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Electroactive polymers containing crown ether or polyether ligands as cation-responsive materials

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Contents

Abstract

The functionalization of electroactive polymers (electroconducting conjugated and redox-type polymers) by monocyclic and acyclic polyether groups is reviewed. In general, materials were chemically or electrochemically deposited as a film onto electrode surfaces from the oxidation of the substituted monomers. The ability of such structures for complexing cations could be evidenced from the modification of their electrochemical and optical properties. In the class of the conjugated polymers, functionalized polythiophenes and polyphenylenes led to numerous representative examples showing they were suited for the building of cation-

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responsive electrodes. Accordingly, some of these polymers were successfully used for the recognition and the extraction of a large variety of cations including alkali, heavy and precious metal cations. Different strategies were developed not only to enhance the affinity between the ligand and the cation, but also to obtain chemically reversible and selective ionic sensors.

Keywords: Electroactive polymers; Crown ether; Polyether

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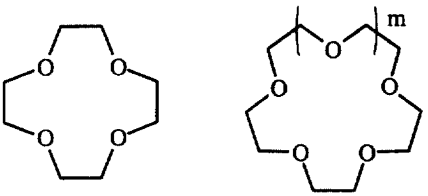
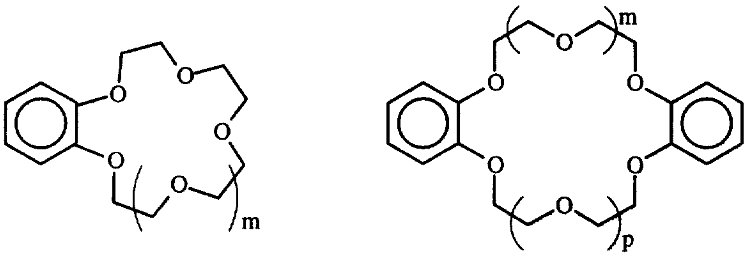
1. Introduction

The monocyclic polyethers called crown ethers were discovered in 1967 by Pedersen [1,2] and can be defined as uncharged macroheterocycles containing the repeat unit (–O–CH_2–CH_2–$)_n$ (Fig. 1). They are designed as molecular hosts able to complex alkali and alkaline earth cations, transition metal cations and ammonium cations. Since then, other ligands such as the cryptands of Lehn [3,4], the spherands and the chiral crown ethers of Cram [5] have been synthesized and their complexing properties have been extensively studied. In addition to these compounds, acyclic



12-crown-4 (12C4)

m = 1 15-crown-5 (15C5)
m = 2 18-crown-6 (18C6)



m = 1 benzo-15-crown-5 (B15C5)
m = 2 benzo-18-crown-6 (B18C6)

m = 0, p = 0 dibenzo-12-crown-4 (DB12C4)
m = 1, p = 0 dibenzo-15-crown-5 (DB15C5)
m = 1, p = 1 dibenzo-18-crown-6 (DB18C6)
m = 2, p = 2 dibenzo-24-crown-8 (DB24C8)

Fig. 1. Some examples of crown ethers and related compounds.

polyethers known as podands can also have strong interactions towards cations when the number of oxygen atoms is suitable [6].

Important review papers devoted to the chemistry of the crown ethers [7–9] and their analytical, chemical and biological applications have been published [10,11]. It has been also demonstrated that the introduction of functional groups, such as lipophilic substituents, acid-dissociable groups, chromophores and chiral centers into the skeleton of crown ethers provided more ample applications in analytical chemistry and related fields [12].

The cation:polyether complexation phenomenon appears to be a Lewis acid–base phenomenon and is principally a function of the size relationship between the crown diameter and the ionic diameter. Generally, the most stable complexes are formed when the ionic diameter is closely equal to the crown diameter [13,14]. In this case, the stoichiometry of the complex is frequently 1:1 with the cation assumed to be located inside the cavity of the polyether ring. When the cation is larger than the cavity, 1:2 and 2:3 complexes are formed. For the 1:2 complex, the most probable structure is a "sandwich" structure in which the ion is located between two polyether rings whereas the 2:3 complex consists of the flatwise arrangement of three polyether rings, each separated from the next by a cation ("club sandwich" structure). However, the binding of cations by crowns is not only influenced by the relative sizes of the polyether cavity and the cations. For example, it has been found that a 1:1 complex was formed between the silver ion (diameter, 2.52 Å) and benzo-15-crown-5 (diameter of cavity, 1.7–2.2 Å) [8] and that the stability constants of numerous 1:1 complexes of cyclic polyethers were much higher in methanol than in water [15]. According to Gokel et al., other factors such as the solvation enthalpies and entropies of the cation and ligand, the number of donor atoms participating in binding and the conformation of the bound and unbound polyether rings must be also considered [16].

The complexation equilibrium between the ligand (L) and the cation (C^{n+}) can be written as

$$L + C^{n+} \overset{K_S}{\rightleftarrows} [LC]^{n+}$$

with the stability constant K_S defined as

$$K_S = \frac{[LC^{n+}]}{[L][C^{n+}]}$$

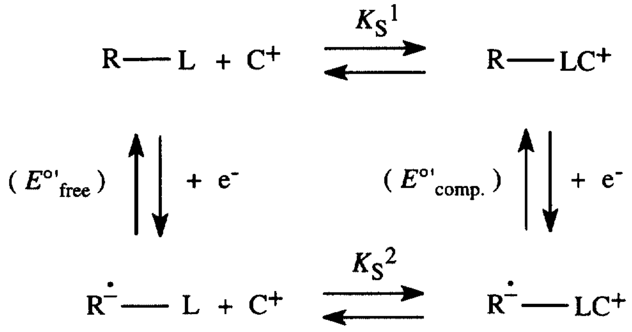
In this expression, [L], [C^{n+}] and [LC^{n+}] are respectively the concentrations of the ligand, the cation and the complex. More precisely, activities should be used instead of concentrations. However, the ratio of the activity coefficients of [C^{n+}] and [LC^{n+}] can be considered close to one for monovalent cations studied in solvents with a dielectric constant greater than about 40 and at ionic strength lower than 0.05–0.10 [10]. Experimentally, the stability constants can be determined by calorimetry, spectroscopy and electrochemistry. The latter method was principally devoted to the electroreduction on a mercury electrode of monovalent metal ion complexes (K^+, Cs^+, Rb^+, Na^+, Tl^+) of macrocyclic polyethers (dicyclohexyl-18-crown-6, dibenzo-18-crown-6) [17–19]. The shift of the reduction potential of the cation in the presence of the ligand was used for the determination of the stability constants. It was demonstrated that the electrochemical behavior of these complexes was strongly dependent on physicochemical parameters such as the size of the cavity and the number of oxygen heteroatoms in the ligand.

Nevertheless, these electrochemical investigations were principally restricted to cations reducible at a mercury electrode. With the aim to enhance the binding power of the ligand towards the cation, numerous authors have synthesized ionophoric compounds of the crown ether or polyether type attached to a redox center, such as ferrocene, quinone and derivatives and nitrobenzene [20–26]. Indeed, the cation binding should be enhanced by electrostatic interaction when the redox center is reduced. In addition, the binding affinity may be accompanied by selective discrimination towards one cation relative to others. Thus these systems can in principle be designed to *recognize electrochemically* the binding of the cations. The electrochemical reactions and the complexation equilibria for this type of systems can be summarized in Scheme 1 for a monovalent cation and a reversibly (fast charge transfer) reduced redox center. K_S^1, K_S^2, $E^{\circ'}_{\text{free}}$ and $E^{\circ'}_{\text{comp.}}$ represent respectively the stability (binding) constants for the neutral ligand–cation and the radical anionic reduced ligand–cation complexes, and the formal redox potentials for the free ligand and the complex. From the four processes, it can be easily demonstrated that

$$\frac{K_S^2}{K_S^1} = \exp\left[-\frac{F}{RT}\left(E^{\circ'}_{\text{free}} - E^{\circ'}_{\text{comp.}}\right)\right]$$

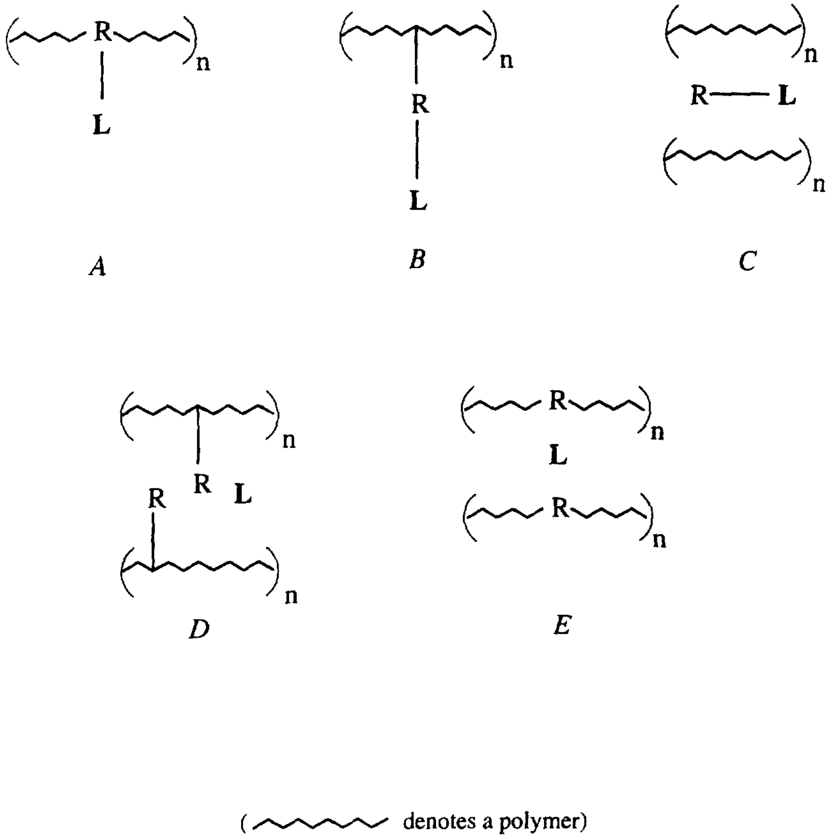
Consequently, the binding constant enhancement upon electrochemical reduction (reflected by the ratio K_S^2/K_S^1) can be calculated from the difference of formal potentials.

Now, in the case where the redox center is incorporated in a solid polymeric matrix, it becomes thus possible to modify electrode surfaces with cation-responsive macromolecular assemblies. Scheme 2 represents the different approaches to incorporate a redox center R in a polymer functionalized with a ligand L. R may be a unit of the polymer chain (cases A and E) or covalently bound to this (B and D) whereas



(R, redox center; L, ligand and C+, monovalent cation)

Scheme 1. Square scheme for the complexation of a cation by an electoactive ligand.



Scheme 2. Different incorporation techniques of a ligand into an electroactive polymer (L, ligand and R, redox center). (A) R covalently linked to L is a component of the polymer backbone; the R———L group is (B) covalently linked to a polymer or (C) entrapped in an electroinactive polymer; L is entrapped in (D) a pendant R groups-substituted or (E) a R-composed polymer.

L may be entrapped in the polymer (C, D and E) or covalently bound to this (A and B).

If the properties of the functional group are not perturbed after its immobilization onto the electrode surface and if it is in close proximity to the redox center, the electrochemical behavior of the redox center is expected to be modified upon the complexation effect.

This review is concerned with polyether or crown ether ligands containing electroactive polymers which are designed for this type of molecular recognition.

Two types of polymers will be described: (i) the electroconducting conjugated polymers characterized by delocalized electronic states and (ii) the redox polymers characterized by localized electronic states. It will be demonstrated from representative examples that other characteristic properties of the polymers can be also modified upon the complexation effect.

2. Electronically conducting polymers functionalized by crown ether or polyether ligands

Electronically conducting polymers (ECPs) are an exciting class of materials with unique electronic, electrochemical and optical properties. The common characteristic of ECPs is a delocalized electronic structure along the conjugated organic backbone which is composed of successive aromatic units. One of the most interesting aspects of these polymers is that they can be reversibly converted upon electron transfer from an electronically insulating, neutral form to a conducting, oxidized form.

The synthesis of ECPs can be electrochemically or chemically achieved. The advantage of the electrochemical method is that the polymer is obtained in one step as a film deposited on the electrode surface from the oxidation of the corresponding monomer in solution. The film thickness can be easily controlled from the electric charge consumed during the electropolymerization reaction.

