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PAPER

Electropolymerization of chiral chromium–salen complexes: new materials for heterogeneous asymmetric catalysis

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Electrochemical oxidation is described as a very efficient polymerization procedure for the heterogenization of metallic chiral catalysts. From chromium chiral complexes based on salen–thiophene ligands, this methodology provided an efficient access to various polymers. Recovered as insoluble powders, these materials were tested in different enantioselective heterogeneous catalytic reactions. Structural modifications were introduced on the salen core in order to evaluate their influence on redox polymer properties and on the enantioselectivity of the catalysis. Electrochemical experiments showed the particular stability of these deposited materials at the electrode surface and SEM analyses suggested the influence of the electropolymerization conditions on their morphology.

Introduction

Chiral metallic complexes are one of the keystones of modern asymmetric catalysis: they have been applied to numerous reactions, allowing synthesis of sophisticated molecules with high enantioselectivities. Even if some homogeneous enantioselective catalytic procedures have been successfully developed at the industrial scale, they remain disputable because of prohibitive costs, mainly due to the loss of the catalyst at the end of the reaction. Furthermore, some of these metallic complexes can be considered as harmful pollutants, especially in medicinal chemistry. In this context, heterogeneous catalysis presents many advantages. Many efforts are thus being directed nowadays towards the efficient recovery and re-use of such selective catalysts. The main trend consists in rendering catalysts insoluble and recycling them by simple filtration of the reaction mixture media.[1]

In this field the tetradentate Schiff base (salen) family has been successfully associated to numerous metals (Mn, Co, V, Ni, Cr, Fe…) and promoted a wide range of enantioselective transformations.[2] Heterogeneous procedures have been applied to various catalytic reactions with some success but there is room for improvement in terms of enantioselectivity, activity and recycling efficiency.[3] Identified problems for the limitations in terms of efficiency are metal leaching, catalysts structure degradation or accessibility of the catalytic sites. In the last several years, we have developed our own solution to this problem based on the heterogenization of chiral salen complexes by electrochemical polymerization.[4] Because chromium complexes are well known to promote various enantioselective reactions such as epoxide ring opening,[5] epoxidation,[6] hetero Diels–Alder reaction[7] or Nozaki–Hiyama–Kishi reaction,[8] we have successfully evaluated the electrogenerated new insoluble materials in asymmetric heterogeneous catalysis based on chromium.[9,10] Considering the electrochemical polymerization mechanism, we have obtained a catalytic heterogeneous material with linear arrangement in which each monomer unit is a catalytic site. The targeted structure allowed the asymmetric catalyst to operate under the best conditions for maintaining its high efficiency for several cycles.

Many electrochemical investigations were carried out with salen complexes, because of their straightforward synthesis, their ability to incorporate various transition metals and their easy electrochemical analysis. Anodic polymerisation of these compounds has been investigated with varied objectives such as new materials for energy storage,[11] electrochemical sensors[12] or catalysis.[13] Furthermore, it has been demonstrated that the anodic polymerization of various salen complexes such as nickel, cobalt, copper, iron, manganese or palladium allowed for efficient preparation of metal–salen based modified electrodes.[14] In most cases, the polymerization was realised by cyclic voltammetry or constant-potential electrolysis in weak donor organic solvents like acetonitrile or dichloromethane.[15] The properties of the coated electrodes have been particularly studied in the reduction of halo- and dihaloalkanes,[16] in the development of electrochemical sensors for the determination of NO concentration in solution,[12a,b] for medicinal products such as dipyrone[17] or metal ions in aqueous media.[18,19] Enantioselective electrocatalytic epoxidation of styrene and stilbene was achieved with chiral manganese–salen complexes polymerized on a glassy carbon electrode using molecular dioxygen as oxidant.[20] In order to better understand the relationship between the ligand structure and the properties of the modified

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electrode, both Reynolds and Swager groups described the synthesis and the electrochemical behavior of salen transition metal complexes tagged with thiophene moieties.[21,22] The introduction of thiophene units allowed for electrochemical polymerization at much lower potentials than the parent salen complexes. These structural modifications suppressed side reactions and improved the stability of the resulting polymers. Of particular note, Kingsborough and Swager prepared various monomers that were electropolymerized at lower potentials especially for 3,4-ethylenedioxythiophene modified-salen and they were able to perform oxygen reduction with very high efficiency.[21c]

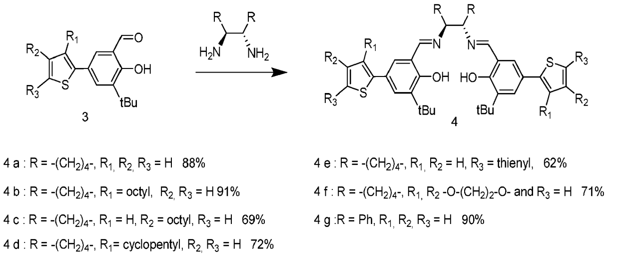
We report herein the results of our investigations on the synthesis of stable polymeric materials efficient for heterogeneous asymmetric catalytic applications. We focused our studies on the influence of the ligand structure and electropolymerization conditions. To evaluate the influence of these structural modifications on both electrochemical polymerization and catalytic activity, each new salen–thiophene complex was analyzed by electrochemistry.

