Synthesis and Electrochemical Investigations of Bis(salen) Complex Precursors Allowing the Formation of a Ladder-type Polymer

P.-H. Aubert,*,† P. Audebert,*,‡ M. Roche,† P. Capdevielle,§ M. Maumy,§ and G. Ricart‖

Laboratoire de Chimie et d'Electrochimie Moléculaire, Université de Franche-Comté, 25 030 Besançon, France, PPSM (CNRS, UMR 8531), ENS Cachan, 94 235 Cachan, France, Laboratoire de Chimie Organique (CNRS, ESA 7084), ESPCI, 10 rue Vauquelin, 75 231 Paris cedex 05, France, Laboratoire de Chimie Macromoléculaire (CNRS, UPRESA 8009), Université de Lille I, France

The synthesis and characterization of bis(salen)-type complexes are reported. Using a "template" method, bimetallic complexes as dyssymmetric ligands can easily be built, giving birth to an unprecedented class of metal Schiff-base salen complexes. Electrochemical investigations allow us to study the overoxidation process that occurs during the polymerization. Furthermore, chronoamperometry studies indicate higher kinetics of electron charge transfer as a proof of an improvement in the polymer framework.

1. Introduction

Building superstructured polymers containing complexed transition metals is raising more and more interest,[1] especially when two or more metal centers can be electrically connected via the polymer skeleton. Various applications may arise including electrode modifiers,[2−6] electrocatalysis,[7−11] sensors,[12−16] and possibly nonlinear and near-field optics.[17,18] Also the build-

ing of new magnetic materials is to be considered in the case where more than one metal is present in the structure.

More recently, several examples of superstructured polymers have been reported in the literature.[19] Among them, the case of "ladder" polymers containing redox metal centers units is especially interesting, since original properties may be expected from this type of compound. Although ladder polymers have been prepared by several groups,[19,20] only very few examples of ladder polymers containing active redox metal centers have been reported to date.[21−24]

Among polymers containing transition metal complexes, poly(metal−salens)[25−33] are of special interest,

* To whom correspondence should be addressed.
† Université de Franche-Comté.
‡ PPSM (CNRS, UMR 8531).
§ Laboratoire de Chimie Organique (CNRS, ESA 7084).
‖ Université de Lille I.
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Scheme 1. Synopsis of Strategy Used for the Synthesis of Bis(salen) Complexes[a]
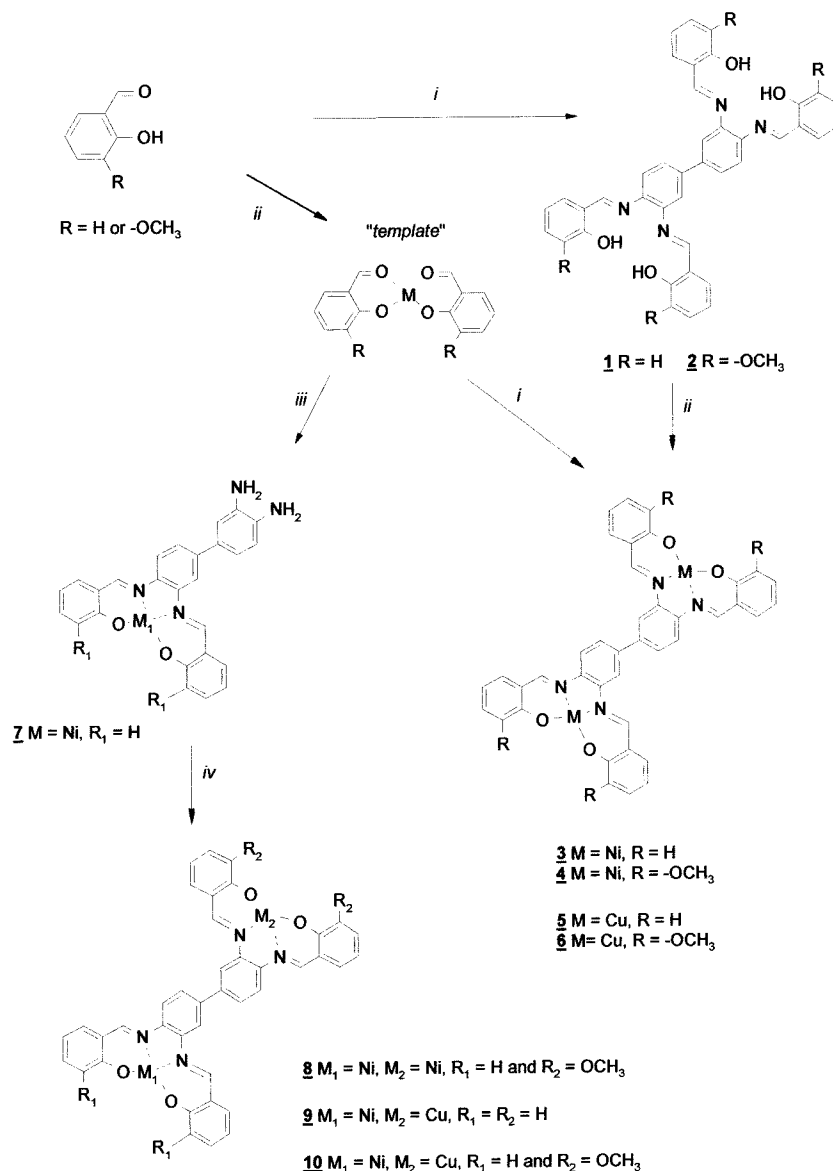
[a] *(i)* 3,3′-Diaminobenzidine, EtOH, reflux, 36 h. *(ii)* KHCO$_3$ in EtOH/H$_2$O and then Ni(ClO$_4$)$_2$ or Cu(ClO$_4$)$_2$ in EtOH. *(iii)* 1 equiv of 3,3′-diaminobenzidine, EtOH, reflux. *(iv)* 1 equiv of template complex, EtOH, reflux.

