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Electrogenerated functional conjugated polymers as advanced electrode materials

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Functional conjugated polymers prepared by electrochemical polymerization are reviewed. Various classes of functionalized polymers are considered such as polymers for energy storage and sensor applications, small band gap polymers and novel polymeric materials with original macromolecular structure. Particular emphasis is placed on the thiophene-based polymers and on the relationships between the structures of the various kinds of derivatized precursors, their aptitude for electropolymerisation and the electronic properties of the resulting polymers.

1. Introduction

Electrochemical polymerisation represents a widely employed route for the synthesis of some important classes of conjugated polymers such as poly(pyrrole) (PPy), poly(thiophene) (PT) and poly(aniline).[1] During the past two decades, these materials have been a focus of considerable interest motivated by both the fundamental problems posed by their structure and electronic properties and their multiple potential technological applications.

Since their first electrochemical synthesis almost 20 years ago,[2–4] PPy and PT have occupied a particular position due to the unique combination formed by the association of their structural versatility with electrochemical synthesis. Although it is evident that low-cost and large scale chemical processes are essential for bulk applications such as coatings for electrostatic charge dissipation or EMI shielding, electropolymerisation presents several advantages which makes it a unique tool for electrochemical studies as well as for some specific electrochemically oriented technological applications of conjugated polymers.

Rapidity is probably the most immediate feature of electropolymerisation. The growth of a polymer film of a few hundred nanometers thickness, which is generally convenient for most electrochemical and spectroscopic characterizations, requires only a few seconds. This is of course nothing compared to the several hours and tedious work-up required by chemical methods.

Simplicity is another evident advantage; at a most rudimentary level, electropolymerisation can be done on a kitchen table with a disposable battery. While more elaborate electrodeposition conditions or detailed electrochemical investigations evidently require more sophisticated equipment, electrochemical polymerisation remains basically a rather simple experiment. Another remarkable advantage is that electrogenerated conjugated polymers (ECPs) are directly obtained in their oxidized (doped) conducting form. Besides further time saving, this specific one-step process leads to more heavily and more homogeneously doped materials than post-polymerisation doped chemically synthesized polymers; this is probably the reason why ECPs are in general significantly more conductive.

Perhaps the most attractive feature of electropolymerisation is that it represents one of the simplest and most straightforward methods for the elaboration of modified electrodes in which the inherent electrochemical and/or optical properties of the conjugated polymer backbone of ECPs are associated with specific properties afforded by covalently bound functional groups. Such electrodes can be designed for numerous applications including energy conversion and storage, electrochromism, electrocatalysis, and sensors for a large variety of chemical species extending from ions to biomolecules.

Despite an apparent simplicity, the realization of this concept poses a number of complex problems related to the direct or indirect effects of the electronic and steric parameters of the attached functional group on i) the electropolymerisation process and ii) the electronic properties of the resulting ECP.

Electropolymerisation basically involves an electrogenerated cation radical as the reactive species. Polymer formation proceeds then through a series of radical coupling reactions and electrochemical reoxidations according to a general $E(CCE)_n$ mechanism.[5,6] Since the elemental step in chain growth is the coupling of two radicals, it is clear that all structural factors which affect this process are of crucial importance for the propagation of the polymerisation and hence for the structure and properties of the resulting ECP.

The interactions between substituents grafted on adjacent monomer units can produce a departure from coplanarity with the aperture of a dihedral angle (θ) which depends on both the size of the substituents and their distance from the linking site. Since electron delocalization varies approximatively with the cosine of the dihedral angle, when θ approaches 90° the conjugation is interrupted resulting in the inhibition of the polymerisation. Intermediate values still compatible with polymerization ($\theta \sim 45^\circ$) drastically limit the π-electron delocalization along the polymer chain causing a partial loss of its relevant electronic properties.[7]

The inductive and/or mesomeric electronic effects of substituents directly connected to the monomer control the reactivity of the corresponding cation radical and hence the efficiency of the polymerisation reaction. Electron-withdrawing groups can increase the oxidation potential up to values which are incompatible with the limit of stability of solvents and electrolytes used in electrochemistry.[8] In contrast donating groups tend to stabilise the cation radical and hence decrease its reactivity. Furthermore, even when electronically disconnected from the monomer, easily oxidizable groups can interfere with the polymerisation process by scavenging the cation radicals.[9] From a different viewpoint, a functional group with an oxidation potential largely inferior to that of the linked monomer may be irreversibly degraded upon electropolymerisation.

Based on these various considerations, some rudimentary rules for precursor design emerged in the mid-eighties and since this period a huge number of functional ECPs based on pyrrole and thiophene monomers have been synthesized. While this 'classical' approach is still widely employed, the field of functional ECPs has considerably evolved in recent years with simultaneous development of new materials for novel applications, and of alternative synthetic strategies for functionalization.

The aim of this review is to give a state-of-the-art of functional ECPs through the presentation of some recent developments of the fields. In addition to a discussion of the novel properties resulting from the functionalization, special emphasis is put on the relationships between precursor structure, polymerizability and electronic properties of the ECP in an effort to identify the main unresolved problems and the emerging areas for possible further development.

2. ECPs for electrochemical energy storage

Applications of ECPs as active electrode materials for rechargeable batteries were widely investigated during the 1980–90 period.[10] While research in this area has been somewhat depressed in recent years, the emergence of electrolytic supercapacitors has triggered a renewed interest in the applications of ECPs in electrochemical energy storage.[11,12] The development of such capacitors or more generally of electrochemical devices for charge storage applications requires polymers with a high doping level and good reversibility in both the p and n doped states. Whereas many ECPs show satisfactory performances in terms of p doping, a key issue remains the synthesis of ECPs with a high n doping level and long-term stability under repetitive redox cycling.

The improvement of the n doping capacity of PT by covalent grafting of a phenyl group at the 3-position of the precursor (**1a**) was first demonstrated in 1987,[13] while the positive effect of *p*-fluorophenyl alkyl substituents (**2b**) on the cyclability of the n-doped state was first reported in 1990.[14] In the past few years, several new classes of electrogenerated PTs 3-substituted by diversely substituted phenyl groups have been described.[15–21] Ferraris *et al.* have synthesized a large series of substituted poly(3-phenylthiophenes) (monomers: **1a–i**) and analysed their electrochemical properties. A good correlation was observed between the oxidation and reduction potentials of the ECPs and the Hammett σ constants.[16] These studies have evidenced the promising properties of poly(*p*-fluorophenylthiophene) (monomer: **1d**) for supercapacitor applications. The effects of the number and relative position of fluorine atoms in a series of poly(fluorophenylthiophenes) (monomers: **3–8**) have been analysed. The oxidation potentials of the monomers were correlated to the corresponding Hammett σ values and increased with the fluorine content.[17] The maximum n doping level of the corresponding ECPs was also correlated to Hammett constants and increased with the number of fluorine atoms on the phenyl ring. However, all the polymers exhibited rather similar band gaps and cycling efficiencies. Test cells fabricated with these ECPs as anode and cathode material exhibited a discharge voltage of about 2.5 V and capacities of 9.5 to 11.5 mAh g^{-1}.[17]

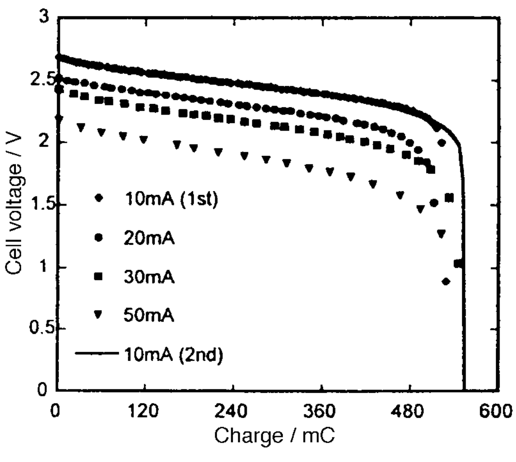
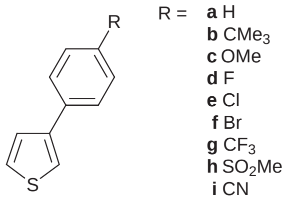


Fig. 1 Potential *vs.* discharge curves obtained for a poly(**5**)-based capacitor grown and cycled in 0.2 M Et_4NBF_4–MeCN, recorded at various discharge rates between 2.8 and 1.0 V for 5–10 cycles each followed by a repeated discharge cycle at 10 mA cm^{-2}, after charging at a current of 2 mA cm^{-2}. (Reprinted from Ref. 18, Copyright 1998, American Chemical Society).



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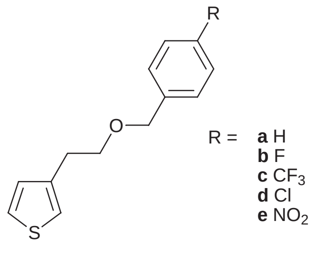

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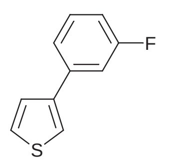

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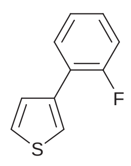

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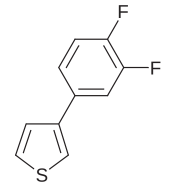

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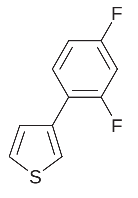

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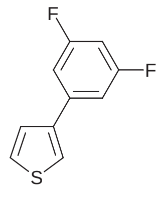

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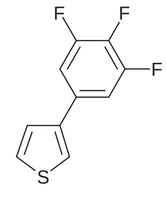

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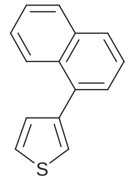

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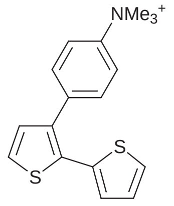

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A comparative study of electrochemical capacitors involving ECPs derived from monomers **1d**, **1h**, **1i** and **5** as active material has been carried out.[18] The best stability was obtained with the polymer derived from the difluorophenyl monomer **5** which exhibited a cycle efficiency (ratio of the recovered charge : injected charge) of 96 ± 1% and very low degradation after 100 cycles.[18] The morphologies and electrochemical performances of the films were shown to depend on both the growth and the cycling electrolytes. Energy and power densities up to 50 Wh Kg^{-1} and 5 kW Kg^{-1} were achieved at discharge rates of 50 and 10 mA cm^{-2} (Fig. 1).[18]

A series of ECPs derived from dithienyl-phenylenes substituted at the phenyl ring by fluorine have also been considered for supercapacitor applications.[19] As for previous series, the oxidation potentials and doping level were dependent on the number of fluorine atoms on the phenyl ring. However, the ECPs were found to oxidize at higher potentials than their respective precursors which is indicative of a restricted conjugation length, probably due to a limited polymerisation efficiency.[19]

Other attempts to improve the n-doping capacity and stability of PTs have involved substitution by naphthyl (**9**) and *p*-trimethylammoniophenyl groups (**10**) but only the latter polymer can undergo an n-doping process.[20,21]

Polypyrroles bearing polyether chains at the 3-position have also been considered for energy storage applications.[22,23] The idea was to design an ECP possessing also ionic conductivity in order to improve the quality of the interface with polymeric ionic conductors such as poly(ethylene oxide). In fact, significant improvements in the charge–discharge characteristics were obtained only when these substituted pyrroles were copolymerised with pyrrole.[23]

3. Small band gap ECPs

The high current interest in small band gap conjugated polymers is motivated by their expected improved nonlinear optical properties, transparency in the visible spectral region and intrinsic conductivity.[24] Furthermore, since reduction of the band gap is generally associated with a positive shift of the reduction potential, small band gap ECPs can be expected to exhibit a stabilisation of the n doped state which represents a key issue for applications in electrochemical energy storage.

Due to a unique combination of stability, moderate aromatic character and structural versatility, thiophene-based linear π-conjugated systems still represent the most widely investigated basic structure for the synthesis of molecular or polymeric materials with a narrow band gap.

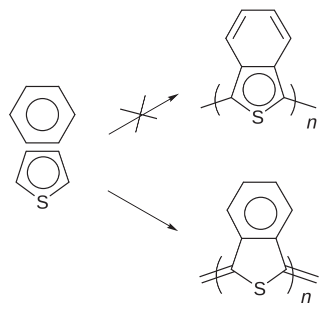
The synthetic principles for band gap control of linear π-conjugated systems resort to three main strategies, namely, the increase of the quinoid character of the conjugated system to the detriment of its aromaticity, the rigidification of the conjugated structure in order to minimize rotational and vibrational disorder and the creation of an alternance of electron-donating and electron-withdrawing sites along the conjugated chain.[24]

Poly(isothianaphthene) (**11**) is the prototype of small band gap conjugated polymers.[25] The fusion of the thiophene and benzene rings leads to a 10 electron system in which only one of the two rings can accommodate the aromatic sextet. Owing to the higher aromatic resonance energy of benzene (1.56 eV *versus* 1.26 eV for thiophene), benzene has a greater tendency to remain aromatic thus contributing to imposing a quinoid geometry on the PT backbone.