Results and discussion

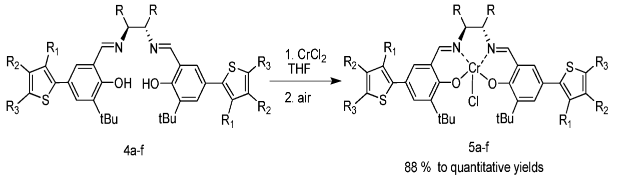
Monomers synthesis

We have developed a general strategy for the efficient synthesis of chiral salen derivatives modified by thiophene groups on the 5,5′-position of the phenolic rings (Scheme 1).[4] Several variations were introduced to the general structure of the chiral salen–thiophene based ligands. The electrochemical behaviour of these monomers and of the corresponding polymers was studied according to the structural variations. Using this synthetic strategy, were prepared various salicylaldehyde precursors **3**. The functionalization introduced on the thiophene moieties allowed the subsequent evaluation of steric and/or electronic effects. Finally the aldehydes were condensed with a chiral diamine to form the corresponding new chiral ligands **4** (Scheme 1).

We then synthesized the corresponding chromium complexes, as monomers for electrochemical polymerization. All chromium complexes were obtained according to the same procedure (Scheme 2) and were isolated after extraction without any purification as powders with nearly quantitative yields. The complexation was carried out using chromium chloride ($CrCl_2$) under inert atmosphere to form chromium(II) complexes, then a simple air oxidation led to the desired chromium(III) complexes.[7a]



Scheme 1 Chiral salen ligands modified by various substituted thiophene derivatives.



Scheme 2 Synthesis of chiral salen thiophene chromium complexes.

Electrochemical polymerization

According to the results reported by Swager *et al.*[21] and our previous work,[4] the polymerization could only occur with salen complexed with the metal. All our attempts for electropolymerization of metal-free salen–thiophene ligands were indeed unsuccessful. Current-potential curves for electropolymerization of metal-free salen–thiophene in dichloromethane solution in the presence of $n\mathrm{Bu_4NBF_4}$ (0.05 M) as electrolyte support were recorded. The potential started from 0.0 V *vs.* SCE and was generally cycled between 0.0 and 1.2 V *vs.* SCE at a potential rate of 0.1 V s^{-1}.[1] A typical example of the cyclic voltammogram obtained for the attempted electrochemical growth of poly-salen thiophene (poly-**4a**) on a platinum electrode is shown in Fig. 1. A large anodic current wave at +0.77 V/SCE was observed during the first cycle that probably arose from the anodic oxidation of the salen thiophene ligand. This peak vanished after a few scans (5–10) and the current of the second positive peak at a potential of about 1.00 V quickly reached stable values during the successive potential scans. The absence of variation indicated that the oligomeric thiophene–salen ligand formed at the electrode was insulating. A negative peak appeared at +0.7 V corresponding to the reduction of the oxidized product at the electrode surface. Finally after about five cycles a perfectly stable redox system was observed. This cyclic voltammetry can be explained by the formation of non-conjugated short oligomers such as dimers or trimers. Electropolymerization of metal-free salen–thiophene yielded thus species that are not much more conjugated than the initial monomer. Consequently, the resulting electrodeposited material is oxidized at the same potential, probably corresponding to the oxidation of the thiophene–phenol ring, which is independent of the chain length in a non-conjugated polymer. A preparative electrochemical oxidation of ligand **4a** led indeed to a soluble species in THF. Maldi-TOF analyses confirmed the formation of only dimers in a low amount.

In contrast, when the electropolymerization was carried out from the corresponding complexes, the evolution of the voltammograms was consistent with the formation of conductive organic polymers at the electrode surface. We have previously reported the oxidative electropolymerization of various thiophene–salen chiral

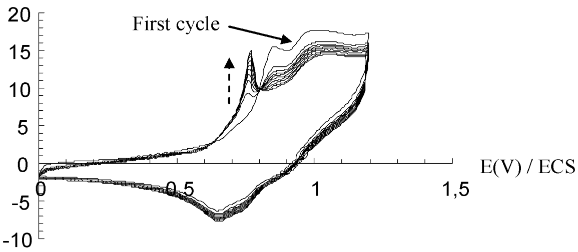


Fig. 1 Electropolymerization of the chiral salen ligand **4a**.

complexes and contrarily to their corresponding ligands the polymerization proceeded smoothly in each case.[4] In order to find the optimal conditions to obtain a more electroactive redox response, the factors affecting the electroactivity of the polymers such as the scan rate, potential cyclic limits and number of cycles were examined. The best conditions to form the polymer film on platinum or glassy carbon electrode surfaces were found for a continuous potential sweep between 0 and 1.5 V/SCE for more than 20 cycles at different scan rates. The continuous current increased in the cyclic voltammetric peaks during repeated potential scans from 0.0 to 1.5 V indicating film growth at the electrode surface. Visual inspection of the electrode also showed the deposition of a dark green-black film.

For every salen–thiophene complex the polymerization led to the formation of robust films at the platinum electrode surface. As illustration, Fig. 2 depicts the evolution of consecutive cyclic voltammograms on a platinum electrode in dichloromethane solution containing 5×10^{-3} M of thiophene–salen complex **5e**. A gradual increase in the amplitude of cyclic voltammetric peaks was observed as a consequence of consecutive potential cycling, indicative of the electropolymerization of thiophene–salen complex **5e** and subsequent deposition of a conductive polymeric film at the electrode.

