligomers **EC_nT 1** ($n = 3, 5$), spectroscopic and electrochemical data, as expected, revealed bathochromic shifts of the optical transitions and a shift of the redox transitions to more negative potentials due to the electron-donating character of the crown ether oxygen atoms. The investigation of the electrochemical behaviour of oligomers **20** clearly revealed that the successive

addition of different cations (Li^+ , Na^+ , K^+ , NH_4^+ , Ba^{2+}) leads to a specific modulation of the redox properties of the conjugated oligomer backbone. Typically, the redox waves are substantially shifted to more positive potentials depending on the selective host–guest interaction, the charge/radius ratio of the cation, the length of the oligothiophene core, and the polarity of the solvent used (Fig. 9). The highest anodic shifts were observed for the 18-crown-6 oligomers **20** in the presence of barium ions ($\Delta E = 296 \text{ mV}$) which is extraordinary in comparison to other redox active macrocycles [14]. Competition experiments in the presence of other alkali metal cations showed a remarkable selectivity towards barium ions even in polar solvents.

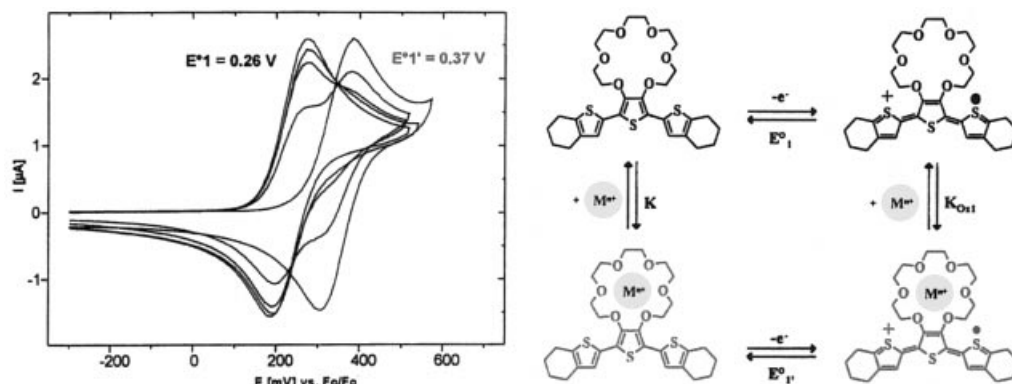


Fig. 9 Electrochemical characterization of 18-crown-6 terthiophene **20** ($n = 2$, $m = 0$) in CH_2Cl_2 (Bu_4NPF_6 (0.1 M), $c = 1 \times 10^{-3} \text{ mol/l}$, scan rate 100 mV/s) in the presence of different equivalents (0 eq, 0.2 eq, 0.5 eq, 0.75 eq, 1 eq) of NaClO_4 (left). Different oxidation and complexation states involved in the equilibria electrochemically investigated (right).

The synthesis and characterization of oligothiophenes **20** clearly demonstrated that the transduction of a selective recognition process into a change in an electrical signal occurs to an even higher extent than in the polymeric counterparts, indicating promising candidates for sensory devices. The effects determined can mainly be attributed to direct electrostatic interactions between the complexed ion and the macrocyclic redox centre.

CONCLUSIONS

In summary, we have shown that the functionalization of conjugated oligothiophenes with a well-defined length, constitution, and conformation leads to valuable structure–property relationships and to promising novel materials for technological applications.

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REFERENCES

- (a) *Handbook of Oligo- and Polythiophenes* (D. Fichou, ed.), Wiley-VCH, Weinheim (1999). (b) P. Bäuerle. Oligothiophenes. In *Electronic Materials: The Oligomer Approach* (G. Wegner, K. Müllen, eds), pp. 105–197. Wiley-VCH, Weinheim (1998). (c) J. Roncali. *Chem. Rev.* **97**, 173–205 (1997).
- R. E. Martin, F. Diederich. *Angew. Chem. Int. Ed.* **38**, 1350–1377 (1999).
- J. M. Tour. *Chem. Rev.* **96**, 537–553 (1996).
- G. Horowitz. *Adv. Mater.* **10**, 365–377 (1998).
- F. Geiger, M. Stoldt, P. Bäuerle, H. Schweizer, E. Umbach. *Adv. Mater.* **5**, 922–925 (1993).
- N. Noma, T. Tsuzuki, Y. Shirota. *Adv. Mater.* **7**, 647–648 (1995).

- 7 P. Bäuerle. *Adv. Mater.* **4**, 102–107 (1992).
- 8 H. Neureiter, W. Gebauer, C. Väterlein, M. Sokolowski, P. Bäuerle, E. Umbach. *Synth. Met.* **67**, 173–176 (1994).
- 9 (a) U. Mitschke, E. Mena-Osteritz, T. Debaerdemaeker, M. Sokolowski, P. Bäuerle. *Chem. Eur. J.* **4**, 2211–2224 (1998). (b) U. Mitschke, T. Debaerdemaeker, P. Bäuerle. *Eur. J. Org. Chem.* 425–437 (2000).
- 10 P. Bäuerle, U. Mitschke, E. Mena-Osteritz, M. Sokolowski, D. Müller, M. Groß, K. Meerholz. *Proc. SPIE Int. Soc. Opt. Eng.* **3476**, 32–39 (1998).
- 11 (a) D. D. Graf, N. C. Day, K. R. Mann. *Inorg. Chem.* **34**, 1562–1575 (1995). (b) D. D. Graf, K. R. Mann. *Inorg. Chem.* **36**, 141–149 (1997). (c) D. D. Graf, K. R. Mann. *Inorg. Chem.* **36**, 150–157 (1997).
- 12 G. Grüner, T. Debaerdemaeker, P. Bäuerle. *Chem. Commun.* 1097–1098 (1999).
- 13 O. V. Gusev, M. A. Ievlev, M. G. Peterleitner, S. M. Peregudova, L. I. Denisovich, P. V. Petrovskii, N. A. Ustynyuk. *J. Organomet. Chem.* **534**, 57–66 (1997) (*E* vs. SCE corresponds to *E* vs. Fc/Fc⁺ – 0.4 V).
- 14 P. L. Boulas, M. Gómez-Kaifer, L. Echegoyen. *Angew. Chem. Int. Ed.* **37**, 216–247 (1998).
- 15 (a) P. Bäuerle, S. Scheib. *Adv. Mater.* **5**, 848–853 (1993). (b) M. J. Marsella, T. M. Swager. *J. Am. Chem. Soc.* **115**, 12214–12215 (1993). (c) P. Bäuerle, S. Scheib. *Acta Polym.* **46**, 124–129 (1995). (d) S. Scheib, P. Bäuerle. *J. Mater. Chem.* **9**, 2139–2151 (1999).
- 16 H. K. Youssoufi, M. Hmyene, F. Garnier, D. Delabouglise. *J. Chem. Soc., Chem. Commun.* 1550–1552 (1993).
- 17 G. Rimmel, P. Bäuerle. *Synth. Met.* **102**, 1323–1324 (1999).