Whereas electropolymerisation of isothianaphthene was initially reported as delicate,[25] improved electrochemical procedures have recently been described.[26,27] Contrary to initial reports, the redox system corresponding to the reduction (n-doping) of the polymer was clearly apparent in the CVs of films produced in optimized conditions.

Several modifications of the structure of isothianaphthene have been described. The aim was to achieve either a further reduction of the band gap or an improvement of the soublility of the polymers. Soluble analogs of **11** have been prepared by grafting alkyl chains on the phenyl ring. Introduction of a methyl group decreases the electropolymerisation potential but increases the oxidation potential of the resulting ECP.[28] Halogen substitution induces a large positive shift of the potential for n doping but does not drastically modify the width of the band gap.[29] Introduction of fluorine at the 5-position leads to a positive shift of the onset potential for n-doping, whereas substitution at the 4-position produces the reverse effect due to steric hindrance.[29]

The insertion of the ITN moiety in the terthiophene structure has been described by several groups.[30–32] The oxidation potential of the resulting precursor (**12**) is lower than that of terthienyl (0.80 *vs.* 1.05 V/SCE) and the partial reversibility of the CV is indicative of a stabilisation of the cation radical. Potentiodynamic electropolymerisation produces an ECP with an estimated band gap of 1.70 eV, intermediate between those of PT and **11**.[30] The terthienyl containing a central isonaphthothiophene (**13**) absorbs at longer wavelengths and oxidizes at a lower potential than **12**. This further stabilisation of the cation radical renders the electropolymerisation and the exact determination of the gap value more difficult than for **12**.[33]



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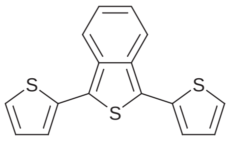

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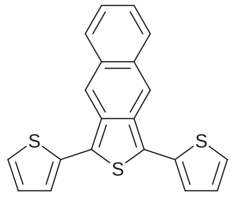

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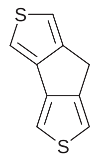

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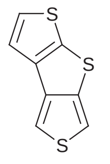

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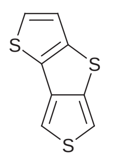

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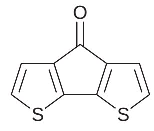
Poly(dithieno[3,4-*b*;3′,4′-*d*]thiophene) (**14**) was the first example of a small band gap ECP based on thienothiophenes.[34] Recently two other members of this class of polymers have been synthesized by electropolymerisation of dithieno[3,4-*b*;3′,2′-*d*]thiophene (**15**) and dithieno[3,4-*b*;2′,3′-*d*]thiophene (**16**). These polymers have band gap values around 1.10–1.20 eV and undergo n doping around −1.50 V *vs.* Ag, a property which has been considered for applications in redox supercapacitors.[35]

In 1991 Ferraris *et al.* reported that electropolymerisation of cyclopenta[2,1-*b*:3′,4′-*b*′]dithiophen-4-one 17 leads to a new type of low band gap polymer.[36] This approach was based on the idea that the electron-withdrawing effects of the ketone group should decrease the aromaticity of the system and hence increase the quinoid character of the polymer. The lowest π–π* transition of **17** at 474 nm is red shifted by 174 nm compared to bithiophene (BT) while the slight increase of the oxidation potential suggests that the carbonyl group has only a moderate effect on the HOMO level. Similarly the resulting ECP exhibits only a modest increase of the oxidation potential compared to poly(BT). Poly(**17**) shows an optical band gap of 1.10–1.20 eV, consistent with CV data.[37] Another representative example of this class of ECPs is derived from 4-dicyanomethylene-4*H*-cyclopenta[2,1-*b*;3,4-*b*′]dithiophene (**18**).[38] The electron-withdrawing effect of the dicyanomethylene group lowers the LUMO level which results in a decrease of the HOMO–LUMO gap confirmed by a further 100 nm red shift of the lowest energy transition. The optical spectrum of poly(**18**) is strongly reminiscent of that of poly(**17**) with the emergence of a new absorption band extending to the near IR and with an absorption onset at *ca.* 0.80 eV.[38] Along the same lines, electropolymerisation of cyclopenta[2,1-*b*;4,3-*b*′]dithiophenylidene-4-[cyano(nonafluorobutylsulfonyl)]methane



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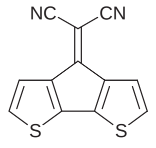

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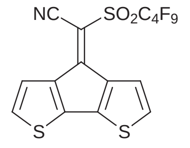

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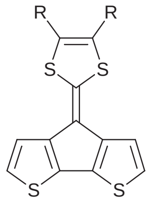

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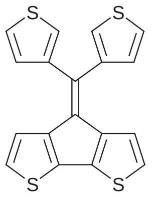

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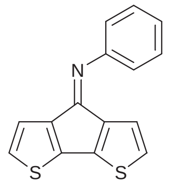

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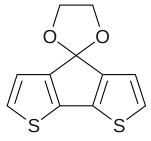

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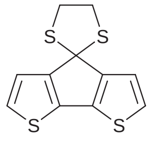

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(**19**) was reported to produce a polymer with an estimated band gap of 0.67 eV.[39]

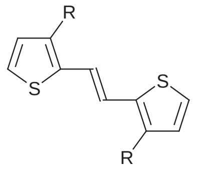
Theoretical calculations on a geometric structure optimized by a semi-empirical technique have concluded that introduction of the dicyanomethylene group at the sp^2 bridging carbon induces major geometrical changes within each ring resulting in a structure which can be viewed as a combination of aromatic and quinoid geometries. The small gap value calculated for poly(**18**) (0.59 eV) was related to HOMO and LUMO levels located between those of aromatic and quinoid PT chains.[40]

Introduction of the electron donating 1,3-dithiole moiety at the sp^2 bridging carbon (**20**) produces a 0.30–0.50 V decrease of the oxidation potential and a 100 nm red shift of the absorption maximum compared to BT. Similar trends are observed for the corresponding ECPs which absorb at longer wavelengths than poly(BT), and exhibit band gap values down to 1.40 eV. Some of these polymers show high conductivities, attributed to strong intermolecular S···S interactions.[41] Other examples of polymers derived from bithiophene bridged by an sp^2 carbon have been obtained from compounds **21** and **22** which led to ECPs with band gaps of 1.30–1.40 eV.[42–44]

Small band gap polymers have also been obtained from bithiophenic precursors bridged by an sp^3 carbon such as the dioxolane **23** or the dithioacetal **24**.[42,43] The CV of poly(**23**) exhibits a potential difference between oxidation and reduction even smaller than poly(**17**).[42] This small gap is due in part to the low oxidation potential of the polymer (0.70 V/SCE *vs.* 0.85 V for poly(**17**), which indicates that the dioxolane group has less influence on the HOMO level than the ketone or dicyano groups. The optical spectrum of poly(**23**) indicates a band gap similar to poly(**17**) (1.10–1.20 eV). The dioxolane group considerably increases the hydrophilicity of the polymer which remains fully electroactive in aqueous medium in contrast to other polymers of this series.[44]

The reduced band gap of the ECPs derived from precursors bridged by an sp^3 carbon such as **23** and **24** poses intringuing problems. The interpretation based on the electron-withdrawing effects of the CO and $(CN)_2$ groups proposed for poly(**17**) and poly(**18**) cannot be invoked here and the reduction of the band gap must have another origin. While enhanced planarity and a possible decrease of bond length alternation are probably important factors, this question is not fully elucidated and still subject to theoretical investigations.[45]

Conjugated polymers obtained by electropolymerisation of dithienylethylenes (DTEs) (**25**) constitute interesting models of the corresponding poly(thienylenevinylenes) while preserving the advantages of electropolymerisation. In recent years, DTEs or more generally diheteroaryleneethylenes have been widely investigated as basic structures for the design of low band gap ECPs.[24]



R = H, Me, Bu^n, Oct^n

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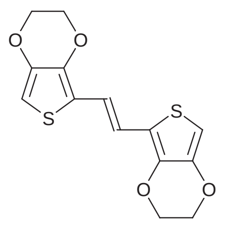

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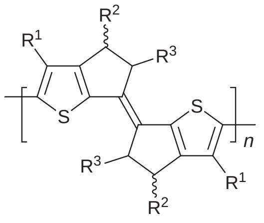
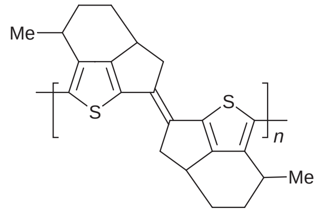




27 **a** $R^1=R^2=R^3=H$
b $R^1=R^2=H$, $R^3=Me$
c $R^1=R^3=H$, $R^2=Me$
d $R^1=R^3=H$, $R^2=Bu^n$
e $R^1=R^3=H$, $R^2=Oct^n$
f $R^1=Oct^n$, $R^2=R^3=H$

28

However, as for other π-conjugated precursors, the poor solubility and the stability of the electrogenerated cation radical significantly limit the efficiency of the electropolymerisation.[6] Electropolymerisation of unsubstituted DTE was first reported in 1985.[46] Shortly after, the definition of optimized electrodeposition conditions led to a highly conducting polymer with a band gap of 1.80 eV.[47] Introduction of alkyl chains at the 4,4′ positions of thiophene improves the solubility of the polymer and leads to a slight reduction of the band gap.[48] These polymers do not exhibit any thermochromic effect thus confirming that they are more rigid than poly(3-alkylthiophenes).[49]

Replacing thiophene by 3,4-ethylenedioxythiophene (EDOT) in *E*-1,2-[2,2′-di(3,4-ethylenedioxythienyl)ethylene] (**26**) leads to an ECP showing an optical band gap of 1.40–1.48 eV and a fast optical switching rate.[50,51]

Roncali *et al.* have developed an alternative approach to reduce the band gap of poly(DTEs) which consists in the rigidification of the DTE precursor by covalent bridging of the thiophene rings with the central double bond.[52–56] This structural modification (**27a**) produces noticeable changes in the electronic spectrum with a red-shift of the absorption maximum and a strong enhancement of the vibronic fine structure while the oxidation potential decreases from 1.10 to 0.72 V *vs.* SCE. The CV of the corresponding ECP presents a negative shift of the oxidation potential from 0.98 to 0.58 V and a considerable improvement of reversibility while the optical spectrum of the neutral polymer reveals a reduction of the band gap from 1.80 to 1.40 eV.[52] Theoretical and experimental works have shown that the 0.40 V decrease of oxidation potential and band gap are related to an increase of the HOMO level and to a reduction of bond length alternation.[53] Alkyl chains have been introduced at different positions of the DTE molecule in order to improve the solubility of the precursor and that of the resulting ECP (**27b–f**). Due to steric interactions, substitution at the R^3 position (**27b**) produces a distortion of the conjugated system which has detrimental effects on the electropolymerisation reaction.[54] In contrast, alkyl substitution at the R^2 position (**27c–e**) improves the electropolymerisation efficiency and leads to a considerable decrease of the oxidation potential of the polymer (Fig. 2).

However, the band gap of the polymer is practically unaffected by substitution and remains in the range 1.40–1.50 eV.[54] Due to the rather tedious synthetic procedures required by this type of substitution, a precursor bearing an octyl chain directly attached at the 3-position of the thiophene ring has been synthesized (**27f**). However, steric interactions between substituents led to an inhibition of electropolymerisation.[55] Interestingly, further cyclization at the 3-position (**28**) allows reduction of this steric hindrance and electropolymerisation again becomes possible leading to an ECP with a band gap of 1.40–1.50 eV.[56]

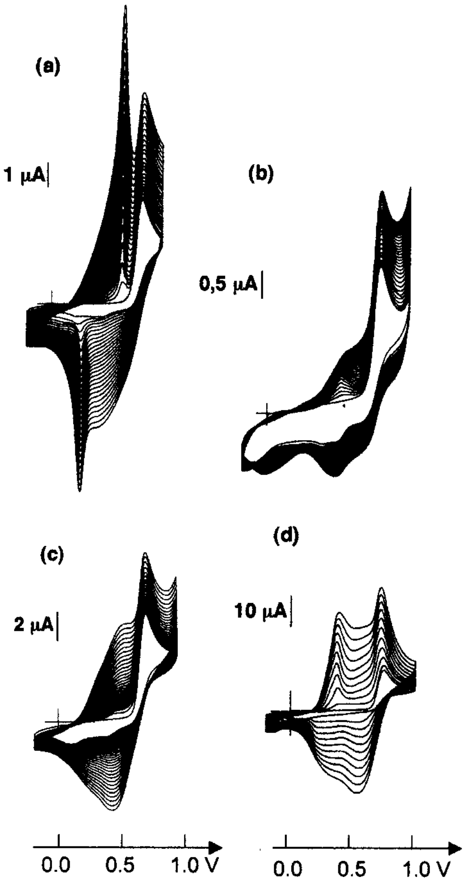


Fig. 2 Potentiodynamic electropolymerisation curves recorded in 0.10 M Bu_4NPF_6–MeCN, substrate concentration 1×10^{-2} M, scan rate 100 mV s^{-1}, ref. SCE. (a) **27a**, (b) **27b**, (c) **27c**, (d) **27d**. (Reprinted from Ref. 54, Copyright 1997, American Chemical Society).