Thus, the functionalization of ECPs by polyether or crown ether ligands is a suitable approach to attach these specific molecules onto electrode surfaces. The functionalized polymer is generally obtained from the oxidation of the starting monomer substituted by a group containing the ligand (case A of Scheme 2). So, it is conceivable that the host–guest interaction between the ligand and a given cation may be "recognized" by the polymer from the modification of its electrochemical response. As illustrated in the following, other characteristic properties can be also changed upon the complexation effect.

2.1. Polythiophenes as polymer matrices

2.1.1. Oligo(oxyethylene)-substituted polythiophenes

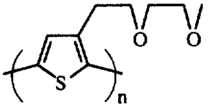
The substitution of polythiophene films by linear oligo(oxyethylene) (polyether) chains has been largely used to obtain materials not only endowed with complexing properties towards cations, but also soluble with a highly hydrophilic character [27].

The electrochemical synthesis of such functionalized polymers can be successfully achieved when two principal conditions are fulfilled. Firstly, two or more CH_2 groups must be used as a spacer between the thiophene ring and the first oxygen atom [28]. When only one methylene group separated the first oxygen atom from the heterocycle, the conjugation and the electronic conductivity of the corresponding polymer was seen to decrease owing to an enhancement of the oxidation potential of the monomer. As demonstrated later with regioregular polyether-substituted polythiophenes, the direct grafting of the polyether chain to the monomer or the presence of only one methylene group is not redhibitory for obtaining the corresponding polymer. As a matter of fact, the problem can be circumvented by chemically oxidizing the monomer, with ferric chloride for example.

Secondly, the impediment of the electropolymerization reaction caused by the steric bulkiness of the functional group should be avoided if the polyether chain is not too long. As reported by Lemaire et al., above seven ether groups, the electrosynthesis of the substituted polythiophene was unsuccessful [28].

In the case where these two conditions are fulfilled, the electropolymerization of polyether-substituted thiophenes could be potentiostatically, galvanostatically or potentiodynamically achieved. It seems that the three electrochemical methods are equivalent to obtain good electroactive films, although it was reported for polythiophenes that the most homogeneous and conducting films were obtained in galvanostatic conditions [27]. The electrosynthesis medium was generally acetonitrile or nitrobenzene containing a tetrafluoroborate, perchlorate or hexafluorophosphate salt as the supporting electrolyte.

Among the polythiophenes 3-substituted by oligo(oxyethylene) chains of different length, the best electroactive and conducting properties were exhibited by the poly[3-(3,6-dioxaheptyl)thiophene] **1** (PDHT) with conductivity values contained in the range 80–250 S cm^{-1} [28,29].



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Furthermore, this polymer when electrosynthesized appeared more conjugated than its alkyl analogue poly(3-heptylthiophene), as revealed by the absorption maximum of the $\pi \rightarrow \pi^*$ transition band located around 550 nm. It must be noted that the chemically synthesized PDHT was less conjugated owing to the poor regio- and stereoselectivity of the chemical polymerization [30].

Even if chemically synthesized polythiophenes 3-substituted by $-OC_2H_4OC_4H_9$ and $-OC_2H_4OC_2H_4OCH_3$ groups were reported as more conjugated ($\lambda_{max}=580$–590 nm) [31], PDHT exhibited original electrochemical, structural and optical properties [32,33].

Firstly, compared to poly(3-alkylthiophene)s, the presence of the polyether chain in PDHT stabilizes more planar conformations and induces a higher degree of electrochemical reversibility [33]. Moreover, this substitution also induces a strong hydrophilic character, as shown by the cyclic voltammograms of Fig. 2 recorded both in aqueous and acetonitrile media [34,35]. The electroactivity and the electrochemical reversibility of PDHT are almost unmodified in the aqueous medium, contrary to poly(3-heptylthiophene) and poly[3-(3-oxaheptyl)thiophene]. The effect of factors such as the nature and the concentration of the electrolyte cation on the electrochemical and optical responses of PDHT has been largely examined by Roncali et al. [32,36,37]. The replacement of NBu_4^+ by Li^+ in acetonitrile resulted in the shift towards more negative values of the oxidation potential of PDHT, i.e. about 100 to 150 mV for a concentration of 0.1M [32]. An increase of the Li^+ concentration from 0.1 to 1.0M led to a better resolution of the cyclic voltammograms, an increase of the doping level and a ca. 150 mV negative shift of the peak potentials (Fig. 3(a)). In contrast, an electroactivity loss and a ca. 150 mV positive shift of the peak potentials were observed when the concentration of NBu_4^+ was varied in the same magnitude (Fig. 3(b)). The improvement of the rate and efficiency of the processes of charge and mass transport in the polymer in the presence of Li^+ could be explained by the complexation of this cation by the oligo(oxyethylene) chains. Indeed this complexation would contribute to localize the counter-anion of

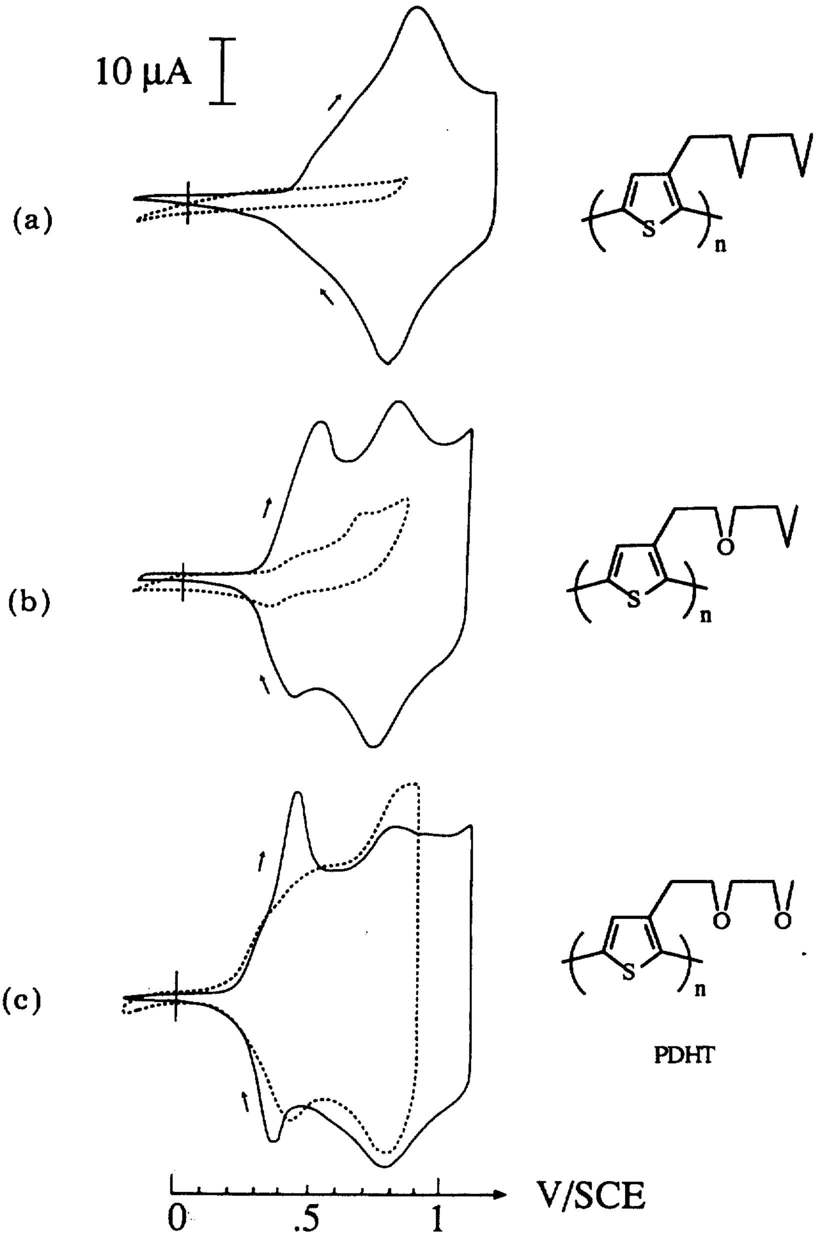


Fig. 2. Cyclic voltammograms on Pt of (a) poly(3-heptylthiophene), (b) poly[3-(3-oxaheptyl)thiophene] and (c) PDHT in 0.5M $LiClO_4+CH_3CN$ (———); in 0.5M $LiClO_4+H_2O$ (- - -). Scan rate, 30 mV s^{-1}; deposition charge, 100 mC cm^{-2}. (Reprinted from Roncali et al. [35], copyright 1990, with permission from Elsevier Science.)

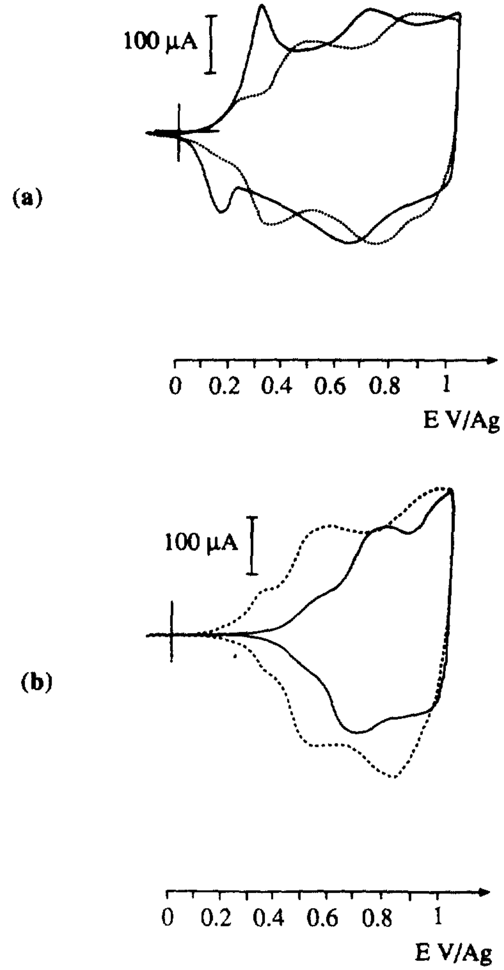


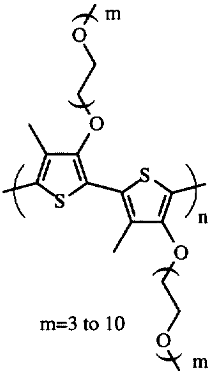
Fig. 3. Cyclic voltammograms of PDHT films on indium–tin oxide (ITO) coated glass electrodes. Deposition charge, 60 mC cm^{-2}; scan rate, 10 mV s^{-1}. Dotted lines: (a) 0.1M $LiClO_4$, (b) 0.1M $Bu_4NClO_4+CH_3CN$. Full lines: (a) 1.0M $LiClO_4$, (b) 1.0M $Bu_4NClO_4+CH_3CN$. (Reprinted from Roncali et al. [32], copyright 1991, with permission from the American Chemical Society.)

the electrolyte in the vicinity of the conjugated backbone by electrostatic interactions, or to dissociation of ion pairs present in the polymer structure [32].

However, changes in the structure and the geometry of the polymer chains can also modify the redox behavior of the polymer to the same extent. From UV–visible absorption spectroscopy complementary data, Roncali et al. suggested that the complexation of Li^+ by the polyether side chains simultaneously increased the coplanarity of the conjugated backbone and the rigidity of the polymer framework [32,36]. Nevertheless, the ionic effect observed with PDHT in the solid state could be considered as weak because of the slight bathochromic shift of the absorption maximum of the polymer (about 10 nm).

More dramatic effects were observed with regioregular polyether-substituted polythiophenes. As reported by Lévesque and Leclerc, chemically synthesized head-to-tail poly[3-oligo(oxyethylene)-4-methylthiophene] **2** led to ionochromic effects with the presence of a clear isosbestic point on the UV–visible absorption spectrum, indicating the coexistence of long sequences of non-planar and planar thiophene units [38,39]. Upon the addition of a cation such as K^+, the twisting of the main chain occurred. However, contrary to PDHT, this phenomenon was only observed with the polymer in solution.

In contrast, ionochromic effects were seen with head-to-tail poly[3-(2,5,8-trioxanonyl)thiophene] **3** both in solution and the solid state [40–43]. Upon the addition of cations such as Pb^{2+} and Hg^{2+}, the conjugation of this polymer, characterized by an absorption maximum at 439 nm in $CHCl_3$ and 486 nm in the solid state, was completely removed [41]. Thus, the cationic complexation would induce the twisting of the polymer backbone away from planarity. However, although the response was chemoselective (Li^+ and Zn^{2+} were found not to interfere), the ionochromic effects observed with Pb^{2+} and Hg^{2+} were irreversible as the conjugation of the polymer was not restored after the complexation.