The coated electrodes were rinsed thoroughly and further tested under cyclic voltammetry conditions in a fresh acetonitrile solution containing 10^{-1} M $n\mathrm{Bu_4NBF_4}$ as supporting electrolyte without any monomer. The effect of scan repetition on the electroactivity of the obtained polymer film was studied between 0.0 and 1.3 V *vs.* SCE at a scanning rate of 100 mV s^{-1}. In this potential range, the polymer exhibited a pair of coupled peaks at 0.82 and 0.7 V as shown in Fig. 3. The peaks observed correspond to the electrochemical behaviour of the polymer formed at the electrode surface, placed in the electrolytic media free of monomers. The voltammograms depicted in Fig. 3 resulted from more than fifty potential scans between 0.0 and 1.3 V. This electrochemical behaviour indicated a reversible redox system without variation of the intensity and clearly proved the formation of a chemically and electrochemically very stable film at the platinum electrode surface. The modified electrode transferred to clean electrolyte solution exhibits only one redox couple with a diffusional profile. Every chromium complex showed the same cyclic voltammogram profiles for the electrochemical polymerization and for its electroactivity when it was analyzed. In Table 1, the characteristic redox potentials E_{ox} and E_{red} for each complex are reported according to its structure. The recorded potentials are in agreement with the electronic effects of each substituent introduced on the thiophene core. Thus, when thiophene is substituted by ethylene dioxide at positions 3,4 (EDOT **5f**) its oxidation potential was strongly lowered, 0.56 V/SCE instead of 1.10 V for nonsubstituted thiophene. Alkyl chains such as octyl or cyclopentyl (**5b**, **5c** and **5d**) introduced on positions 3 or 4 have the same influence with a slight lowering of the potential around 200 mV compared to non-substituted thiophene.

The modification of the ligand by the introduction of a bisthiophene unit (**5e**) emphasized this decrease in the potential totally in agreement with a more conjugated heteroaromatic system. The change of the chiral bridge, using diphenylethylene diamine (**5g**) instead of cyclohexane diamine in **5a**, did not apparently lead to any change in the oxidation potential. In the case of a chemically stable redox species and an electrochemically reversible system, the voltammetric behavior of an electrode coated with a monolayer of a redox couple is characterized by symmetrical anodic and cathodic waves with a difference in the peak potential values (ΔE) close to zero.

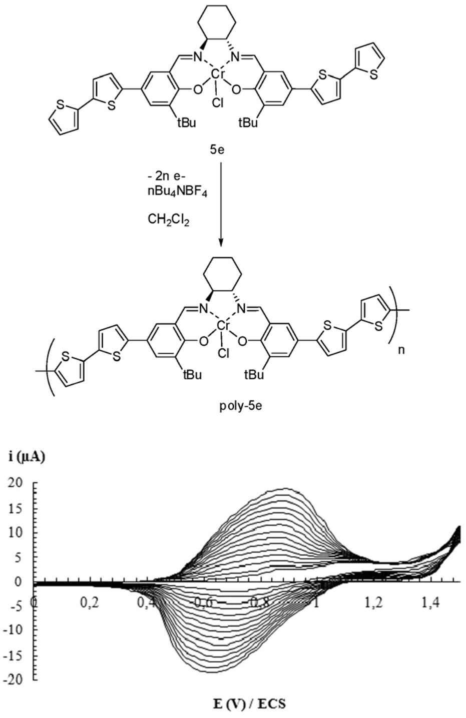


Fig. 2 Anodic polymerization of chromium complex **5e** (0.05 M) with $n\mathrm{Bu_4NBF_4}$ (0.1 M) in CH_2Cl_2, v = 100 mV s^{-1}.

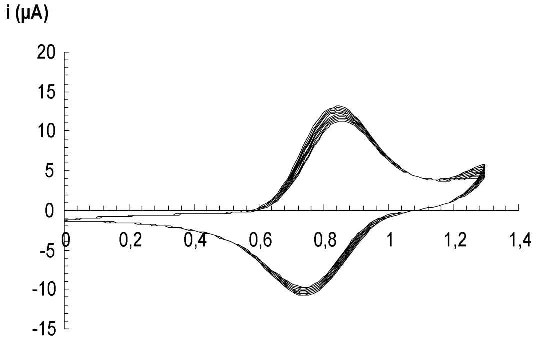


Fig. 3 Analysis of the polymer poly-**5e** coated electrode in CH_3CN, $n\mathrm{Bu_4NBF_4}$ (0.1 M), v = 100 mV s^{-1}.

Table 1 Structure effect of the complex on the potentials of oxidation and reduction

Polymer	E_{ox} (V/SCE)	E_{red} (V/SCE)	ΔE	Q_a/Q_c
Poly-**5a**	1.10	0.56	0.54	1.18
Poly-**5b**	0.89	0.70	0.19	1.26
Poly-**5c**	0.89	0.59	0.30	1.13
Poly-**5d**	0.95	0.76	0.19	0.93
Poly-**5e**	0.82	0.73	0.09	1.15
Poly-**5f**	0.56	0.51	0.05	1.04
Poly-**5g**	1.08	0.52	0.56	1.02

The ΔE values are generally dependent on charge-transfer kinetics, the scan rate and mass transport for relatively thicker films. In our case, for all films, the cyclic voltammetry waves exhibited peak potential separations between 50 and 560 mV at 100 mV s^{-1} according to the structure modifications and diffusional shape, thus indicating a relatively slow charge transfer rate from the interface between the electrode and the redox centers through the film.

Another characteristic value of the stability of the polymers is the charge Q_a/Q_c ratio. These Q_a/Q_c ratios are reported in Table 1, and for all polymers, Q_a/Q_c was found to be close to 1, demonstrating the particular stability of those materials able to exchange reversibly a similar quantity of charge.

SEM analyses

Scanning electron microscopy (SEM) analyses were performed to find some information about the morphology and the strength of the interaction between the electrode and the polymeric material.

This SEM study of a polychromium–salen complex-coated electrode was realized by delimiting three areas on a vitreous carbon electrode, on which the number of potential scans between 0.0 and 1.3 V/ECS were varied. The electrode surface modification was carried out using the conditions optimised for complex **5a** electropolymerization.

SEM analysis showed that each electrode was completely coated with the polymer. The first one obtained after five scans (Fig. 4a) showed dispersed particles on the electrode surface with an average particle size of about 500 nm, leading to a porous structure.

