

Poly(thiophenes) derivatized with linear and macrocyclic polyethers: from cation detection to molecular actuation

Dora Demeter · Philippe Blanchard ·
Ion Grosu · Jean Roncali

Received: 15 November 2007 / Accepted: 25 February 2008 / Published online: 22 March 2008
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Abstract The association of linear or macrocyclic polyethers with the electronic properties of the π -conjugated polythiophene backbone leads to functional conducting polymers that exhibit metal cation dependent electronic properties. Based on this concept, various classes of cation sensors have been proposed and investigated for almost two decades. The interactions of metal cations with linear or macrocyclic polyether functional groups lead to modifications of the electronic properties of the π -conjugated backbone through various mechanisms including direct electronic effects on a single conjugated chain, collective electrochemical processes, or conformational changes. Conjugated polymers and oligomers representative of these various processes are discussed with an emphasis on recent examples of derivatized conjugated systems in which the interactions between metal cations and polyether groups serve as driving force to create molecular motion in conjugated systems.

Keywords Polythiophene · Crown ether · Complexation · Actuation

Introduction

Sensors based on extended thiophene-based π -conjugated systems has been a focus of sustained academic and technological interest for more than two decades [1–4]. Despite the huge variety of sensors based on conjugated systems proposed and investigated, all of them have in common the fact that their sensing mechanism resorts more or less directly to an alteration of the electronic properties of the extended π -conjugated system.

In their neutral state, conjugated polythiophenes are large band gap semiconductors ($E_g \sim 1.80$ – 2.00 eV) [5]. Reduction, or in most cases oxidation, of the conjugated systems results in the creation of charge states associated with a local geometrical relaxation of the structure namely polarons or bipolarons that confer electrical conductivity on the material. Since this so-called “doping process” is chemically or electrochemically reversible, a first generation of rather rudimentary sensors has been based on the variation of the electrical resistance of conjugated polymers in the presence of a chemical species e.g. nitrogen dioxide, or ammonia capable to induce changes in the doping level. Sensors based on this principle have been considered at an early stage [6, 7] but the interest in this first generation of sensors rapidly declined because of their lack of sensitivity, selectivity and reproducibility.

A specificity of conjugated polymers based on aromatic units like poly(thiophenes) lies in the extreme sensitivity of their electronic properties on changes in the geometry of the conjugated system [5]. Whereas a fully planar geometry leads to optimal electron delocalization, any departure from planarity caused by a local torsion of the conjugated system induces a localization of π -electrons and thus an increase of the energy gap with

D. Demeter · P. Blanchard · J. Roncali (✉)
CNRS, CIMA, Linear Conjugated Systems Group,
University of Angers, 2 Bd Lavoisier, 49045 Angers, France
e-mail: jean.roncali@univ-angers.fr

D. Demeter · I. Grosu
Organic Chemistry Department and CCOCCAN,
“Babes-Bolyai” University, 11 Arany Janos str, 400028
Cluj-Napoca, Romania

changes in the optical and redox properties of the system. This mechanism is at the origin of many examples of sensors in which interactions of the polymer with a target species generate a modification of the geometry of the conjugated system and thus of its electronic properties. This principle presents several potential advantages over the old “variable resistor” concept in terms of stability and reproducibility and allows to read the sensing event by means of various optical and electrochemical techniques both in solution and in the solid state.

During the past two decades this concept has been widely developed and a large number of conjugated polymers tethered by functional groups specifically designed to recognize a huge variety of chemical or biochemical species have been synthesized and investigated in view of evaluating their sensing properties [1–4].

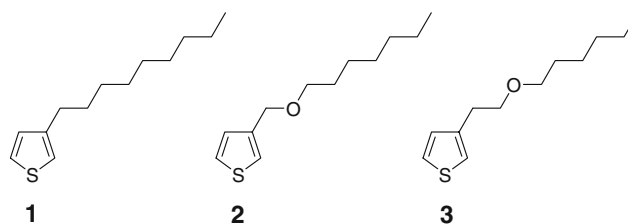
Among the numerous classes of functional conjugated polymers designed for sensor applications, polythiophenes functionalized by linear or macrocyclic polyethers form a specific class of materials combining enhanced hydrophilicity with metal-cation sensitive electronic properties. Intensive studies on these materials have demonstrated that the interactions between these functional polymers or oligomers and metal cations can give rise to various interesting combinations of electronic and geometrical effects. More specifically, in several cases, it has been shown that the interactions of the attached polyether with metal cations could generate large geometrical changes. The goal of this short review is to present a brief survey of this particular class of functional conjugated systems in order to try to identify possible directions for future research with an emphasis on the potentialities offered by these compounds for the generation of molecular motion.

Polythiophenes derivatized with linear polyether chains

Polythiophenes derivatized by linear polyether chains are among the very first classes of functional polythiophenes synthesized [8–12]. Initial work in this area was motivated by the development of electroactive polymers potentially capable to act as cation sensors but also by the search for more polythiophenes with enhanced hydrophilicity [11]. The polymerization of thiophenes derivatized by polyether chains is in general more delicate than for the parent alkyl-thiophenes. In this regard, the position of the first oxygen atom in the side chain has been identified as a crucial parameter which controls both the reactivity

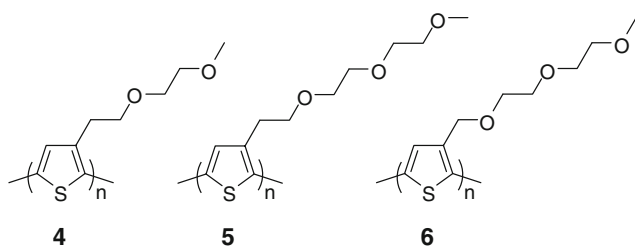
of the monomer and hence the maximum degree of polymerization of the polymer, as well as the electrical, electrochemical and optical properties of the final polymer.

When directly attached at the 3 or 3 and 4 positions of the thiophene ring, an ether group exerts a strong electron-donating mesomeric effect which produces an increase of the HOMO level and hence a decrease of the oxidation potential of the thiophene ring. This effect leads to a stabilization of the corresponding cation radical at the 2-position adjacent to the methoxy group and thus to a drop of reactivity of the 5 position which strongly limits the growth of the polymer chain [12]. A noticeable exception is 3,4-ethylenedioxythiophene (EDOT) which presents a unique combination of reduced oxidation potential and high reactivity of the 2 and 5 positions [13].



