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Polypyrrole films containing metal complexes: syntheses and applications

Alain Deronzier, Jean-Claude Moutet

Laboratoire d'Electrochimie Organique et de Photochimie Rédox (URA CNRS 1210),
Université Joseph Fourier Grenoble 1, BP 53, 38041 Grenoble Cedex 9, France

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Contents

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Abstract

The deliberate modification of electrode surfaces by polymer films containing metal complexes to control the properties of the interface forms a new field that combines coordination chemistry with polymer chemistry and electrochemistry, and which aims at developing new materials for electrocatalysis, electroanalysis and photoelectrochemistry. This review describes the powerful method to prepare polymer coatings on a carrier electrode based on electropolymerization of pyrrole and substituted pyrroles. An overview of prospective applications is given.

Keywords: Electrode surfaces; Metal complexes; Polymer coatings; Polypyrrole films

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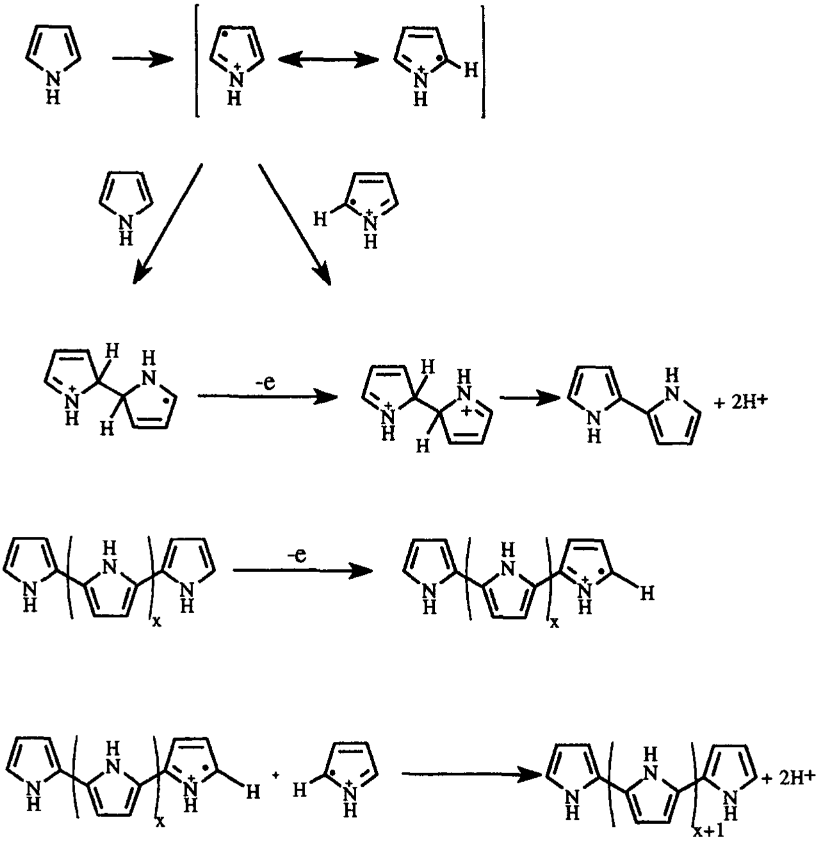
1. Introduction

Redox processes involving metallic complexes constitute an extensive field of chemical reactions, embracing reactions occurring in both living nature and industrial processes. Electrochemistry is the ideal tool to investigate in detail these types of reaction, and also for instance to use the redox properties of metallic complexes for electrocatalysis.

However, one of the major fields of modern electrochemistry concerns the deliberate modification of electrode surfaces by chemical reagents. In this context, the immobilization of metallic complexes appears of great interest and much effort has been recently expended to achieve this goal. The modification of electrode surfaces by polymer layers is a simpler, more effective and more versatile method than the chemical derivatization of surfaces via, for example, covalent bonding. The various methods for the preparation of polymer-coated electrodes have recently been reviewed [1–3]. The electrochemical polymerization and precipitation of films directly onto an electrode surface offer some advantages compared with the deposition of chemically preformed polymers. Electropolymerization allows the deposition of insoluble polymers, a uniform coating on irregular surfaces, and easy electrochemical control of the film thickness.

Among the various chemical functions that could undergo electrochemical polymerization, the pyrrole group appears exceptionally convenient for carrying out the coating of electrode surfaces by non-passivating polymer films containing active centres, especially transition metal complexes [4,5]. This review describes the generation of this type of functionalized polypyrrole film and some relevant applications of these molecular electrode materials in fields such as electrocatalysis, photoelectrochemical devices and sensors.



Scheme 1. Mechanism for pyrrole electropolymerization [10].

2. Making functionalized polypyrrole films

2.1. General principles

The formation of conductive and highly stable polypyrrole films on a platinum electrode by the anodic oxidation of pyrrole in acetonitrile was first reported in 1979 [6,7]. Electropolymerization of pyrrole occurs at a moderately positive potential ($E_{1/2}=1$ to 1.3 V vs. standard calomel electrode (SCE)). The mechanism of electropolymerization has still not yet been fully elucidated [8,9]. The initial step involves oxidation to a pyrrole radical cation which couples with another radical cation, or with pyrrole followed by a further charge transfer. Two protons are eliminated, forming a neutral dimer. The latter is immediately oxidized at the applied potential, since it is more oxidizable than the monomer, leading to a new radical cation. The continuing reaction is a lengthening of the oligomer chain, and this leads to the growth of polypyrrole on the electrode surface. The resulting polymer contains mainly structural units of 2,5-linkage (Scheme 1).

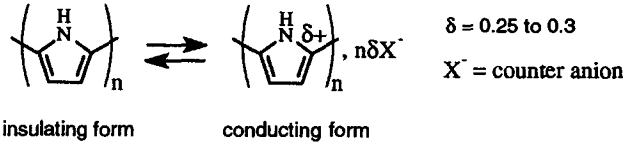
Potentiostatic and potentiodynamic as well as galvanostatic techniques can be used to polymerize pyrrole in both aqueous and organic electrolytes and form the corresponding polypyrrole films on various materials (Pt, C, Au, SnO_2, etc.) [11]. However, most studies have been conducted in organic systems from which pyrrole and numerous substituted pyrroles readily polymerize from dilute solutions (10^{-3} M). From the numerous results in the literature, it appears that acetonitrile containing a non-nucleophilic electrolyte, e.g. $LiClO_4$, R_4NClO_4, R_4NBF_4, is the most common medium. Since polymers from pyrrole have markedly lower oxidation potentials (0 to 0.4 V(SCE)) than the monomer, they are obtained in an oxidized state which is electrically conducting, allowing the growth of the film. The oxidized state contains approximately one positive charge for three to four pyrrole rings. Cyclic voltammetry studies show that the polymer can be cycled between the conducting (oxidized, doped) and the neutral (reduced, undoped) states (Scheme 2). The counter-anions from the electrolyte diffuse into and out of the polymer during the oxidative and reductive processes to ensure the electroneutrality of the film.

2.2. *Functionalization of polypyrrole by metallic complexes*

There are basically two major ways to functionalize polypyrrole films. The first involves the polymerization of a functionalized monomeric molecule; the pyrrole ring can be substituted on the nitrogen atom, or on its 3,4 positions. The second technique makes use of the anion exchange properties of the oxidized form of the polymer; for instance, anionic complexes can be trapped in polypyrrole during its preparation.

2.2.1. *Electropolymerization of N-substituted pyrrole monomers*

N-substituted pyrroles are excellent electropolymerizable monomers for the preparation of polymer films containing active centres. The *N*-substitution is responsible for a slower polymerization rate and a marked drop in the conductivity of the polypyrrole matrix, due to non-planarity of the polypyrrole chains induced by the substituents [12]. However, the remaining conductivity of the polymeric chain is large enough to allow the steady growth of films, without the help of the electroactivity in the anodic region of some pendant redox groups. This behaviour distinguishes pyrrole polymerization from other non-passivating electropolymerizations such as those involving vinyl or amino compounds [13]. Generally, derivatization begins with substitution at the *N*-centre by the appropriate ligand, followed by complexation



Scheme 2. Reversible oxidation of polypyrrole.

with the desired metal and electropolymerization of the resulting complex. A large variety of complexes has been immobilized via this strategy.