The synthesis and electropolymerisation of the bridged compound **27a** were recently reproduced by others who confirmed the previous conclusions.[57]

The electron withdrawing properties of the cyano group have been widely used in order to decrease the LUMO level and the band gap of conjugated oligomers and polymers.[24] In the specific case of ECPs, introduction of a CN group results in a considerable increase of the oxidation potential of the monomer which can have deleterious consequences for the electropolymerisation. Consequently, this electron withdrawing effect must be counterbalanced either by introduction of an electron releasing substituent or by extending the conjugation length of the precursor. This is exemplified by bithiophene **29** with cyano and methoxy groups at the 3,3′-positions. Cyclic voltammetry and spectroelectrochemistry of the resulting ECP reveal two distinct oxidation steps which have been attributed to a strong stabilisation of the polaron state caused by the localization of positive charges in this specific electronic structure.[58] However, the strong steric hindrance to planarity associated with the 3,3′-disubstitution probably also represents a major obstacle to electron delocalization, as indicated by the large band gap of the polymer. In this context, the hitherto unknown 3,4′ precursor (**30**) should represent an interesting target as a possible route towards a regioregular polymer which may exhibit a much smaller band gap.

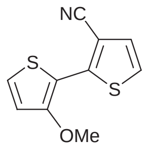
A further reduction of the band gap of poly(DTE) has been achieved by introduction of a cyano group at the ethylene linkage of the precursor (**31a**).[59] While electrochemical and optical data show that the electrodeposited material contains some fractions of a polymer with very narrow band gap (~0.50 eV), electropolymerisation was rendered difficult by the very poor solubility of the precursor.[59] Introduction of a methyl group on the thiophene ring (**31b**) has deleterious consequences for the electropolymerisation whereas incorporation of furan in the structure (**32**) greatly improves the film-forming properties allowing deposition of free-standing films with a conductivity of 4.8 S cm^{-1}. An ECP with a band gap of 1.30–1.40 eV has been obtained from compound **33**.[60] Contrary to **31a**, this precursor was reported to polymerise efficiently due probably to the presence of EDOT in the structure.

Whereas longer precursors designed along the same lines such as **34** and **35** were quite difficult to polymerise, incorporation of a dioxolane bridged bithiophene or of a 3′-octyl terthiophene in the structure **36**, **37** allows the facile electrodeposition of highly cathode-active materials with moderate band gaps (~1.50 eV).[61]

This strategy was recently extended to pyrrole-based precursors (**38–40**) leading in that case too to an important gap reduction. For example poly(**38**) shows a band gap of 2.20 eV instead of 2.85 eV for PPy.[62] Interestingly, introduction of pyrrole in the structure of the extended precursors **34** and **35** (**39,40**) significantly improves the electropolymerisation efficiency. However, the band gaps of these polymers remain rather large. On the other hand, the same group has reported that electropolymerisation of 2,2′-azopyrrole (**41**) produces an ECP with a band gap of ~1.0 eV.[63]

The use of conjugated precursors for electrochemical polymerisation is inherently limited by the rapid decrease of the reactivity of the cation radical as the conjugation length of the molecule increases. Despite this major drawback, this approach presents the advantage of allowing the design of complex molecular architectures combining building blocks with different electronic properties. Furthermore, the stabilisation of rather unstable fused ring systems into an extended conjugated structure allows a first evaluation of their impact on the electronic properties of π-conjugated systems.

This strategy has been extensively developed by Yamashita *et al.* who have synthesized various series of tricyclic precursors built around median ring systems combining strong electron-



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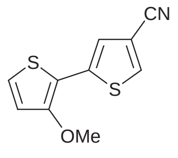

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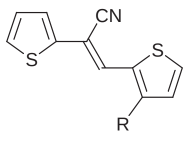
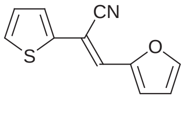


31 a R = H
b R = Me



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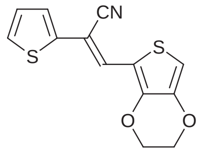

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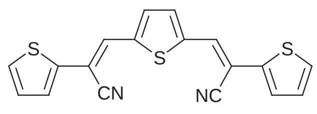

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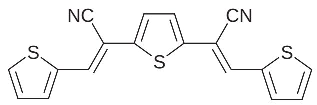

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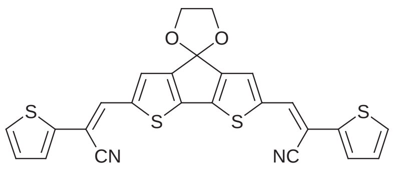

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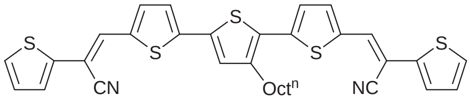

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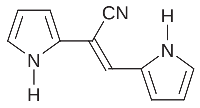

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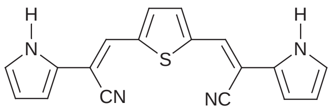

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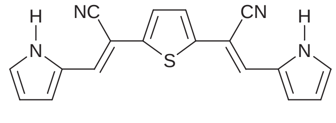

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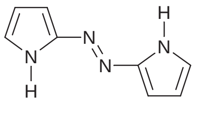

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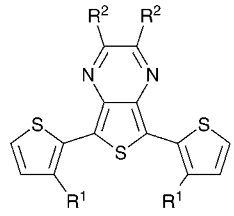

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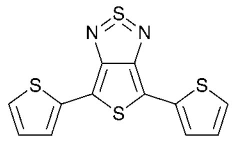

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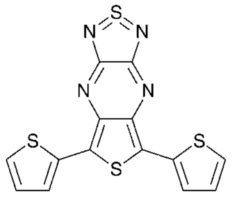

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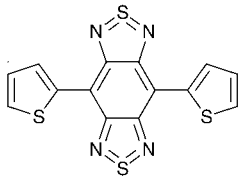

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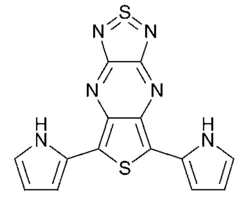

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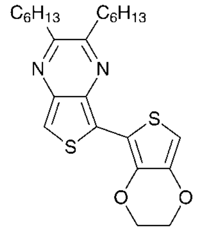


47

accepting properties with a marked propensity to impose a quinoid geometry on the structure of the π-conjugated polymer backbone. These synergic effects have led to several ECPs that exhibit some of the smallest band gaps known to date.[64–69]

Thus, the electronic absorption spectra of compounds **42** with a median thieno[3,4-*b*]pyrazine ring system show appreciable red shifts compared to **12** with λ_{max} ranging from 484 nm for $R^1 = n$-hexyl to 529 nm for the unsubstituted compound.[64] These compounds are irreversibly oxidized at 0.80–1.00 V/SCE, and reversibly reduced in the −1.10 to −1.50 V region. The ECPs prepared by potentiodynamic electropolymerisation showed band gaps in the range 1.00–1.50 eV based on both electrochemical and optical data. The trimeric fused-ring system built around a thieno[3,4-*c*][1,2,5]thiadiazole median ring (**43**) has a smaller HOMO–LUMO gap than isothianaphthene. Furthermore, the X-ray structure shows that the three rings in the molecule are nearly coplanar and stabilised by intramolecular interactions between the nitrogen atoms and the sulfur of the adjacent thiophene. The lowest π–π* transition occurs at 618 nm and oxidation and reduction potentials occur at +0.85 and −0.93 V/SCE respectively. The resulting ECP shows an absorption maximum at 934 nm in the neutral state and a band gap of *ca.* 0.90 eV.[65] A similar approach has given rise to the synthesis of other trimeric precursors such as **44** in which a tricyclic median ring system used as an electron-deficient unit leads to a larger red shift of the lowest π–π* transition to 990 nm. As expected, the electronic spectrum of the resulting ECP exhibits an absorption edge below 0.50 eV ranking among the smallest band gaps reported so far.[66] Compound **45** with a benzobis(1,2,5-thiadiazole) electron-withdrawing moiety exhibits a larger HOMO–LUMO gap than **44** ($\lambda_{max} = 702$ nm). However, the resulting ECP exhibits an optical spectrum and a band gap similar to those of poly(**44**) which might reflect a higher degree of polymerisation.[67]

Recently, these authors have reported that replacement of thiophene by pyrrole in compound **44** (**46**) produces a considerable shift of λ_{max} to 1345 nm.[68] The ECP exhibits a very small electrochemical band gap (0.30 eV) indicating that compound **46** appears well suited for the synthesis of intrinsically conducting materials.[69]

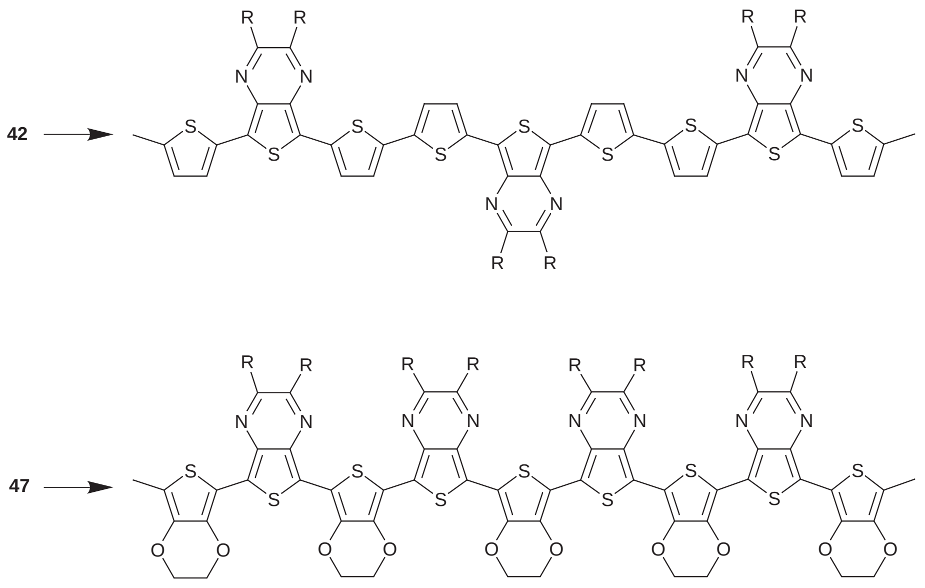
While these various examples clearly confirm the interest of Yamashita's pro-quinoid acceptors, some of these precursors appear difficult to polymerize and lead to polymers of limited stability under redox cycling.[70] These problems reflect the limitations inherent in the electropolymerisation of conjugated precursors. In fact, in several cases, the considerable effects observed on the HOMO–LUMO gap of the precursor molecule are hardly reflected by the band gap of the resulting ECP.

In an attempt to solve these problems a bithiophenic precursor in which thienopyrazine is associated with EDOT has been synthesized (**47**).[71] This precursor combines the superior polymerisability of bithiophenic structures over more conjugated ones, the solubility imparted by the dihexyl chains on the pyrazine moiety, the high HOMO level of EDOT and the well-known stability of its polymers.[72] Furthermore, unlike tricyclic precursors, this dimeric structure could in principle allow the formation of a regular alternance of donor and acceptor moieties in the chain (Scheme 1).

Electropolymerisation of **47** occurs readily at very low potential (0.72 V *vs.* SCE) leading to a polymer with an oxidation potential close to 0.0 V *vs.* SCE and a large n-doping capacity (Fig. 3).