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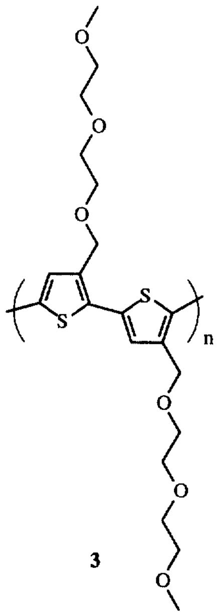

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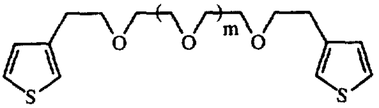
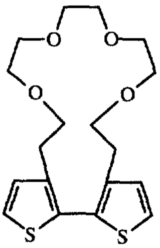
For all examples reported before, the integrity of the functional group was kept after the chemical or electrochemical polymerization step and the complexation of cations was ensured by an acyclic ligand.

An original approach developed by some authors consisted in the electroformation of complexing macrocyclic cavities from the oxidation of the thiophene derivatives substituted with acyclic polyether chains. In this context, symmetrical monomers possessing two thiophene units linked together by a polyether subunit have been synthesized [44–47] and their electrochemical behavior has been investigated [44,46,47]. Based on electrochemical considerations, Roncali et al. claimed that the oxidation of 1,14-(3-thienyl)-3,6,9,12-tetraoxatetradecane **4b** in the presence of Li^+ yielded conducting polythiophene containing pseudo-crown ether cavities [44]. As a matter of fact, the complexation of this cation by the polyether chain would promote the cyclization (template effect) and the concomitant polymerization of the terminal thiophene groups. Although the authors justified this mechanism by a significant shift of the electropolymerization potential of **4b** (250–300 mV) relatively to that of 3-alkylthiophenes or of other thiophenes 3-substituted by ether groups, the occurrence of such an effect was not really demonstrated.



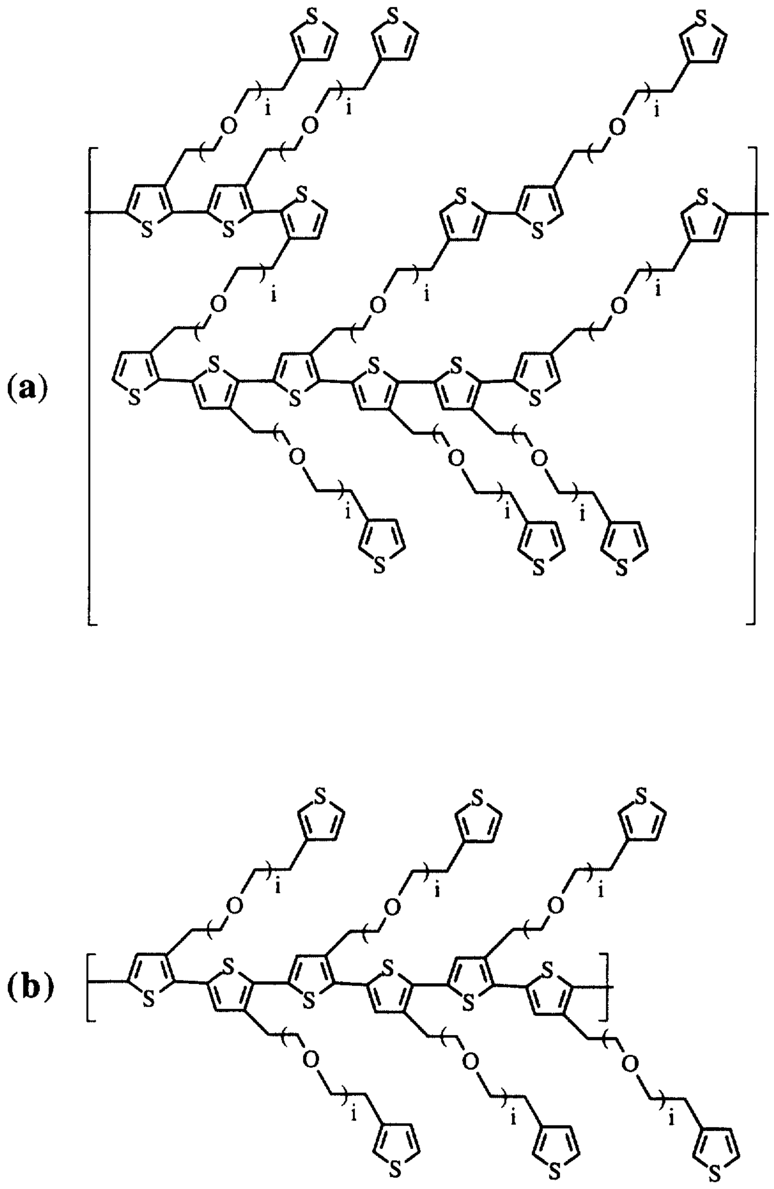
m=1 **4a** m=4 **4d**
m=2 **4b** m=5 **4e**
m=3 **4c**



4cycl

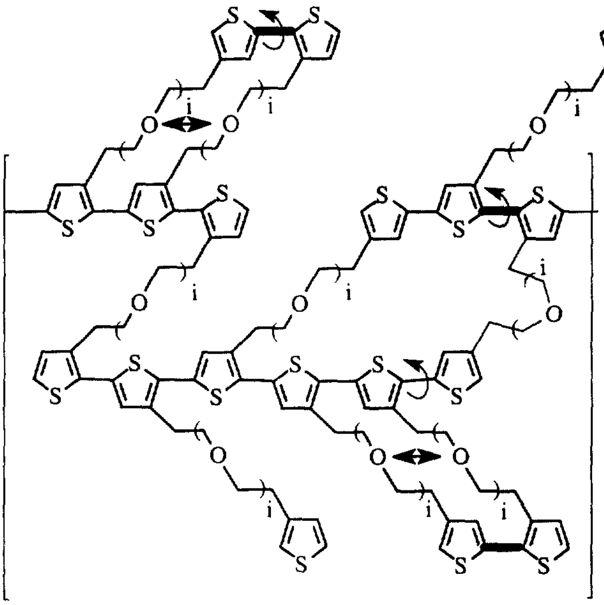
A recent study from the Simonet's laboratory has clearly demonstrated that such an effect could not be involved in the electropolymerization of **4b** [47]. Indeed no significant shift of the oxidation potential of **4b** was observed when the nature of the electrolyte cation was changed. Moreover, the electrochemical and spectroscopic responses of poly(**4b**) were different from those obtained for poly(**4cycl**). In 0.1M $Bu_4NBF_4+CH_3CN$, the cyclic voltammograms of poly(**4b**) showed two oxidation steps at 0.40 and 0.62 V (vs $Ag/10^{-1}M\ Ag^+$) whereas poly(**4cycl**) exhibited only one oxidation step at 0.70 V [46,47]. Additionally, the absorption maximum of the $\pi\rightarrow\pi^*$ transition band was located at 420 and 360 nm respectively for poly(**4b**) and poly(**4cycl**).

From coulometric measurements, the electropolymerization of **4b** and its derivatives bearing polyether groups of different length (**4a** and **4c**–**4e**) was found to consume two electrons per molecule of substrate for the polymer formation and about 0.65 electrons per molecule for the doping. Because only half of the thiophene units are involved in the electropolymerization process, the nature of the polymer electrogenerated in the first step and particularly of the redox centers is difficult to define. The electrochemical and UV–visible spectroelectrochemical results would be more consistent with a redox polymer possessing long-chain oligomeric units (e.g. pentathiophene or sexithiophene) (Scheme 3(a)) alone or mixed with an electronically conducting polymer possessing pendant polyether chains (Scheme 3(b)).



Scheme 3. Possible structures of the polymer electrogenerated from the one-step oxidation of **4**. (a) Redox-type polymer possessing sexithiophene units; (b) electronically conducting polymer bearing pendant polyether 3-substituted thiophene groups. (From Ref. [47].)

The anodic coupling of thiophene or oligothiophene units remaining within the polymer structure could be performed under potentiostatic conditions and led to a decrease of the mean conjugation length compared with the as-grown polymer.



Scheme 4. Formation of macrocyclic cavities from the potentiostatic oxidation of poly(**4**). (From Ref. [47].)

Therefore, this post-polymerization electrochemical modification would result in the distortion of the conjugated π-system and the formation of macrocyclic cavities within the polymer matrix (Scheme 4).

The properties of complexation of different undoped poly(**4**) toward inorganic cations (Ag^+, Mn^{2+}, Co^{2+} and Sb^{3+}) have been investigated by gamma-spectrometry and the principal results are summarized in Table 1. It can be seen that these polymers exhibit a binding power which is much stronger towards Mn^{2+} and Co^{2+} than towards Sb^{3+}. Furthermore, the same affinity was obtained for Co^{2+} (ionic radius, 0.72 Å [48]) whatever the polymer, whereas Mn^{2+} (0.80 Å) and Ag^+ (1.26 Å) were more specifically complexed by poly(**4a**) and poly(**4c**), respectively. Thus this result is well correlated with the length of the polyether chain.

In the course of their investigations concerning the electroformation of complexing

Table 1

Proportions of uncomplexed cations (in %) remaining after the reaction for 24 h of 0.3 g of undoped polymer with an aqueous solution initially containing 4×10^{-7}M of cation; the detection was achieved by gamma-spectrometry (from Ref. [46])

Polymer	Cation			
	Ag^+	Mn^{2+}	Co^{2+}	Sb^{3+}
poly(**4a**)	48.5	2.4	4.4	77.5
poly(**4b**)	51.4	10	1.0	80
poly(**4c**)	10	15	4.0	82

Table 2

Voltammetric data of **5** and their corresponding polymers; the films were potentiodynamically grown at 100 mV s^{-1} on Pt in 0.1M $Bu_4NBF_4+CH_2Cl_2$ (deposition charge: 64 mC cm^{-2}) and studied in 0.1M $Bu_4NBF_4+CH_3CN$ (from Ref. [46])

Monomer	E_{pa} (V)[a]	Polymer p-doping E_{pa} (V)	E_{pc} (V)	n-doping E_{pa} (V)	E_{pc} (V)
5a	1.60	0.68	0.57	−2.10	−2.12
5b	1.48	0.75	0.60	−2.12	−2.14
5c	1.61	0.70	0.65	−2.20	−2.25
5d	1.74	0.60	0.60	−1.98	−2.00
5e[b]	1.40	–	–	–	–
5f[b]	1.35	–	–	–	–

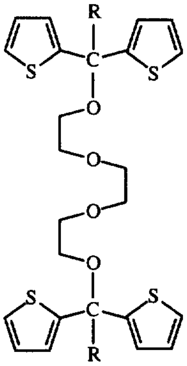
[a] Anodic peak potentials relative to monomers (concentration: 10^{-2}M).

[b] These compounds do not electropolymerize.

All potentials are referred to the system Ag/10^{-1}M Ag^+ in CH_3CN. Scan rate: 100 mV s^{-1}.

macrocyclic cavities from acyclic podands, Simonet and co-workers have recently synthesized new thiophene derivatives **5** substituted in the 2 position by acyclic polyether chains [46,49]. Contrary to the thiophenes functionalized in the 3 position, the oxidation of such compounds led to unconjugated, redox-type polymer films, except for **5e** and **5f** which did not electropolymerize. These were expected to consist in the succession of bithiophene units separated by the carbon atom bearing the R group and the polyether chain.

The oxidation potential of the monomers was found to be dependent on the electronic character of the R aromatic group substituting the quaternary benzylic carbon atom (Table 2). Therefore, owing to the presence of the electron-withdrawing nitro group, **5d** was oxidized at a potential higher than **5a**, whereas inversely **5e** and **5f** were oxidized at a lower potential than **5a**.



R= phenyl **5a**	*p*-nitrophenyl **5d**
2-naphthyl **5b**	*p*-methoxyphenyl **5e**
2-thienyl **5c**	*o*-methoxyphenyl **5f**

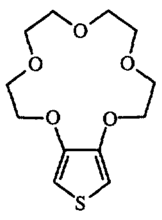
All the electrogenerated polymers exhibited two reversible redox systems corresponding to the n-doping and p-doping processes (Table 2). They could be cycled between the two states without apparent decrease of their electroactivity. Although the potential complexation properties towards some cations have not yet been investigated, this type of polymers, capable of being negatively and positively charged, should be of great interest for the development of chemically reversible ionic sensors. Indeed, the cation binding should be enhanced when the polymer is in its n-doped state and disfavored when it is in its p-doped state.