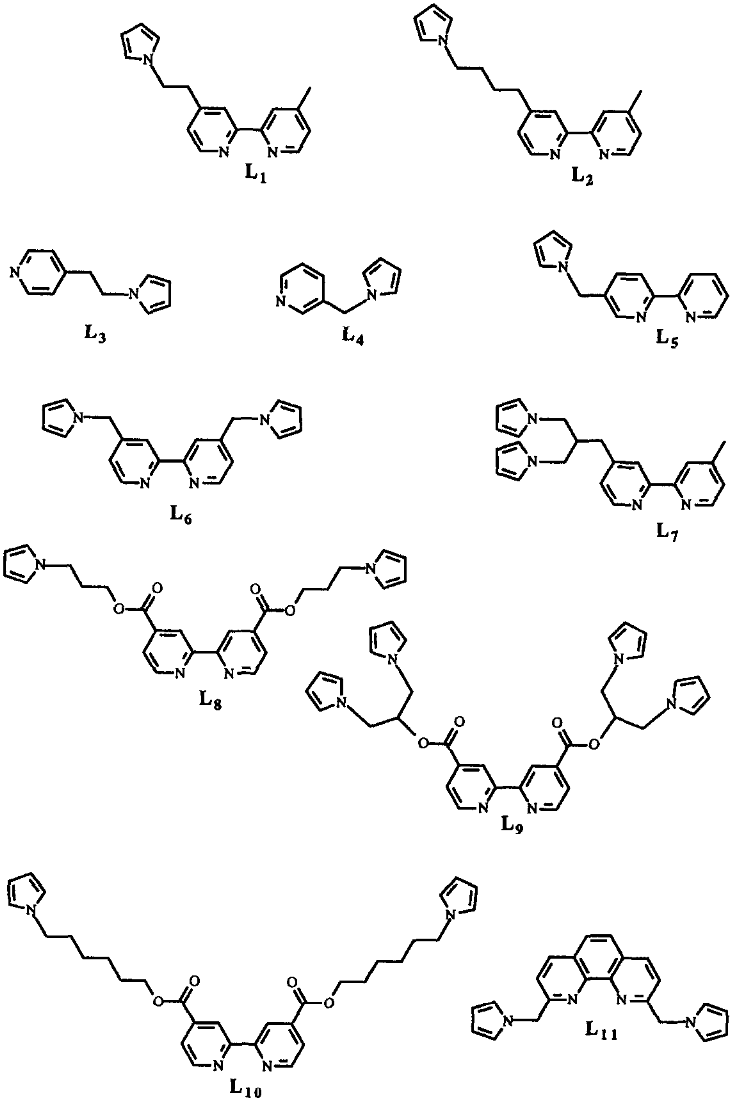
2.2.1.1. Polypyridyl complexes Synthesis with this class of complexes has been considerably developed. A series of pyrrole-substituted pyridine, 2,2′-bipyridine, 1,10-phenanthroline and 2,2′:6-2″-terpyridine ligands has been prepared (Scheme 3) and numerous corresponding Ru(II) [14–26], Fe(II) [16,17,22], Re(I) [27–29], Cu(II) [30], Co(II) [22,31,32], Ni(II) [22,33,34], Rh(III) [35–40], Mn(III) [22], Pd(II) [32,41,42], Cu(I), Zn(II) [32], Ag(I) [32] and Ir(III) [43] complexes have been synthesized.

In most cases, films of polypyrrole bearing these complexes can be obtained by anodic electropolymerization of the monomer, and polymeric films generally exhibit the regular electroactivity of the immobilized complex. For example, films corresponding to more than 10 000 monolayers of ruthenium complex could be readily grown from 5×10^{-4} M $[Ru(bpy)(L_1)_2]^{2+}$ in CH_3CN electrolyte [15].

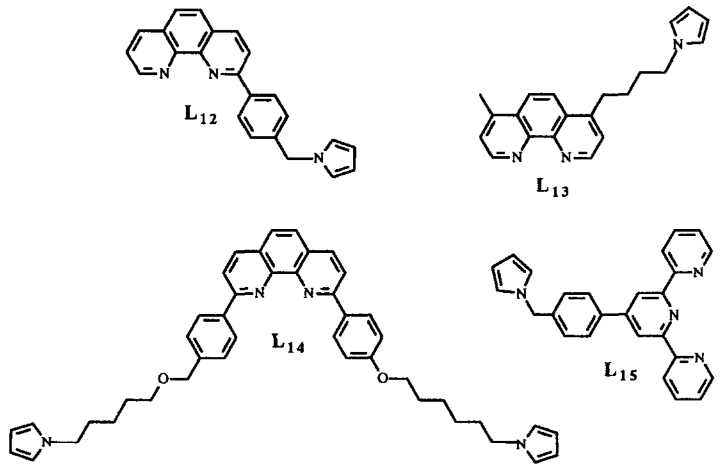
In most cases, i.e. when the polymer films do not contain pendant groups able to ensure a redox conductivity in the positive potential area, it is of great importance that the polypyrrole chain keeps its conductivity to grow thick and homogeneous films. Degradation of this conductivity during polymer growth would be responsible for the formation of very thin films. The reversible oxidation of regular polypyrrole is followed at a higher potential by an irreversible oxidation process called over-oxidation, leading to the destruction of its conductivity [44]. The over-oxidation corresponds to the formation of a dication which reacts with traces of water, forming substitution products. Thus it is recommended that electropolymerization is performed at potentials only slightly more positive than the potential of the polymerization threshold. From an experimental point of view, the polymerization potential must be choosen as the potential of the foot of the pyrrole oxidation wave.

To illustrate this over-oxidation phenomenon, a striking example based on the $[Ru(bpy)_2(L_9)]^{2+}$ monomer is given in Fig. 1. Films prepared at 0.7 V exhibit the polypyrrole electroactivity ($E_{1/2}\sim0.2$ to 0.3 V vs. Ag/10^{-2} M Ag^+; Fig. 1, curve (a)) in a clean electrolyte, followed by the Ru(III/II) wave ($E_{1/2}=1.05$ V). Scanning the potential to 1.6 V induces the emergence of a broad irreversible peak at about 1.4 V (Fig. 1, curve (b)) due to the over-oxidation of the polypyrrole matrix. On the reverse scan the reversible wave of the polypyrrole has totally vanished. Its regular oxidation wave is replaced by a pre-peak located at the foot of the Ru(III/II) oxidation wave (Fig. 1, curve (c)), indicating that the film is now non-conducting [45] through the polymer skeleton. It is noteworthy that the electroactivity of the complex remains unchanged and stable, demonstrating that the transformed, non-conductive polypyrrole retains its polymeric character and adherence. The same feature was obtained after the electrode was potentiostated at 1.5 V, or by using a higher anodic potential for its preparation ($E=1.1$ V, for instance, instead of 0.7 V) since the conductivity of the polypyrrole chain is destroyed as it is formed [21].

Moreover, film formation can be demonstrated by repeated cyclic voltammetric scans between, for instance, -0.4 and $+1.2$ V. Fig. 2 shows the continuous increase in the size of the cyclic voltammogram peaks for the Ru(II/III) couple during the growth of a poly$[Ru(bpy)(L_1)_2]^{2+}$ film [15]. The efficiency of the electropolymerization is strongly dependent on the number of pyrrole groups per monomer. As an example, it has been demonstrated that the film-forming ability of $[Ru(bpy)_{3-n}(L_1)_n]^{2+}$ complexes (bpy = 2,2′-bipyridine) increased when the number of pyrrole groups (n) was increased [15]. When starting with $[Ru^{II}(bpy)_2(L_1)]^{2+}$, the film accumulation remained limited to 10^{-9} mol cm^{-2}, while a coverage of 10^{-7} mol cm^{-2} of ruthenium(II) complex can easily be reached with $[Ru(L_1)_3]^{2+}$.



Scheme 3. Pyrrole-substituted pyridyl ligands.



Scheme 3. (Continued).

As pointed out previously, electropolymerization has mostly been conducted in CH_3CN electrolyte. However, in some cases it may be more convenient to use a less coordinating solvent. For instance, electropolymerization of pyrrole-substituted ruthenium(II) aquo complexes $[Ru(trpy)(L_2)(H_2O)]^{2+}$ (trpy = 2,2′:6′,2″-terpyridine) and $[Ru(L_{15})(L_2)(H_2O)]^{2+}$ cannot be accomplished in CH_3CN, since fast irreversible transformation occurs owing to the substitution of the aquo ligand by the

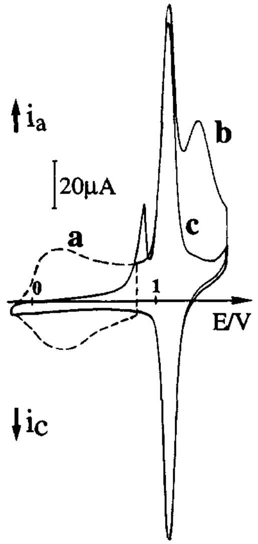


Fig. 1. Cyclic voltammogram of a glassy carbon disk electrode (5 mm diameter) modified by a poly$[Ru(bpy)_2(L_9)]^{2+}$ film ($\Gamma = 9 \times 10^{-9}$ mol cm^{-2}) prepared by electropolymerization at 0.7 V and transferred in fresh 0.1 M nBu_4NClO_4–CH_3CN ($v = 0.1$ V s^{-1}; V vs. Ag/10^{-2} M Ag^+): curve (a), scan range, −0.2 to +0.8 V; curves (b) and (c), first and second scans between −0.2 and +1.6 V.