After 10 scans (Fig. 4b), the polymer growth is obvious with the modification of the surface morphology due to an increase in the particle size, ranging between 11 and 19 μm. Finally, after 15 scans of potential (Fig. 4c) a thickening of the deposit is observed. The pores are filled with growing polymers until complete obstruction and a smooth surface is formed equivalent to a conventional film of conducting polymer deposited at the electrode. Moreover, when this deposit is dried with air to eliminate solvents from polymerization, the film is cracked and detached from the electrode (Fig. 4d). Based on these observations, it seems clear that the conditions of polymerization will influence the morphology of the polymer. However to obtain an efficient heterogeneous catalyst, porosity or specific surface area are important factors. For example, porosity increases the specific surface area and is therefore a highly valued property in polymerized catalysts.

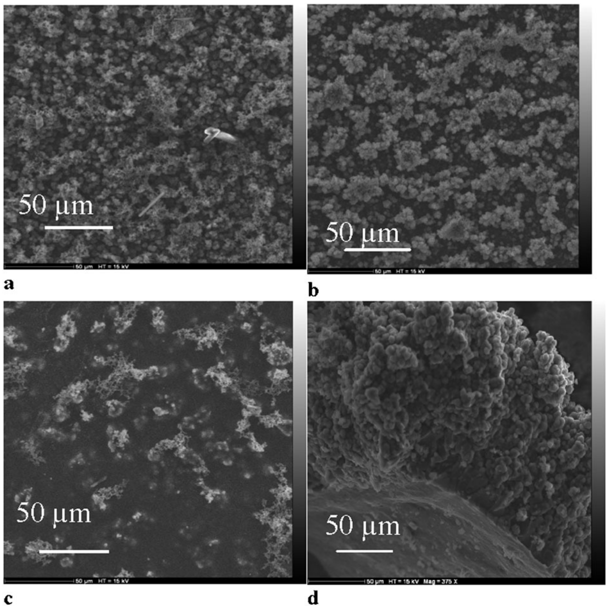


Fig. 4 SEM images of anodic polymerization of chromium complex **5a** (0.05 M) with $n\mathrm{Bu_4NBF_4}$ (0.1 M) in CH_2Cl_2; v = 100 mV s^{-1} running between 0 and 1.2 V *vs* ECS. (a) After 5 potential scans, (b) after 10 potential scans, (c) after 15 potential scans and (d) polymer recovered from the electrode.

We have performed the oxidative electropolymerization of these new chiral thiophene–salen complexes at a preparative scale, for the formation of insoluble polymers recovered as black powders from the electrode surface. The electrosynthesis was performed at a constant current of 50 mA in an undivided electrochemical cell fitted with two vitreous carbon (16 cm^2) electrodes in Bu_4NBF_4 2.0 × 10^{-2} M in CH_3CN or CH_2Cl_2 as electrolytic medium. The anode potential was monitored by a saturated calomel electrode (SCE) during the electrolysis. After more than 2 hours the vitreous carbon anode was recovered and the deposited polymer removed from the electrode surface. The residue was washed with various solvents and dried under vacuum before their use in asymmetric catalysis.

Asymmetric heterogeneous catalysis

These new insoluble polymers, based on chromium complexes, were tested for their ability to promote successfully heterogeneous catalysis in various asymmetric transformations.

As most accessible monomeric chromium complex, **5a** was evaluated in numerous asymmetric reactions and its efficiency was compared to the results described by the group of Jacobsen in the presence of the analogous *tert*-butyl substituted complex.[5,7,23,24] We particularly performed hetero Diels–Alder reactions,[10a] nitroaldol transformations[10c] and epoxides ring opening with trimethylsilylazide,[10b] for which high activities and enantioselectivities were reached, albeit with slightly diminished values compared to those obtained using the Jacobsen complex. Replacing the ^{t}Bu-groups on the salen core by thiophene ones led thus to a detrimental effect probably due to different electronic and steric constraints. Correspondingly, the efficiency of poly-**5a** was previously evaluated and we able to report its high efficiency in those reactions, in terms of both activity and enantioselectivity. For instance, the asymmetric hetero Diels–Alder reaction of various aldehydes was performed and poly-**5a** was nicely reused in successive catalytic cycles for up to 15 times. This polymer was then successfully used in a multi-substrate procedure; with the same batch of poly-**5a** twenty runs were performed leading to the synthesis of ten structurally varied pyranones with stable activities and enantioselectivities. We also described the first use of a chiral heterogenized salen complex active in the Henry reaction between various aldehydes and nitromethane. The same heterogeneous catalystpoly-**5a** was used five times with a slight loss of yield and enantioselectivity. We have finally recovered the same catalyst batch (poly-**5a**) in different consecutive epoxides ring opening reactions with nitrogen-based nucleophiles leading however to poor results, compared with the values obtained under homogeneous conditions. This is probably due to the structure of the polymeric catalyst itself, with the chromium coordinating sites arranged in a pearl necklace manner. The essential position of the catalytic sites for an optimal cooperative bimetallic pathway is possibly, in this case, not feasible.

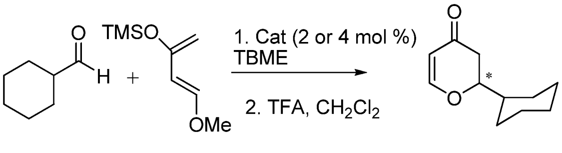
Analogous poly-**5b** and poly-**5e** were therefore also engaged in those diverse reactions and their ability to promote asymmetric catalysis is here discussed, in comparison with their homogeneous analogues and poly-**5a**.