When introduced at the 3-position of the thiophene ring after one methylene group, the ether group exerts an inductive electron-withdrawing effect which raises the oxidation potential of the thiophene ring by ca 0.15 V [8,10]. However, this increased reactivity of the cation radical has deleterious consequences for the efficiency of the electropolymerization process and for the electronic properties of the resulting polymer. Thus, compared to poly(3-nonylthiophene) (1), poly(2) shows an oxidation potential higher by 200 mV, an absorption maximum hypsochromically shifted from 540 to 435 nm and a three orders of magnitude lower conductivity. All these results indicate a considerable decrease of the effective conjugation length [10]. Finally, the introduction of two methylene groups before the first oxygen atom as in compound 3, neutralizes its electronic effects thus allowing the thiophene ring to recover an oxidation potential identical to that of 3-alkylthiophenes while the resulting polymers shows electronic properties quite similar to those of their alkyl-substituted analogs [8, 10].

The characterization of the polymers synthesized taking these results into account has shown that increasing the number of ether groups in the side chain strongly increases the hydrophilicity, thus leading to polymers (4, 5) that are fully electroactive in aqueous media [11].



Poly[3-(3,6-dioxaheptyl)thiophene] (**4**) and the parent poly(**5**) are generally acknowledged as the first examples of conjugated polymers on which cation dependent electrochemical properties have been observed [9, 10]. In the presence of tetrabutylammonium cation in acetonitrile the cyclic voltammogram (CV) of poly(**4**) displays two redox systems at ca 0.50 and 0.80 V vs SCE. Replacing Bu_4N^+ by Li^+ produces a 100–150 mV negative shift of the first oxidation potential of the polymer. This shift increases up to 250 mV at high concentrations of Li^+ . Optical and spectroelectrochemical experiments have shown that this potential shift is accompanied by a 2–13 nm bathochromic shift of the absorption maximum of the polymer and by an exaltation of the vibronic fine structure in the optical spectrum [14–16]. These results have been interpreted as the consequences of the combined effects of cation complexation by the side polyether chains namely (i) a planarization of the conjugated backbone, and (ii) a rigidification of the polymer network through “ionic crosslinking”. Changing the solvent to water led to a significant blue shift of the absorption spectrum which was attributed to a distortion of the conjugated backbone by steric crowding due to the large effective volume of the solvated Li^+ [11, 15].

Solvation-induced steric effects were also observed when immersing films of poly(**4**) in a strong hydrogen-bonding solvent such as hexafluoroisopropanol. In such case, solvation of the polyether side chain indirectly produces a torsion of the conjugated backbone due again to steric crowding which results in considerable loss of conjugation with a 140 nm blue shift of the absorption maximum [16]. Furthermore, experiments carried out on films that have been cycled in the presence of Bu_4N^+ or Li^+ provided first evidences of solid-state ionochromism on polythiophene derivatives [16].

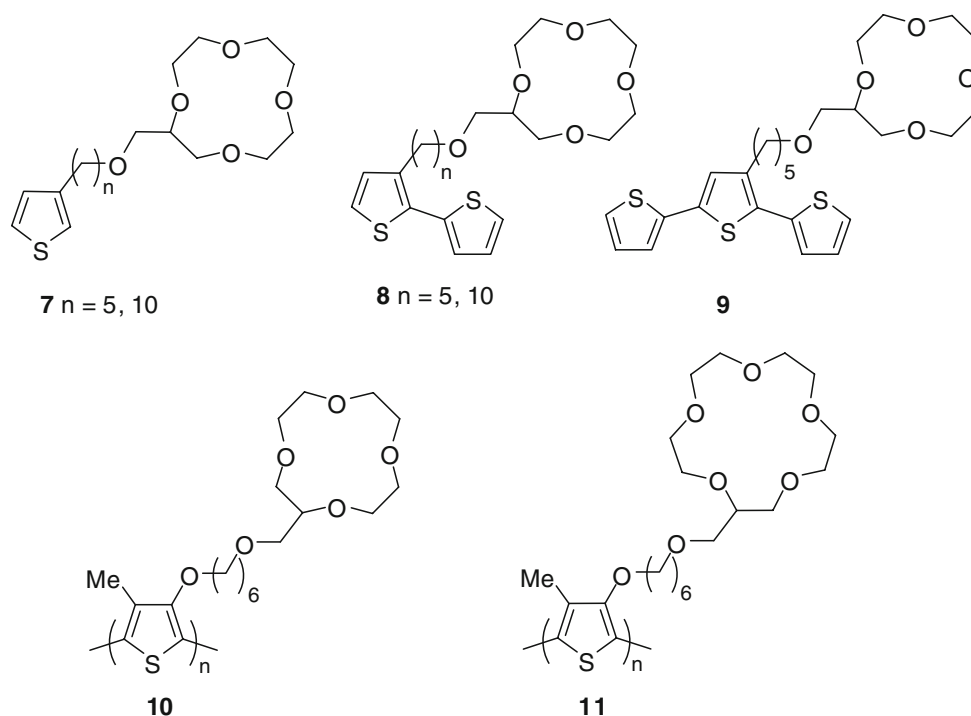
Ionochromic effects have also been observed in the case of the chemically synthesized regio-regular polymer **6** [17]. Interactions of the polymer with Pb^{2+} and Hg^{2+} in chloroform solutions produces a loss of conjugation with complete disappearance of the absorption band in the visible region. It was proposed that this effect was not associated with cation complexation by the polyether side chain but resulted from a direct coordination of the metal to the thiophene sulfur atom [17].

Crown-ether derivatized polythiophenes

The first examples of polythiophenes functionalized with covalently attached crown ethers have been reported by Bäuerle and coworkers who synthesized mono-, bi- and tert-thiophene substituted with pendant 12-crown-4 receptor linked to the thiophene ring via an alkyl spacer (**7–9**) [18]. Electropolymerization of monomeric precursors (**7**) remained essentially unsuccessful. Precursors based on bi- and terthiophenes (**8, 9**) were successfully polymerized but the best results were obtained with bithiophenic precursors (**8**) which led to extensively conjugated polymers. The analysis of the electrochemical properties of these polymers showed that addition of increasing amounts of Li^+ , Na^+ or K^+ produces a steady positive shift of the anodic peak potential and a decrease of the electroactivity expressed by the amount of charge reversibly exchanged upon redox cycling. The maximum sensitivity towards Li^+ was observed with poly(**8**) with a short alkyl spacer. These effects were observed to a lesser extent in the case of poly(**9**), as could be expected from the lower ratio crown ether/thiophene. To interpret these results the authors have proposed that cation complexation by the crown ethers results in the formation of a positively charged “shell” surrounding the conjugated backbone. This shell acts as a potential barrier that impedes the migration of the charge-compensating counter-anions during the electrochemical doping process of the polymer and thus give rise to the development of a Donnan potential [18].