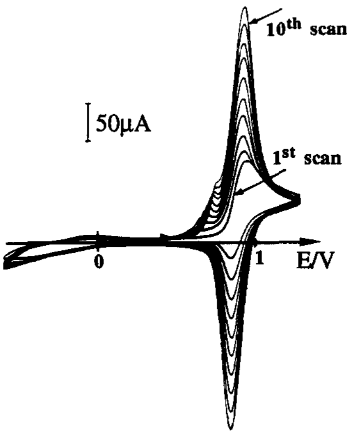


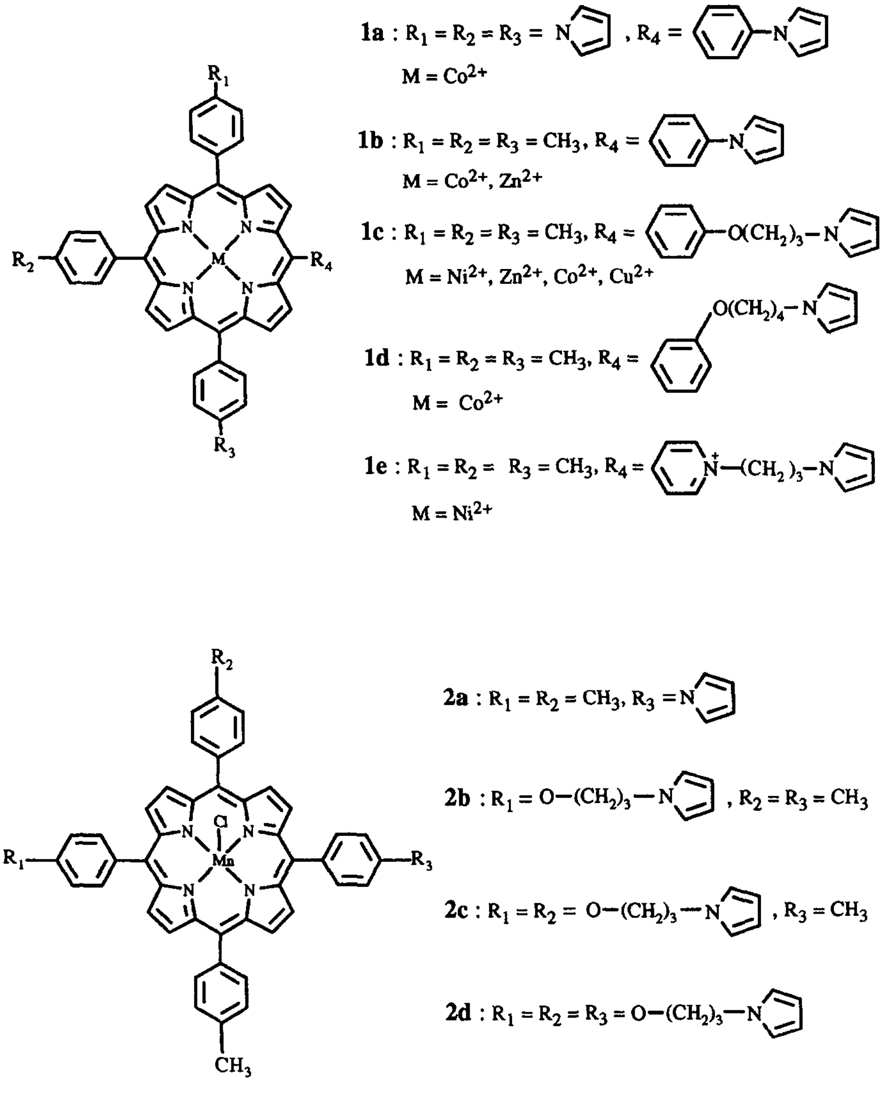
Fig. 2. Growth of a poly$[Ru(bpy)(L_1)_2]^{2+}$ film during the first ten cyclic scans at 0.1 V s^{-1} on a 5 mm diameter Pt disk electrode in a 0.5 mM solution of Ru(II) complex in 0.1 M nBu_4NClO_4–CH_3CN.

solvent. However, electropolymerization of $[Ru(L_{15})(bpy)(H_2O)]^{2+}$ in aqueous electrolyte gave only erratic results [22]. The coating of the electrode surface by undamaged aquo-complexes was successfully achieved by electropolymerization of $[Ru(trpy)(L_2)(H_2O)]^{2+}$ and $[Ru(L_{15})(L_2)(H_2O)]^{2+}$ complexes in less-coordinating organic solvents such as methylene chloride and acetone [23]. The cyclic voltammogram of a C/poly$[Ru(L_{15})(L_2)(H_2O)]^{2+}$-modified electrode transferred in phosphate buffer shows waves for both the the $Ru^{III/II}$ and $Ru^{IV/III}$ redox systems, demonstrating the formation of catalytically active $Ru^{IV}{=}O$ species, in spite of the slowness of the first couple.

All these polymeric materials need a fast mass-transport rate with a view to their application in electrocatalysis. Their permeability depends on several factors. The utilization of a bulky anion (toluenesulphonate, for instance) instead of ClO_4^- or BF_4^- in the polymerization step followed by its exchange with a smaller one (ClO_4^-) markedly improves the permeability of the films (×6). This results from an irreversible expansion of the polymeric structure by tosylate anions entrapped during polymerization. Scanning electron microscopy analysis corroborated the formation of an expanded structure. The efficiency of solute permeation is increased with films having a high degree of cross-linking ($[polyRu(L_1)_3]^{2+} > [Ru(bpy)(L_1)_2]^{2+}$) as a consequence of the better rigidity of the polymeric structure [46].

The technique of electropolymerization of *N*-substituted pyrrole complexes may also be used to build more sophisticated microstructures, including copolymers [47] and supramolecules [48,49] containing different redox active centres, especially ruthenium complexes which can behave as molecular electronic devices, e.g. p–n junction analogues.

The oxidation of these polypyridine ligands does not lead to the formation of a conductive polymer on the electrode surface. The amine function acts as nucleophile towards the pyrrole cationic centres and prevents their polymerization [50,51]. Usually, addition of a few equivalents of a strong acid (perchloric acid, for instance)



Scheme 4. Pyrrole-substituted metallic porphyrins.

protonates the basic centres and allows electropolymerization. The resulting polymer contains ligands in their protonated form [14,30,34,51]. Poly(pyrrole-Ni(II) bipyridine complex) films can be prepared in situ from a preformed poly(pyrrole–bipyridine ligand) film and a nickel salt in solution [34].

2.2.1.2. Metallic porphyrins Considerable effort has also been made to develop synthetic routes for the grafting of pyrrole to tetraphenylporphyrin derivatives [52–59]. There are two types of pyrrole-substituted metallic tetraphenylporphyrins

($M = Ni^{2+}$, Zn^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}); one involving the connection of the pyrrole group directly on the phenyl group, the other through a flexible chain. Scheme 4 summarizes the structures of the monomeric complexes prepared.

All the complexes investigated lead to the corresponding polypyrrole films. However, it appears that the efficiency of electropolymerization is lower for complexes in which the pyrrole is connected directly to the macrocycle. With this configuration, steric hindrance and mesomeric effects limit the efficiency of the electrochemical polymerization process. This is illustrated by the comparison between electropolymerization of **1b**-Co^{2+} [54] and **1d**-Co^{2+} [57] by repeated potential scans. The increase in the amplitude of the peaks is markedly faster and larger for **1d** (Fig. 3).

In addition, polypyrrole–cobalt(II) porphyrin films have some striking features [58]. The oxidation of the metal centre (Co(II)/Co(III) process) which is intrinsically a slow process in fluid solution is clearly observed only at very low sweep rates

Fig. 3. Growth of (a) poly **1b**-Co^{2+} (40th to 75th cycle) and (b) poly **1d**-Co^{2+} (1st to 20th cycle) films on a 3 mm diameter glassy carbon electrode in 2 mM solutions of monomers in 0.1 M nBu_4NBF_4–CH_3CN ($v = 0.15\ V\ s^{-1}$).

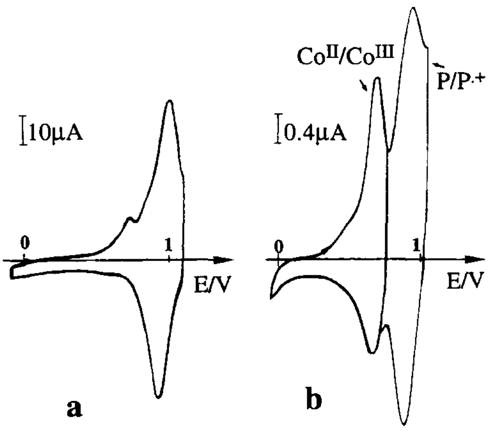


Fig. 4. Cyclic voltammetry of a Pt disk electrode (5 mm diameter) coated with a film of poly 1c-Co^{2+} ($\Gamma = 5.5 \times 10^{-9}$ mol cm^{-2}) in clean 0.1 M nBu_4NClO_4–CH_3CN; (a) $\nu = 0.1$ V s^{-1}; (b) $\nu = 0.005$ V s^{-1}.

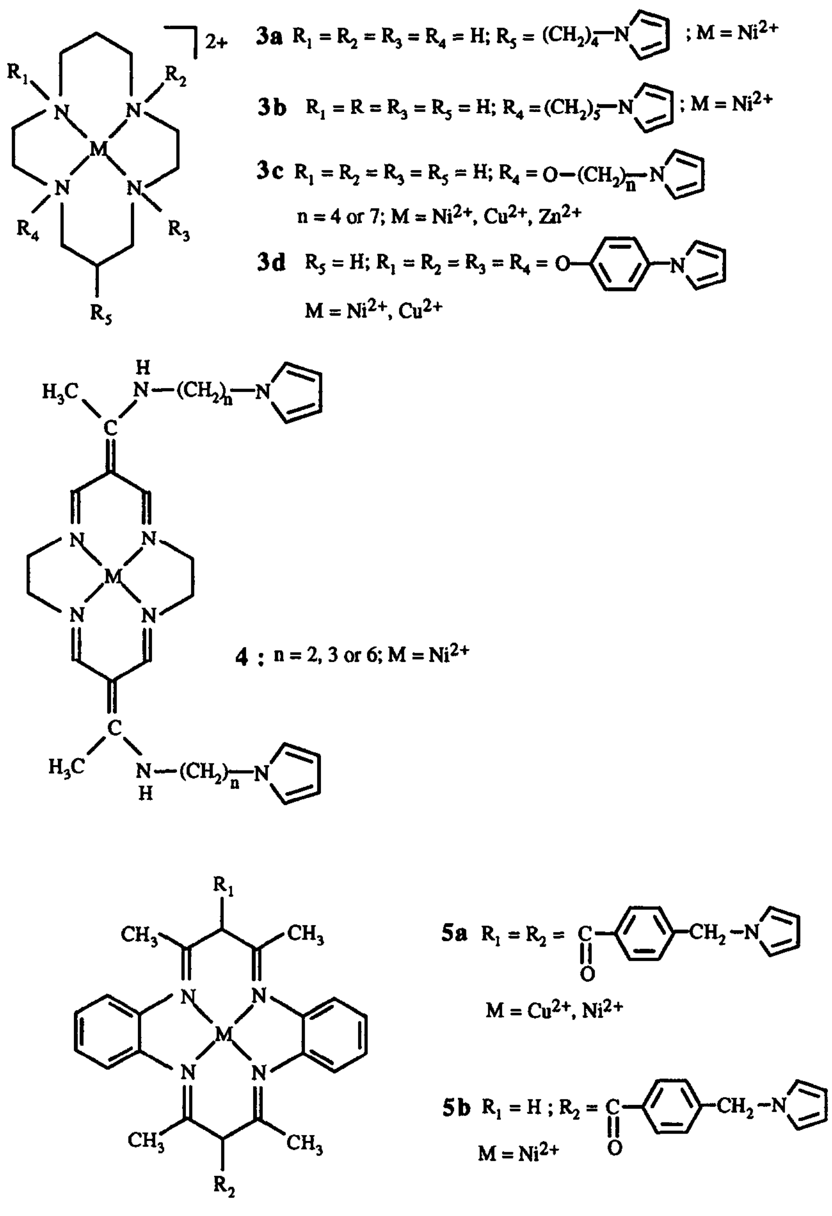
($\nu = 0.005$ V s^{-1}; Fig. 4(b)). In classical experimental conditions ($\nu = 0.1$ V s^{-1}) only a single pair of peaks is clearly observed as a consequence of the overlapping of the Co(II)/Co(III) and the P/P^+ (oxidation of the macrocycle) electron transfers (Fig. 4(a)).