To illustrate the hetero Diels–Alder transformation, the synthesis of 2-cyclohexyl-2,3-dihydro-pyran-4-one was attempted through reaction between cyclohexanecarboxaldehyde and Danishefsky's diene.[25] Jacobsen and co-workers described this reaction yielding the targeted product with an ee of 93% (71% isolated yield) using the tetrafluoroborate chromium complex of (*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine at −20 °C in MTBE (Table 2).[7a]

Delightfully complexes **5b** and **5e** were also efficient catalysts for the synthesis of 2-cyclohexyl-2,3-dihydro-pyran-4-one and were furthermore more active species than **5a** since the targeted compound was isolated in high yield within the same reaction time. The highest enantioselectivity value was obtained with **5b** as catalyst and reached 78% ee. The increase in the steric bulk on the thiophene ring arising from the introduction of the octyl group was thus beneficial in terms of enantioselectivity. The corresponding polymeric complexes catalyzed also the transformation and as previously observed in the case of the use of poly-**5a** this heterogeneous procedure afforded the desired product albeit with slightly diminished ee values with regards to the homogeneous cases. The polymers were nevertheless very active and could be reused twice with relatively stable efficiencies. As for its homogeneous counterpart **5b**, poly-**5b** was the most enantioselective catalyst of the polymeric species.

Since poly-**5b** proved to be more efficient than the unsubstituted poly-**5a** in the hetero Diels–Alder transformation, we wondered if we could demonstrate a broad activity for this catalytic species in other transformations. The Henry reaction was thus investigated as an atom economic transformation allowing the synthesis of nitroalcohol building blocks, valuable synthons for the preparation of biologically active compounds.[26] The homogeneous reaction between *o*-anisaldehyde and nitromethane was conducted in dichloromethane at room temperature and both catalysts **5a** and **5b** delivered the expected nitroalcohol in satisfying yield but moderate enantioselectivity. In this case again, catalyst **5b** was the most enantioselective promoter. As a comparison, this transformation has been studied by Skarżewski and coworkers using the classical ^{t}Bu-salen modified Jacobsen's catalyst. They performed the reaction in dichloromethane at −78 °C and isolated 1-(2-methoxy-phenyl)-2-nitro-ethanol in 88% yield and 73% ee (Table 3).[24a]

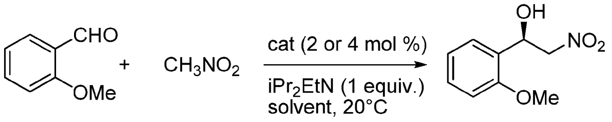
Table 2 Hetero Diels–Alder reaction



Entry	Cat (mol%)	*t*/h	Temp./°C	Yield[a] (%)	ee[b] (%)
1	**5a** (2)	22	20	79	72
2	**5b** (2)	23	20	92	78
3	**5e** (2)	23	20	>99	71
4	Poly-**5a** (4)	21	25	61	60
5	Poly-**5b** (4)	24	25	89	72
6	(1st reuse)	24	25	88	65
7	(2nd reuse)	24	25	93	69
8	Poly-**5e** (4)	23	25	71	62
9	(1st reuse)	23	25	74	63
10	(2nd reuse)	23	25	80	62

[a] Isolated yields, [b] ee determined by chiral HPLC analysis.

Table 3 Henry reaction



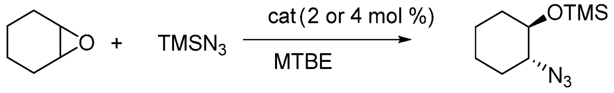
Entry	Cat (mol%)	*t*/h	Solvent	Yield[a] (%)	ee[b] (%)
1	**5a** (2)	24	CH_2Cl_2	74	34
2	**5b** (2)	24	CH_2Cl_2	70	54
3	Poly-**5a** (4)	24	MTBE	>99	65
4	Poly-**5b** (4)	24	MTBE	67	47
5	(1st reuse)	24	MTBE	43	46
6	(2nd reuse)	24	MTBE	40	51

[a] Isolated yields, [b] ee determined by chiral HPLC analysis.

The heterogeneous catalysis was performed in MTBE as best solvent for this procedure as was previously optimized in the presence of poly-**5a**.[10c] The *n*-octylthiophene-substituted chromium salen polymer poly-**5b** catalysed the same reaction and delivered 1-(2-methoxy-phenyl)-2-nitro-ethanol in 67% isolated yield and 47% ee. Surprisingly, these values are worse than those obtained through poly-**5a** catalysis, contrarily to the results arising from the homogeneous case. The heterogeneous catalyst was nevertheless reused two times showing a nice stability, at least if one considers the enantioselectivity values. Only few catalytic systems have been described in the literature that can promote successively and with a good stability the asymmetric Henry reaction. Electrogenerated poly-salen complexes described here showed thus promising results in this context.

Salen derivatives have furthermore proven their high ability to catalyze the epoxides ring-opening with a variety of nucleophiles.[27] Jacobsen *et al.* reported indeed that the ^{t}Bu-substituted chromium chloride Jacobsen complex promoted the ring opening of 7-oxa-bicyclo[4.1.0]heptane with trimethylsilylazide as nucleophile and delivered the targeted product in 80% yield and with 88% ee when the reaction was conducted in ether.[5a] The thiophene-modified derivatives **5a** and **5b** were analogously tested, but the reaction was performed at 50 °C in MTBE leading successfully to (2-azido-cyclohexyloxy)-trimethylsilane in high yield and promising enantioselectivities. Complex **5b** led again to the best values. We described earlier that the use of poly-**5a** as heterogeneous catalyst under the same conditions yielded the opened product in high yield albeit in its nearly racemic form. We assumed in this case that the arrangement of the catalytic sites in the linear polymeric