Polythiophenes derivatized by crown ethers attached at the 3-position of thiophene by an alkoxy linker (**10, 11**) have been synthesized chemically [19, 20]. In acetone solution poly(**10**) exhibits a ionochromic behavior with a red shift of the absorption maximum from 444 to 544 nm in the presence of Li^+ , Na^+ or K^+ . The largest effect was observed in the presence of Na^+ and the smallest with Li^+ . This unexpected results were attributed to the formation of 2:1 sandwiches with Na^+ and K^+ which results in larger conformational changes in the conjugated backbone than in the case of a 1:1 complex [19, 20].

In order to improve the electronic communication between the π -conjugated system and the complexing site, Bäuerle and coworkers have developed a series of polymers derived from mono- bi- and terthiophene in which the complexing macrocycle was fused to the conjugated system by attaching a polyether loop between the 3 and 4 positions of the thiophene ring (**12–14**) [21]. Only compounds **12** and **13** based on thiophene and bithiophene could be efficiently electropolymerized while the trimer **14** could not. Whereas poly(**13**) was practically insensitive to the presence of alkali cations, the CV of poly(**12**) showed a large positive shift of the anodic peak potential in the



presence of Na^+ , in agreement with the size of the cavity of 15-crown-5 ether. This change in the electrochemical behavior was ascribed to the combined effects of a more difficult diffusion of the counter anion, and to the decrease of the electron-donating properties of the two ether groups after metal cation complexation. These combined effects resulted in larger electrochemical responses than those observed for polymers with pendant crown ether (**7–9**).

The same group has reported a series of oligothiophenes with fused crown ether and pendant polyiodants (**15–17**). The analysis of the cyclic voltammetric response in the presence of various cations showed that oligomers with a 18-C6 unit exhibit the largest positive shifts of the oxidation peak in the presence of K^+ whereas those containing a 15-C5 were more sensitive to Li^+ . Experiments carried out in the presence of equimolar mixtures of various cations allowed to conclude that oligomers **15** with a 15-C5 unit were able to selectively recognize Ba^{2+} in the presence of alkali cations [22,23].

Berlin et al. have synthesized terthiophenes **18** and **19** with a 18-crown-6 unit fused to the median thiophene ring. Electrochemical quartz crystal microbalance analyses, showed that the complexation constants of the macrocyclic crown ether ring towards alkali metal cations was two orders of magnitude lower for the electrogenerated polymers than those typical for 18-crown-6-ether molecules [24].

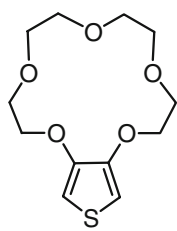
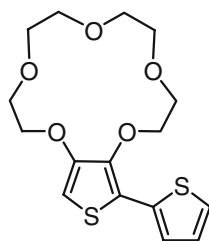
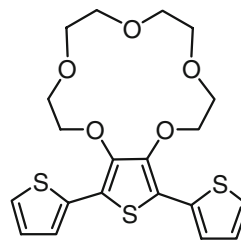
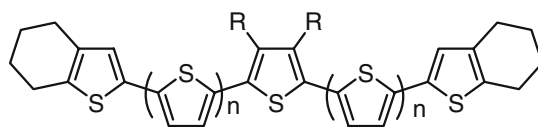
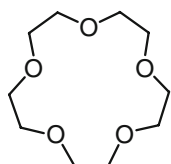
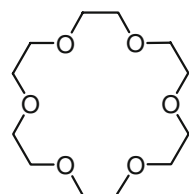
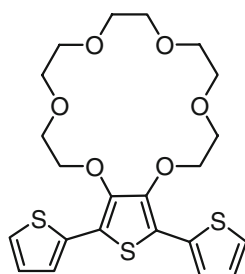
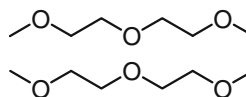
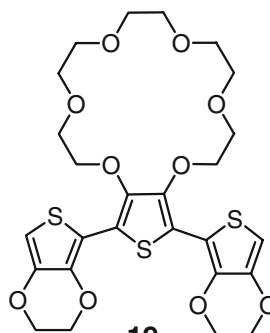
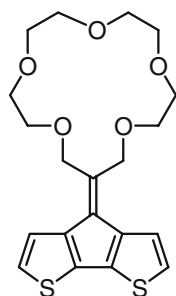
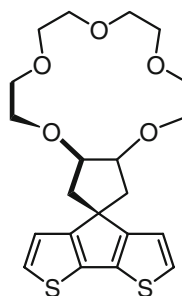
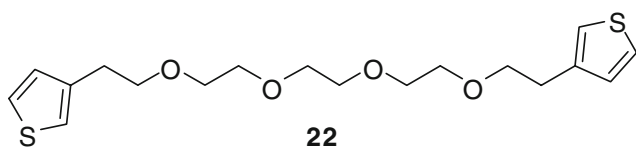
Sannicolò et al. have developed an original class of polymers based on cyclopentabithiophene precursors with

either a 16-C5-ether ring coplanar to the bithiophene moiety (**20**) or a 15-C5 perpendicular to it (**21**) [25]. This design allows to combine good electronic communication between the complexing site and the conjugated system with reduced steric hindrance to planarity. Both precursors were readily electropolymerized into extensively conjugated polymers as confirmed by optical data. The analysis of electrochemical properties of the polymers in the presence of alkali cations showed that whereas poly(**21**) is quite insensitive to the nature of the cationic species, the anodic peak potential of poly(**20**) undergoes a 350 mV positive shift in the presence of Na^+ [25].