given their ease of preparation by electropolymerization as well as their conducting character; in addition, in some cases they exhibit electrocatalytic properties.[34−36] Connecting two salen units to form a ladder precursor represents therefore an attractive challenge, especially if two metals can be introduced at the same level of the ladder. This can be realized if the diamine precursor bridge is replaced by a tetramine one. We describe here the preparation and the electrochemical behaviors of a new series of bimetallic complexes related to the salen family, starting from biphenylene-3,3′,4,4′-tetramine. Each complex is built according to Scheme 2, the bridged biphenylene entities making the connection between the two salen units. In this way, it should be possible to get electronic interactions between the two metals

through the bridging units. Furthermore, during the electrochemical polymerization, ladder-type chains should be formed because of the proximity of the second reactive positions and given the rigidity of the spacer link. The electrochemical investigations on the synthesis of the polymers bring indications that ladders are indeed built through the electrochemical electrooxidation in a definite potential range.

In addition, the particular synthetic strategy followed allows us to build step by step each complex, therefore allowing the specific introduction of either the same metal or, on the other hand, two different redox metal centers in the same complex. Similarly, each side of the complex may contain identically or differently substituted bis-salicylaldehyde moieties (see Scheme 1).
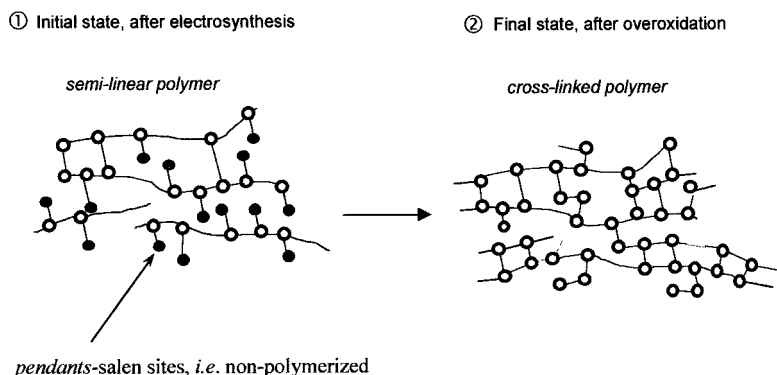
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2. Experimental Section

2.1. Reagents and Apparatus. 3,3′-Diaminobenzidine (Fluka, 99%), salicylaldehyde (Aldrich, 99%), and *o*-vanillin

Scheme 2

① Initial state, after electrosynthesis   ② Final state, after overoxidation

semi-linear polymer   *cross-linked polymer*

pendants-salen sites, *i.e.* non-polymerized

(Aldrich, 99%) were used for synthesis without any purification. Concerning electrochemical synthesis and analysis, acetonitrile (Aldrich, spectroscopic grade) was distilled over P_4O_{10} and stored on molecular sieves. Tetraethylammonium perchlorate[37] was used as supporting electrolyte after recrystallization in a CH_3CN/Et_2O (50/50) mixture and stored under inert atmosphere.