2.1.2. Crown ether-substituted polythiophenes

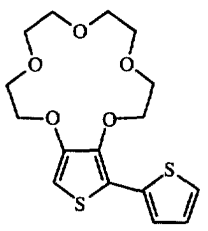
Large modifications of the characteristic properties of a conducting polymer substituted by a macrocyclic ligand are expected when the binding site is in close proximity to the conjugated backbone. Therefore, the cationic complexation should be efficiently and rapidly recognized.

However, in this case, it is predictable that an electrochemical-type recognition based on the shift of the redox potentials of the electroactive polymer will be strongly dependent on environmental events. Firstly, in the course of its oxidation, positive charges are generated along the polymer chain which result in electrostatic repulsions with the inorganic cation. Secondly, the short distance between the ligand and the polymer backbone may hinder the migration and transport of the cation into the polymer.

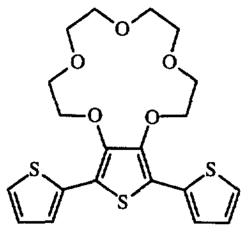
These features have been considered by Bäuerle and co-workers with the study of novel 15-crown-5 substituted (oligo-)thiophenes **6** in which the macrocycle is directly grafted to the thiophene moiety [50].



6a



6b



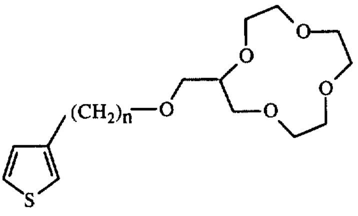
6c

These compounds could be potentiodynamically polymerized, except **6c** which did not form adhering films at an electrode surface.

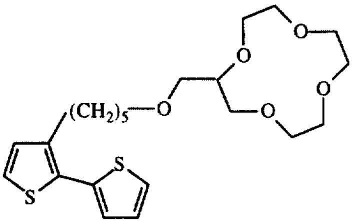
The influence of alkali cations such as Na^+, Li^+ and K^+ on the redox behavior of poly(**6a**) and poly(**6b**) has been analyzed from multi-sweep cyclic voltammetry experiments. The electrochemical response of poly(**6b**) was found to be not affected by the presence of alkali cations. In contrast, a large shift of the oxidation peak of poly(**6a**) towards more positive potentials was observed in the presence of Na^+. Additionally, the cyclic voltammograms became flatter with increasing number of scans. Weaker effects were visible when Li^+ and K^+ were added to the electrolyte. As poly(**6a**) was stable towards electrochemical cycling when Bu_4N^+ was used, it could be concluded that the potential shift was caused by the complexation phenomenon. Indeed, upon the cationic complexation, the electron density donated by the oxygen atoms of the crown ether into the conjugated polymer backbone is decreased and consequently, the oxidation potential of the polymer is enhanced. Also, a deviation from coplanarity of the conjugated chain can induce a similar effect.

For all these three cations, the anodic peak potential of poly(**6a**) was linearly dependent on the number of scans. The sensitivity of this polymer towards alkali cations deduced from the slopes of the straight lines was $Na^+ \gg Li^+ > K^+$. Thus, this result is in accordance with the size of cations, Li^+ (diameter, 1.20 Å), Na^+ (1.90 Å) and K^+ (2.66 Å) relatively to the diameter of the macrocyclic cavity (1.7–2.2 Å) [8]. Nevertheless, as the cyclic voltammograms were stabilized after only a very large number of scans, poly(**6a**) was not suitable to electrochemically recognize cations in real time.

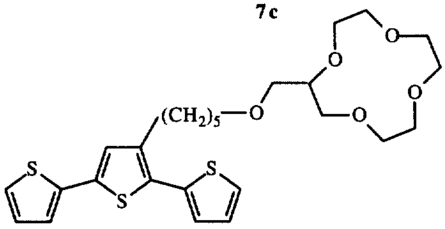
A faster electrochemical detection could be achieved if the cation binding was enhanced or the transport of the cation in the polymer structure was facilitated. The first condition would be fulfilled if the polythiophene substituted by a crown ether could be n-doped. Such a type of doping has been claimed for a chemically synthesized polythiophene derivative substituted by a 15-crown-5 moiety [51,52]. However, the reported experimental results were not really convincing because the redox system assigned to a so-called n-doping was totally irreversible and poorly defined.



n=5 **7a**
n=10 **7b**



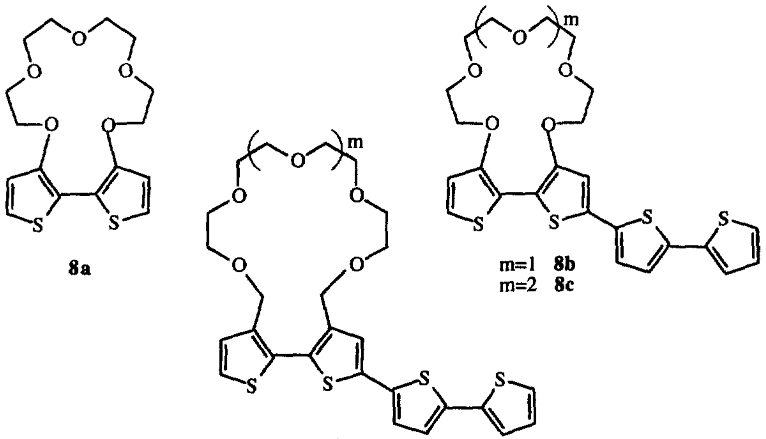
7c



7d

The increase of the distance between the conjugated backbone and the crown ether could contribute not only to facilitate the transport of the cation in the polymer but also to diminish the steric constraints of the macrocycle on the polymer. The negative effect is that the interaction between the crown ether and the conjugated system would be lowered and consequently the electrochemical recognition of cations would be less sensitive.

As reported by Bäuerle et al., sensitive and selective cation-responsive polymers can be obtained when the length of the spacer group separating the macrocycle from the polymer is suitable. This aim has been reached with 12-crown-4-functionalized poly(alkylthiophene)s (poly(**7**)) in which the crown ether was linked to the thiophene ring via an oxaalkyl chain [53,54]. Electroactive polymer films were electrogenerated from the oxidation of **7c** and **7d** whereas the oxidation of **7a** and **7b** led only to soluble oligomers. After the addition of alkali cations to the electrolyte solution, the cyclic voltammograms of poly(**7c**) and poly(**7d**) were shifted towards more positive potentials but contrary to poly(**6**), their stability was reached after a few scans for a given cation concentration. The sensitivity of poly(**7c**) towards cations was found to be $Li^+ > Na^+ > K^+$ and the detection limit was lower than 5×10^{-5}M for Li^+. Thus, the observed sensitivity is well in accordance with the relative sizes of cations and the macrocyclic cavity (1.2–1.5 Å) [8]. For poly(**7d**), much smaller electrochemical modifications were observed in the presence of alkali cations.



8a

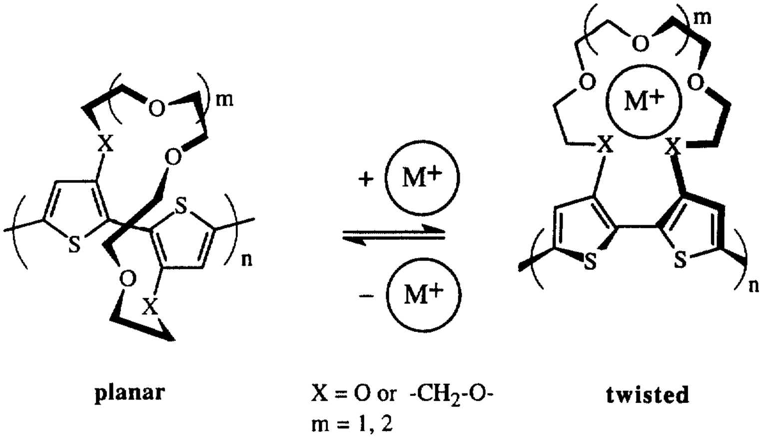
m=1 **8b**
m=2 **8c**

m=1 **8d**
m=2 **8e**

Until now, the electrochemical detection of cations by crown ether-substituted polythiophenes was based on the perturbation of the doping/undoping process upon the complexation effect. Therefore, the presence of positive charges along the conjugated polymer backbone may affect the complexing properties of the ligand. Moreover, the modification of the redox potential of the polymer may be caused either by electronic effects or conformational changes in the polymer. Accordingly, the contribution of each component is difficult to estimate when only electrochemical considerations are taken into account.

The original approach developed by Marsella and Swager consists of an optical detection of the cation binding. In this way, only conformational changes in the polymer are considered.

They have synthesized and characterized crown ether-substituted polythiophenes (poly(**8**)) which underwent large band gap changes in response to alkali metal ions [55–59]. Their synthesis could be achieved by both electrochemical and chemical oxidation as well as through chemical coupling reactions. For **8d** and **8e**, the methy-



Scheme 5. Conformational change of crown ether-substituted polythiophenes (poly(**8**)) induced by the cation complexation. (From Ref. [55].)

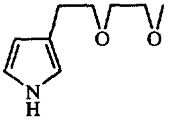
lene spacer between the bithiophene and the polyether chain has the effect of increasing the size of the macrocyclic cavity and also prevents electron donation from the macrocycle's oxygen to the thiophene ring. From UV–visible absorption spectroscopy data, poly(**8d**) and poly(**8e**) were found to be less conjugated than the other polymers because of greater conformational restrictions. After the addition of alkali cations (K^+, Na^+ or Li^+), large ionochromic effects were observed with a hypsochromic shift of the absorption maximum and an increase in the band gap of the polymer. As a matter of fact, the metal complexation forces a rotation of the thiophene rings in order to accommodate maximum chelation (Scheme 5). Poly(**8a**) and poly(**8b**) showed the largest shift for Na^+ whereas poly(**8c**) was most responsive to K^+. The observed differences between ions resulted from the varying degree of rotation imposed on the bithiophene unit by the ligand's distinct conformational requirements for each metal [55]. In contrast, poly(**8d**) and poly(**8e**) exhibited poor ionochromic activity, principally explained by their poor binding affinity which resulted in failure of the twist-inducing mechanism.

In several recent papers, Swager and co-workers have reported a new approach to polymer-based sensors illustrated by polythiophene-based pseudopolyrotaxanes which transduced molecular recognition events into measurable changes in conductivity [60–62].

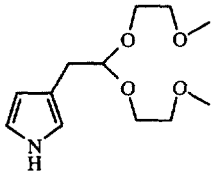
2.2. Polypyrroles

Comparatively to polythiophenes, the functionalization of polypyrroles by crown ether and oligo(oxyethylene) ligands has been much less exploited. Apart from an example of polypyrrole incorporating tetrasulfonated dibenzo-18-crown-6 as doping anion [63], the specific group was covalently bound to the polymer.

The substitution at the 3 position has been preferred by Garnier and co-workers owing to the excellent conducting properties of the resulting polypyrrole films. Accordingly, they have reported the synthesis and electrochemical behavior of a new polypyrrole 3-substituted by a polyether chain [64]. 3-(3,6-dioxaheptyl)Pyrrole **9a** was potentiostatically electropolymerized whereas the electrooxidation of **9b** did not give rise to a polymer film because of the steric effect caused by the substituents.



9a



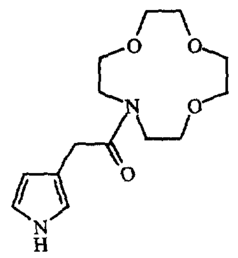
9b

Poly(**9a**) exhibited an enhanced redox reversibility compared to the unsubstituted polypyrrole. This result which is interesting for battery applications was explained by a greater mobility of the ionic species inside the polymer caused by the pendant polyether chain.

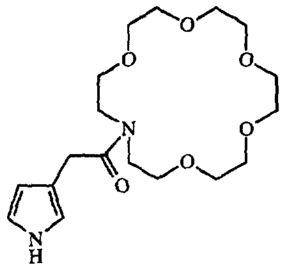
The grafting of an azacrown ether moiety at the 3 position of pyrrole has also been reported as a promising route towards selective cation-responsive polymers [65–67]. Indeed, the voltammetric response of poly(**10b**) in acetonitrile was shifted towards more positive potentials when Na^+ or K^+ was added to the electrolyte solution whereas Li^+ had no effect (Fig. 4). In contrast, the redox behavior of poly(**10a**) was not affected whatever the alkali cation. The absence of any recognition from this polymer could be ascribed to the small size of the aza-12-crown-4 cavity (ca. 1 Å) unsuited for the tested alkali cations.