2.2.1.3. Other macrocyclic complexes Successful electropolymerization of other pyrrole–macrocyclic complexes such as metallated cyclam [60–62] and tetraazaannulene [63–66] complexes has also been reported. The formulae of these molecules are represented in Scheme 5.

Fig. 5 shows, for instance, the growth of a polymer film from nickel–cyclam **3a** by repeated cyclic potential scans [60]. The main electrochemical process in the film corresponds to the Ni(III/II) couple. In contrast, the film is totally electroinactive in the cathodic area, where no redox process involving the Ni(II/I) couple is detected. This has been attributed to the fact that this process involves a purely metal localized redox orbital. Nickel–cyclam substituted by pyrrole at an N atom of the macrocycle can also lead to modified electrodes containing the Ni complex [62], although some previous attempts were unsuccessful [61].

Concerning the tetraazaannulene compounds, besides the development of modified electrodes following the regular pyrrole route, we noted an original procedure based on copolymerization of pyrrole and nickel tetraazaannulene [67]. Both compounds are known to lead separately to polymers at a comparable potential value.

2.2.1.4. Organometallics Several polymerizable ferrocene derivatives have been synthesized [68–72]. However, only a few are able to form electroactive polymers by direct anodic electropolymerization. Most involve their copolymerization with unsubstituted pyrrole.



Scheme 5. Pyrrole-substituted metallated cyclams and tetraazaannulenes.

2.2.2. *Electropolymerization of 3-substituted pyrrole monomers*

An alternative to *N*-substitution is to derivatize polypyrrole in the 3-position. The literature suggests that these materials would require a less anodic potential for their oxidation and would be more conductive than the *N*-substituted polypyrrole [73,74].

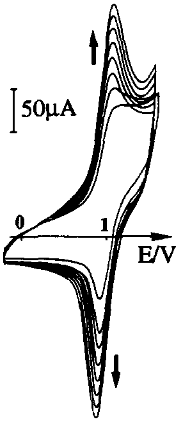
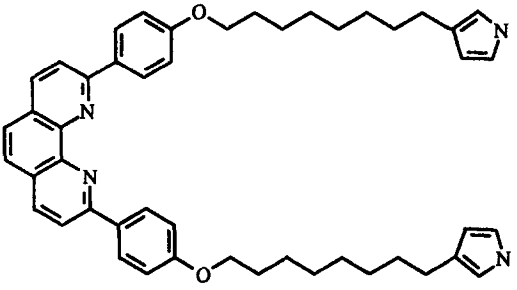


Fig. 5. Growth of a poly **3a**-Ni^{2+} film on a glassy carbon disk electrode by repeated potential scans ($\nu = 0.05$ V s^{-1}) in 0.1 M nBu_4NClO_4–CH_3CN.

However, preparation of derivatized ligands needs multistep synthesis, and pyrrole monomers substituted at the 3-position with metallic complexes remain restricted to a few examples. The first one [75,76] involves ferrocene derivatives, and the second one an entwining phenanthroline Cu(I) complex. The latter was prepared from the ligand L_{16} [77].



L_{16}

As expected, the electrochemical activity of the resulting polypyrrole matrix is shifted markedly in a negative direction (about 300 mV) compared with that of the corresponding film obtained from a similar complex in which phenanthroline ligands (L_{14}) contain *N*-substituted pyrrole.

2.2.3. *Incorporation of active species in polypyrrole films*

Another important route for the creation of polypyrrole-based materials is to trap active sites in polypyrrole or functionalized polypyrroles. Several approaches have been used to incorporate metallic complexes in polypyrrole films.

2.2.3.1. Trapping of chemicals during the electrochemical growth of the polypyrrolefilm or by anion-exchange procedure Since polypyrrole is obtained in an oxidized doped state containing counter-anions from the electrolyte, the electropolymerization of pyrrole in a medium containing an anionic species as the supporting electrolyte allows the development of polypyrrole films functionalized by this species. In such a way polypyrrole has been doped by several metallic tetraphenylporphyrin tetrasulphonates [78] or carboxylates [79,80] (Co(II), Fe(II), Mn(II)) and metallic phthalocyanine mono and tetrasulphonates (Co(II), Fe(II), Cu(II)) [81–87]. Some other complexes have also been incorporated by this technique. Polypyrrole films containing cobalt salts [88,89], thiomolybdate anions [90], nickel and palladium complexes of maleonitriledithiol [91], heteropolyanions [91–94], a chromium oxalate complex [95], an iron trisphenanthroline sulphonic acid complex [96] or ferri/ferrocyanide [97–102] and Prussian blue [103] have been prepared by electropolymerization in a medium containing these anions as supporting electrolyte. It is expected that the polymer frame would be formed around the trapped anion and retain it strongly. However, such electrode materials are less stable than those in which the substituent is covalently attached to the polymeric skeleton, owing to some exchange of dopant anions with counter-anions of the electrolyte [82]. The rate of release is high [104] with small dopant anions such as $[(Fe(CN)_6]^{4-}$. Moreover, polypyrrole loses its anion-exchange properties when it is reduced, and the process of removing the anions present in the film is competitive with the incorporation of cations of the supporting electrolyte.

Generally the large background current due to capacitive charging of polypyrrole renders the characterization of polypyrrole-doped films difficult by classical electrochemical methods. However, the visible electroreflectance technique, coupled to capacitive and voltammetric measurements [80] and in situ Raman spectroscopy [86] have been successfully used to characterize the redox properties of polypyrrole incorporating large macrocycles. The development of functionalized polypyrrole films by electropolymerization of pyrrole in the presence of anionic species appears simple and versatile. However, this technique has severe limitations. Its requires the use of large amounts of chemicals. It must also be emphasized that, even if the size of coating can be controlled by coulometry, the quantity of trapped molecules cannot be easily controlled and determined. Moreover, polypyrrole acts only as an anion-exchange material. Its exchange capacity is restricted to one negative charge per three or four pyrrole rings, and vanishes when it is reduced.

2.2.3.2. Polypyrrole films with improved ion-exchange properties Ion-exchange properties of polypyrrole can be dramatically improved by linking ionic substituents to its backbone. The validity of this approach has been demonstrated with the poly(3-methyl pyrrole-4-carboxylic acid) which has permanent cation-exchange properties and extracts the cobalt(II) trisbipyridine cation from diluted solutions [105]. Other positive multiply-charged complexes such as ruthenium(II) hexaamine and trisbipyridine have also been efficiently bound into a copolymer comprising pyrrole and 3-(pyrrol-1-yl) propanesulphonate [106].

Films with permanent anion-exchange capacity have been obtained by electropolymerization of pyrrole *N*- or 3- substituted with alkylammonium or pyridinium groups [107–111]. These improved anion-exchange properties have been exploited to bind some inorganic anions such as hexacyanoferrate(III) [107,111], octacyanomolybdate(IV) [111], iron–sulphur clusters [112–114], heteropolyanions [115] and metallic porphyrins [116,117].

Moreover, catalytic materials have also been built by trapping heterogeneous catalysts in polypyrrole films functionalized by cationic redox-active groups. The latter allows easy incorporation of metal or metal oxide microparticles by an ion-exchange procedure including electroreductive precipitation of particles. Suitable redox couples endow the polymer with a stable and well-defined conductivity at the potentials where the polypyrrole electronic conductivity is very weak. For instance, a poly[(pyrrole-Ru(II) trisbipyridine complex)-RuO_4^{2-}]-modified electrode displays the redox activity of both constituents of the material. After reductive precipitation of RuO_4^{2-} as RuO_2, the electrode exhibits the catalytic activity of the oxide [18].

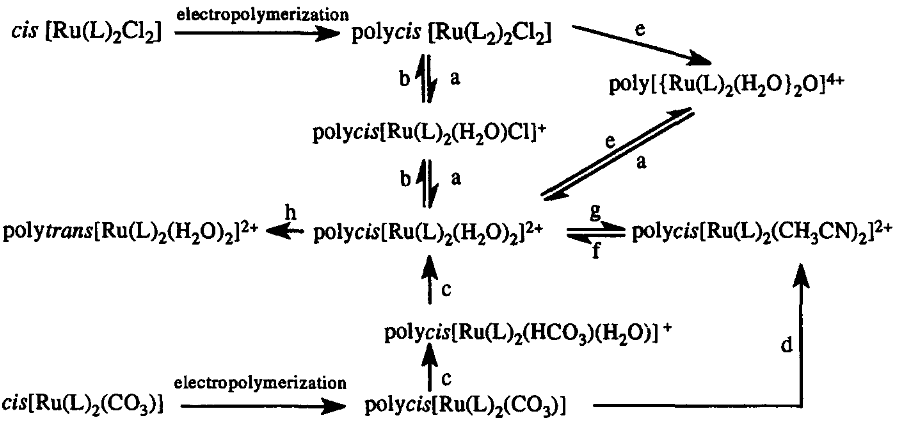
2.2.4. *Other methods*

2.2.4.1. Direct functionalization of polypyrrole films The amine functionality of polypyrrole is chemically reactive and can generate covalent bonds with suitable groups. Nevertheless, direct chemical derivatization of polypyrrole coatings remains restricted to a few examples. The functionalization of polypyrrole by ferrocene [118] or dithiocarbamate moieties [119] following this procedure has been attempted. However, this chemical modification appears limited to the outer surface of the film. Steric effects arising from the three-dimensional structure of the polymer and the size of the derivatizing agent limit the functionalization reaction.