The low energy absorption edge of the optical spectrum indicates a band gap of 0.36 eV which ranks among the lowest values ever reported for a conjugated polymer. The narrowness of the absorption band appears consistent with a well-defined polymer. This polymer differs from other known low band gap polymers by having an exceptional stability under reductive redox cycling. Thus, whereas most low band gap polymers undergo rapid degradation after a few reduction cycles poly(**47**) retains 80% of its initial electroactivity after 1500 reduction cycles.[71]

To summarize, the development of new synthetic strategies or the combination of known approaches with recent advances in the chemistry of thiophene-based conjugated systems has



Scheme 1

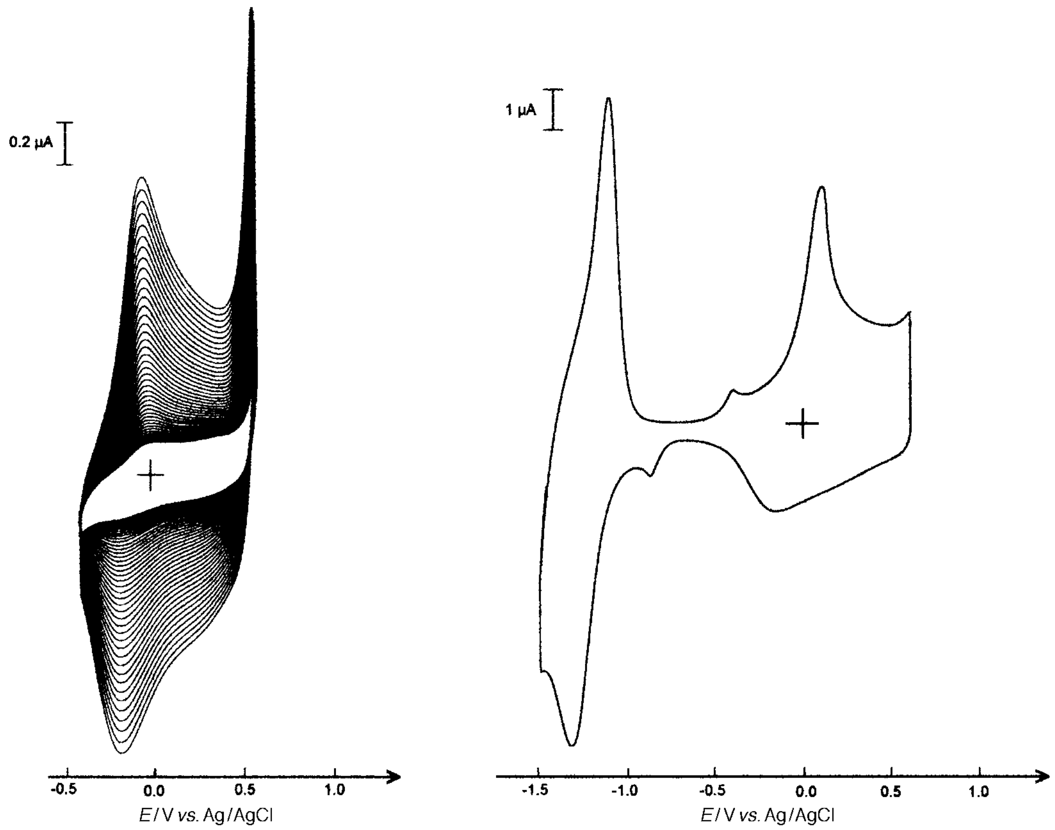


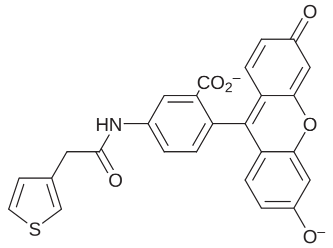
Fig. 3 Left: potentiodynamic electropolymerisation of **47** in 0.10 M Bu_4NPF_6–MeCN, substrate concentration 1×10^{-4} M, scan rate 100 mV s^{-1}. Right: Cyclic voltammogram of poly(**47**) in 0.10 M Bu_4NPF_6–MeCN, (Reprinted from Ref. 71, Copyright 1998, Royal Society of Chemistry).

led to significant progress in the control of the band gap and stable materials with extremely narrow band gaps are now available. This combination of low band gap and improved stability under redox cycling can be expected to have a large impact on many of the potential technological applications of ECPs. On the other hand, the electronic data reported by Yamashita *et al.* for some of the above discussed precursors suggest that the design of new bithiophenic precursors combining these acceptors with EDOT can represent a very exciting goal for future work.

4. Functional ECPs for sensors applications

The use of ECPs for applications in electrochemical sensors represents a strong stimulation for the development of functional ECPs. Such sensors are intended to cover a wide range of applications extending from simple pH sensors to more sophisticated systems based on molecular recognition of ions or of molecules of biological interest.

An ECP based on a fluorescein derivatized thiophene (**48**) has been described. Electropolymerisation required application of an unusually high potential (2.60 V *vs.* Ag/Ag$^+$) and led to a yellow film.[73] Since extensively conjugated PTs are dark blue in their doped form, this yellow color reveals a very short conjugation length due probably to large steric hindrance to conjugation caused by interactions between the attached bulky substituents. The pH titration curve of the electrodeposited film showed a well-defined titration with, however, a lower pH sensitivity compared to the precursor in solution.[73] Another type of pH sensor based on poly(pyrrole) derivatized with hydroquinone has been synthesized (**49**). The polymer exhibited a sub-Nernstian response of 46 mV pH^{-1}.[74]



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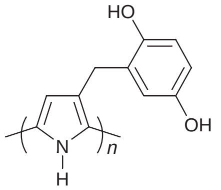

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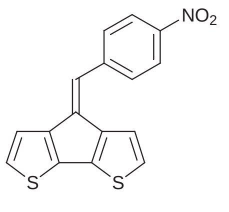

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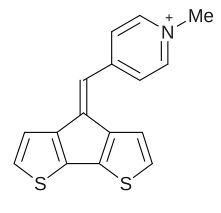

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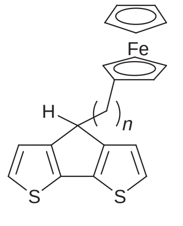
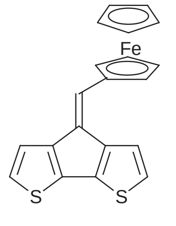


52 **a** n=1
b n=6



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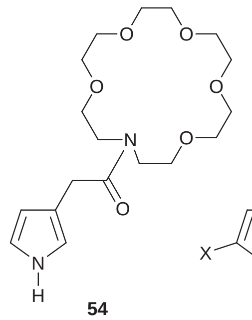
A particularly interesting class of precursors has been synthesized using bridged cyclopentadithiophene as a basic structure. The analysis of the *in-situ* conductivity changes associated with the redox process of ECPs containing redox active groups such as nitrophenyl (**50**) and methylpyridinium (**51**) provided evidence for a high redox conductivity attributed to favorable intersite distance and high exchange rate.[75] Ferrocene derivatized ECPs based on bridged bithiophene have also been synthesized (**52, 53**). The decrease of the distance between the ferrocene group and the conjugated backbone (**52b**) or the direct conjugation (**53**) was found to enhance the electron hopping rate and hence the redox conductivity associated with the ferrocene group.[76]

ECPs possessing cation recognition properties have been subject to a sustained interest in recent years. Cation-dependent electrochemical and optical properties were initially observed on PTs derivatized with polyether side chains.[77,78]



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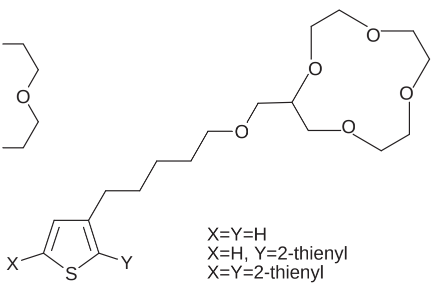

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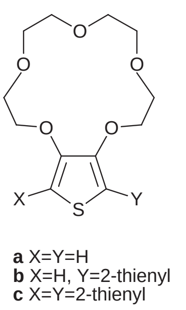

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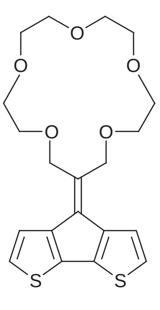

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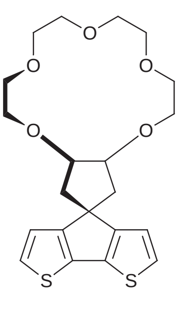

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More recently ECPs containing macrocyclic crown ethers have been developed by several groups. Thus, when cycled in the presence of $NaClO_4$ or $KClO_4$, the CV of the ECPs obtained by electropolymerisation of pyrrole 3-substituted by an aza crown ether **54** shows a progressive positive shift of the anodic peak potential and a loss of electroactivity attributed to the binding of the cation by the side crown ether.[79]

This polymer was reported to complex Co^{2+} ions and the resulting modified electrodes were investigated for oxygen reduction.[80] Bäuerle *et al.* have synthesized PTs with pendent crown ether linked *via* an alkyl spacer (**55**).[81] Functionalized monomers were difficult to electropolymerise and the best results were obtained with bithiophenic precursors which led to extensively conjugated polymers. The electrochemical properties were analysed in the presence of different alkali cations (Li$^+$, Na$^+$, K$^+$). In each case addition of incremental amounts of cation produces a positive shift of the anodic peak potential and a decrease of electroactivity. The highest sensitivity was found for Li$^+$, as could be expected for a 12-crown-4. Nevertheless for all cations, a linear dependence was found between the decrease of the anodic peak current measured at fixed potential and the concentration of cation. These effects were attributed to a shielding of the conjugated backbone caused by the potential barrier formed by the host–guest complex.[81] In order to improve the electrical communication between the complexing cavity and the conjugated backbone, the same group has synthesized ECPs derived from precursors

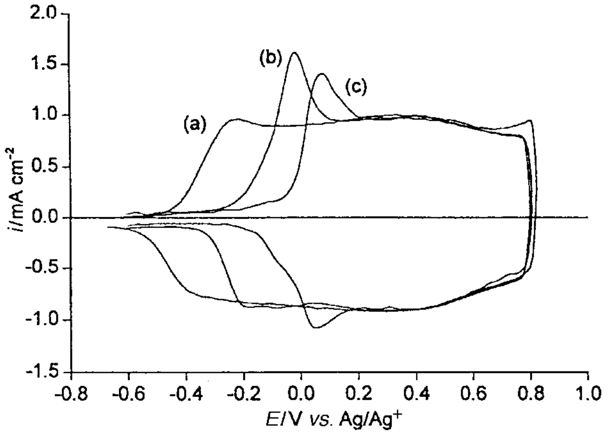


Fig. 4 Cyclic voltammogram for poly(**57**) in acetonitrile + (a) 0.1 M Et_4NClO_4, (b) 0.1 M $LiClO_4$, (c) 0.1 M $NaClO_4$. (Reprinted from Ref. 83, Copyright 1998, American Chemical Society).

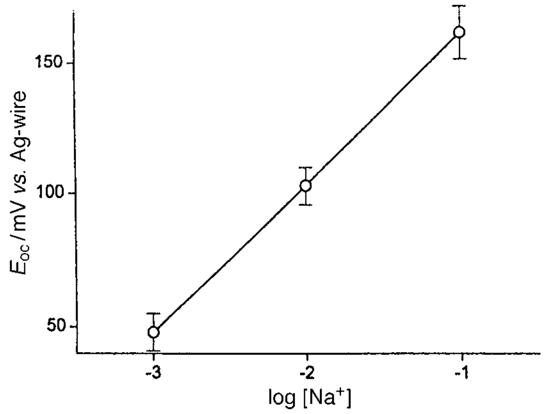


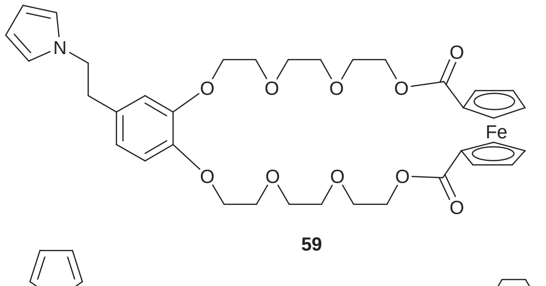
Fig. 5 Open circuit voltage (*vs.* Ag wire) *vs.* log of sodium ion concentration of a poly(**57**) film on Pt in acetonitrile (Reprinted from Ref. 83, Copyright 1998, American Chemical Society).

56. In contrast to the previous series, the monomer could be polymerised but not the trimer.[82] This different behavior is probably due to the presence of the two strongly electron donating alkoxy groups. While the oxidation potential of the precursors showed a gradual positive shift upon addition of alkali cation, the behavior of the ECPs in the same conditions was less clear due to the difficulties in reaching a stable voltammogram.[82]

Another strategy proposed by Sannicolò *et al.* consists of the use of cyclopentabithiophene precursors with either a 16-crown-5-ether ring coplanar to the bithiophene moiety (**57**) or a 15-crown-5-ether perpendicular to it (**58**).[83] This approach allows a considerable reduction of steric problems and the precursors were readily electropolymerised into extensively conjugated polymers as confirmed by their optical data. The analysis of their electrochemical properties in the presence of alkali cations revealed quite different behaviors. Thus, while poly(**58**) is completely insensitive to change of the cationic species, the redox potential of poly(**57**) shifts positively from -0.30 to $+0.05$ V *vs.* Ag/Ag$^+$ when replacing Et_4NClO_4 by $NaClO_4$ (Fig. 4).