All NMR spectra were recorded with an AC 300 MHz Brucker instrument. FTIR spectra were realized in the 400–4000 cm^{-1} range on a Brucker Electrospin IFS-45. Mass spectra were measured on a Finningan spectrometer using a MALDI-TOF procedure. The electrochemical apparatus was a homemade potentiostat, equipped with an ohmic drop compensation system, fitted with a PAR 173 Universal Programmer, a Nicolet digital oscilloscope, and a Sefram 164 plotter.

2.2. Synthesis of the Ligands N,N,N',N'''-**Tetrakis-(salicylidene)-3,3',4,4'-biphenylene Tetramine (1) and** N,N,N',N'''-**Tetrakis(o-vanillidene)-3,3',4,4'-biphenylenetetramine (2).** To a solution of 1.14 g of salicyladehyde or 1.40 g of o-vaniline (9.0×10^{-3} mol) are slowly added 0.50 g of diaminobenzidine in solution in ethanol at 60 °C. The mixture is then refluxed for 36 h. After 30 min, a light brown precipitate forms, which turns dark brown after several hours. The solution is filtered and the precipitate washed two times with ethanol and diethyle oxide, respectively. Yields: 90–95%. Elementary analysis for **1** ($C_{40}H_{30}N_4O_4$). Calc %: C, 76.18; H, 4.79; N, 8.88. Found %: C, 75.95; H, 4.66; N, 9.21. ^{1}H NMR (DMSO-d_6, TMS): $\delta = 6.80$–7.95, m; $\delta = 8.95$, s; $\delta = 12.85$ ppm, s. FTIR (ν, cm^{-1}): 3195, 2845, 1590, 835. Elementary analysis for **2** ($C_{44}H_{38}N_4O_8$). Calc %: C, 70.39; H, 5.10; N, 7.46. Found %: C, 70.21; H, 5.05; N, 7.60. ^{1}H NMR (DMSO-d_6, TMS): $\delta = 2.25$ ppm, s; $\delta = 6.85$–8.15, m; $\delta = 9.05$, s; $\delta = 13.25$ ppm, s. FTIR (ν, cm^{-1}): 3190, 2905, 2835, 1592, 1070, 832.

2.3. Synthesis of the Monomers N,N,N',N'''-**Tetrakis(salicylidene)-3,3',4,4'-biphenylene Tetraimino Dinickel(II) (3) and** N,N,N',N'''-**Tetrakis(o-vanillidene)-3,3',4,4'-biphenylene Tetra imino Dinickel(II) (4) and the Dicopper(II) Analogues 5 and 6.** The syntheses are performed following the "template" method: Ni^{II} (or Cu^{II}) bissalicylate (or bis-o-vanillate) is synthesized as described in the literature.[38] The conditions of synthesis are similar to the procedure described in section 2.1. The reaction is held at reflux of ethanol for 3 days, using a stoichiometric amount of reactants. Yields: 80–95%. Elementary analysis for **3** ($C_{40}H_{26}N_4Ni_2O_4$). Calc %: C, 64.57; H, 3.52; N, 7.53; Ni, 15.78. Found %: C, 64.76; H, 3.46; N, 7.21; Ni, 15.90. FTIR (ν, cm^{-1}): 2844, 1640, 827. Elementary analysis for **4** ($C_{44}H_{34}N_4Ni_2O_8$). Calc %: C, 61.15; H, 3.97; N, 6.48; Ni, 13.59. Found %: C, 61.70; H, 3.76; N, 6.82; Ni, 13.23. FTIR (ν cm^{-1}): 2907, 2835, 1637, 1082, 840. Elementary analysis for **5** ($C_{40}H_{26}Cu_2N_4O_4$). Calc %: C, 63.74; H, 3.84; N, 7.43; Cu, 16.86. Found %: C, 62.22;

H, 3.58; N, 7.92; Cu, 16.94. FTIR (ν, cm^{-1}): 2840, 1672, 832. Elementary analysis for **6** ($C_{44}H_{34}Cu_2N_4O_8$). Calc %: C, 60.48; H, 3.92; N, 6.41; Cu, 14.54. Found %: C, 59.40; H, 3.50; N, 6.62; Cu, 15.05. FTIR (ν cm^{-1}) 2910, 2824, 1667, 1087, 838.

2.4. Synthesis of the Monomer Complexes 7–10. The following complexes are prepared in two steps. The monoadduct **7** is first prepared according to the following process: to a solution of 0.50 g of 3,3'-diaminobenzidine (2.4×10^{-3} mol) is added drop by drop 0.70 g (2.4×10^{-3}mol) of nickel(II) bis-(salicylate), and the mixture is refluxed for 10h. The monometalated compound is then filtered, washed, and dried in an oven (50 °C), before being engaged in the second step without further purification.