2.2.4.2. Chemical and electrochemical transformation of functionalized polypyrroles The chemical reactivity of polypyrrole can be modulated and improved by the introduction of chemically reactive functions. A striking example is the chemical binding of an iron–sulphur cluster by ligand exchange in a polypyrrole film substituted with cysteinyl groups, obtained by a chemical treatment of a poly(pyrrole alkylammonium–pyrrole cystine) copolymer [113,114].

Electroinduced chemical and chemical transformations in functionalized polypyrrole films are also known. For instance films of polypyrrole containing polypyridyl aquo ruthenium complexes like *cis*-$[Ru(bpy)_2(H_2O)_2]^{2+}$ can be formed easily by transformation of films of poly *cis*-$[Ru(L_1 \text{ or } L_2)_2Cl_2]$ and poly *cis*-$[Ru(L_1)_2(CO_3)]$ prepared by regular electropolymerization of the corresponding monomers in non-aqueous solution [24,26]. Aquation of films to give first the mono-aquo, then the bis-aquo complex can be accomplished by continuously cycling the potential of poly *cis*-$[Ru(L_1 \text{ or } L_2)_2Cl_2]$ or by soaking a poly *cis*-$[Ru(L_1)_2(CO_3)]$ electrode in acidic aqueous solution. The same type of solvolysis can be accomplished in CH_3CN to form the poly *cis*-$[Ru(L_1 \text{ or } L_2)_2(CH_3CN)_2]^{2+}$ complex. However, polymerized *cis*-$[Ru(L_1)_2(H_2O)_2]^{2+}$ is readily converted into *trans*-$[Ru(L_1)_2(H_2O)_2]^{2+}$ by exposing the film to ambient light. The μ-oxo complex $[\{Ru(L_1)_2(H_2O)\}_2O]^{4+}$ could be obtained by soaking the electrode in an Ag^+ solution at 80 °C for 30 min. Scheme 6 summarizes the different transformations implied.

Finally, it was observed that a poly$[Ni(II)(L_2)_3]^{2+}$ is obtained by cycling a



Scheme 6. Chemical and electrochemical transformations in poly *cis*-[Ru(L)$_2$Cl$_2$] (L=L$_1$, L$_2$) and poly *cis*-[Ru(L)CO$_3$] (L=L$_1$): (a) scans between 0 and 1 V in 0.1 M CF_3SO_3H/H_2O, or between 0 and 1.2 V in 0.1 M aqueous $HClO_4$; (b) soaking in saturated NaCl for 1 h; (c) exposure to aqueous 0.1 M aqueous $HClO_4$ or HPF_6; (d) scans between 0 and 1.6 V in CH_3CN+0.1 M tetrabutylammonium perchlorate (TBAP); (e) soaking in 1% aqueous $AgNO_3$ at 80 °C for 30 min; (f) scans between 0 and 1.6 V in 0.1 M aqueous $HClO_4$; (g) scans between 0 and 1.6 V in CH_3CN+0.1 M TBAP; (h) ambient light for 72 h in aqueous 0.1 M CF_3SO_3H.

poly[(L$_2$)(H)$_2$]$^{2+}$-modified electrode in DMSO containing Ni(II) cations. The polymer–nickel complex formed in situ contains a larger quantity of electroactive Ni(II) sites than poly[Ni(II)(L$_2$)$_3$]$^{2+}$ films prepared by electropolymerization of the pyrrole-substituted Ni(II) complex, and has similar electrochemical behaviour [34].

3. Applications

3.1. Electrocatalysis

Electrocatalysis is in principle a process of great industrial interest. The aim is to drive selective oxidations or reductions of substrates efficiently at a modest potential. In comparison with classical electrodes, molecular electrode materials are presently at a fundamental stage of research. They possess the advantage of a wide area of application owing to the great variety of catalysts that can be confined on the electrode, but they have the disadvantage of less stability. However, recent developments in the electrochemistry of polypyrrolic coating have allowed laboratory-scale electrosynthesis to be carried out [4]. A large part of this development is attributable to the high chemical stability of polypyrrole films and the possibility to immobilize very efficient and selective transition-metal complexes catalysts into this polymer. An inherent problem with electrochemistry is that at least one heterogeneous step is involved. Mediated electrolysis makes use of electron-transfer catalysts that shuttle electrons between the metallic electrode and the substrate, avoiding adverse effects which result in the necessity to apply a large over-potential.

Two cases of electrochemical catalysis have been distinguished [120,121]. *Electrochemical redox catalysis* concerns the acceleration of sluggish electron transfers by means of a mediator (reversible redox system) which exchanges electrons rapidly with both the electrode and the substrate, the latter via an outer-sphere process. Pure homogeneous electron transfers must be clearly distinguished from electron transfers associated with a chemical step, such as the existence of a specific interaction and/or exchange of atoms or molecules between the electrocatalyst and the substrate through an inner-sphere process. The latter case is called *chemical catalysis*. Great efficiency and selectivity will arise from the double role played by the chemical catalyst.

From a general point of view, electrocatalysis with a catalyst immobilized in a film at an electrode surface has a number of obvious advantages over the homogeneous case, including easier recovery of products and catalyst, and the use of much lower quantities of catalyst, highly concentrated in the reaction layer. The latter point is of huge importance for the use of costly catalysts such as transition-metal complexes. Moreover, in many cases the immobilization of the catalyst on the electron source provides its stabilization, and allows the number of catalytic cycles which can be effected by a catalytic site to increased markedly, as compared to the corresponding homogeneous system.

3.1.1. Electrochemical redox catalysis

Although without real synthetic value, the mediated reduction of vicinal dibromides to olefins has been examined with a polypyrrole Co (II)-catenand modified electrode [122]. In the same way, the electrocatalytic oxidation of benzylalcohol to benzaldehyde has been achieved with a triruthenium cluster–polypyrrole film [20].

3.1.2. Chemical catalysis

3.1.2.1. Alkyl chloride reduction The poly $[Co(L_2)_3]^{2+}$ electrode is an efficient electrode material for alkyl chloride catalytic reduction [31] in a manner similar to that observed in homogeneous solution [123]. In the latter case, it was proposed that the loss of one bipyridine ligand is the slow step which controls the catalytic process. Thus it appears that the linkage of the ligand to a polymeric film does not prevent this key step.

3.1.2.2. Activation of dioxygen A large number of studies relative to the reduction of dioxygen to water or hydrogen peroxide on polypyrrole films containing oxygen-reductive electrocatalysts, especially metal phthalocyanines and porphyrins [78,80,81,83,85], have been made. However, they remain restricted to cyclic or rotating-disc voltammetry experiments.

More interesting are biomimetic oxidations of hydrocarbons by dioxygen using manganese porphyrin-coated electrodes as the electrocatalytic system. The only example of quantitative electrosynthesis on an anionic catalyst-doped polypyrrole film is the electroassisted oxidation by molecular oxygen of 2,6-di-t-butylphenol with a polypyrrole-containing manganese porphyrin [79,80]. More attractive results have

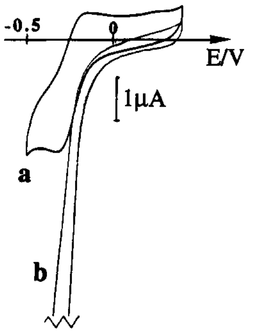
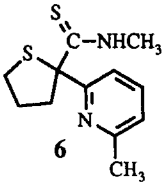


Fig. 6. Mn(III/II) redox couple in a poly **2a** film coated on a 5 mm carbon disk electrode in 0.1 M nBu_4NClO_4–CH_3CN containing 1-methylimidazole and benzoic anhydride under argon (curve (a)) and dioxygen (curve (b)) ($v = 0.02$ V s^{-1}).

been obtained by oxidative electropolymerization of pyrrole-substituted porphyrins. The principle of an homogeneous electrocatalytic model cytochrome-P450 has been described by Creager et al. [124]. Using the same principle, catalytic oxidation of 2,6-di-t-butylphenol [125,126] to its quinone and dibenzoquinone derivatives and epoxidation of *cis*-cyclooctene [53,59,125,126] were carried out with electropolymerized manganese pyrrole-substituted porphyrins.

Fig. 6 shows the strong catalytic wave observed with a poly(pyrrole–Mn porphyrin)-modified electrode in the presence of O_2, 1-methylimidazole as axial base and benzoic anhydride as activator [59]. The confinement of the catalyst in the polymer film markedly improves its stability. For instance, a turnover per porphyrin site greater than 2500 and a high current efficiency (85%) were obtained for the catalytic epoxidation of *cis*-cyclooctene on a 10 mm × 10 mm × 4 mm carbon felt electrode coated with a poly **2d** film containing 2×10^{-8} mol of catalyst [59]. In homogeneous experiments, the best turnover was only 10 and the current efficiency reached only 56% [124]. Miscellaneous hydrocarbons, i.e. tetraline, indane, cyclohexene, cyclooctane [127] and stilbene [59], have been also oxidized with this system, with acceptable catalytic efficiencies (up to 500 turnovers per hour).

An important objective of the use of biomimetic catalytic systems is to reproduce drug metabolism, which would allow oxidized metabolites of a given biologically active molecule to be prepared. In this context, oxidation of the thioacetamide **6**, which has interesting anti-secretory and anti-ulcer activities, has been successfully accomplished on poly **2b**-modified electrodes [59]. Its five oxidized derivatives **7a**–**7e** were produced in quantifiable (micromolar) amounts and identified by comparison with metabolites formed in vitro in the presence of rat liver microsomes. It should be noted that increasing the surface concentration of catalyst by using monomers **2c** or **2d** containing two and three pyrrole groups, and hence having a better polymerizability, gave cross-linked polymers which presented a lower activity than a polymer film prepared from monomer **2b** containing only one pyrrole group.