Polythiophenes derived from two-site precursors

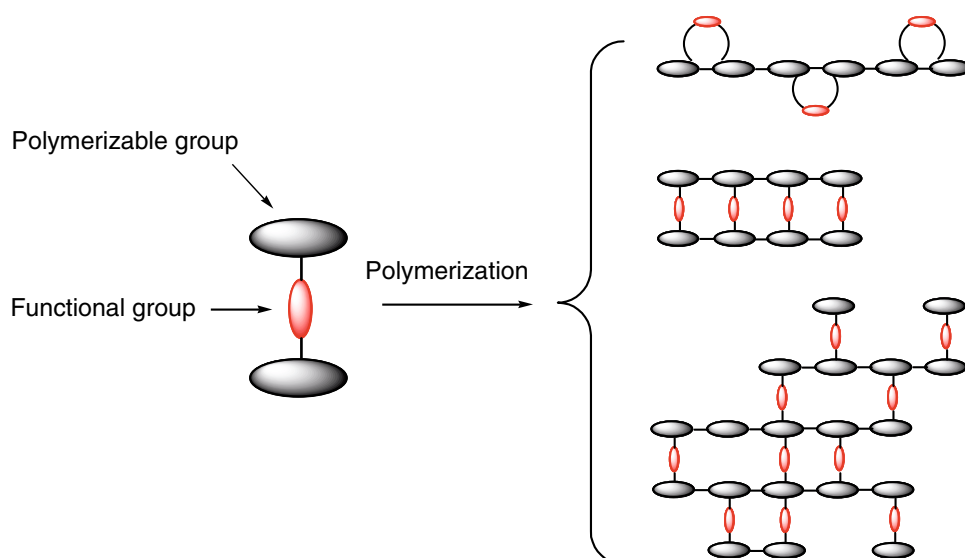
A quite different approach consists in the creation of a macrocyclic cavity between two consecutive thiophene units by polymerizing a precursor involving two polymerizable groups linked by a flexible polyether chain (Scheme 1).

This idea was initially investigated in the case of compound **22** [26]. More recently, other two-site thiophenic precursors based on different polymerizable groups and containing polyether chains of various length (**23–28**) have been synthesized and investigated [27–30].

**12****13****14****15** R-R =**16** R-R =**17** R, R =**18****19****20****21****22**

Although the formation of crown ethers or ladder polymers represent ideal limiting situations, it must be underlined that even in the case of a completely random process, which is the most probable situation, polymerization of two-site precursors will always lead to the

Scheme 1



formation of macrocyclic cavities with two sides constituted by polyether links and the two others by conjugated chains (Scheme 1). Of course, such cavities are potentially capable to interact with guest species either during the polymerization process or after. In the former case, template effects of imprinting effects may be anticipated.

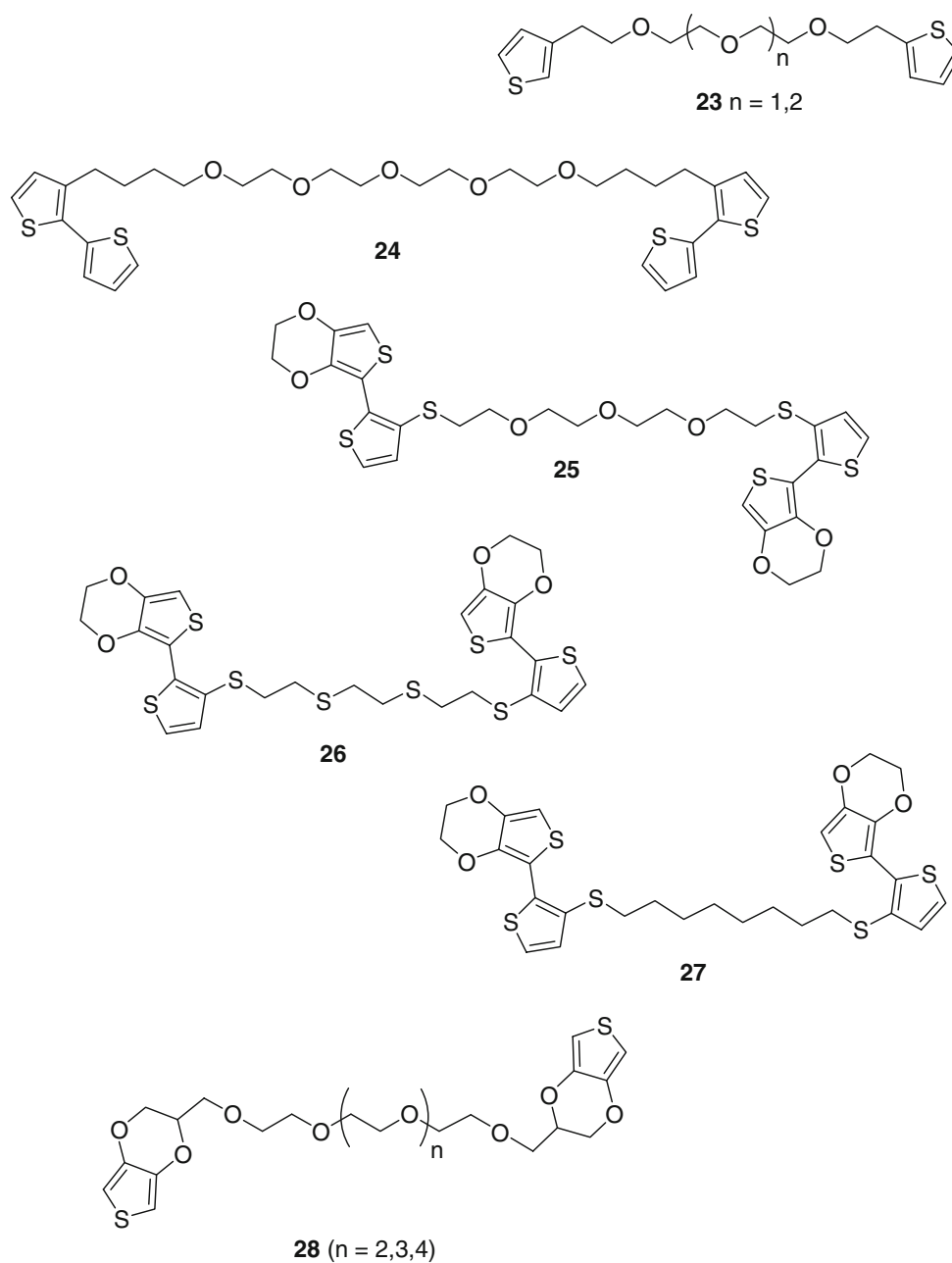
In fact such a template effect has been observed when applying this concept to the synthesis of a related system containing bithiophenic polymerizable groups [28]. Thus, the analysis of the electropolymerization of precursor (**24**) in the presence of Li^+ , Na^+ or Ba^{2+} showed that the nature of the cation present during the polymerization process strongly affects the structure of the resulting polymer. In particular, the electrochemical and optical properties of the polymer synthesized in the presence of Ba^{2+} exhibited a 300 mV decrease of the oxidation potential together with a significant red shift of the absorption maximum compared to the polymer synthesized in the presence of Bu_4N^+ [28]. These results thus provide first evidences for a metal cation template effect during electropolymerization. More recently, the same approach has been extended to the electropolymerization of precursors based on hybrid bithiophenic structures containing an EDOT unit (**25–27**) [29]. Electrochemical investigations carried out in the presence of various metal cations showed that polymers **26** and **27** present some sensitivity towards cadmium and lead cations. However, the largest positive shifts of the anodic peak potentials were observed with polymer **27** which contains only two sulfide groups attached at the internal β -position of the thiophene units. This result thus underlines the predominance of changes in the