Such an increase of the oxidation potential of the polymer upon the complexation effect has already been observed for crown ether-substituted polythiophenes [50,53,54] and could be interpreted as a consequence of the deviation from coplanarity of the polypyrrole chain. This explanation was supported by the results obtained with polypyrrole *N*-substituted with a benzo-15-crown-5 unit which did not show any electrochemical recognition property towards alkali cations [68]. As a matter of fact, the *N*-substitution induced a much weaker configurational flexibility to the polymer backbone than the 3-substitution [65]. A possible answer to this problem has been provided by Ion et al. with polypyrrole *N*-substituted by ferrocene crown ether, designed as a Ba^{2+} and Ca^{2+}-responsive material [69]. In this case, the recognition of the cation binding was based on the changes in the electrochemical response of the ferrocene/ferrocenium couple instead of polypyrrole, according to the principle depicted in Scheme 1.

The complexation of transition metals such as Co^{2+} by azacrown ether-substituted polypyrroles has also been reported [70]. Co^{2+}-functionalized films were directly obtained from the potentiodynamical electropolymerization of **10a** and **10b** in the presence of Co^{2+} and showed an electrochemical response characteristic of polypyrrole and the incorporated metallic center. For poly(**10b**), a 1:1 complex was proposed with the cation located within the cavity of the azacrown ether whereas a sandwich-type structure with Co^{2+} located between two macrocycles was proposed for



10a



10b

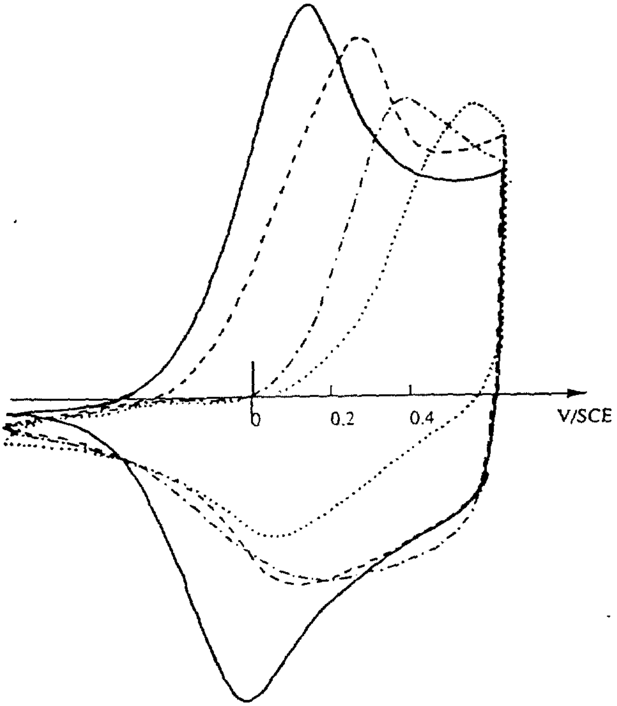
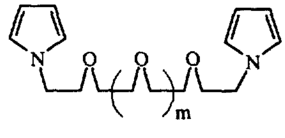


Fig. 4. Cyclic voltammograms on Pt of poly(**10b**) in 0.1M $Bu_4NClO_4 + CH_3CN$ in the presence of increasing $NaClO_4$ concentration: 0M (———); 10^{-5}M (– – –); 10^{-3}M (- · -); 10^{-2}M (· · ·). The film was electrosynthesized at 0.9 V (vs SCE) in 0.5M $Bu_4NClO_4 + CH_3CN$ containing 0.1M of **10b** (deposition charge, 500 mC cm^{-2}). Scan rate, 20 mV s^{-1}. (Reprinted from Korri-Youssefi et al. [66], copyright 1994, with permission from Elsevier Science.)

poly(**10a**). Moreover, the Co^{2+}-complexed poly(**10a**) was reported to exhibit an electrocatalytic activity towards the two-electron oxygen reduction.

Very recently, Garnier and co-workers have proposed a new route to functionalize a polypyrrole film. The grafting of a crown ether unit to the polymer has been achieved after the polymerization step with the substitution of aminomethyl-18-crown-6 to polypyrrole bearing an easily removable leaving group [71].

Using an approach analogous to that developed for polythiophenes, Simonet and co-workers have synthesized monomers consisting of two pyrrolyl units linked together by long chain polyether spacers **11** [72,73].



11

In accordance with the electrochemical results obtained for **4** [47], macrocyclic cavities could be potentiostatically generated after the polymerization step of **11**. However, contrary to **4**, **11** was less efficiently electropolymerized, probably owing to the lower conducting and electroactive properties of the corresponding *N*-substituted polypyrroles. Furthermore, the electrochemical behavior of poly(**11**) was nearly independent of the length of the polyether chain. The complexing properties of such polymers, exemplified by poly[1,11-di(1-pyrrolyl)-3,6,9-trioxaundecane] (**11**, $m = 1$), have been investigated by gamma-spectrometry with the extraction of cations contained in radioactive wastes [72]. A strong affinity towards Co^{2+} was obtained whereas Cs^+ and K^+ were much less complexed by this polymer.

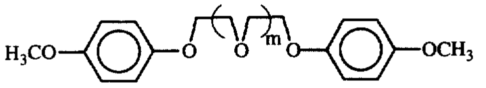
2.3. Polyphenylenes and related fused systems

The functionalization of this class of polymers by polyethers or crown ethers has been principally developed by Simonet's group. Such electroactive polymers could be electrogenerated from the oxidation of crown ether-substituted benzenes and naphthalenes as well as oligo(oxyethylene)-substituted benzenes.

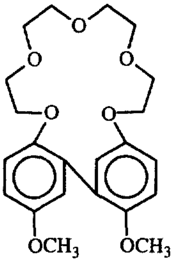
2.3.1. Polymers electrogenerated from the functionalized benzene derivatives

As already demonstrated for 1,4-dimethoxybenzene and related compounds [74,75], the electrochemical behavior of **12** was strongly dependent on the experimental conditions used. In 0.2M $Bu_4NBF_4 + CH_2Cl_2$ containing **12** at 10^{-2}M, the electrooxidation of **12** between 1.3 and 1.5 V (vs Ag/10^{-1}M Ag^+) led to the corresponding electroactive polyphenylene films [72]. With increasing of the length of the polyether chain, the electropolymerization yield was lowered from 50 to 30% whereas the doping level of the polymers was relatively constant at about 0.55 positive charges per aromatic ring. From thin-layer cyclic voltammetry experiments, the electropolymerization of **12** was found to consume between two and three electrons per molecule of substrate depending on the oxidation potential value. This result which is typical of polymers electroformed from compounds consisting of two identical aromatic units suggests that the anodic coupling of benzene units remaining within the polymer structure can be performed under potentiostatic conditions.

In contrast with the results obtained in CH_2Cl_2, intramolecular coupling reactions occurred when the electrochemical study of **12** was investigated in CH_3CN containing low concentrations of substrate. The cyclization product **12d** was obtained with a low yield of 5% from the oxidation at 1.0 V of **12c**.



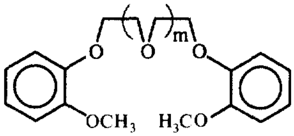
m = 1 **12a**
m = 2 **12b**
m = 3 **12c**



12d

When the substituents of the two aromatic rings were placed in the *ortho* position, specific trimerizations on each ring occurred and gave rise to electroactive polymers possessing triphenylene moieties. It must be noted that such an electrochemical trimerization reaction has already been reported for numerous aromatic orthodiethers [76,77]. Thus, the polymer obtained from the oxidation of **13** was found to be thermically stable and strongly paramagnetic under its p-doped state characterized by 0.35 to 0.50 holes per triphenylene moiety [78]. The voltammetric behavior of poly(**13**) which can be defined as a redox-type polymer showed two well reversible steps corresponding to 0.5 electrons each per triphenylene.

In spite of an open structure (Scheme 6), poly(**13**) in its neutral form was able to extract a large palette of cations (Au^{3+}, Hg^{2+}, Pt^{2+} and Ag^{+}) especially from water.

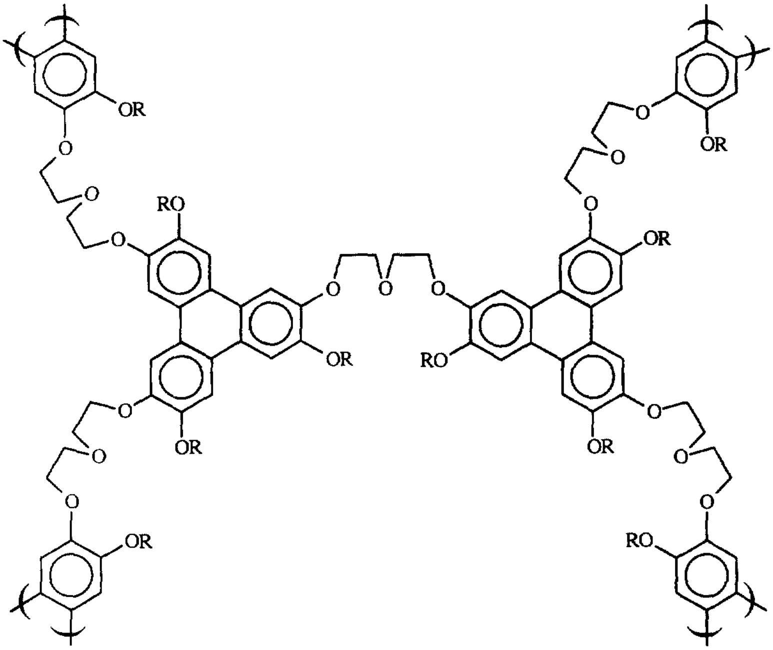


R_1, R_2 H

13

Trimerization reactions were also reported for most of the benzo- and dibenzo-crown ethers.

Accordingly, new tricyclic molecules such as **14** could be electrogenerated from the oxidation of benzo-15-crown-5 [79] and benzo-18-crown-6 [80,81]. As a matter of fact, the anodic coupling of the benzo-crown ether led directly to the corresponding trimer radical cation. Taking into account the relative instability of the radical cation towards nucleophilic species, the synthesis of such trimers required a non-nucleophilic medium, such as a $CH_2Cl_2+CF_3COOH$ mixture (90/10 v/v) and the use of a flow redox cell with a porous electrode. Under these conditions, the trimer radical cation was found to be stable and reversibly reducible into the neutral species in

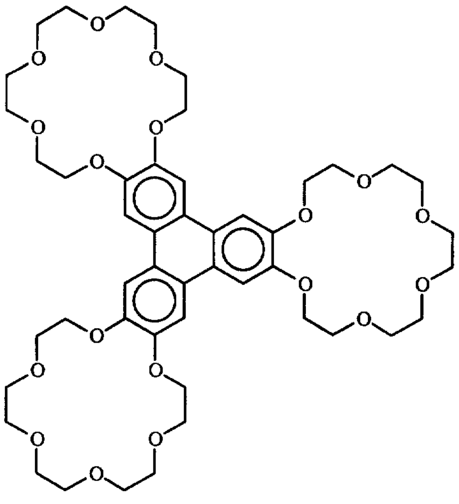


Scheme 6. Idealized representation of the poly(triphenylene) electrogenerated from the oxidation of **13** ($m=1$).

CH_3CN. Finally, this type of electron donor molecules could be very interesting for the formation of charge transfer complexes with acceptor organic or inorganic compounds. Moreover, as a hexasubstituted triphenylene, it may also present the mesogenic properties of a discotic liquid crystal [82,83].

The synthesis of electroactive polytriphenylenes possessing macrocyclic complexing cavities has been achieved from the anodic oxidation of dibenzo-crown ethers. The triphenylene moieties were presumably two-dimensionally linked via polyether bridges (Scheme 7). The structure of these poly(dibenzo-crown ether)s has been established [84–86] by means of different physicochemical methods, such as scanning electron microscopy, infrared, UV–visible, EPR and solid state ^{13}C-NMR [87] spectroscopies.