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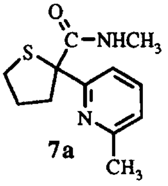
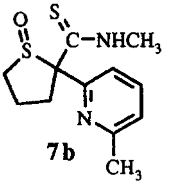


7a



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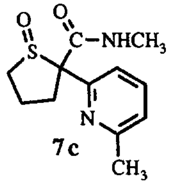

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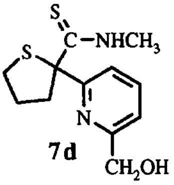

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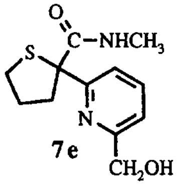


7e

3.1.2.3. Carbon dioxide reduction Another relevant example of catalysis is the electrocatalytic reduction of carbon dioxide using electrodes modified by electropolymerization of pyrrole-containing transition metal complexes.

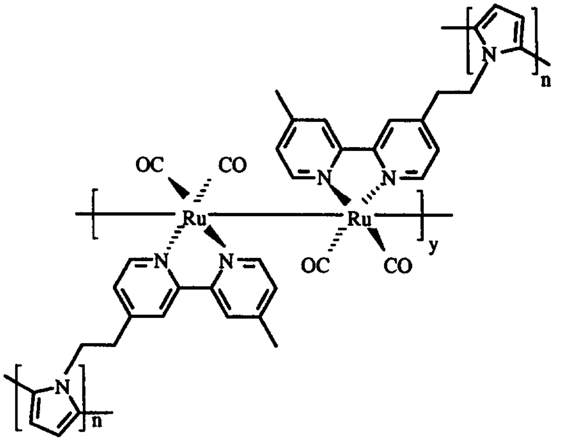
Carbon dioxide activation has been studied by cyclic voltammetry and preparative electrolysis on platinum and carbon electrodes modified by electropolymerization of *fac*-[Re(L)(CO)$_3$Cl] (L = L_2, L_6, L_7) complexes [27–29]. The large enhancement of the peak current for the reduction (Re(I)→Re(0)) of the immobilized rhenium species in the presence of CO_2 illustrated the strong electrocatalytic activity of this molecular electrode material towards CO_2 activation. Preparative-scale electrolysis in acetonitrile electrolyte on large-area (platinum gauze or carbon felt) modified electrodes gave mainly carbon monoxide, with current efficiencies higher than 90%, according to the following equation:

$$2CO_2+2e^- \rightarrow CO+CO_3^{2-}$$

The production of CO increased when the surface concentration of the rhenium complex increased. The optimal film thickness for maximum catalytic efficiency corresponded to about 4000 monolayers of catalyst. However, current densities remained low, ranging between 0.2 and 1 mA cm^{-2} according to the film thickness.

Among the number of metal complexes which have been examined as electrocatalysts for CO_2 reduction, only a few appeared effective in aqueous electrolytes, because the accompanying reduction of protons is usually observed [128]. This problem could be avoided by using polymer-confined catalytic systems deposited on a cathode surface. Nickel(II)–cyclam presents efficient and selective electrocatalytic properties towards reduction of CO_2 to CO in aqueous electrolytes [129]. Unfortunately, poly(pyrrole–Ni(II) cyclam) films are insulating in the cathodic region, preventing the use of the Ni(II)/Ni(I) couple in electroreductive reactions [60].

Selective and quantitative production of CO by reduction of CO_2 in pure aqueous electrolyte has been achieved on carbon electrodes coated by a film of an inorganic $\{Ru(bpy)(CO)_2\}_n$ polymer, containing Ru^0–Ru^0 bonds and formed upon cathodic



Scheme 7. Polypyrrole[$\{Ru(L_1)(CO)_2\}_n$] composite.

reduction of the [$Ru(bpy)(CO)_2Cl_2$] complex by a two-electron process associated with the loss of two Cl^- ligands [130–132]. The operational stability of these materials is markedly improved when the metal–metal bonds are electrochemically generated in a preformed polypyrrole film substituted by [$Ru(bpy)(CO)_2Cl_2$] units [131]. The latter was obtained by electropolymerization of [$Ru(L_1)(CO)_2Cl_2$] [25]. Scheme 7 shows the proposed structure for the polypyrrole [$\{Ru(L_1)(CO)_2\}_n$] composite material.

3.1.2.4. Alcohol oxidation Polypyridyl oxo complexes of ruthenium are known as active oxidants for a variety of organic substrates and, particularly, the [$Ru(trpy)(bpy)O]^{2+}$ complex is capable of oxidizing alcohols, aldehydes, cyclic ketones and C–H bonds adjacent to olefinic or aromatic groups [133]. The catalytic activity of the corresponding polymeric material poly-[$Ru(trpy)(L_2)(H_2O)]^{2+}$ and poly-[$Ru(L_{15})(L_2)(H_2O)]^{2+}$ was demonstrated by cyclic voltammetry experiments (Fig. 7) and preparative-scale oxidation of alcohols. For instance, benzyl alcohol and 1-phenylethanol were oxidized to benzaldehyde and acetophenone with 85% and 82% electrical yield respectively in a phosphate buffer of pH 6.8 at a poly-[$Ru(L_{15})(L_2)(H_2O)]^{2+}$-modified electrode [23]. Poly-[$Ru(trpy)(L_2)(H_2O)]^{2+}$ film is markedly less stable under catalytic conditions than poly-[$Ru(L_{15})(L_2)(H_2O)]^{2+}$. Analytical and preparative-scale capability as oxidant of poly-[$Ru(L_2)_2(H_2O)_2]^{2+}$ films has been tested toward alcohols and chloride ions. As an example, the selective transformation of benzyl alcohol to benzaldehyde was accomplished on a carbon-felt modified electrode with 89% current efficiency and 2200 turnovers [24]. Controlled-potential electrolysis in 0.1 M CF_3SO_3H of a 1.0 M solution of Cl^- led to Cl_2 in 49% yield. The partial deactivation of the modified electrodes comes from the anation of the complex to give poly-[$Ru(L_2)_2(H_2O)Cl]^+$. However, the catalytic activity can be restored by soaking the electrode in 0.1 M $HClO_4$ and then in water for several hours [26].

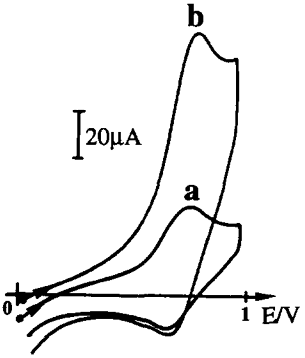
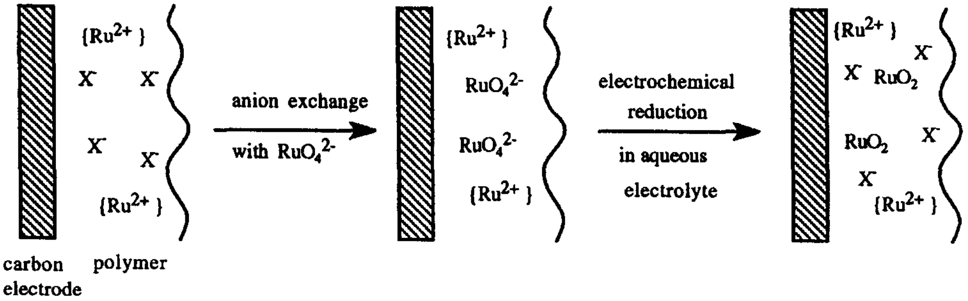


Fig. 7. Cyclic voltammetry of a Pt/poly$[Ru(trpy)(L_2)(H_2O)]^{2+}$-modified electrode in a phosphate buffer of pH 6.8 before (curve (a)) and after (curve (b)) addition of 0.05 M allyl alcohol ($v = 0.1$ V s^{-1}).

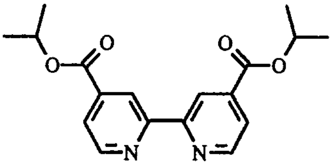


Scheme 8. Elaboration of a C/poly[pyrrole-Ru(II) complex-RuO_2] catalytic anode ($X^- = ClO_4^-$).

One of the most efficient electrocatalytic systems for the oxidation of organic substrates is based on the utilization of ruthenium tetraoxide as an oxidizing agent. The latter can be electrochemically generated from RuO_2. Catalytic anodes have been prepared by trapping RuO_2 microparticles in $[Ru(L_2)_3]^{2+}$ films [18,134]. The ion-exchange method for RuO_2 incorporation is depicted in Scheme 8.

The trisbipyridine ruthenium(II) complex acts as a stable and efficient electron relay ($E_{1/2}$ Ru(III/II)$=0.92$ V) for the electrochemical generation at 1.1 V of the oxidizing RuO_4^{2-} species. Analytical proof of its formation in the polymer film and of the electrocatalytic activity of the modified electrodes towards benzyl alcohol oxidation was obtained from cyclic voltammetry experiments. Preparative-scale oxidation of a number of carbinols was accomplished in $LiClO_4/CH_3CN$ electrolyte containing 4% of water, with turnovers above 10^4 (Table 1).

Formation of the higher-oxidizing RuO_4^- species could be achieved with a poly$[Ru(L_{17})_2(L_9)]^{2+}$ matrix, since electron-withdrawing carboxyester groups at the 4,4′-positions of the bipyridyl ligands induce a large positive shift in the Ru(III/II) redox couple up to 1.24 V.



L_{17}

A higher catalytic activity and an increase in turnover (up to 14 000) was then obtained [134]. Moreover, oxidation of cinnamyl alcohol at 1.35 V gave appreciable amounts of glyoxal and benzaldehyde, resulting from a six-electron oxidation process, in addition to cinnamaldehyde. This result is consistent with the electrogeneration of the highly oxidizing RuO_4^- species in the film.