electronic effects of the sulfide groups in direct communication with the conjugated system on cation sensitivity [29].

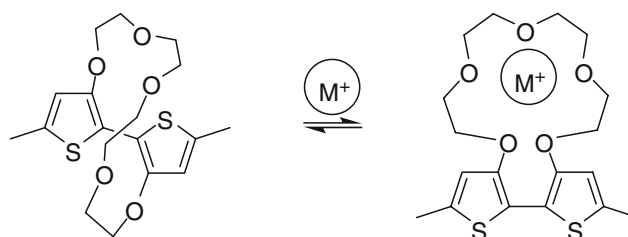
A quite different behavior has been observed for polymers derived from precursors in which two EDOT units are linked by long oligooxyethylene chains (**28**) [30]. The cyclic voltammograms of these polymers recorded in the presence of various metal cations show that depending on the length of the oligooxyethylene linker, doubly charge cations such as Sr^{2+} , Ca^{2+} or Ba^{2+} , produce considerable positive shifts of the anodic peak potentials. Thus, the CV of poly(**28**) ($n = 3$) undergoes a 400 mV positive shift in the presence of Ba^{2+} . These polymers presents several unique properties such as an extreme sensitivity to water. Thus, transferring a film of poly(**28**) ($n = 3$) from acetonitrile to water leads after electrochemical undoping to a 100 nm red shift of the absorption maximum. Furthermore, these polymer films exhibit fast solid-state chromism by simple immersion in acetonitrile solutions containing different cations. Thus removing a film from a MeCN solution of Bu_4N^+ and immersing it into a Ba^{2+} MeCN solution leads to an immediate 80 nm blue shift of λ_{max} . This process is fully reversible and the initial spectrum is restored by immersion in a Bu_4N^+ solution [30].

Poly(thiophenes) with inter-ring macrocyclic crown ethers

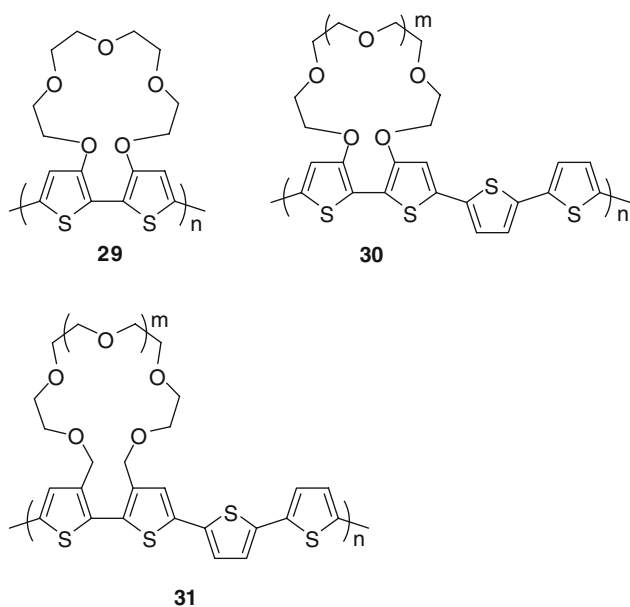
Bithiophenic precursors containing macrocyclic receptor cavities of variable size (**29–31**) have been synthesized by Marsella and Swager [31]. The corresponding polymers



were synthesized by Stille coupling or oxidative coupling in the presence of $\text{Fe}(\text{acac})_3$. The UV-vis spectra of the polymers showed that connecting the polyether loop by methylene groups (**31**) leads to an hypsochromic shift of the absorption maximum of the polymer due to the larger steric hindrance of the methylene groups as compared to oxygen. The cation complexing properties of the polymers were analyzed in acetonitrile solutions in the presence of 0.10 M of Li^+ , Na^+ and K^+ .



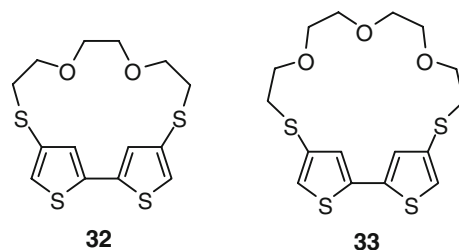
Scheme 2



Addition of Li^+ , Na^+ or K^+ to solutions of the polymers induces a hypsochromic shift of the absorption maximum. This effect was attributed to a transition from a planar conformation of the non-complexed polymer to a more twisted structure when the polyether loop unfolds to adopt an optimal geometry for cation complexation (Scheme 2). The largest effects were observed for polymers **29** and **30** while the less conjugated polymer **31** exhibited little ionochromic activity [31].