The monometalated compound prepared as above (0.20 g, 4.30×10^{-3} mol) is dissolved in absolute ethanol and brought to reflux; then 1 equiv of Ni^{II} bis(o-vanillate), Cu^{II} bis-(salicylate), or Cu^{II} bis(o-vanillate) is progressively added and left for 48 h at reflux of ethanol. The reaction mixture is extracted as above and the filtrate washed with ether.

Elementary analysis for **7** ($C_{26}H_{20}N_4NiO_2$). Calc %: C, 65.17; H, 4.21; N, 11.69; Ni, 12.25. Found %: C, 64.85; H, 4.15; N, 11.78; Ni, 12.70. FTIR (ν, cm^{-1}) 3382, 3369, 3128, 2842, 1635, 830. Elementary analysis for **8** ($C_{42}H_{30}N_4Ni_2O_6$). Calc %: C, 62.73; H, 3.76; N, 7.48; Ni, 14.60. Found %: C, 62.34; H, 3.45; N, 7.52; Ni, 14.75. FTIR (ν cm^{-1}): 2900, 2832, 1685, 841. Mass spectrometry: $M^* = 802.34$ and 804.25. Elementary analysis for **9** ($C_{40}H_{26}CuN_4NiO_4$). Calc %: C, 64.15; H, 3.50; Cu, 8.48; N, 7.48; Ni, 7.84. Found %: C, 63.74; H, 3.26; Cu, 8.27; N, 7.72; Ni, 7.90. FTIR (ν cm^{-1}): 2910, 1685, 1660, 860. Mass spectrometry: $M^* = 747.31$ and 748.94. Elementary analysis for **10** ($C_{42}H_{30}CuN_4NiO_6$). Calc %: C, 62.36; H, 3.74; Cu, 7.86; N, 6.93; Ni, 7.26. Found %: C, 61.95; H, 3.45; Cu, 8.08; N, 7.06; Ni, 7.46. FTIR (ν cm^{-1}): 2910, 2840, 1690–1672, 835. Mass spectrometry: $M^* = 807.33$ and 808.96.

2.5. Electrochemical Setup. Analytical experiments were performed in a three-compartment cell fitted with a saturated calomel reference, a glassy carbon electrode (diameter 1.2 mm), or a platinum electrode (diameter 1.0 mm) and a 1 cm^2 platinum counter electrode. The concentration of the monomeric substrates was usually saturation in CH_3CN, due to the low solubility of the complexes (concentration is estimated to be approximately 5×10^{-4} to 10^{-3} M). The concentration of electrolyte was 0.1 M. The cells were stored in dry atmosphere and flushed with argon throughout the electrochemical synthesis or experiments. For film studies, two cells were used in parallel, the films being prepared in the first cell containing the monomer solution and then being transferred to the second cell containing monomer-free electrolyte for further investigations (cyclic voltammetry, doping charge determination, chronoamperometry). Cross-linking experiments have to be more detailed: the films were prepared potentiostatically in the cell containing the monomers. Then, polymers were rinsed and dedoped in the free-monomer solution to determine the redox charge of the initial polymer. The polymer was finally overoxidized (total charge was measured taking account of the initial redox charge) and the complete cross-linked polymer

(37) Warning: perchlorates are hazardous and may explode spontaneously.

(38) Purcel, K. F.; Kutz, J. C. *Inorganic Chemistry;* W. B. Saunders Company: Philadelphia, PA, 1977; p 784.

was then reduced to finally determine the redox charge of the fully cross-linked polymer. Experiments were repeated at least three times, but the charge values did not differ by more than 5% usually. The electrodes were carefully cleaned between each experiment. The films were prepared potentiostatically at various potentials (see Discussion). Due to the morphology change of the polymer when it is overoxidized, the determination of the apparent diffusion coefficient is more complicated: thus, experiments have to be realized once and repeated (usually 3−5 times) in order to get reproducible measurements (see discussion in cross-linking section).

When precise potential determination was desired, ferrocene was used as an internal standard, and its potential was assumed to be +0.405 V versus SCE; in such a case, the ferrocene potential was checked after each set of experiments, but the values in the tables are given against SCE.

3. Results and Discussion

3.1. Synthesis of the Monomers. The preparation of polyfunctional compounds is always delicate, since when different substituents have to be set into different equally reactive sites of a molecule, the number of isomers grows as a power law. In the case of our complexes, substituting four salicylates and/or *o*-vanillates on one diphenylene tetramine results in 12 possible isomers according to the nature and the position of the aldehydes on the tetramine. This difficulty has been overcome using the template method, which allows the successive introduction of two aldehyde entities at the same time on one edge of the tetramine, while leaving the other unreacted (see Scheme 1, *iii* and *iv*). The selectivity of the monoaddition is certainly due to the decrease of the nucleophilicity of the amino groups on the second benzenic ring, induced by the imine formation on the first one. In addition, since the solubility of all complexes decreases also with the substitution ratio, the weak proportion of monosubstituted complex in solution also helps to slow the second substitution kinetics and increases the selectivity of the monoaddition.