3.1.2.5. Electrocatalytic hydrogenation Although the literature has some relevant examples of efficient photo- [135,136] and electro-reduction [35,36] of protons to hydrogen by using metallic complexes, especially rhodium, transition metal complexes have only been used recently as catalysts for the electrochemical hydrogenation of organic compounds [137]. It was assumed that reduction of protons or water with metal complexes in a low valence state leads to a metal–hydride intermediate from which hydrogen gas is evolved [135]. This has recently been clearly demonstrated with an iridium complex such as $[(C_5Me_5)Ir(bpy)Cl]^+$. The corresponding hydrido complex $[(C_5Me_5)Ir(bpy)H]^+$ is quantitatively electrogenerated by reduc-

Table 1
Electrocatalytic oxidation at 1.16 V of primary and secondary alcohols with a C/poly$[Ru(L_2)_3]^{2+}$ RuO_2 electrode in 4% aqueous CH_3CN containing 0.1 M $LiClO_4$ and Na_2CO_3

Alcohol	E_p^a (V)	Components of modified electrode		Amount of aldehyde or ketone (10^{-3} mol)	Current efficiency (%) (turnover)
		$[Ru(L_2)_3]^{2+}$ (10^{-7} mol)	RuO_2 (10^{-7} mol)		
Benzyl alcohol	2.00	7.00	6.80	7.16	99 (10500)
Cinnamyl alcohol	1.85 2.11 2.29	7.05	7.05	3.64	95 (5150)
1-Naphthyl methanol	1.48	6.95	7.01	2.64	98 (3750)
Benzhydrol	1.96	7.10	7.10	4.39	97 (6200)
Fluorenol	1.70	7.00	7.02	2.28	96 (3250)
4,4′-Dichlorobenzhydrol	1.93	7.05	7.05	2.80	98 (3950)

[a] Anodic peak potential measured by cyclic voltammetry.

tion of $[(C_5Me_5)Ir(bpy)Cl]^+$ in solution [138] or in a polypyrrole film [139] in the presence of protons or residual water. The polypyrrole films derived from $[(C_5Me_5)Rh^{III}(L)Cl]^+$ ($L=L_7$, L_{10} or L_{12}) has allowed the build-up of molecularly-based cathode materials for hydrogen evolution in aqueous media [35,36]. A modified electrode obtained by electropolymerization of a metal–hydride complex such as pyrrole-substituted $[Rh^{III}(H)_2(PPh_2Et)_2(bpy)]^+$ is active towards the reduction of water [40].

Preliminary results have shown that a C/poly $[Rh^{III}(L_8)_2Cl_2]^+$ electrode could hydrogenate cyclohexanone to cyclohexanol, at a potential where the catalytically active Rh(I) intermediate is formed [38]. Further investigations have shown that this catalytic electrode could efficiently hydrogenate substituted cyclohexanones and carvone, with turnovers around 10^3 [140]. It was assumed that a rhodium–hydride intermediate is involved in the hydrogenation mechanism. It is noteworthy that the supported catalytic system appeared more efficient than the homogeneous one, as demonstrated by the comparison with electrocatalytic hydrogenation using a similar complex in homogeneous media. Moreover, a noticeable difference in regio- and stereoselectivity was found for the hydrogenation of bulky substrates on the catalytic cathode, as compared with their homogeneous catalytic and electrocatalytic hydrogenation. For example, the distribution of the diastereoisomers of the dihydrocarveol formed by hydrogenation of carvone was quite different depending on the electrocatalytic system (modified electrode or homogeneous system) used. This demonstrates that the microenvironment of the polymer matrix in which the complex is embedded has a strong influence on its selectivity.

Recent studies carried out with carbon electrodes modified by electropolymerization of $[Ru^{II}(L)_2Cl_2]^+$ complexes ($L=L_2$ or L_{13}) have shown that the use of an alkyl chain to link the complexes to the polypyrrolic skeleton, instead of a carboxy-ester group as in L_8, markedly improves the operational stability of these cathodes. Turnovers as high as 5000 have been obtained for the electrocatalytic hydrogenation of various organic substrates, without appreciable loss of the catalytic activity of the cathodes [141].

Electrode materials synthesized from electropolymerization of the $[Pd^{II}(L_1)_2]^{2+}$ complex have also been shown to be active for the selective hydrogenation of the carbon–carbon double bond of a number of enones [41]. It is noteworthy that the catalytically active Pd(0) form of the complex is stable in its polymeric film form, while it quickly decomposes in homogeneous media.

3.1.2.6. Electrochemical regeneration of NADH Non-enzymatic regeneration of reduced nicotinamide adenine dinucleotide (NADH) requires the regioselective transfer of two electrons and a proton to NAD^+. Various polypyridinyl rhodium(III) complexes have been used as electrocatalysts for this purpose. However, NADH electrochemical regeneration always goes with the formation of non-biochemically-active dimers and isomers via direct reduction of NAD^+. An attractive alternative is the use of an electrode modified with a polymer film containing the catalyst, to prevent single-electron reduction of NAD^+ at the bare electrode. NAD^+ reduction at carbon electrodes modified with poly$[pyrrole\text{-}Rh^{III}(C_5Me_5)(L_1)Cl]^+$ [142] and poly[pyrrole-$Rh^{III}(L_{15})_2]^{3+}$ [37] films has shown the validity of this approach. Successful enzymic reduction of pyruvate to L-lactate in the presence of lactate dehydrogenase and cyclohexanone to cyclohexanol in the presence of alcohol dehydrogenase has demonstrated the regiospecific reduction of NAD^+ on these functionalized polypyrrole film electrodes.

3.2. Photochemistry

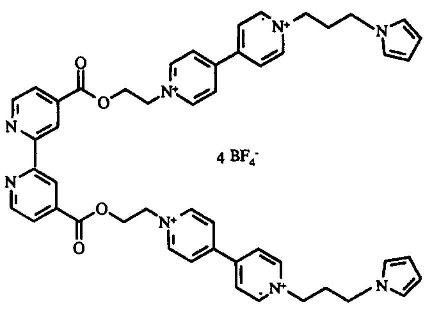
3.2.1. Molecular photoelectrodes

Photoconversion processes based on the electron-transfer quenching of molecular excited states are well established. In simple homogeneous systems, there is no spatial control over the photoproduced oxidative and reductive equivalents, and the redox energy is stored only transiently because of recombination by back electron transfer. One solution to this problem is to construct assemblies of chromophores and quenchers as polymeric films on an electrode surface, with the aim of achieving spatial separation of the photogenerated species. In this context, molecular photoelectrodes have been developed by electropolymerization of conveniently substituted pyrrole monomers. Thin polypyrrolic films containing a conventional photosensitizer such as a polypyridyl complex of ruthenium(II), chromophore-quencher assemblies have been prepared for this purpose.

Platinum electrodes coated by oxidatively electropolymerized $[Ru(bpy)(L_3)_2]^{2+}$ or $[Ru(bpy)(L_1)_2]^{2+}$ complexes gave appreciable (up to 3 $\mu A\ cm^{-2}$) and moderately stable cathodic photocurrents when irradiated in the presence of an irreversible electron acceptor such as aryldiazonium salts [143]. The steady-state current increased first with the film thickness, to reach a limiting value. This current should be regarded as the result of the irreversible oxidative quenching of the excited state of the immobilized ruthenium complexes by diazonium molecules which diffuse in the film.

Film-based pyrrole chemistry has also been utilized to assemble a variety of derivatized polypyrrole film structures, containing the chromophore $[Ru(bpy)_3]^{2+}$, the reversible electron-transfer acceptor viologen (4,4′-bipyridinium salt) and/or the reversible electron donor phenothiazine. Similarly, copolymeric films, as spatially segregated bi- and trilayers (each layer containing a different component) have been prepared from $[Ru(L_1)_3]^{2+}$, phenothiazine and viologen monomers functionalized with pyrrole groups [47]. The photoelectrochemical response of these different films has been studied in the presence of the irreversible reductive scavenger triethanolamine [144]. The magnitude of the photocurrent depends on the composition and microstructure array of the chromophore/quencher assembly. A copolymeric film appears as the best arrangement with a large dilution of the chromophore sites vs. quencher sites. Under optima conditions, per-photon adsorbed quantum efficiencies for photocurrent production of greater than 10% have been achieved.

However, photoresponses fifteen times larger and stable for hours were obtained with polypyrrole films based on an unimolecular photosensitizer–electron acceptor system, constructed by electropolymerization of the $[Ru(bpy)_2(L_{18})]^{2+}$ complex [48].