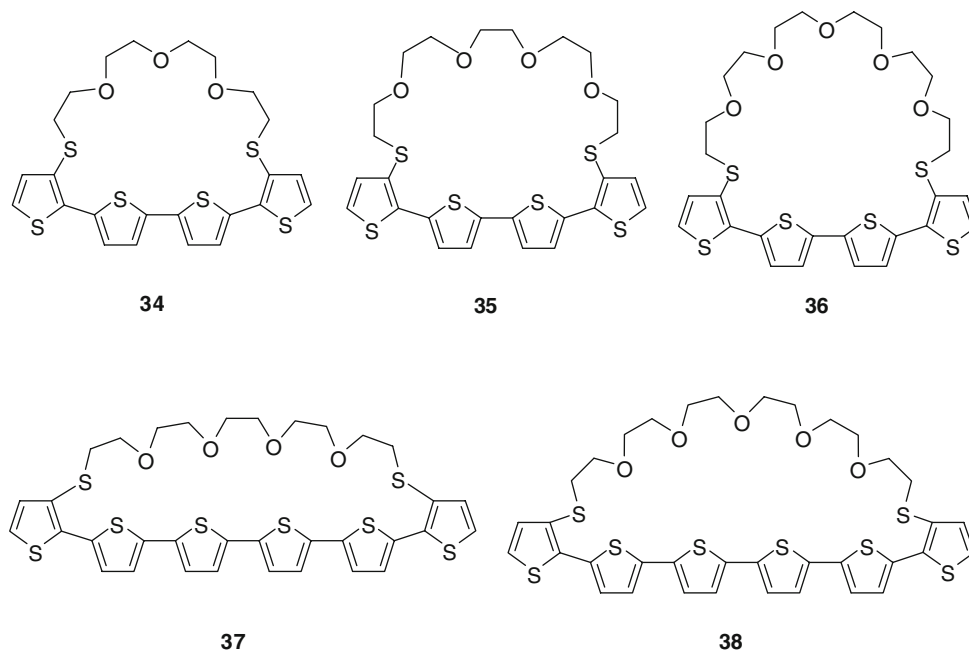
Another class of polymers containing preformed crown ether cavities have been synthesized by electropolymerization of crown annelated bithiophenes **32** and **33** in which the external β -positions are linked together by a polyether

chain connected via a sulfide linkage [32]. The UV–Vis absorption spectra recorded in methylene chloride solutions show that compound **33** absorbs at a shorter wavelength than compound **32**, (306 vs 333 nm) a difference which reflects the larger dihedral angle between the two thiophenes caused by the size of the polyether loop in compound **33**.

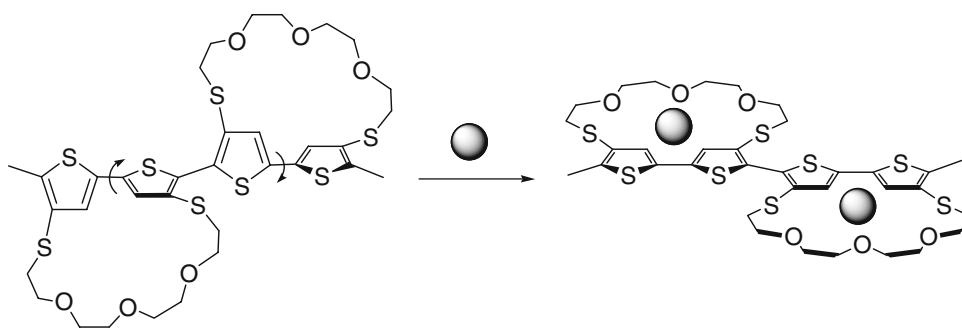


Both compounds were readily electropolymerized into the corresponding polymers. The shorter effective conjugation associated with the more distorted structure of bithiophene **33** was also apparent in the higher oxidation potential of the corresponding polymer. The analysis of the cyclic voltammetric response of the polymers in the presence of various metal cations showed that whereas poly(**32**) is quite insensitive to the presence of metal cations, for poly(**33**) replacing Bu_4N^+ by Li^+ produces a *ca* 100 mV negative shift of the main anodic peak potential. This behavior strongly reminiscent of that of poly(**1**) has been attributed again to a planarization of the conjugated system consecutive to cation complexation (Scheme 3) [32].

The above summarized results show that the cation recognition properties of the various classes of



Scheme 3



polythiophenes derivatized with linear and macrocyclic polyethers resorts to very different concepts and mechanisms including (i) the development of a Donnan potential due to the pinning of the counter anions by the immobilized positive charges of the cations, (ii) purely electrostatic effects involving a decrease of the electron-releasing properties of oxygen or sulfur atoms directly attached to the π -conjugated system and (iii) chemo-mechanical effects in which cation complexation induces geometrical changes which are more or less directly transmitted to the conjugated backbone to in turn modify its conformation and electronic properties. On the basis of this latter mechanism, one can envision to adopt a different point of view by considering cation complexation no longer in terms of sensing properties but as a tool to generate motion at the molecular level.

Cation complexation as driving force for molecular actuation

In order to test this idea, we have synthesized oligothiophenes **34–38** in which a polyether loop is attached at two fixed points of the conjugated backbone. In those systems, metal cation complexation will be used as a driving force to produce geometrical changes in the structure of the conjugated system and hence to modify its electronic properties [33].

The analysis of the cation complexing properties of compounds **34–36** by ^1H NMR (500 MHz) titration experiments with solutions of Li^+ , Na^+ , in 1:1 $\text{CDCl}_3/\text{CD}_3\text{CN}$ showed that alkali cations have essentially no effect on the ^1H NMR spectrum. In contrast, addition of sub-stoichiometric amounts of Ba^{2+} , Sr^{2+} , or Pb^{2+} induces significant changes in the chemical shifts of the aliphatic protons of the polyether chain confirming that complexation essentially occurs within the macrocyclic cavity. The binding constant estimated by treatment of ^1H NMR data show that the compounds form 1:1 complexes with low to moderate binding constants with alkali-earth cations. Definitive evidence for 1:1 complex formation was given by mass spectrometry. As expected, the binding constant increases

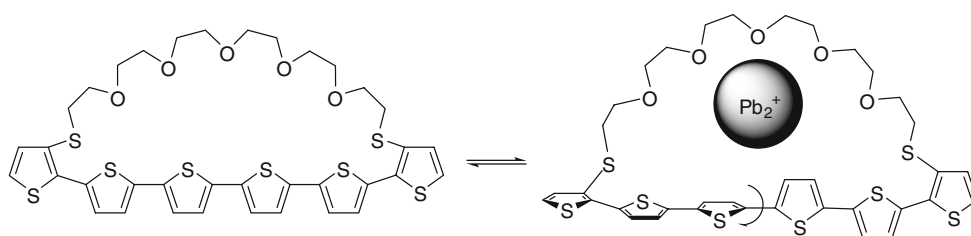
with the size of the macrocyclic cavity and compound **36**, exhibits the largest value ($K = 7200 \text{ M}^{-1}$ for Ba^{2+}) [33].