The large number of papers devoted to poly(dibenzo-crown ether)s and especially to poly(DB18C6) has demonstrated that such electroactive polymers exhibited remarkable structural, electrochemical and complexing properties. Poly(DB12C4), poly(DB15C5) and poly(DB18C6) could be obtained as a film coating an electrode surface from the oxidation of the monomer in dried CH_2Cl_2 or a $CH_2Cl_2+CH_3CN$ mixture containing Bu_4NBF_4 or Bu_4NPF_6 as the supporting electrolyte [84,86,88]. The electropolymerization was performed either by repeated potential linear scanning (upper limit, about 1.45 V vs $Ag/10^{-1}M\ Ag^+$) or by electrolysis at a constant potential of 1.05 V. The electrochemical behavior of DB24C8 was somewhat similar but no tractable deposit was obtained from its



14

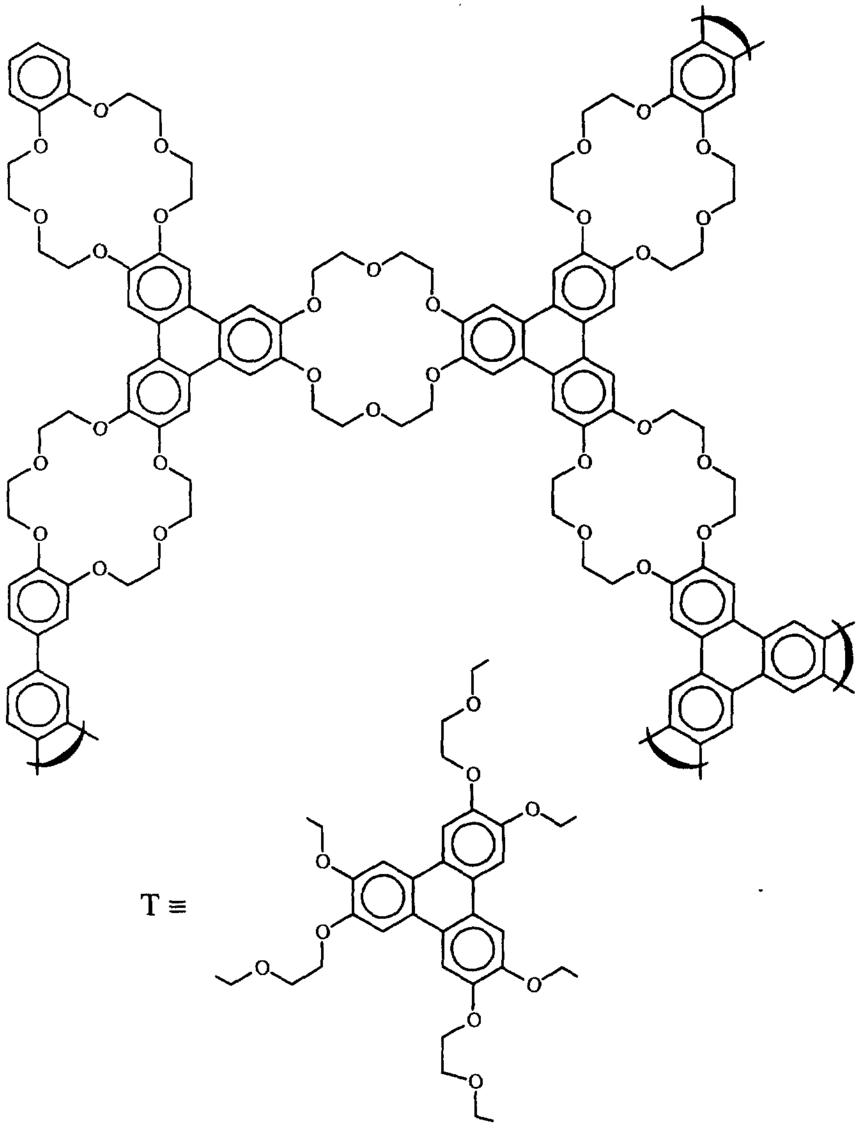
oxidation. The electroactive properties of the p-doped polymers obtained just after their electrosynthesis were found to be nearly independent of the size of the complexing cavity and were characterized by several (up to four) redox processes attributed to the triphenylene moieties. For poly(DB18C6), it has been argued that this polymer exhibited three fully reversible steps followed by an irreversible one, each one corresponding to a 0.5 electron redox exchange.

$$\begin{tikzcd}
{[\mathrm{T}]_n} \arrow[r, shift left, "-0.5n\,e^-"] & {[\mathrm{T}^{0.5+}, 0.5\,\mathrm{X}^-]_n} \arrow[l, shift left, "1"] \arrow[r, shift left, "-0.5n\,e^-"] & {[\mathrm{T}^{+}, \mathrm{X}^-]_n} \arrow[l, shift left, "2"] \arrow[r, shift left, "-0.5n\,e^-"] & {[\mathrm{T}^{1.5+}, 1.5\,\mathrm{X}^-]_n} \arrow[l, shift left, "3"] \arrow[d, "4"', "-0.5n\,e^-"] \\
 & & & {[\mathrm{T}^{2+}, 2\,\mathrm{X}^-]_n}
\end{tikzcd}$$

$$\underbrace{\phantom{[\mathrm{T}]_n}}_{\textbf{Neutral polymer}}\quad\underbrace{\phantom{[\mathrm{T}^{0.5+}, 0.5\,\mathrm{X}^-]_n\quad[\mathrm{T}^{+}, \mathrm{X}^-]_n\quad[\mathrm{T}^{1.5+}, 1.5\,\mathrm{X}^-]_n}}_{\textbf{p-doped polymer}}$$

Where T symbolizes the electroactive hexasubstituted triphenylene unit and X^- is the doping anion ensuring the electroneutrality of the material.

From the elemental analysis and voltammetric data, the most stable structure of the p-doped polymer films was thought to be $[T^{0.5+}, 0.5X^-]_n$. Indeed, remarkably compact and homogeneous films were obtained for a doping level of 0.5 positive charges per triphenylene unit. Moreover, a continuous cycling on the redox step **2** did not affect the stability and the electrochemical response of the film (Fig. 5) whereas cycles reaching more oxidizing potentials might result in a sudden drop in the conductivity, proper to a completely self-inhibiting process. It has been also



Scheme 7. Structure of poly(dibenzo-18-crown-6). (T symbolizes the electroactive triphenylene unit.)

proved from potentiometric measurements that the doping anion was more strongly retained in the polymer structure when $X^- = BF_4^-$, ClO_4^- or SCN^- [89].

The ionophoric properties of the poly(dibenzo-crown ether)s have been investigated in their p-doped, oxidized form as well as in their undoped, neutral form. Their undoping could be quickly and efficiently achieved by a chemical treatment of the as-grown p-doped polymer with a reducing agent, such as the electrogenerated

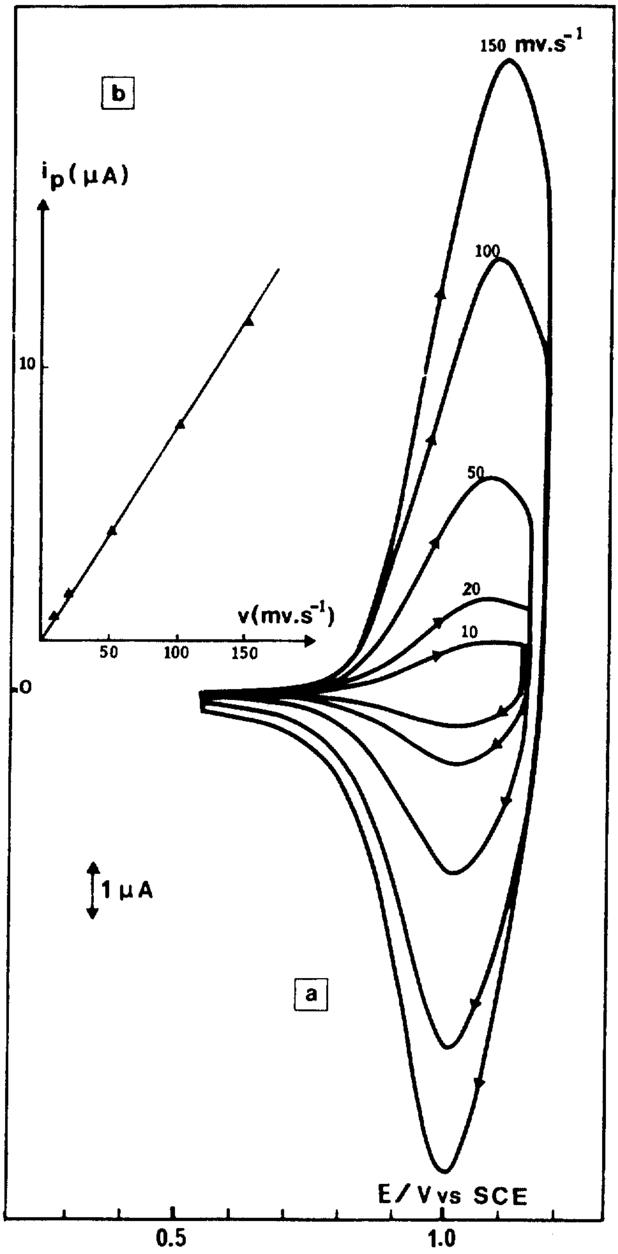


Fig. 5. (a) Cyclic voltammograms of poly(DB15C5)-coated Pt electrode in a CH_2Cl_2+CH_3CN (9/1 v/v) mixture containing 0.1M Bu_4NBF_4, as a function of the potential scan rate v. (b) Linear relationship between the peak current intensity I_p and v, as expected for surface-immobilized redox species. (From Ref. [86].)

superoxide anion $O_2^{\cdot -}$, primary and tertiary amines in acetonitrile or tetraalkylammonium hydroxide [90,91].

When the reduction of the p-doped polymer was performed with R_4NOH (R = alkyl) or $O_2^{\cdot -}$ in CH_3CN containing Bu_4NBF_4, it was demonstrated that a large amount of R_4N^+ and OH^- ions were incorporated and strongly retained in the polymer [91]. Thus, in the case of a polymer initially doped with BF_4^-, the undoping process can be described as

$$[T^{x+}, xBF_4^-]_n + nm(R_4N^+, OH^-) \rightarrow [T, m(R_4N^+, OH^-)]_n + nxBF_4^-$$

Qualitatively, the behavior of BF_4^--doped poly(DB15C5) and poly(DB18C6) towards alkali cations was very close to that observed in solution with the monomers, i.e. the strongest affinity was obtained with K^+ and Na^+ in the case of poly(DB18C6) and with Li^+ for poly(DB15C5) [92]. Furthermore, this effect was all the larger as the doping level of the starting material was low.

This feature underlines that the complexing properties of poly(dibenzo-crown ether)s are not dependent only on the affinity of the crown ether towards a given cation. Other experimental parameters, such as the oxidation level of the polymer, the undoping method used, the nature of the counter-anion associated to the complexed cation and the nature of the solvent must be also taken into account. The influence of these various parameters has been analyzed by Rault-Berthelot et al. with poly(DB18C6) as a model material.

Firstly, the affinity of the polymer towards a large variety of cations including heavy metal and precious metal cations was greatly improved when the polymer was previously undoped [93–97]. As shown in Table 3, the ratio of one cation per two triphenylene units could be reached with cations like K^+, Cs^+, Rb^+, Hg^{2+}, Ni^{2+} and Pd^{2+} [95,96]. The worst results were obtained with La^{3+} and Mn^{2+}, and to a lesser extent with Ca^{2+}, Ba^{2+}, Co^{2+} and Sr^{2+}. In contrast, the ratio of one cation per two triphenylene units was overtaken for Ag^+ and Au^{3+}.

Additionally, poly(DB18C6) exhibited a moderate selectivity when several cations were mixed [95,97].

The influence of the solvent on the complexing properties of poly(DB18C6) was not easy to rationalize. Indeed, Ag^+, Sr^{2+}, Ba^{2+}, Ca^{2+}, Hg^{2+}, Ni^{2+} and La^{3+} were found to be more efficiently extracted from H_2O whereas K^+ and Rb^+ were more efficiently extracted from CH_3CN.

Moreover, the effect of the counter-anion was also unclear. As an example, for Ni^{2+} or Zn^{2+} extracted from CH_3CN, the results appeared better when using acetylacetonate than when using acetate anion. An opposite result was found in the case of the extraction of Sr^{2+}.