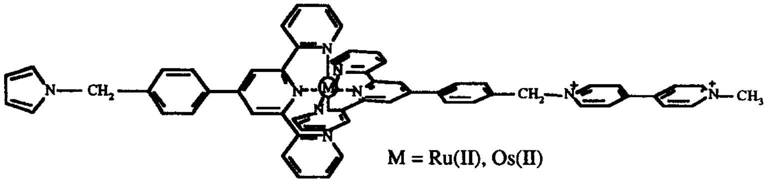


L_{18}

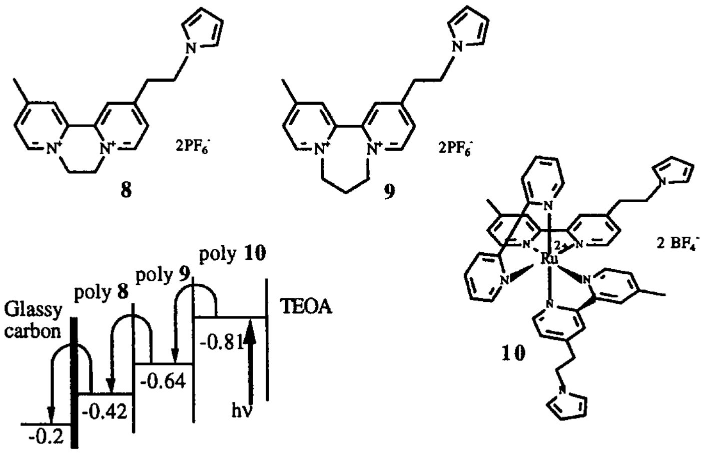
The efficiency of photoelectrodes based on such electropolymerized molecular diads was confirmed with electrodes modified with poly$[Ru^{II}(trpy)_2]^{2+}$ films (trpy = 2,2′:6,2″-terpyridine), where one trpy is substituted by a pyrrole group (L_{15}), the other covalently linked to a 4,4′-bipyridinium group [49] (Scheme 9). Here the particular disposition of molecular assemblies is made in order to obtain an efficient spatial charge separation, since such ruthenium terpyridine complexes have only short excited-state lifetimes in solution in comparison with corresponding bipyridine complexes [145]. These studies demonstrate that light-energy conversion with an integrated system is much more efficient than for the analogous electrode material prepared by copolymerization of the two separate components, i.e. pyrrole-substituted viologen and ruthenium complex monomers.

Significant photocurrents have been also obtained with a polymeric triad based on polypyrrole systems [146,147]. Sequential electropolymerization of the electron acceptors **8** and **9**, and of the chromophore **10** leads to a trilayer C/poly **8**/poly **9**/poly **10** which acts as a molecular photoelectrode under irradiation with visible light in the presence of triethanolamine. Here the redox cascade can assist the photoinduced charge separation in sensitized thin-film assemblies (Scheme 10). The electrode was maintained at −0.2 V(SCE) to ensure the reduction of the acceptor group.

It has also recently been demonstrated that coating of electrode surfaces with stable and photosensitive films of polypyrrole derivatized with polypyridyl complexes of ruthenium can be accomplished by an uncommon procedure. This procedure involves first the electroreductive deposition of multilayers of amphiphilic polypyridyl complexes substituted by pyrrole groups such as $[Ru(L_{19})_3]^{2+}$ and $[Ru(bpy)(L_{19})_2]^{2+}$. Multilayers of monomers are then photo- or electro-polymerized

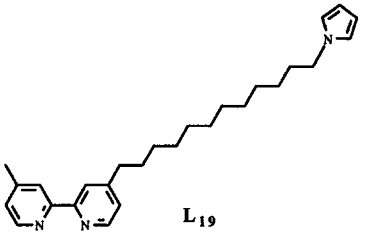


Scheme 9. Pyrrole-substituted molecular diad.



Scheme 10. Mechanistic interpretation of the photoelectrode working principle in terms of forward-biased intrinsic diode.

in organic or aqueous electrolytes [148]. This original polymerization process can be applied to the coating of materials poorly conductive or non-conductive in the anodic region. Preliminary results have shown that TiO_2 surfaces could readily be coated in this way by photosensitive films.

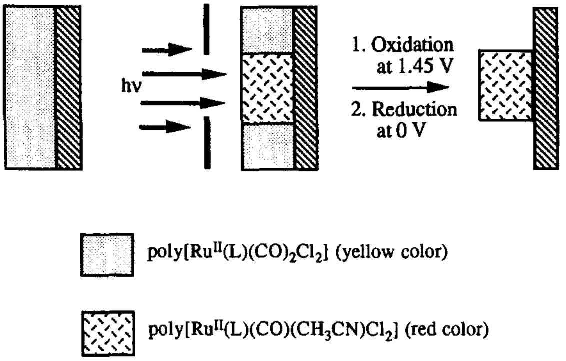


L_{19}

3.2.2. Photoimaging

Spatially controlled microstructured films can be built on a conductive surface by using the photomask technique. For instance, the visible photolysis of an acetonitrile solution of $[Ru(L_1)_3^{2+}]$ and a reversible quencher such as methylviologen sandwiched between conductive and ordinary glass induces a coating of poly$[Ru(L_1)_3^{2+}]$ on the plate. Spatially restricted photolysis leads to a well-defined polymeric image on the transparent surface [149].

Another device is based on the photochromic properties of films of poly$[Ru(L_1)(CO)_2Cl_2]$ deposited on an electrode. Photolysis at 366 nm of this film immersed in CH_3CN leads to successive photosubstitution of two CO ligands and of a Cl^- ligand by CH_3CN. On the basis of this photochemistry (mono CH_3CN photosubstitution essentially), images can be created in the films by using masking techniques. In a subsequent step, the unphotolysed area can be removed from the electrode surface by electrolysis. This procedure leaves a spatially controlled image



Scheme 11. Construction of a spatially controlled microstructure by a sequence of photochemical/electrochemical steps.

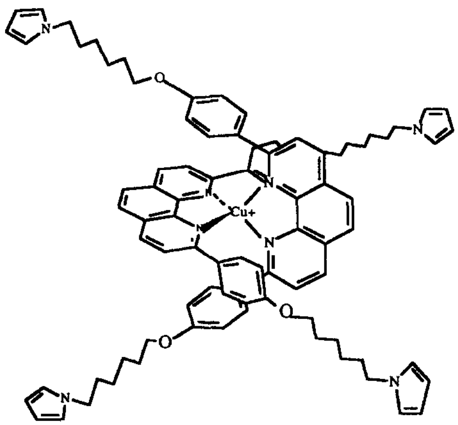
of the original mask as a red film of poly[Ru(L_1)(CO)(CH_3CN)Cl_2] [25]. The sequence of photochemical–electrochemical steps is summarized in Scheme 11.

3.3. Sensors and biosensors

3.3.1. Sensors

Functionalized polypyrrole films have some potential applications in the field of analysis. As an example, the ability of poly(pyrrole-*N*-carbodithiate) films to take up metal ions from solution and the subsequent voltammetry of the complex formed on the electrode surface suggested that analytical applications may be feasible [119]. Under specific uptake conditions and by use of cyclic voltammetry, a detection limit for copper of 1 ppm was estimated.

N-functionalized polypyrrole films with Cu(I) (Scheme 12), Co(II) and Zn(II) complexes having two entwined 2,9-diphenyl-1,10 phenanthroline (L_{14}) can be revers-



Scheme 12. Electropolymerizable Cu(I) bisphenanthroline complex.

ibly demetallated and remetallated [32,42]. Demetallation was performed by dipping the modified electrodes into KCN (Cu(I) complex) or into KSCN (Co(II) and Zn(II) complexes) solution. Remetallation was accomplished in the presence of $[Cu(MeCN)_4][BF_4]_2$. From the Zn(II) demetallated films, Zn^{2+} cations can be reincorporated and Cu^+ replaced by Zn^{2+}. In the same manner, Co^{2+} can be replaced in the polymeric network by Cu^+. However, in some cases, complete demetallation of the films inhibits further recomplexation. This material retains partial memory of its complex precursor as a consequence of the highly entangled nature of the polymeric matrix helping to maintain the relatively rigid complexing cavities of the film. These materials could be used as electrochemical sensors for metallic cation determination.

3.3.2. Biosensors

The construction of biosensors is also possible with the functionalized polypyrrole technique. A number of enzymes have been immobilized in this way in polypyrrole films. Generally, direct electron transfer from an electrode to the redox centres of an enzyme is not observed. Most of the studies have been carried out using the redox enzyme glucose oxidase with oxygen as an electron relay to ensure the reoxidation of the reduced form of glucose oxidase. More sophisticated devices have been proposed using an artificial electron relay, especially some metallic complexes immobilized in the biosensor. In this connection, the use of a polypyrrole film *N*-substituted by ferrocene groups allowed the build-up of an attractive stable reagentless biosensor [72].

A poly(pyrrole–nickel cyclam) film modifying an electrode surface [60] acts as a catalyst for the oxidation of hydrogen peroxide, at a potential (about 0.4 V) at which no significant oxidation of H_2O_2 takes place at a carbon surface. So, it is an excellent electrode material for hydrogen peroxide detection. It has been demonstrated that this modified electrode is applicable to the preparation of an interesting amperometric glucose sensor, after immobilization of glucose oxidase on the poly(pyrrole–catalyst) film via classic glutaraldehyde cross-linking [150].

Anionic metalloporphyrins have been firmly entrapped in alkylammonium polypyrrole films [116,117]. Iron porphyrins are known to react with nitrate in acidic media. In these pH conditions, free NO is generated in solution from the disproportionation of nitrous acid [151]. Thus, once formed, NO can react directly with the Fe(III) centre to give the porphyrin complex $[Fe^{II}(NO^+)]^+$. This type of film can serve as an amperometric sensor for the analysis of nitric oxide [117,151].

4. Conclusion and outlook

The development of modified electrodes based on functionalized polypyrrole by metallic complexes has been spectacular over the past decade. Easy to deposit from non-aqueous electrolytes, allowing the anchorage of supramolecular microstructures based on multifunctional complexes or spatially segregated multilayers, for example, and giving remarkably adherent films, functionalized polypyrrole materials are attractive for multiple applications. Their specific electronic conductivity brings a matchless advantage for their controlled deposition on metals, carbon or semiconducting surfaces. The examples developed here demonstrate the large and versatile possibilities offered by these molecular electrode materials.

Molecular self-assembly of amphiphilic pyrrole monomers appears as a new concept for the development of well-arranged material [148,152]. Further development in design and construction of ordered polypyrrole films functionalized with appropriate metallic complexes would find potential applications in electronic, photoelectrochemical or sensor devices.

Metallic complex–polypyrrole modified electrodes have already shown useful potential applications in electrocatalysis, owing to the construction of electrode materials based on electropolymerized molecular catalysts or catalyst microparticles embedded in the film. Further development could make use of the grouping in the same polymer matrix of different selected molecular and microparticle partners, with a view to achieving sophisticated electrocatalytic syntheses involving multielectronic steps.

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