Unlike open chain sexithiophenes, the optical spectrum of compounds **37** and **38** shows two absorption band around 380 nm and 440 nm. This result indicates the coexistence of two distinct conjugation lengths generated by rotation around a single bond in the middle of the molecule, thus dividing it into two quasi-orthogonal terthiophene segments. The larger intensity of the 380 nm band observed for **37** compared **38** is consistent with a stronger constraint imposed on the 6T chain by the shorter polyether loop. Addition of Pb^{2+} cation to solutions of **37** and **38** produces a decrease of the 440 nm band with a concomitant increase of the 380 nm one around an isobestic point, indicating the interconversion of two distinct species (Scheme 4). The largest changes are observed for **38**, in agreement with the larger degree of freedom of the conjugated chain allowed by the longer polyether loop.

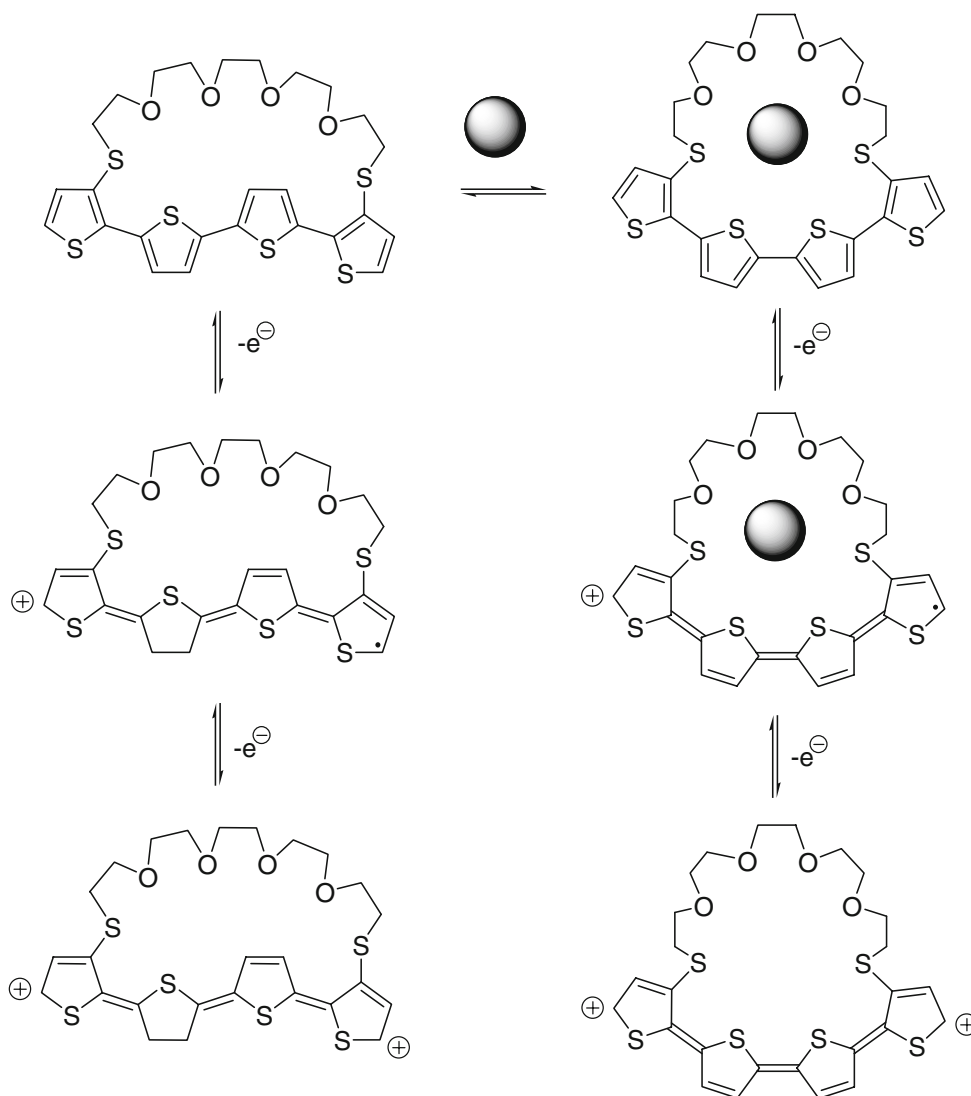
The cation complexing properties of the macrocyclic oligothiophenes **35** and **36** have been investigated by cyclic voltammetry in the presence of Ba^{2+} , Sr^{2+} , or Pb^{2+} . In the absence of metal cation, the CV of compounds **35** and **36** shows two reversible one-electron oxidation processes with redox potentials E^{o1} and E^{o2} at ca 0.90 and 1.10 V, corresponding to the successive generation of the oligothiophene cation radical and dication. Depending on the value of the binding constant, the addition of sub-stoichiometric amounts of metal cation to electrolytic solutions of compounds **35** and **36** produces a slight negative or positive shift of E^{o1} but always a negative shift of E^{o2} .

This unusual behavior has been attributed to the different conformation imposed to the oligothiophene chain by cation complexation. As shown by crystallographic data, in the absence of guest species, the quaterthiophene chain presents an *anti-anti-syn* conformation (Scheme 5, top). Complexation of a metal cation forces the macrocyclic cavity to adopt the optimal geometry for complexation with in particular a reduction of the distance between the two sulfur atoms. This exerts a constraint on the conjugated chain and after the flip of one thiophene ring the systems adopts an *anti-syn-anti* conformation.