Consequently, the data collected in Table 3 suggest that poly(DB18C6) acted as an ion exchanging membrane more than a complexing polymer. Indeed, the tetraalkylammonium and hydroxide ions present initially in the undoped polymer could be partially exchanged with the cation and the counter-anion of the salt in solution. Information about the location of the cation within the undoped polymer structure has been provided from EXAFS measurements. It has been concluded that the

Table 3
Extraction of various cations by poly(DB18C6), previously undoped with electrogenerated superoxide anion in 0.2M $Bu_4NBF_4+CH_3CN$; procedure: 100 mg of undoped polymer in 20 mL of solution (H_2O or CH_3CN) containing the salt at about 0.1M; duration of contact: one week (from Ref. [95])

Cation	Counter-anion	Calculated ratio of cations per triphenylene unit T	
		Extraction from H_2O solution	Extraction from CH_3CN solution
Ag^+	BF_4^-		0.73
	NO_3^-		0.58
	NO_3^-	0.60	
Au^{3+}	Cl^-	1.35	
Ba^{2+}	$CH_3CO_2^-$		0.03
	$CH_3CO_2^-$	0.20	
Ca^{2+}	$CH_3CO_2^-$		0.02
	$CH_3CO_2^-$	0.12	
Co^{2+}	$CH_3CO_2^-$	0.16	
Cr^{3+}	$CH_3CO_2^-$	0.37	
Cs^+	BF_4^-	0.53	
	NO_3^-	0.28	
Hg^{2+}	$CH_3CO_2^-$	0.63	
	$CH_3CO_2^-$		0.52
K^+	$AcAc^-$[a]	0.45	
	$AcAc^-$[a]		0.55
La^{3+}	F^-		0.00
	F^-	0.03	
Mn^{2+}	NO_3^-	0.04	
Ni^{2+}	$AcAc^-$[a]		0.44
	$CH_3CO_2^-$		0.06
	$CH_3CO_2^-$	0.18	
Pd^{2+}	Cl^-	0.60	
Pt^{4+}	Cl^-	0.22	
Rb^+	NO_3^-	0.32	
	NO_3^-		0.48
Sr^{2+}	$CH_3CO_2^-$		0.06
	$AcAc^-$[a]		0.00
	NO_3^-		0.11
	NO_3^-	0.18	
Zn^{2+}	$CH_3CO_2^-$		0.25
	$AcAc^-$[a]		0.33

[a] $AcAc^-$ = acetylacetonate.

divalent cation Sr^{2+} as well as the monovalent ones Ag^+ and Cs^+ were located in poly(DB18C6) at the center of the crown ether [98,99].

In these complexation studies, the occurrence of a redox process was not observed and poly(DB18C6) remained in a neutral form. As reported by De Backer et al., the reduction of the triphenylene units could be performed when the polymer was treated with alkali metals. By this treatment, undoped poly(DB18C6) was converted into a new n-doped material similar to polyelectride [100].

The electrodeposition onto an electrode surface of the polymer films obtained from the oxidation of benzo- and dibenzo-crown ethers has been also described by

Lunsford et al. and the modified electrodes were used for the amperometric or potentiometric detection of catechols and catecholamines (e.g. dopamine) [101–103]. However, it seems very likely that the polymers electrosynthesized by these authors were electroinactive and insulating because a strongly positive electropolymerization potential (3.2 V vs Ag/AgCl, in CH_3CN) was used. Moreover, the possibility of a degradation of the crown ether at such a potential value could not be ruled out, although it has been reported that 18-crown-6 was not oxidizable up to 2 V (vs SCE) [104]. Finally, the interest to use a crown ether for the detection of catechols and catecholamines has not really been demonstrated in these papers and numerous studies have shown that insulating, overoxidized polypyrrole films could be also successfully used for the voltammetric determination of dopamine [105–109].

2.3.2. Polymers electrogenerated from the functionalized naphthalene derivatives

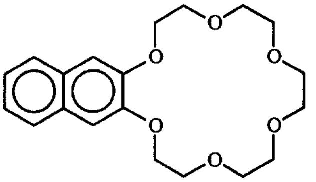
In the preceding section, the oxidation of dibenzo-crown ethers in appropriate experimental conditions led to the corresponding unconjugated, redox-type polymers in which the triphenylene units were the electroactive centers. In order to promote the anodic coupling of aromatic moieties and consequently to obtain electronically conducting fused polyarylenes functionalized by crown ethers, Simonet and co-workers have synthesized various naphthalene and binaphthalene crown ethers [110–113].

Poorly electroactive films were synthesized in low yield (< 10%) from the electrooxidation of naphtho-15-crown-5 whereas attempts to electrogenerate films from naphtho-18-crown-6 **15** failed. In contrast, the oxidation at about 1.1 V (vs $Ag/10^{-1}M\ Ag^+$) of dinaphtho-18-crown-6 **16** in CH_3CN or CH_2Cl_2 containing 0.1M Bu_4NBF_4 yielded the corresponding polymer film (electropolymerization yield, 30%) [111]. The BF_4^--doped film showed a conductivity of about 0.1 S cm^{-1} and its doping level was 0.35 BF_4^- per monomeric unit.

In the 1970s, Cram and co-workers developed an important concept in complexation based on a new class of crown ethers which had properties of chiral recognition due to their atropoisomerism [5,114]. Among the host molecules synthesized by Cram, those containing crown-6-ether and binaphthalene units showed abilities in distinguishing enantiomers of protonated amines and amino acids [115], as well as trapping spherical cations like alkali metal ions [116]. Systems such as bis-binaphtho-22-crown-6 **18a** and its derivatives were extensively studied and used in many applications [117–119] (e.g. preparative optical resolution by chromatography, chiral recognition in transport).

Thus the attachment of such ionophores onto electrode surfaces in order to take advantage of these specific properties observed in solution is of great interest. In this context of modified electrodes design and their potential use as ion-sensitive electrodes, Simonet and co-workers have demonstrated that p-doped electroactive polymer films could be electrogenerated from the oxidation of **18a** ([*SS*] or [*RR*] enantiomeric form) and **17** ([*S*] form) in an appropriate dried electrolytic medium, i.e. 0.1M $Bu_4NBF_4+CH_2Cl_2$ [110,112]. The doping level of these films was estimated at 0.35 BF_4^- per binaphthalene unit and their conductivity was below 10^{-4} S cm^{-1}.

It must be noted that the enantiomeric form of the monomers did not at all affect



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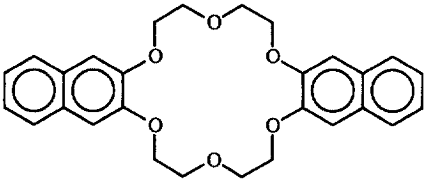

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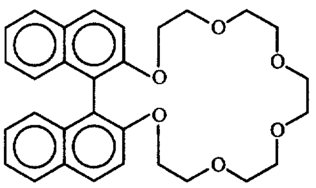

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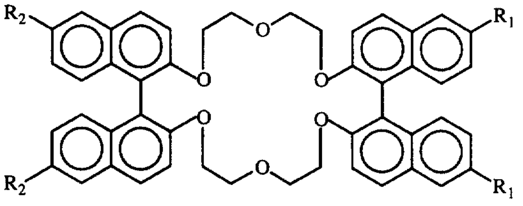
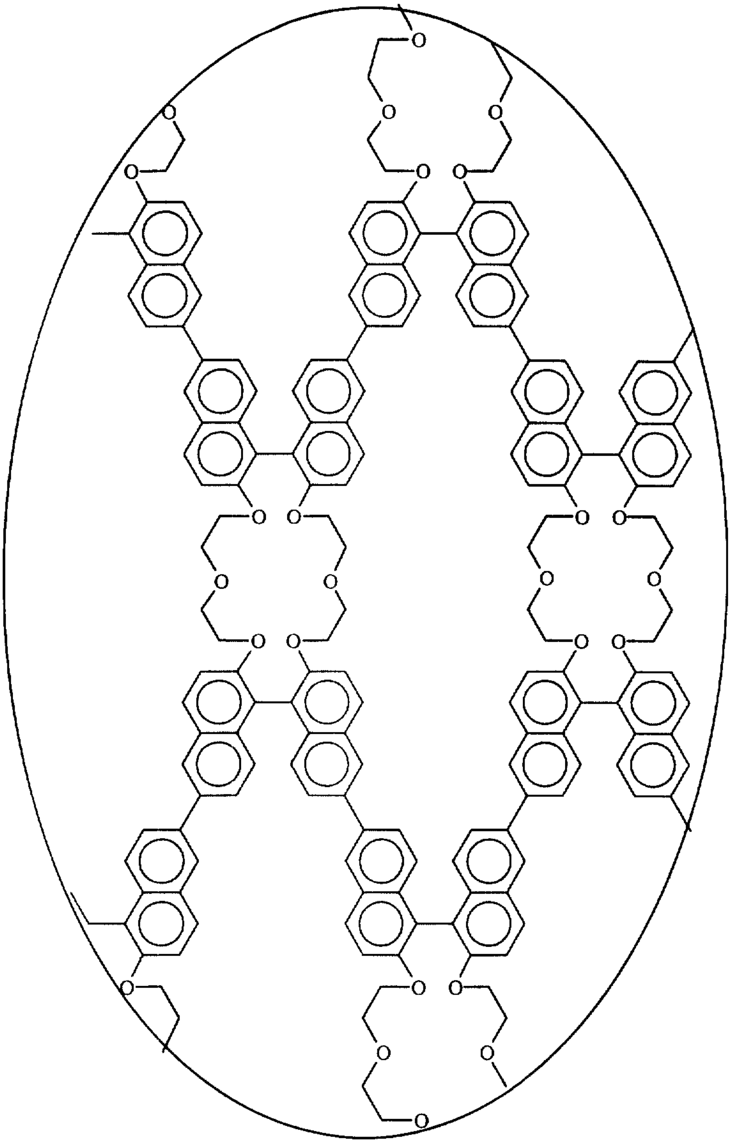


$R_1 = R_2 = H$ **18a**
$R_1 = R_2 =$ *tert*-butyl **18b**
$R_1 = H, R_2 = Br$ **18c**
$R_1 = H, R_2 =$ nitrophenyl **18d**

the electrochemical response and other characteristic properties of the corresponding polymers. The voltammetric behaviors of BF_4^--doped poly(**18a**) and poly(**17**) were somewhat similar with a reversible redox system at about 0.90 V (vs Ag/10^{-1}M Ag^+) corresponding to the doping/undoping process of the polymers. The electropolymerization of **17** has also been investigated by Ma et al. but the experimental conditions used (3.2 V vs Ag/AgCl, in CH_3CN) were unsuited to obtain electroactive films [120,121]. From the voltammetric study of two non-electropolymerizable substituted binaphthalene and bis-binaphthalene **18b** derivatives, Simonet and co-workers provided evidence for regioselectivity of the oxidative carbon–carbon coupling reaction [112]. By also taking into account the UV–visible and IR spectroscopic data of poly(**18a**), a structure was proposed for this polymer in which the binaphthalene groups are linked on the 6 and 6′ positions (Scheme 8). Furthermore, such a conjugated polymer exhibited the complexation properties of the monomeric unit [110].

However, although the binaphthalene crown ether derivatives could be reversibly reduced at about −2.9 V (vs Ag/10^{-1}M Ag^+), the occurrence of a reversible n-doping has not been demonstrated for the corresponding polymers. As a matter of fact, an unstable and irreversible process was observed whatever the electrolytic medium used. A reversibly n-doped and p-doped material has been obtained from the oxidation of substituted bis-binaphthalene crown ethers **18c** and **18d**. Polymers derived from these compounds in which the 6 and 6′ positions on one of the binaphthalenes are free led to conjugated polynaphthalenes while on the other



Scheme 8. Hypothetical structure of poly(bis-binaphtho-22-crown-6) (poly(**18a**)). (From Ref. [112].)

binaphthalene subunit, the blocking of these positions induced the formation of electroreducible perylenes by internal coupling between the 8 and 8′ positions [110,113]. Such functionalized polymers seem of great interest for an electrochemically switched complexation. Indeed, an enhancement of the cation binding through electrostatic interactions is expected when the polymer is negatively charged.

Contrariwise, a lowering of the cation binding is expected when the polymer is in its p-doped state.

2.3.3. Other electronically conducting polymers

With regard to the numerous papers devoted to polythiophenes, polypyrroles and polyphenylenes, the functionalization of other conducting polymers by polyether and crown ether ligands has received little attention. The approach consisting in the electrochemical conversion of linear polyether into pseudo-crown ether containing polymers has been generalized to polycarbazoles [122] and polyfluorenes [123]. These polymers were electrogenerated from the oxidation of dicarbazyls **20** and difluorenyls **21** linked together by a polyether spacer. As the electropolymerization reaction consumed only two electrons per molecule of substrate [123], the polyether functionalized material still contained electropolymerizable units. Therefore, the subsequent oxidation of the polymer could promote internal coupling reactions, giving rise to macrocyclic cavities. In the case of carbazoles *N*-substituted with a polyether chain **19**, only dimers were anodically formed [122].