Table 4 Ring opening of 7-oxa-bicyclo[4.1.0]heptane with trimethylsilylazide as nucleophile



Entry	Cat (mol%)	t/h	Temp./°C	Yield[a] (%)	ee[b] (%)
1	**5a** (2)	24	50	70	59
2	**5b** (2)	24	50	97	74
3	Poly-**5a** (4)	24	50	85	5
4	Poly-**5b** (4)	72	20	60	34
5	(1st reuse)	72	20	47	29
6	(2nd reuse)	72	20	74	25

[a] Isolated yields, [b] ee determined by chiral HPLC analysis.

structure was probably not suitable for the necessary cooperative bimetallic pathway of this demanding reaction. We therefore tested the use of poly-**5b** possessing sterically hindering substituents on the thiophene rings that could thus have led to a different global structure compared to that of the unsubstituted analogue poly-**5a** (Table 4).

The same reaction was tested under milder conditions at room temperature and the reaction time was raised up to 72 h to obtain reasonable conversions. The azide-opened epoxide was in this case nicely obtained with up to 34% ee and the heterogeneous polymeric catalyst was reused two more times delivering again the expected product, even if the selectivity values suffered from a slight decrease.

Preparative electropolymerization afforded therefore insoluble chiral salen-based complexes that could interestingly promote asymmetric transformations. They mainly retained the activity of their homogeneous counterparts but furnished the targeted products with slightly diminished enantioselectivities. The modification of the thiophene structure of the polymeric catalyst has been shown to have an influence on the enantioselectivity of the tested asymmetric reaction. Furthermore these catalysts were easily recovered by simple filtration and could be reused in a subsequent transformation showing their good stability.[28]

Conclusions

We have prepared by electrochemical oxidation a range of polymers starting from several structurally different chromium complexes modified by thiophene derivatives. The polymerization took place only starting from the complexes and not from the ligands, probably due to the loss of the conjugation in the salen. Under these conditions the metal center acted as an electronic bridge rendering the polymerization feasible. Many modifications were made onto the structure of ligand and all the corresponding chromium complexes were polymerized efficiently. The electrochemical analyses revealed particularly stable polymers with redox responses in agreement with the electronic effects of the introduced substituents. SEM analysis enabled to appreciate the evolution of the material deposited at the electrode surface during the electropolymerization by cyclic voltammetry. These SEM analyses suggested the importance of the electropolymerization conditions especially to obtain efficient porous materials for heterogeneous asymmetric catalysis. The application of several polymers (poly-**5a**, poly-**5b** and poly-**5e**) in various enantioselective transformations demonstrated the particular stability of these new chiral polymers with a potential application in very original procedures *i.e.* multisubstrates or multireactions heterogeneous asymmetric catalysis. Finally, this work may open important perspectives for new enantioselective catalytic processes by preparing modified surfaces by electrooxidation, to investigate supported- or fixed bed catalysis.

Experimental section

Chemicals, instrumentation and analysis

All reactions were conducted under an argon atmosphere in oven-dried glassware with magnetic stirring. Solvents were distilled before use: THF from sodium metal/benzophenone, CH_3CN and CH_2Cl_2 from calcium hydride. 3-*tert*-Butyl-5-bromo-2-hydroxy-benzaldehyde was synthesized according to ref. 4. ^1H NMR and ^{13}C NMR spectra were recorded on either a Bruker AM 360 (360 MHz), AM 300 (300 MHz) or AM 250 (250 MHz) instrument with samples dissolved in $CDCl_3$ and data are reported in ppm with the solvent signal as reference (7.27 ppm for ^1H NMR and 77.0 ppm for ^{13}C NMR). Optical rotations were measured in solution in 10 cm cells at the sodium D line using a PERKIN ELMER 241 polarimeter. IR spectra were recorded as KBr disks using a PERKIN-ELMER spectrometer. Mass spectra were recorded on a micrOTOF-q Brucker Daltonics spectrometer. Elemental analyses were performed by the Microanalytical laboratory of the Institut de Chimie des Substances Naturelles, Gif sur Yvette. Electrochemical measurements were performed using a EG&G Princeton Applied Research (model 362) scanning potentiostat equipped with an IFELEC (IF 2502) recorder, in an undivided three electrode cell containing a Pt working electrode, a Pt counter electrode and a saturated calomel electrode (SCE) as reference. The solutions were degassed by argon bubbling prior to electropolymerization. The cell was stored in a dry atmosphere and flushed with argon before the electrochemical experiments. Energy Dispersive Spectroscopy (EDS) was performed on a Field Emission Gun Scanning Electron Microscope (FEG-SEM) Zeiss Supra 55 VP. The EDS is a SAMx IDFix analysis package using a new Silicon Drift detector (SDD) working at 15 kV.

Thiophene–salen chromium complex **5a** was synthesized according to ref. 4. **5b**, **5d**, **5f** and **5g** were synthesized as previously reported.[10a] The synthesis of complex **5c** was also previously reported.[10c]

Synthesis and procedures

Synthesis of 3-*tert*-butyl-2-hydroxy-5-(5-(thiophene-2-yl)thiophene-2-yl)benzaldehyde (3e). A Schlenk tube was charged with 3-*tert*-butyl-5-bromo-2-hydroxybenzaldehyde (416 mg, 1.62 mmol), 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene (945.7 mg, 3.24 mmol), $Pd(PPh_3)_4$ (280 mg, 0.24 mmol) and Na_2CO_3 (257 mg, 2.43 mmol) and was maintained under argon by successive vacuum–argon cycles (3 h). Thoroughly degassed DME (3 mL) and degassed water (1 mL) were introduced with a cannula in the Schlenk. The mixture was heated at 100 °C for 24 h. Water (20 mL) was added and the aqueous layer was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$

and the solvents were removed under reduced pressure. The residue was purified by flash chromatography on silica gel (heptane/diethylether 98/2) to afford 3-*tert*-butyl-2-hydroxy-5-(5-(thiophene-2-yl)thiophene-2-yl)benzaldehyde **3e** (537 mg, quantitative yield) as a yellow solid.