Scheme 4

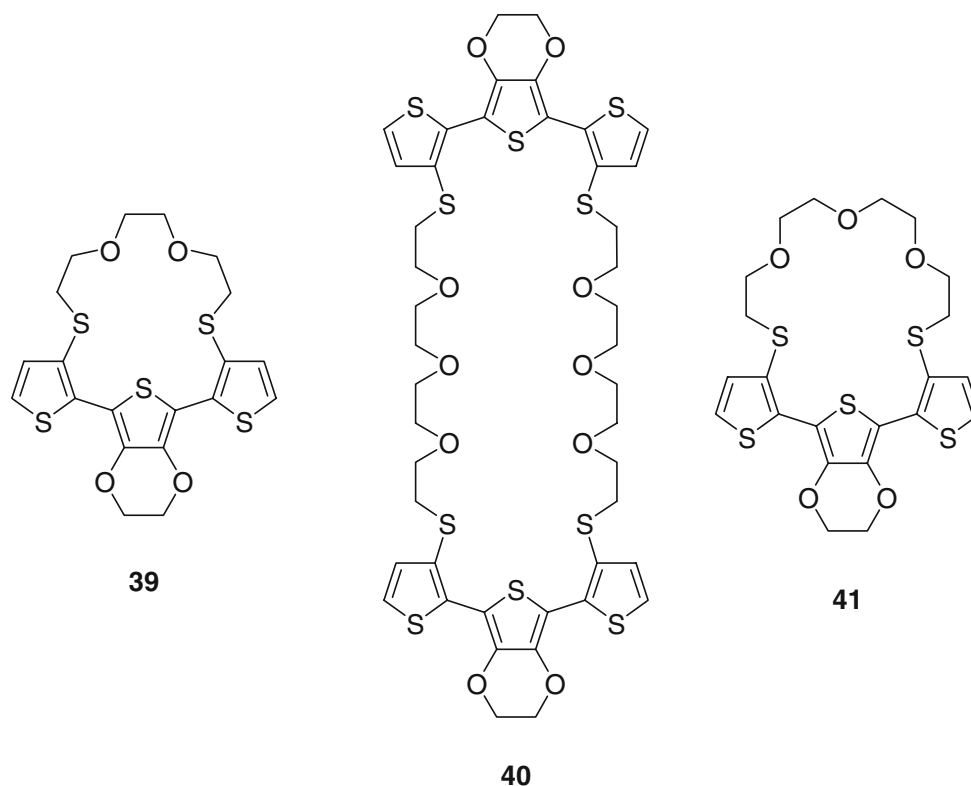


Scheme 5



Oxidation of the oligothiophene to the cation radical state leads to the expulsion of the cation out of the macrocyclic cavity by coulombic repulsion. However, since the oxidation process occurs after cation complexation, the conjugated system which is now locked into a quinoid form, keeps the *anti-syn-anti* conformation imposed by the transient residence of the metal cation in the cavity. Since, as shown by theoretical calculations, the *anti-syn-anti* conformation has a higher HOMO level than the *anti-anti-*

syn one, oxidation of the cation radical into the dication requires a lower potential when the first oxidation step has been preceded by cation complexation (Scheme 5). These results thus provide conclusive evidences showing that cation complexation can induce conformational transitions in the oligothiophene conjugated chain. This process can be utilized either as a means to achieve a reversible mechanical control of the electronic properties of π -conjugated systems or as a source of molecular actuation.



In the continuation of this work, we have synthesized crown-annulated π -conjugated systems based on a hybrid terthiophyl chain containing a median EDOT unit (**39–41**) [34]. Incorporation of EDOT in the terthiophyl chain was expected to stabilize the cation radical due to the synergistic effects associated with the rigidification of the conjugated chain by noncovalent intramolecular sulfur-oxygen interactions [13] and the strong electron-releasing effect of EDOT combined to those of the two lateral sulfide groups.

The electronic absorption spectrum of compounds **39–41** in methylene chloride presents an absorption maximum at 392–393 nm similar to that of an open chain reference compound. The invariance of the absorption maximum clearly shows that contrary to the other series of crown-annulated oligothiophenes (**29** to **38**), the nature and size of the macrocyclic cavity have no effect on the geometry of the oligothiophene chain. This absence of effect is clearly due to the rigidification of the π -conjugated system by noncovalent intramolecular sulfur-oxygen interactions associated with the presence of the median EDOT ring [13].

The cation complexing properties of **39–41** have been analyzed by UV-vis spectroscopy, ^1H NMR spectrometry and cyclic voltammetry. Investigations carried out in the presence of Li^+ , Ag^+ , Ba^{2+} or Pb^{2+} did not provide any evidence of complexing ability for **39** and **40** whereas some sensitivity toward Pb^{2+} was observed for **41** [34].

Addition of successive amounts of Pb^{2+} to a solution of **41** leads to a decrease in the intensity of the main absorption band in the 360–450 nm range and an increase of absorbance in the 250–340 nm region. These changes occur around isobestic points at 360 and 430 nm, which suggest interconversion between defined species. The absence of shift of the absorption maximum shows that complexation does not induce any interannular rotations around single bonds in the terthiophyl chain, as expected for a rigidified conjugated system. A complexation constant K of 4.2×10^4 was obtained from these spectral changes, in good agreement with the value of 6×10^4 obtained from ^1H NMR data. The CV of **41** shows two quasi-reversible redox systems peaking at 0.75 and 1.10 V. Addition of increasing amounts of Pb^{2+} produces a progressive decrease of the intensity of the first anodic wave with the concomitant development of a new anodic wave at *ca.* 0.90 V. This progressive shift of E_{pa1} is due to the combined effects of the coulombic repulsion between the positive charges of the metal cation and cation radical of the conjugated system and the decrease of the electron-releasing effect of the sulfur atoms when involved in the complexation of the metal cation. On the other hand, the fact that the second redox system is not affected by the presence of Pb^{2+} indicates that once the terthiophene chain is oxidized to the cation radical state, repulsion between positive charges leads as expected to the expulsion of the metal cation from the cavity.

Conclusion

Functional conjugated polymers based on the association of polythiophene with linear and macrocyclic polyether have almost 20 years history. Starting from polymers derivatized with simple linear short-chain polyethers the chemistry in the area has progressively evolved toward more sophisticated systems in which crown ethers with well-defined macrocyclic cavities are associated with the polythiophene conjugated backbone. Work carried out on various classes of polymers and oligomers of this type has demonstrated that the creation of a direct communication between the complexing macrocyclic cavity and the π -conjugated backbone leads to a significant improvement of the sensitivity and selectivity of the system for metal cation detection.

Despite the significant progress accomplished in this area, cation recognition does not appear any longer as a priority target and the topic has been progressively supplanted by the development of sensors for molecules of biological interest in the general context of functional π -conjugated systems [2, 4]. From this point of view, the derivatization of polythiophenes by polyether chains represents an invaluable tool for adjusting the hydrophilicity of the conjugated backbone to biological media. On the other hand, the control of the hydrophilicity of conjugated systems can also contribute to progress in the field of sensors based on organic field-effect transistors (OFETs) that represent another emerging topic where conjugated thiophene derivatives with enhanced hydrophilicity can provide an interesting contribution [35]. Recent examples of OFETs based on alkoxyoligothiophenes [36] or on hybrid EDOT-based oligothiophenes [37] represent interesting first steps in this direction.

Among the various processes involved in the interactions of metal cations with polyether-derivatized thiophene-based conjugated systems, complexation triggered single-chain conformational changes appear as a particularly interesting possible source for molecular actuation. Some first illustrations of these ideas have been recently reported and this field clearly represents an interesting direction for future research.

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