A plot of the open circuit voltage of a platinum electrode coated with this polymer in its slightly oxidized state *vs.* the logarithm of the concentration of Na$^+$ gives a linear potentiometric response with a slope of 57 mV in the 10^{-3} to 10^{-1} M range (Fig. 5).[83]

Moutet et al. have proposed an original concept which consists of the incorporation in the crown ether of a ferrocene group (**59**) acting as a detector of the complexing status of the cavity; the electrochemical properties of the corresponding ECP revealed a high sensitivity towards Ba^{2+} cations.[84] The same group has also developed another approach involving the formation of a hybrid bipyridine ruthenium (II) complex involving a pyrrole-substituted bipyridine ligand (**60**) and 2,2′-bipyridine ligands 4,4′-disubstituted to form a complexing host cavity. This concept, first applied to the immobilisation of calixarenes,[85] was recently extended to aza-crown ethers L^1 and L^2. In this case immobilization of the crown ether is achieved *via* the formation of a Ru(II) complex [Ru(**60**)$_2$(L^1)]$^{2+}$ or [Ru(**60**)$_2$(L^2)]$^{2+}$. In the presence of an excess of Li$^+$ and Na$^+$ a positive shift of the ligand centered reduction wave occurs and these cation recognition properties are mainly retained after immobilisation of the complexes by electropolymerisation.[86]



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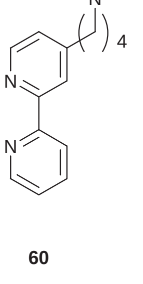

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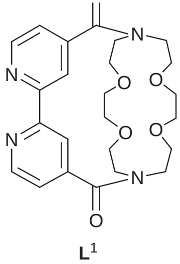
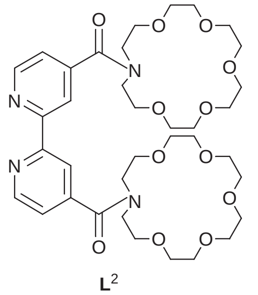


L^1



L^2

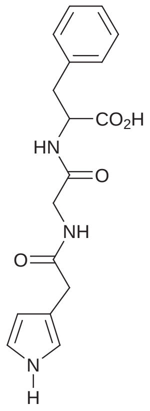
One of the most recent developments in the field of ECP based sensors concerns the design of modified polymers capable of selectively recognising molecules of biological interest. While a considerable amount of work has been devoted to the immobilisation of enzymes by entrapment during the electropolymerisation process, devices based on derivatized ECPs are considerably more scarce.

Electroactive polypyrroles functionalized with bioactive dipeptides have been synthesized in order to achieve the electrochemical recognition of proteolytic enzymes. Thus when cycled in the presence of increasing concentrations of carboxypeptidase A, the CV of poly(**61**) shows a positive shift of the anodic peak potential attributed to the binding of the enzyme.[87] This conclusion was confirmed by the release of the enzyme in an aqueous solution at pH 3. Electrochemical releasing of the enzyme was also achieved by application of a low potential leading to a release of protons from the carboxylic acid groups of the polymer.

Films of copolymers of pyrrole with pyrroles functionalized by covalently linked oligonucleotides (ODN) (**62**) have been electrodeposited in order to form an addressable DNA matrix for the detection of gene mutation. Hybridization of the attached oligonucleotide with a radioactive labelled (5′-^{32}P) complementary single stranded ODN was demonstrated.[88,89]

Bäuerle *et al.* have synthesized nucleobase-functionalized PTs from bithiophenic precursors (**63, 64**).[90] The electrochemical analysis carried out in the presence of the complexing complementary base revealed in both cases a small decrease in electroactivity proportional to the concentration of the complementary base in the electrolytic medium. This effect was attributed to the formation of a potential barrier by the polar hydrogen bonds at the polymer surface.

A possible alternative to the direct electropolymerisation of



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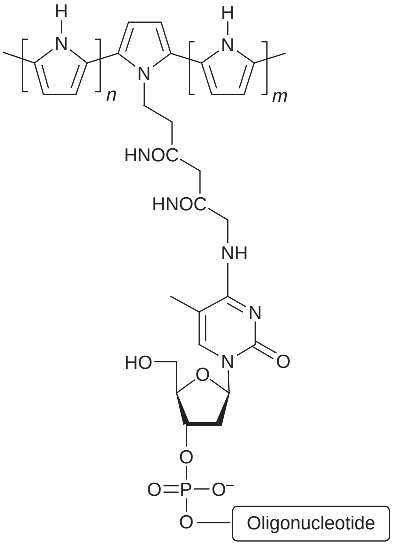

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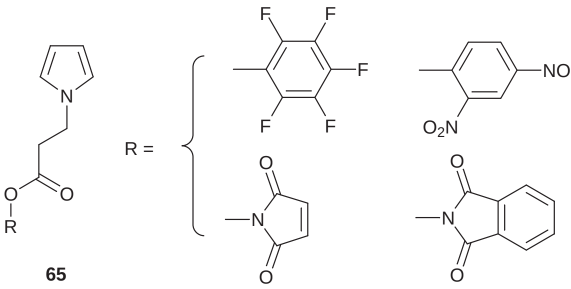

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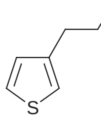

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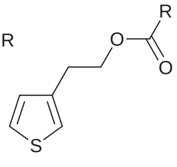

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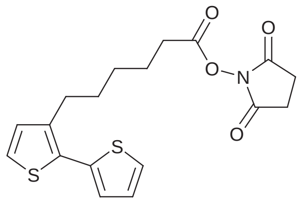

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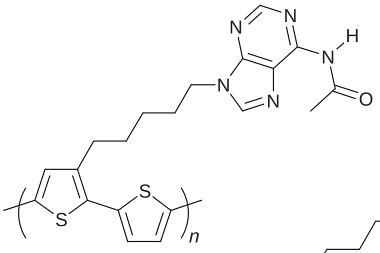

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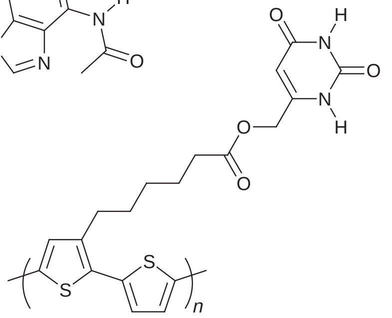

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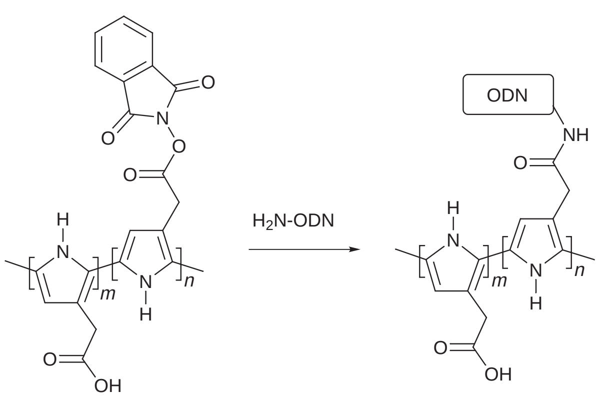


69

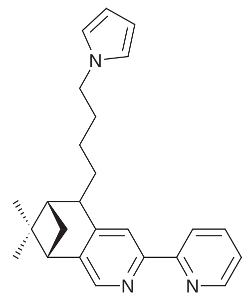
a functionalized monomer consists of the post-polymerisation modification of the polymer. While this method avoids a possible degradation of the functional group during the electropolymerisation, an important limitation is that functionalization can be limited to the outer surface of the polymer film. The roots of this approach can be found in early work of Diaz *et al.* who reported the derivatization of as-grown poly(pyrrole) by reaction with tetrathiafulvalenecarboxylic acid.[91] More recently a different post polymerisation strategy was introduced by Pickett *et al.* who electropolymerised a pentafluorophenolate activated pyrrole (**65**).[92] Reaction of the polymer with molecules possessing hydroxy or amine functions gave rise to an ester or amide derivatised polymer.

This method was then extended to other activating groups such as nitro- and dinitrophenolates, *N*-hydroxysuccinimide or phthalimide esters and conversion of the active leaving group to the corresponding methionine and histidine methyl esters was reported.[93] A related approach has been developed independently by Kossmehl *et al.* for 3-thienylethanol derivatives protected by various ether or ester groups (**66, 67**).[94–96] However, most of these compounds could not be electropolymerised and polymeric films were obtained only by copolymerisation with 3-methylthiophene.[94,96] Only 3-(2-methoxyethyl)-thiophene was successfully converted into the corresponding polymer. After ester cleavage, the resulting hydroxy functionalized polymer was used for the covalent attachment of alcohol dehydrogenase.[95] A similar procedure was applied to the immobilization of chymotrypsin or lactate oxidase.[96]

Electropolymerised bithiophene **68** has been also considered for post-polymerisation functionalisation.[97] The validity of this strategy was first tested in the case of functionalisation with ferrocene and the method was then applied to immobilization of glucose oxidase, leading to an amperometric glucose sensor.[98] Extension of this strategy to ECPs derived from 3-substituted poly(pyrrole) has led to ferrocene functionalised polymers.[99] More recently the preparation of ODN derivatized poly(pyrroles) was also carried out by a similar method.[100] The first step involved electrochemical synthesis of a copolymer of pyrrole-3-acetic acid and 3-*N*-hydroxyphthalimide pyrrole (**69**). The labile ester group was then displaced by an amino-substituted oligonucleotide containing 14 bases. The analysis of the cyclic voltammogram of the copolymer in the presence of an increasing concentration of an ODN of complementary structure to that of the attached one revealed a steady decrease in electroactivity whereas no change was observed in the presence of a non complementary ODN.[100]

5. Metal-containing ECPs

For more than a decade, the synthesis of ECP-based electrode materials containing transition metal centers has represented a major motivation for the development of functional ECPs. The aim is to develop both sensors for small molecules (CO, O_2, CO_2, NO), as well as modified electrodes for electrocatalysis or energy conversion. A large amount of work has been devoted to the development of poly(pyrrole) functionalized with transition metal complexes and this topic has been covered in a recent review.[101] Recent applications of this class of materials have involved electrodes modified by poly(pyridyl) rhodium and iridium complexes for proton reduction and hydrogenation of organics,[102] or the synthesis of a chiral poly(2,2′-bipyridyl rhodium(III) complex) (based on **70**).[103] This material was tested in the electrocatalytic reduction of



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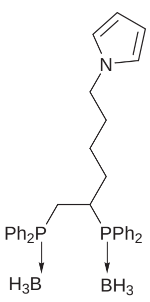

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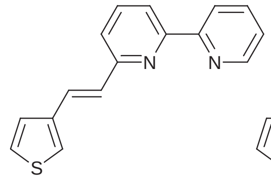

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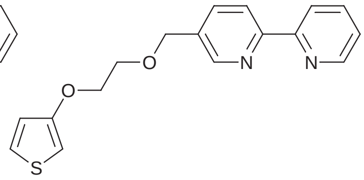

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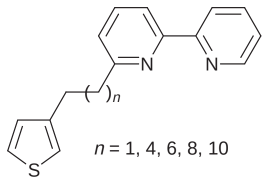

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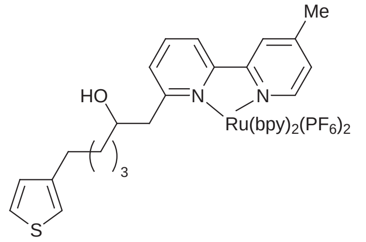

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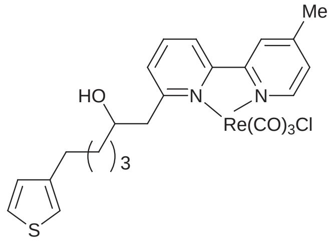

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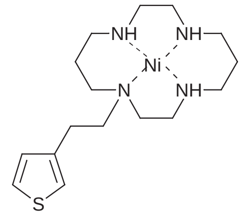


77

several ketones and some asymmetric induction was demonstrated although the optical yields remained modest (5–12%).[103]