^{1}H NMR (360 MHz, CDCl$_3$, δ): 11.87 (s, 1H, OH), 9.91 (s, 1H, H$_9$), 7.77 (s, 1H, H$_6$ ou H$_4$), 7.58 (s, 1H, CH), 7.26–7.21 (m, 2H, CH), 7.15 (s, 2H, H$_6$ ou H$_4$), 7.07–7.05 (m, 1H, CH), 1.52 (s, 9H, H$_8$); ^{13}C NMR (90 MHz, CDCl$_3$, δ): 197.0 (C$_9$), 160.7 (C$_2$), 141.9 (Cq), 139.1 (Cq), 137.2 (Cq), 136.3 (Cq), 131.6 (CH), 128.5 (CH), 127.9 (CH), 125.6 (Cq), 124.5 (CH), 124.4 (CH), 123.6 (CH), 123.1 (CH), 120.6 (Cq), 35.0 (C$_7$), 29.1 (C$_8$); EIMS (*m*/*z* (%)): 342 (100) [M$^+$], 327 (26) [M$^+$–CH$_3$], 299 (12), 149 (17); HRMS (ESI, *m*/*z* (%)):[M$^+$–H] calcd for C$_{19}$H$_{17}$O$_2$S$_2$ (M–H): 341.0670, found 341.0673; mp: 97–99 °C.

Synthesis of (*S*,*S*)-(*N*,*N*′-bis(3-*tert*-butylsalicylidene-5-(thiophene-2-yl))-cyclohexane-1,2-diamine (4e). This product was obtained using 3-*tert*-butyl-2-hydroxy-5-(5-(thiophene-2-yl)-thiophene-2-yl)benzaldehyde **3e** and (*S*,*S*)-cyclohexane-1,2-diamine. The diamine (0.52 eq.) was added to a solution of the targeted aldehyde in ethanol (0.07 M) with continuous stirring, and the mixture was heated at 60 °C for 5 h. The reaction was cooled to room temperature. The solvents were removed under reduced pressure and the residue was purified by flash chromatography on silica gel (heptane/diethylether 9/1) to afford (*S*,*S*)-(*N*,*N*′-bis(3-*tert*-butylsalicylidene-5-(thiophene-2-yl))-cyclohexane-1,2-diamine **4e** (62%) as a yellow solid.

^{1}H NMR (300 MHz, CDCl$_3$, δ) 14.06 (bs, 2H, OH), 8.34 (s, 2H, H$_4$), 7.47 (d, J = 1.9 Hz, 2H), 7.20 (dd, J = 1.1 Hz, 5.3 Hz, 2H), 7.15 (dd, J = 1.1 Hz, 3.6 Hz, 2H), 7.09, 7.08, 7.01 (dd, J = 3.8 Hz, 5.3 Hz, 2H), 3.42–3.38 (m, 2H, H$_1$), 2.05–1.65 (m, 8H, H$_2$ and H$_3$), 1.47 (s, 18H, H$_{8'}$); ^{13}C NMR (62.5 MHz, CDCl$_3$, δ) 165.4 (C$_4$), 160.3 (C$_{2'}$), 143.3 (Cq), 137.9 (Cq), 137.7 (Cq), 135.3 (Cq), 127.8 (CH), 127.2 (CH), 126.8 (CH), 124.4 (CH), 124.1 (Cq), 123.9 (CH), 123.2 (CH), 122.3 (CH), 118.5 (Cq), 72.2 (C$_1$), 34.9 (C$_{7'}$), 32.9 (C$_2$), 29.4 (C$_{8'}$), 14.1 (C$_3$); HRMS (ESI *m*/*z* (%)): [M + H]$^+$ calcd for C$_{44}$H$_{47}$O$_2$N$_2$S$_4$: 763.2520, found: 763.2524; IR (KBr): ν 2931 (w), 2860 (w), 1628 (w), 1474 (s), 1436 (vs), 1271 (vs), 836 (s), 794 (w), 690 (w); mp: 124°C. $[\alpha]_D^{20}$ −28.1 (*c* 1 in CHCl$_3$). UV-vis (CH$_3$CN): $\lambda_{max}(\varepsilon)$ 271 (5000), 351 (12 000).

Preparation of chromium–thiophene–salen complex (5e)

The chiral ligand in dry, degassed THF (0.08 M) was added to a solution of anhydrous Cr(II)Cl$_2$ (1.15 eq.) in dry, degassed THF (0.04 M). The resulting brown solution was stirred for 2 h under argon and then exposed to air. Stirring was continued overnight to give a dark brown solution. It was diluted with CH$_2$Cl$_2$ and washed with sat. NH$_4$Cl and brine. The organic layer was dried over MgSO$_4$ and solvents were removed under reduced pressure to afford the expected complex as a brown solid in 92% yield.

IR (KBr): ν 2945, 2857, 2361, 2347, 1621, 1538, 1432, 1411, 1385, 1345, 1323, 1257, 1163, 795, 691; anal. calc. for C$_{44}$H$_{44}$O$_2$N$_2$S$_4$ClCr + THF: C 62.62; H 5.69; N 3.04; S 13.93 found C 63.19; H 5.91; N 2.75; S 14.94%. UV-vis (CH$_3$CN): $\lambda_{max}(\varepsilon)$ 271 (5000), 369 (12 000).