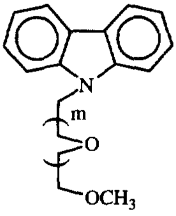
Polyfluorene bearing bis(3,6-dioxaheptyl) side groups (poly(**22**)) has been recently used as a light-emitting material [124]. The conjugated main chain served as an electronic conductor, while the bis(3,6-dioxaheptyl) side groups solvated ions and promoted ion transport. Solid-state light-emitting electrochemical cells based on this polymer and a dissolved lithium salt efficiently emitted bright blue light.

The derivatization of polyaniline by polyether [125] and crown ether [126] moieties has also been reported. In the first work, an unusual electrochemical behavior has been observed for the electrosynthesized poly[*N*-(3,6-dioxaheptyl)aniline] when studied in the presence of Li^+ [125]. It has been claimed that the interaction between this cation and the dioxaheptyl side chain resulted in a n-doping of the polymer. In the second work, the intercalation of 18-crown-6 or 15-crown-5 within the polyaniline structure was achieved from the chemical oxidation of the monomer in the presence of the ligand [126].

2.3.4. Electronically conducting copolymers designed as controlled-size pseudo-crown ether cavities containing materials

Owing to an incomplete electropolymerization reaction, the nature of electroactive polymers derived from compounds consisting of two identical electropolymerizable units linked together by a polyether chain was difficult to define. Furthermore, the subsequent oxidation of these polymers gave rise to the formation of macrocyclic cavities, simultaneously with the decrease of the mean conjugation length due to the distortion of the conjugated π-system. As shown in Scheme 4 for the case of the polythiophene derivative, the size of the complexing cavities within the polymer structure was expected to be variable after the anodic coupling reaction of the remaining aromatic units.

A novel approach to form controlled-size pseudo-crown ethers from acyclic polyethers has been recently proposed by Fabre et al. [46,127]. As conceptualized in Scheme 9, it consisted in the electrosynthesis of electroactive copolymers from compounds possessing two different electropolymerizable aromatic groups


m = 1, 2

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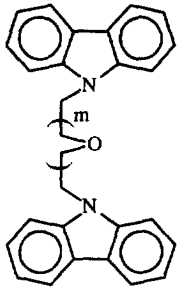
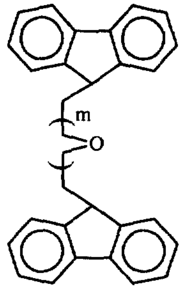
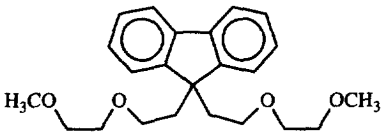

m = 2 to 4

20


m = 2, 3

21



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(pyrrole/thiophene **23**, pyrrole/dimethoxybenzene **24** and thiophene/dimethoxybenzene **25**) linked together by a polyether chain. Such an approach is of interest when functionalized conducting polymers with a defined structure are desired.

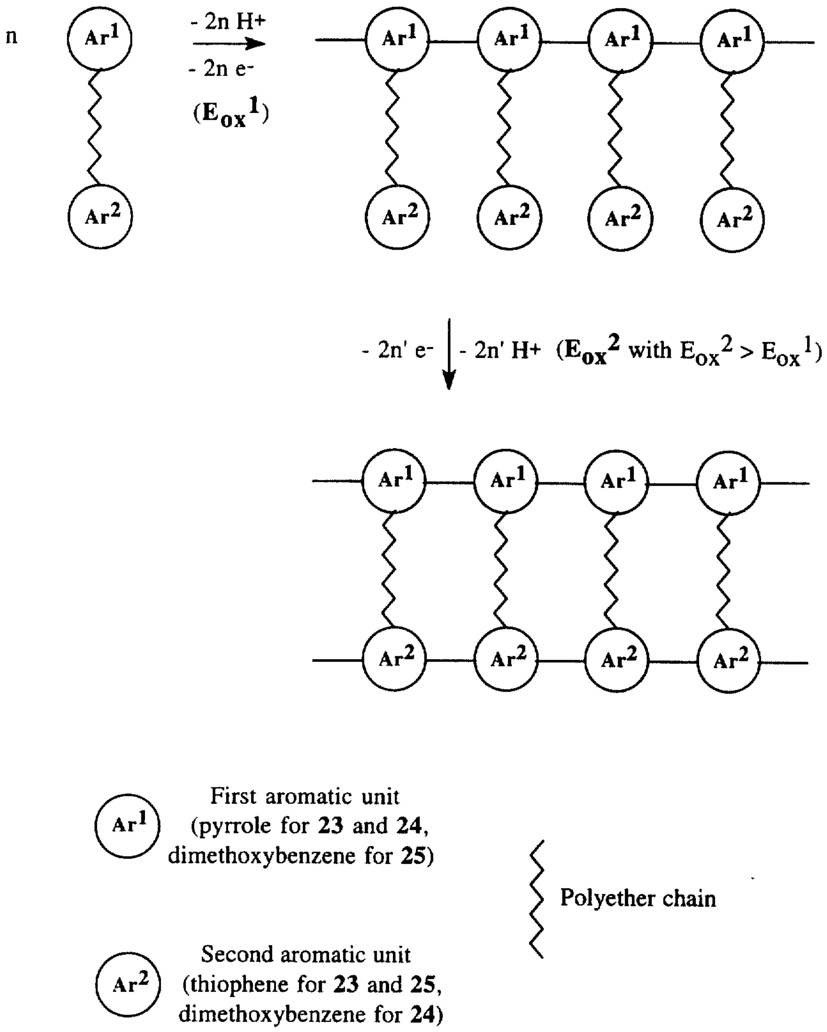
At a low anodic potential, the oxidation of the first electropolymerizable unit led to an electroactive homopolymer film composed of pendant polyether-substituted aromatic moieties. A subsequent oxidation of the polymer by applying a more positive potential promoted the electropolymerization of the second aromatic unit. Therefore, complexing macrocyclic cavities were electrogenerated, the size of which was thought to be adjustable depending on the length of the polyether chain of the starting monomer.

The two aromatic units were chosen so that the electroactivity of the preformed polymer was not degraded through an overoxidation process in the course of the electroformation of the second polymer. Generally this condition was fulfilled when the oxidation potentials of these two units were relatively close.

This type of solid-state electropolymerization has already been observed for biaromatic derivatives consisting of pyrrole and another aromatic group [128,129].

3. Polymers incorporating metallic redox centers

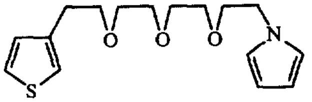
In solution, the electrochemical behavior of a redox center (e.g. ferrocene, quinone, tetrathiafulvalene, metalloporphyrin) in close proximity to a host crown ether could



Scheme 9. Electroformation of macrocyclic cavities from a solid-state electropolymerization reaction.

be modified upon the addition of a guest cation [20,21]. As rationalized in Scheme 1, this event involved redox and complexation equilibria.

With the aim to construct cation sensors, Beer and co-workers have modified electrode surfaces with redox-active polymer films containing benzo- and azacrown ethers [130–132]. These films were obtained from the cathodic electropolymerization of vinyl linked benzo- and aza-15-crown-5 ether–bipyridyl ruthenium(II) complexes, following the technique pioneered by Abruña et al. [133]. The electropolymerization was thought to proceed by a radical–radical hydrodimerization mechanism involving pairs of vinyl groups.



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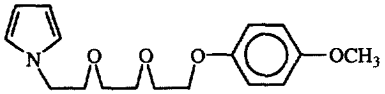

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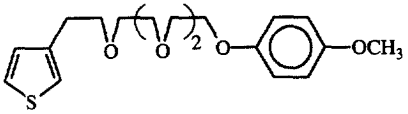

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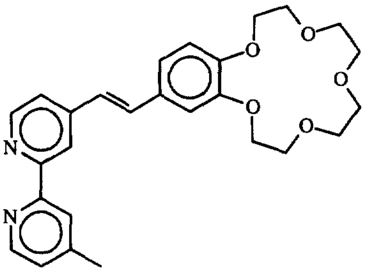
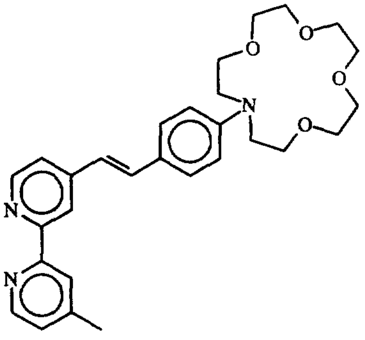
Possibly due to steric bulkiness of the 4,4′ substituents, the complexes $[Ru\mathbf{27}_3][PF_6]_2$ were less efficiently electropolymerized than $[Ru\mathbf{26}_3][PF_6]_2$.

The complexation of alkali and alkaline earth metal cations (Na^+ and Mg^{2+}) by



26a



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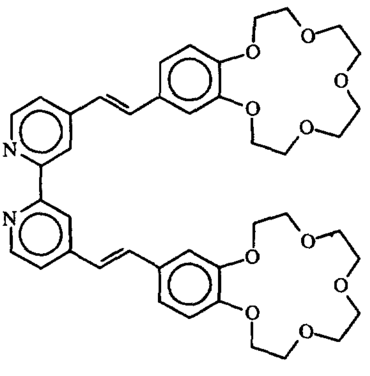
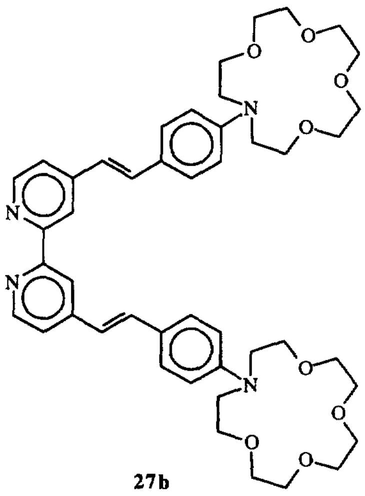


27a



27b

such crown ethers has been investigated by fluorescence emission spectrometry. Similarly to the monomeric complexes, the metal-to-ligand charge transfer emission maximum of the polymers was shifted to lower wavelengths in the presence of these ions. Thus, these functionalized polymers could be designed to spectrochemically recognize the cation binding. In contrast, an electrochemical-type recognition was not observed as the Ru^{III}/Ru^{II} redox response was not perturbed when the cation of the supporting electrolyte was changed. This result was explained by the too large distance between the bound cation and the Ru^{III}/Ru^{II} site as well as the removal of conjugation between the ionophore and the Ru^{III}/Ru^{II} site, caused by the loss of the vinyl linkages on electropolymerization [132].

The conversion of an electroinactive film into electroactive film has been reported by Massaux et al. for a polysiloxane derivative containing the benzo-15-crown-5 moiety [134]. The incorporation of thallium(I) within the polymer structure occurred when a mercury electrode coated with the functionalized polysiloxane was contacted with an acetonitrile solution containing this electroactive metal cation. After transfer to a thallium-free solution, a reversible and stable redox process was observed and assigned to the reduction of crown ether-complexed thallium to mercury amalgam, i.e. $Tl^{+}/Tl^{0}(Hg)_x$.

4. Concluding remarks

The affinity of a crown ether or a polyether towards an appropriate cation constitutes the driving force for the construction of the ion-responsive electrodes. The attachment of such specific groups onto electrode surfaces has been achieved via the chemical or electrochemical deposition of a functionalized polymer film. In most cases involving redox-active polymers (electronically conducting polymers, polymers incorporating metallic centers), the ionophore was directly grafted to the polymer. This procedure was found efficient to strongly and durably retain this group at the electrode surface. For these polymers, the recognition of cations was principally based on the modification of the electrochemical properties of the redox center. However, some examples have demonstrated that the optical and conducting properties of these materials could also be affected upon the complexation effect.

Besides the immobilization in polymer structures, the formation of lipid monolayers [135] and Langmuir–Blodgett multilayers [136] containing macrocyclic ionophores has been proposed as an alternative route to modify electrode surfaces with novel molecular architectures.

Recently, a new investigation field has appeared for this type of ligands. The specific interaction between a crown ether and an ammonium cation has been exploited for the formation of fullerene–crown ether monolayers [137,138]. The principle involved initial derivatization of a gold electrode surface with an ammonium-terminated alkanethiolate monolayer, followed by a secondary self-assembly of a monolayer of a crown ether–fullerene derivative driven by the interaction between the crown ethers and the ammonium groups. This original concept based on the molecular recognition principle could be generalized to other specific groups, such as catalytic, optical, electropolymerizable moieties, which are covalently bound to crown ether derivatives.

Acknowledgements

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