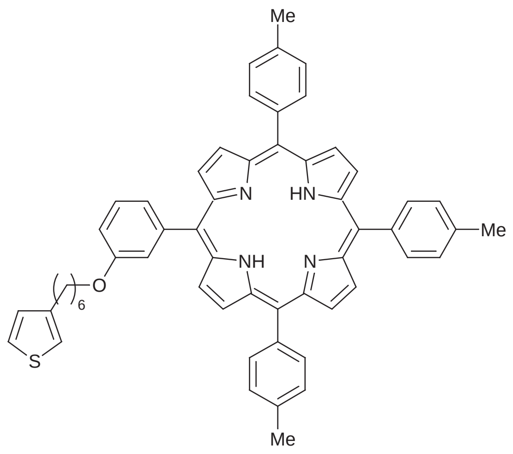
PPys derivatized by diphosphine groups were reported quite recently.[104,105] Jugé *et al.* first reported the synthesis of precursor **71** in which the diphosphine ligand is protected by BH_3 groups. The resulting ECP was then loaded with Pd by soaking in $Pd(OAc)_2$ solution and these modified electrodes were shown to be active in the electrocatalytic reduction of water.[104]

Only a few examples of PT functionalized with pyridyl and bipyridyl groups have been described. The first examples were reported ten years ago by Parker *et al.* who described the electrodeposition of the Fe^{2+} complexes of ligands **72, 73**.[106] More recently Keene *et al.* have synthesized a series of thiophenic ligands with a bipyridine group linked at the 3-position of thiophene through an alkyl spacer of variable length (**74**) and analysed the electropolymerisation of the tris(ligand)ruthenium(II) complexes.[107] A short conference paper reported the synthesis of a thiophene monomer with a bipyridine covalently attached at the 3-position of thiophene *via* a hexyl chain.[108] Reaction with ruthenium bis-2,2′-bipyridyl dichloride and rhenium pentacarbonyl chloride gave metal complexes **75** and **76** respectively. However, unequivocal evidence for the formation of extensively conjugated ECPs was not obtained.[108]

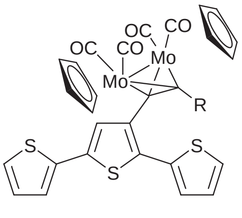
Some examples of PTs containing macrocyclic ligands such as nickel cyclam **77**,[109,110] or porphyrin (**78**),[111] linked at the 3-position of the thiophene ring *via* an alkyl spacer have been reported. In each case homoelectropolymerisation failed probably because of problems related to a lack of solubility and to the large steric hindrance to coplanarity of consecutive monomer units. Copolymers of **77** and **78** were obtained with 3-methylthiophene and bithiophene respectively.[110,111] The copolymer of **78** exhibited some ability to complex Ni(II) ions but the exact coordination environment of the metal ions in the polymer was not ascertained.[111]

These few available examples of PTs containing transition metal complexes seem to reveal a rather common behavior, electropolymerisation is generally difficult to achieve and although the CV of the resulting material exhibits the typical signature of the metal complex, that of the PT backbone is generally absent. Consequently one may wonder if a conjugated backbone is actually formed during the electrodeposition of these materials.

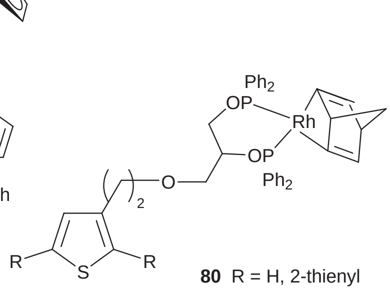
Terthiophenes with pendent organomolybdenum complexes *erythro*-[$Mo_2(\eta^2\text{-}C_5H_5)_2(CO)_4\{\eta\text{-}\eta^2\text{:}\eta^2\text{-}C(R)\equiv C[(C_4H_3S)_2\text{–}2,5]\}1$, (**79**) have been synthesized and characterized by X-ray diffraction.[112]



78



79 R = H, Ph



80 R = H, 2-thienyl

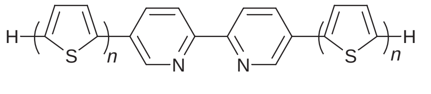
Electrodeposition was achieved by application of recurrent potential scans. While oxidation of the complex core to the cation radical and dication Mo^+ and Mo^{2+} was observed in the CV of the ECP, the wavelength of the absorption maximum of the films suggests a rather limited conjugation length although definitive assignments of the observed optical transitions were not made.[112]

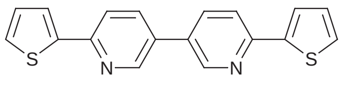
Chiral redox-active Rh(I)(bisdiphenylphosphinite) monomers and trimer (**80**) have been synthesized. These systems were targeted to probe the important factors in the design of polymeric redox-switchable hemilabile ligands.[113] While attempts to electropolymerise the monomeric complex (R=H) remained unsuccessful, the terthienyl based complex was polymerised in potentiodynamic conditions in THF. Exposure of the obtained film to H_2 in THF results in the removal of the

C_7H_8 ligand but leads to a cross-linked polymer where the Rh(I) centers dimerize.[113]

Whereas for a long period substitution of the thiophene ring by covalent derivatization at the 3-position has represented the unique route towards electrogenerated functional PTs,[6] recent years have witnessed the emergence of an alternative strategy consisting of the incorporation of the functional or complexing site within the π-conjugated chain itself. The potential advantages of this approach lie in the expected improved electronic communication between the metal center and the π-conjugated system. A first step in this direction was reported in 1996 by Swager *et al.* who synthesized compounds **81** both as free ligands and as $Ru^{2+}(bipy)_3$ complexes.[114] Although attempts to electropolymerise **81a** or its Ru^{2+} complex failed, the decrease of the oxidation potential resulting from the incorporation of an additional thiophene ring at both ends of the precursor allowed electrodeposition of both the free ligand **81b** and its Ru^{2+} complex.[114]

Pickup *et al.* have synthesized other bis-thienyl bipyridines (**82, 83**) and analysed their electrochemical behavior.[115] Both compounds exhibit large HOMO–LUMO gaps (3.30 and 3.60 eV respectively) and were found difficult to polymerise. The CVs of the electrodeposited materials revealed oxidation potentials considerably higher than that of PT while their high dissymmetry indicates a limited electrochemical reversibility. Better defined voltammograms were observed for the reduction process but the similarity of the oxidation and reduction potentials of the electrodeposited materials to those of their precursors suggests a limited degree of polymerisation.[115]


81 **a** *n* = 1
b *n* = 2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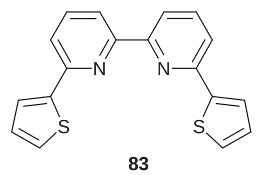
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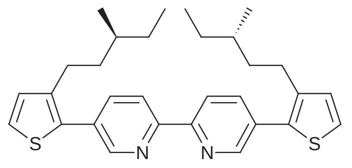

84

In order to orient the above approach towards the development of electrode materials for asymmetric heterogeneous electrocatalysis, Lemaire *et al.* have synthesized the chiral thiophene–bipyridine ligand **84**.[116] This compound was tested as a chiral ligand in the complexation of various metals such as rhodium, iridium, ruthenium and cobalt and the resulting complexes were used in the asymmetric catalytic reduction of acetophenone. While good conversion efficiencies were reached in some cases, only poor enantiomeric excesses were obtained. Attempts to electropolymerise the free ligand remained unsuccessful and film deposition could only be achieved by copolymerisation with 3-methylthiophene. However, the incorporation of the ligand moiety in the conjugated polymer chain was not definitively ascertained.[116]

Polyrotaxanes containing a conjugated thiophene-based backbone have been synthesized *via* a copper(I) template and electropolymerisation of the intertwined complex $[Cu(\mathbf{85,86})BF_4]$. In the case of the bis-monothienyl derivative (**85a**) electrodeposition was accompanied by the vanishing of the electroactivity of the Cu(I) center suggesting the occurrence of demetallation.[117] In contrast, the electrodeposition CV of the bis-bithienyl compound (**85b**) showed the persistence of the electroactivity associated with the Cu(I) ion.

Electrodeposition produced a red–orange film with a CV typical of tetrathiophene. While this result confirms that electrochemical coupling takes place, it also underlines an absence of development of the conjugation through the ligand. After decomplexation of Cu(I) remetallation was possible only when Li^+ was present in the medium (Fig. 6).[118]

Conjugated metallorotaxanes have been also investigated by Swager *et al.* who have described two series of rotaxanes based on various bipyridine thiophene systems such as **81** and **87**.[119,120] Again compound **87a** containing single terminal thiophenes was found difficult to polymerise while as expected, polymerisation of **87b** was easier and occurred at a less positive potential. The CV of the deposited material exhibited two redox systems centered around 0.35 and 0.75 V *versus* Ag wire attributed to the polymer.[120] However, since the redox potential of poly(EDOT) is around 0.0 V *vs.* SCE,[121] this large difference suggests that the observed two redox waves correspond to the formation of the cation radical and dication of the EDOT tetramer which is the redox active conjugated system formed upon electrooxidation.

Complexation of **87b** with Cu^+ or Zn^{2+} in the presence of Sauvage's phenanthroline macrocycle **86** gave rotaxanes **88** which were subsequently electropolymerised. Cyclic voltammetry revealed that metallation produces a slight positive shift of the redox potentials while *in-situ* conductivity measurements led to the conclusion that the poly(rotaxanes) behave as redox conductors.[120]

Thiophene based ECPs incorporating transition metal containing *N,N′*-ethylenebis(salicylidenimine) (salen) complexes such as **89** have been developed by the Reynolds group.[122] Although electropolymerisation of the free ligand could not be achieved, electrodeposition was possible after metal complexation. However, further investigations have shown that in this case polymerisation occurs *via* the *p*-phenylene positions.[123] On the other hand, formation of a poly(thiophene) backbone was made possible by blocking the linking sites ($R^2 = CH_3$) or by using a terthiophene structure as precursor (R^1 = 2-thienyl).[123]

More recently, it has been shown that electrooxidation of

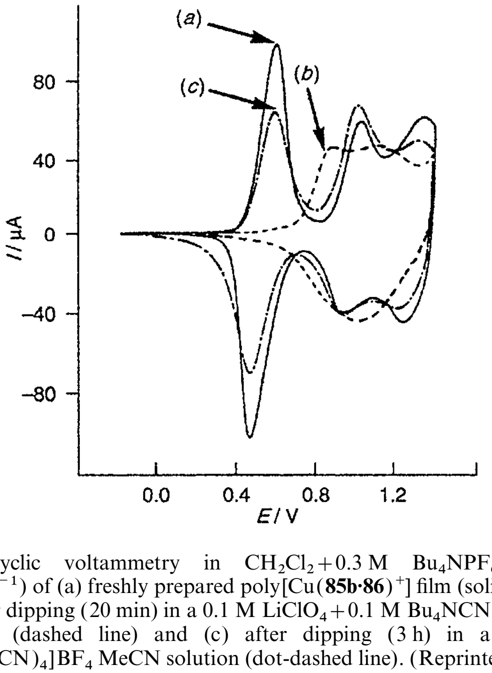
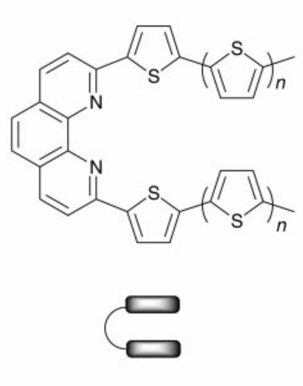
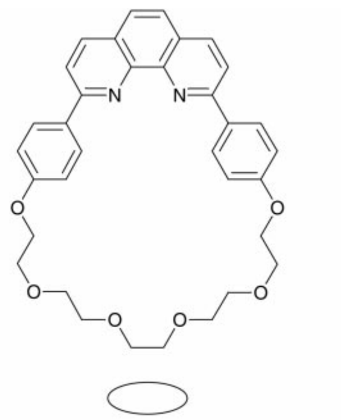


Fig. 6 Cyclic voltammetry in $CH_2Cl_2 + 0.3$ M Bu_4NPF_6 ($v = 50$ mV s^{-1}) of (a) freshly prepared poly$[Cu(\mathbf{85b{\cdot}86})^+]$ film (solid line), (b) after dipping (20 min) in a 0.1 M $LiClO_4 + 0.1$ M Bu_4NCN MeCN solution (dashed line) and (c) after dipping (3 h) in a 0.1 M $[Cu(MeCN)_4]BF_4$ MeCN solution (dot-dashed line). (Reprinted from Ref. 118, Copyright 1998, Royal Society of Chemistry).