Electropolymerization of the chromium–thiophene–salen complex (poly-5e). Complex **5e** (340 mg, 0.5 mmol) was placed in an undivided electrochemical cell fitted with a platinum cathode and a platinum grid (2.25 cm^2) as anode. The anode potential was monitored *versus* a saturated calomel electrode (SCE) throughout the electrolysis. *n*Bu$_4$NBF$_4$ (0.03 M in 15 mL CH$_2$Cl$_2$) was used as a supporting electrolyte and the electrolysis was performed at a constant current of 50 mA during 2 h. The platinum grid was recovered with the polymerized complex. Some insoluble material also settled at the bottom of the cell. The deposited polymer was used as an insoluble catalyst after removal from the support and several washings with acetonitrile and dichloromethane. This residue was dried under vacuum and used without further purification for the asymmetric catalysis. Poly-**5e** was isolated in 59% yield.

Representative procedure for hetero-Diels–Alder reactions

Homogeneous conditions. A Schlenk tube was charged with catalyst **5a**, **5b** or **5e** (2 mol%) and thoroughly maintained under argon by three successive vacuum–argon cycles. MTBE (200 μL), the aldehyde (1 mmol) and Danishefsky's diene (234 μL, 1.2 mmol) were then introduced through a syringe. The resulting solution was stirred at room temperature for the specified amount of time. It was then diluted with CH$_2$Cl$_2$ (2 mL), treated with a drop of trifluoroacetic acid and further stirred for another 30 min. The solvents were removed under reduced pressure and the residue was purified by flash chromatography on silica gel to determine the yield of the reaction and the enantiomeric excess of the product.

Heterogeneous conditions. A Schlenk tube was charged with catalyst poly-**5a**, poly-**5b** or poly-**5e** (4 mol%) and maintained under argon by three successive vacuum–argon cycles. MTBE (400 μL), the aldehyde (1 mmol) and Danishefsky's diene (1.2 mmol) were then introduced through a syringe. The resulting suspension was stirred at room temperature for the specified amount of time. It was then filtered with a filtering syringe and the residue was washed with MTBE. Then the solvents of the combined filtrates were partially removed under reduced pressure. The residue was diluted with CH$_2$Cl$_2$ (2 mL), treated with a drop of trifluoroacetic acid and stirred for another 30 min. The solvents were then removed under reduced pressure and the residue was purified by flash chromatography on silica gel to determine the yield of the reaction and the enantiomeric excess of the product. In the Schlenk tube, the polymer catalyst was dried under vacuum for its reuse and new substrates and solvents were added.

Representative procedure for Henry reactions

Homogeneous conditions. A Schlenk tube was charged with the catalyst **5a** or **5b** (2 mol%) and maintained under an argon atmosphere by three successive vacuum–argon cycles. DCM (4 mL), the aldehyde (1 mmol), and nitromethane (2 mL, 37.5 mmol) were introduced. In the case of reactions performed at low temperature, the mixture was first cooled to the desired temperature, followed by the addition of a solution of diisopropylethylamine (1 or 0.5 equiv.) in DCM (4 mL). The resulting solution was stirred for the specified amount of time. The solvents were then removed under reduced pressure, and the residue was purified by flash chromatography on silica gel for the determination of the yield of the reaction and the enantiomeric excess of the product.

Heterogeneous conditions. A Schlenk tube was charged with the catalyst poly-**5a** or poly-**5b** (4 mol%), and the procedure is analogous to that described above. After the resulting suspension was stirred for the specified amount of time, it was then filtered with a filtering syringe and the precipitate was thoroughly washed twice with MTBE. The solvents of the combined filtrates were removed under reduced pressure, and the residue was purified by flash chromatography on silica gel for the determination of the yield of the reaction and the enantiomeric excess of the product. In the Schlenk tube, the powdered catalyst was washed with water and MTBE then dried under vacuum and new substrates and solvents were added for its recycling.

Representative procedure for ring opening epoxides with trimethylsilylazide

Homogeneous conditions. A Schlenk tube was charged with the catalyst **5a** or **5b** (2 mol%) and thoroughly maintained under an argon atmosphere by three successive vacuum–argon cycles. MTBE (330 µL) and cyclohexene oxide (1 mmol) were introduced with a syringe. The resulting solution was stirred at room temperature and then trimethylsilylazide (197 µL, 1.5 mmol) was introduced. The mixture was stirred for 72 h. The solvents were removed under reduced pressure. The residue was purified by Celite filtration for the determination of the yield of the reaction and the enantiomeric excess of the product.

Heterogeneous conditions. A Schlenk tube was charged with poly-**5a** or poly-**5b** (4 mol%) and placed under an argon atmosphere by three successive vacuum–argon cycles. MTBE (330 mL) and the epoxide (1 mmol) were introduced by using a syringe. The resulting solution was stirred at a given temperature and then trimethylsilylazide (197 mL, 1.5 mmol) was introduced. The mixture was stirred for the specified amount of time and then filtered with a filtering syringe. The solution was purified by filtration through Celite and the solvents were removed under reduced pressure. The residue was purified by flash chromatography on silica gel to give the product, which was used to determine the yield of the reaction and the enantiomeric excess. In the Schlenk tube, the catalyst was dried under vacuum and new substrates and solvents were added for reuse.

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28 We previously proved, in the case of poly-**5a**, that no leaching occurred during the recycling procedure (see ref. 10*a* and *b*). The insoluble polymer was indeed added to hetero Diels–Alder or Henry reaction mixtures, thoroughly stirred and subsequently removed by filtration. The recovered filtrates showed almost no catalytic activity when substrates were added, confirming thus that those transformations were promoted by the catalyst under heterogeneous conditions.