85 a $n = 1$
b $n = 2$



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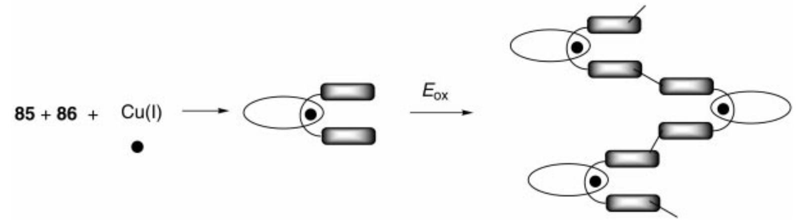
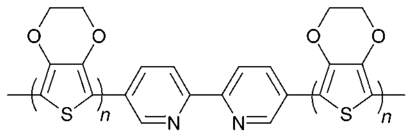
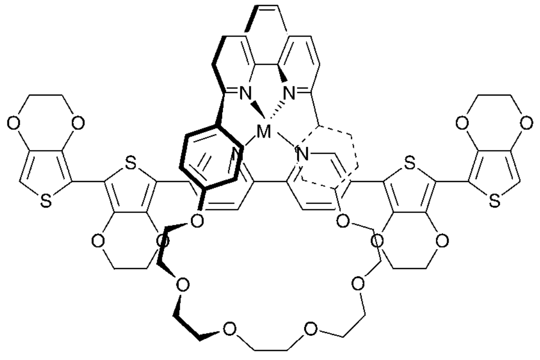
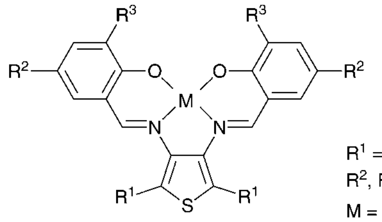




87 a $n = 1$
b $n = 2$

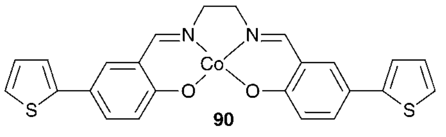


88 M = Zn^{2+}, Cu^{+}



R^1 = H, 2-thienyl
R^2, R^3 = H, CH_3
M = Cu, Ni

89



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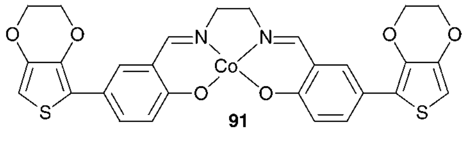


91

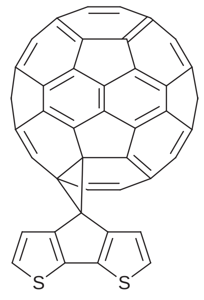
compounds **90** and **91** in acetonitrile leads to film deposition.[124] As expected, replacement of thiophene by EDOT lowers the electrodeposition potential. The CV of the films of poly(**91**) exhibits the electroactivity associated with the $Co^{2+/3+}$ redox couple and *in-situ* conductivity measurements indicate rather high values from which it was inferred that the metal center plays a major role in the development of the conjugation in these systems.[124] However, the conjugation length is noticeably shorter than that of the corresponding homopolymers as shown by the 70–100 nm blue shift of the absorption maximum compared to PT and poly(EDOT) respectively.

In conclusion the development of PTs containing transition metal ligands is one of the most recent research areas in PT functionalisation. Such materials offer many interesting opportunities to develop selective sensors, modified electrodes for electroanalysis, electrocatalysis or energy conversion. Parallel to the continuation of the classical approach involving functionalisation of thiophene at the 3-position, a more recent strategy consists of the incorporation of the metal ligand in the π-conjugated chain. Although this method should in principle contribute to optimizing the interactions between the conjugated chain and the active site, it presents the major drawback of interrupting or at least severely limiting π-electron delocalization along the conjugated system, with in some cases complete inhibition of electropolymerisation. These problems thus underline the need for alternative approaches to PT functionalization in order to expand the multiple potential applications of transition metal-containing ECPs.

6. Functional ECPs as a source of exotic conjugated structures

The synthesis of ECPs by electropolymerisation of thiophenic precursors bearing covalently attached C_{60} fullerenes has been reported by two groups.[125,126] Based on the high photovoltaic conversion efficiency obtained with blends of C_{60} and conjugated polymers,[127] it was hoped that covalent attachment of C_{60} onto a conjugated polymeric backbone could help to improve the photoinduced electron transfer between the conjugated backbone and C_{60}.

A first report described the direct grafting of C_{60} at the



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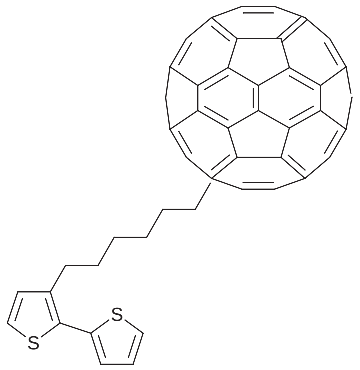

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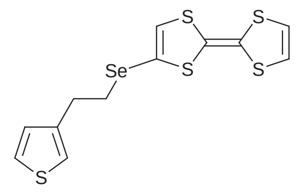

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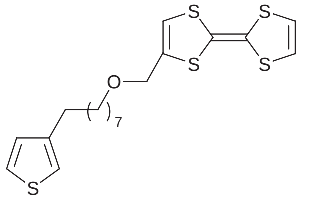

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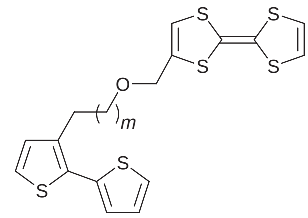

$m = 3, 5$

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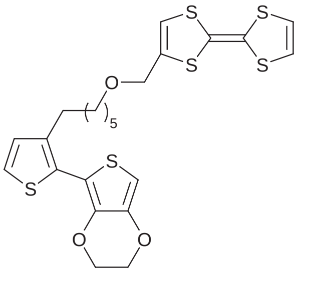

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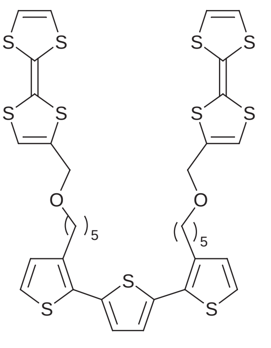

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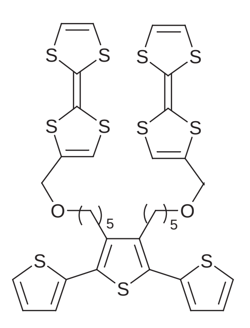

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bridging carbon of cyclopentadithiophene **92**.[125] The material obtained by electropolymerisation in chlorobenzene showed an absorption maximum at 440 nm in the neutral state. This value, which represents a *ca.* 100 nm blue shift compared to that of poly(cyclopentabithiophene), was attributed to a low degree of polymerisation due to the poor solubility of the precursor.[124] A different approach involves the electropolymerisation of a bithiophenic precursor with a C_{60} linked through an alkyl spacer **93**.[126] The resulting ECP exhibited rather high oxidation potential and an absorption maximum at 480 nm, suggesting a larger degree of polymerisation than for poly(**92**).

Derivatization of PT by covalent attachment of tetrathiafulvalene (TTF) has been a focus of considerable interest.[128] In addition to an expected increase of the long-range order in the polymer due to the high propensity of TTF to form regular π-stacks, such materials are expected to pave the way towards a new class of organic conductors in which the overall electrical conductivity would be ensured in parallel by the intra-stack aromaticity transfer associated with mixed-valence interactions in TTF π-stacks and the polaron/bipolaron conduction in the π-conjugated chain. While potential precursors of such ECPs have been synthesized by several groups, most of the attempts to electropolymerise these precursors have remained unsuccessful.[128]

Bryce *et al.* first described the electropolymerisation of compound **94** but the orange colour reported for the polymer suggested a limited conjugated length.[129] The first unequivocal evidence for the electrosynthesis of an extensively conjugated PT–TTF was obtained in the case of compound **95** in which the TTF group is linked *via* an oxadecyl spacer in order to minimize steric interactions.[130] Nevertheless, electropolymerisation remained difficult and proceeded only in nitrobenzene. A major problem posed by the electrosynthesis of PT–TTF lies in the considerable difference between the first oxidation potential of TTF (~0.40 V/SCE) and that of the thiophene ring (~2.0 V). This difference implies that at the potential required to form the PT backbone a large part of the current is consumed by the oxidation of TTF, furthermore TTF can also act as a scavenger for thiophene cation radicals.

In order to solve this problem we have recently synthesized new precursors based on bithiophenic structures (**96, 97**).[131] In addition to a limitation of steric problems by functionalization at an internal β-position, compounds **96** can be electropolymerised at a potential *ca.* 0.50 V less positive than that for **95** (1.32 instead of 1.80 V/SCE) and at a concentration lower by one order of magnitude. Incorporation of EDOT in precursor **97** allows a further decrease of the polymerization potential to 1.18 V. Potentiodynamic electropolymerisation of **96** and **97** leads to the steady growth of the two redox systems associated with the formation of the cation radical and dication of TTF.

Another advantage of the insertion of EDOT in the structure lies in the decrease of the redox potential of the PT backbone in the ECP. Thus, in contrast to poly(**96**), poly(**97**) is already conductive at the first oxidation potential of TTF. This is reflected by the faster intensification of the first TTF redox system due to the improved electrical communication between the electrode and the TTF group (Fig. 7). The extended conjugated structure of the resulting polymers is confirmed by the similarity of their absorption maxima to that of poly(3-alkylthiophenes) ($\lambda_{max} > 500$ nm).[131] A detailed analysis of the electrochemical and spectroelectrochemical properties of these polymers has provided the first evidence for the occurrence of mixed-valence interactions among the attached TTF groups. This was first demonstrated by the additional anodic wave due to the oxidation of the mixed-valence dimer between those corresponding to the cation radical and dication of TTF (Fig. 8) and definitively confirmed by the spectral signature of the mixed-valence dimer at 1850 nm at the begining of the oxidation process.[132]

Quite recently, compounds **98** and **99** have been synthesized with the aim of increasing the TTF concentration in the polymer. Although homoelectropolymerisation failed, mixed-valence interactions were nevertheless observed in the CV of the copolymers with bithiophene. Interestingly, the intensity of the mixed-valence anodic wave was almost independent of the composition of the copolymer, suggesting that mixed-valence interactions involve a significant contribution of intramolecular interactions.[133] These first results should provide a strong incitement to further work towards the development of organic materials with hybrid electronic conduction.

ECPs derived from precursors possessing multiple linking sites represent another class of materials with potentially original structure and electronic and electrochemical properties. This concept was first investigated in the case of precursor

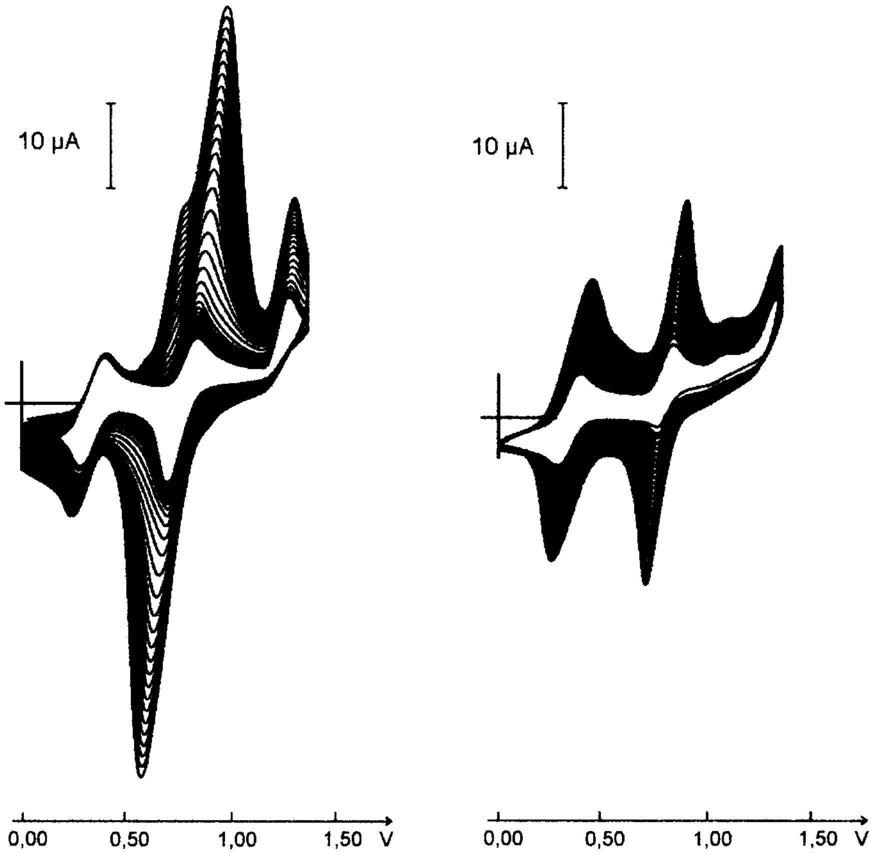


Fig. 7 Potentiodynamic electrodeposition curves of the polymers in 0.1 M Bu_4NPF_6–$PhNO_2$, ref. SCE, scan rate 100 mV s^{-1}. Left: poly(**96**) ($m = 5$), 2×10^{-2} M precursor, right: poly(**97**) 1.5×10^{-2} M precursor (Reprinted from Ref. 131, Copyright 1998, VCH Verlag).

100 in which connection of four terthienyl units to a central silicon atom leads to a precursor with a tetrahedral geometry.[134] It was hoped that upon electrooxidation formation of thiophene–thiophene linkages would lead to a material forming a three-dimensional conjugated network.

The electrochemical and spectroscopic data of the electrodeposited material were consistent with the electrodeposition of a tetrakis cation radical salt. Application of subsequent potential scans to this material leads to conversion into a material containing sexithienyl conjugated units, as indicated by the red shift of the absorption maximum from 380 to 460 nm (Fig. 9).

X-Ray energy dispersion spectrometry data confirmed the persistence of the Si–C bonds after electrochemical conversion.[134] The converted material exhibited an intense and well defined n-doping redox system consistent with a rigid conjugated structure. Recently this idea has been extended to a tetrapyrrole precursor (**101**)[135] and to another tetrahedral thiophenic precursor built around an sp^3 carbon (**102**).[136] In both cases the conductivity of the materials showed a sensitivity towards gases such as ammonia or trimethylamine[135] or to vapor of organic solvents[136] considerably larger than that of the parent polymers prepared from monomeric precursors. These results were attributed to the highly porous structure of these novel electrogenerated materials.

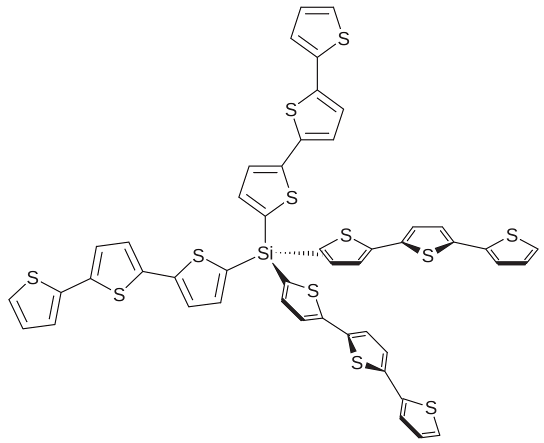
Electropolymerisation of a precursor involving two polymerisable groups linked by a flexible polyether chain was initially proposed by Roncali *et al.* in the case of compound **103** as a possible route to creating ECP containing pseudo crown ethers.[137] Indeed, electropolymerisation of this type of precursor can give rise to polymeric structures containing macrocyclic cavities of various sizes (Scheme 2).

In the presence of Li^+, the onset for polymerisation of compound **103** occurs at a potential *ca.* 0.20–0.30 V less positive than that of thiophene monomers 3-substituted by a linear polyether chain. This negative shift was tentatively attributed to the occurrence of some ring closure by a template effect. While this concept has been extended to other systems such as fluorene,[138] we have recently synthesized a first example of a novel series of this class of precursors with bithiophene as an electropolymerisable group (**104**). Preliminary results have revealed a strong effect of the nature of the electrolyte cation on the structure of the polymer providing evidence for an electrochemical molecular imprinting effect.[139]

While introduction of functional groups in the linker could contribute to the extension of the applications of functional PTs as electrode modifiers, these first results together with those obtained with ECPs derived from tetrahedral precursors suggest possible routes for controlling the porosity of the materials. The control of this parameter will probably acquire a growing importance in the near future as it is likely that beyond appropriate functionalization, the geometry and accessibility of the active site represent key factors for the design of electrode materials for electrocatalysis applications.

7. Conclusion and outlook

For about 15 years the synthesis of functional ECPs has involved essentially a ‘side chain approach’ consisting of the covalent attachment of the functional group on a pyrrole or thiophene ring *via* an electrochemically inert spacer group in order to neutralize undesired electronic and steric effects. While this method has led to the development of a large number of ECPs with specific properties such as ionic or molecular recognition, or electrocatalysis, there have also been many examples of precursors that either do not electropolymerise or lead to ill-defined materials in which most of the relevant electronic properties of the conjugated backbone are lost. These unsuccessful attempts are sometimes consecutive to an



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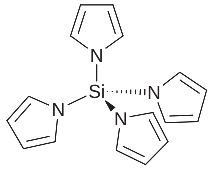

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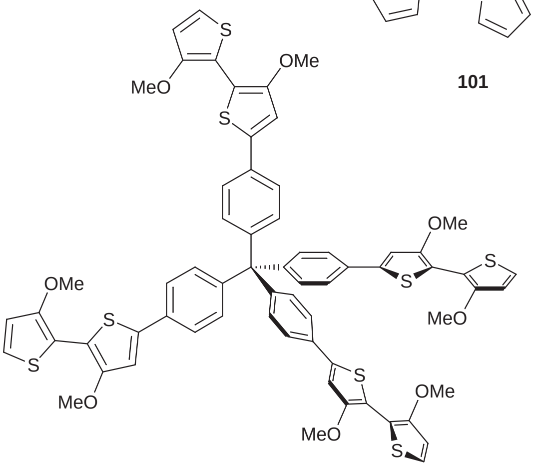

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underestimation of electronic and steric effects in the precursor design but there are also many cases where the lack of polymerisation reflects the inherent limitations of the 'monomer side chain approach' in terms of steric capacity and stability of the functional group at highly positive potentials. Furthermore, the need for extended linkers for the attachment of the functional group poses the problem of the electronic communication between the active center and the π-conjugated backbone.

Possible solutions to these questions resort to different strategies such as the design of precursors with lower polymerisation potential and a different view of steric effects.

As shown by several of the above examples such as crown ethers, nucleobases or TTF, functionalized bithiophenes which combine low polymerisation potential with reduced steric interactions represent an interesting new class of precursors which may well supplant the parent monomers in many instances. Similarly, EDOT appears as a very promising substrate which associates moderate polymerisation potential with an exceptional stability in the doped state. The potentialities offered by this latter substrate have been illustrated by some recent examples of functional ECPs,[140,141] and there is little doubt that ECPs based on substituted EDOT will acquire a growing importance in a near future. However, the reverse of the coin is that functionalization of both bithiophene and EDOT requires more complex synthetic chemistry than that of thiophene.

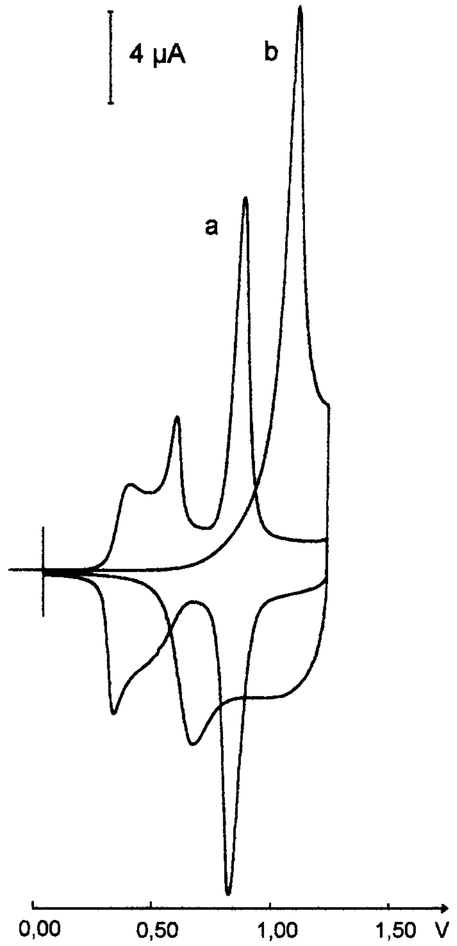


Fig. 8 Cyclic voltammograms recorded in 0.10 M Bu_4NPF_6–CH_3CN, scan rate 100 mV s^{-1}, Ref. SCE. (a) poly(**96**) ($m = 5$), (b) poly(bithiophene) (Reprinted from Ref. 132, Copyright 1998, American Chemical Society).

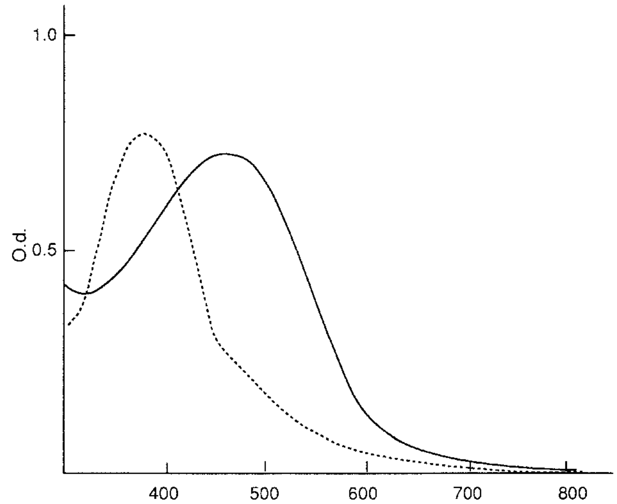
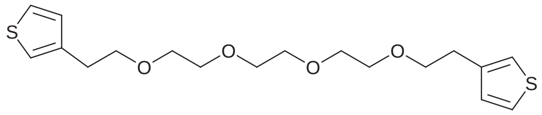


Fig. 9 Electronic absorption spectrum of an electrodeposited film of poly(**100**). Dotted line: as-deposited film. Solid line: same film after several oxidation cycles between 0.0 and 1.40 V *vs.* SCE. (Reprinted from Ref. 134, Copyright 1995, Elsevier).

It is widely acknowledged that conjugated oligomers are inappropriate substrates for electropolymerisation due to the relative stability of their cation radicals.[6,24] However, as pointed out in several recent works, introduction of electron donating methoxy or methylsulfanyl groups at the external β-positions produces a 'reactivation' of the end linking site thus allowing the formation of extended conjugated chains.[142,143]



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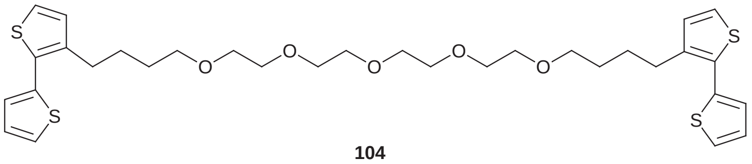

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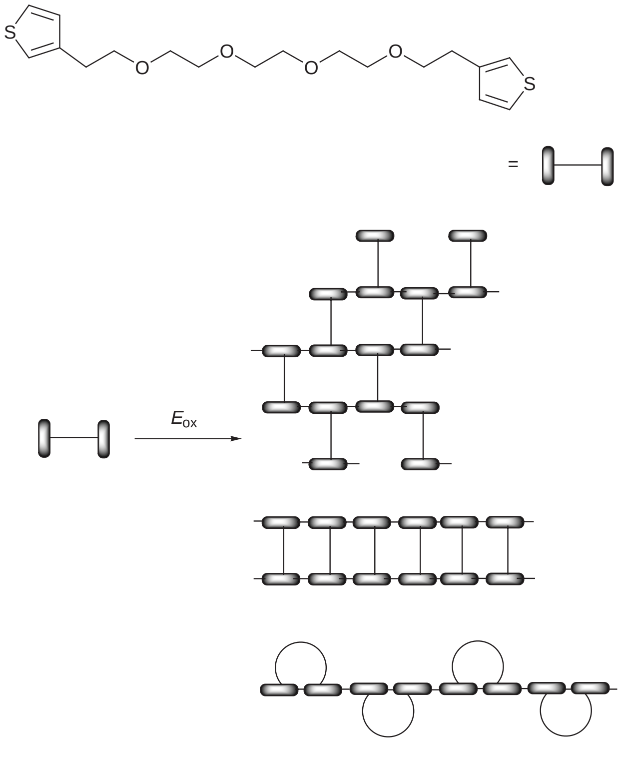
These results can thus stimulate further work in the direction of a rational use of functional oligomers as precursors.

A recently proposed alternative to the 'side chain approach' consists of the insertion of the functional group within the conjugated path. While this 'in-chain approach' should in principle allow optimal interactions between the π-conjugated system and the functional site, the various examples reported so far indicate that this kind of structure leads to an interruption of conjugation with the formation of discrete oligomeric segments. Consequently, and despite the interesting properties exhibited by these original materials, the definition of an 'in chain approach' compatible with the preservation of an extensively conjugated polymer chain remains an open question.

To summarize, functional ECPs remain at the forefront of research on linear π-conjugated systems. The intensive research effort invested in the recent period has led to the development of a huge number of materials with original properties. However, many problems related to the efficient electropolymerisation of modified precursors and to the control of the structure of the resulting ECPs remain largely unresolved, thus underlining more than ever the great need for creative synthetic chemistry.



Scheme 2

Acknowledgements

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