This possibility of forming successively two salens on biphenylene tetramine is especially interesting regarding the preparation of bimetallic compounds. We limited our investigations to the copper and nickel compounds, since they were recognized to give the polymers displaying the most interesting characteristics in the past. Unfortunately, the very low solubility of dicopper(II) and most bimetallic copper(II)/nickel(II) compounds (below 10^{-5} mol/L in all classical solvents for electrochemistry) impeded their electrochemical polymerization. Therefore, we describe only the polymers issuing from the nickel complexes **3**, **4**, and **8**.

3.2. Electrochemical Studies. *3.2.1. Behavior of Complexes.* All complexes were submitted to cyclic voltammetry in the oxidation potential range prior to polymer synthesis; on the basis of the comparison of peak potentials with a ferrocene standard and classical salen behaviors, they exhibit an irreversible two-electron oxidation wave whatever the scan rate (Figure 1) which turns up in polymer formation on the electrodes, as generally observed in the case of salens. However, this shows that, at the time scale of the cyclic voltammetry, there is only one moiety of the molecule which is oxidized at the peak potential. The polymerization is assumed to be the same fast RC−RC
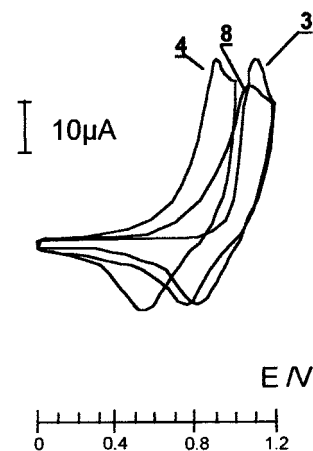

Figure 1. CVs of complexes **3**, **4,** and **8** realized on a 1 mm Pt electrode: scan rate, $v = 100$ mV s^{-1}; electrolyte, CH$_3$CN, 0.1 M TEAP.
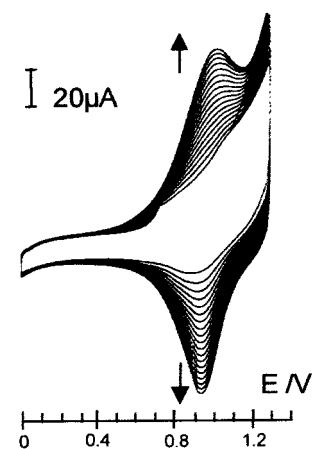

Figure 2. Accumulative synthesis of poly-**3** coated on a Pt electrode: scan rate, $v = 100$ mV s^{-1}; electrolyte, CH$_3$CN, 0.1 M TEAP; total oxidation charge, $Q_{ox} = 1$ mC. The arrow indicates the increase in the successive CVs.

Table 1. Electrochemical Data for Monomers 3, 4, and 8 and Their Related Polymers in Comparison with Their Classical Parent Salen[a]

complex	E_p(monomer) vs SCE	$E°$(polymer) vs SCE	doping level δ	D[b]/ cm^2 s^{-1}
3	1.125	1.050	0.87	3.0×10^{-7}
4	0.870	0.650	0.93	2.1×10^{-6}
8	1.055	0.845	0.85	8.0×10^{-7}
Ni-salphen	1.090	0.950	0.81	1.2×10^{-9}
Ni-salphen (OCH$_3$)$_2$	0.910	0.720	0.89	5.7×10^{-9}

[a] Scan rate, $v = 100$ mV·s^{-1} in CH$_3$CN, 0.1 M TEAP. [b] Experiments under 1.10 V.

mechanism as in the case of classical salens, since bis-salen complexes should behave as two independent salens, due to the weak conjugation through the bridge.[27] Electrochemical data are listed in Table 1, in which values can be compared to those of a parent "classical" salen, *N,N′*-bis(salicylidene)phenylenediamino nickel(II), Ni^{II}-salphen, and *N,N′*-bis(vanillidene)-phenylenediamino nickel(II), Ni^{II}-salphen(OCH$_3$)$_2$. The synthesis of the polymer films may occur either at a controlled potential or upon repetitive cycling, this latter one giving the proof of the conducting character for these polymers; cf. Figure 2. Similarly, the oxidation
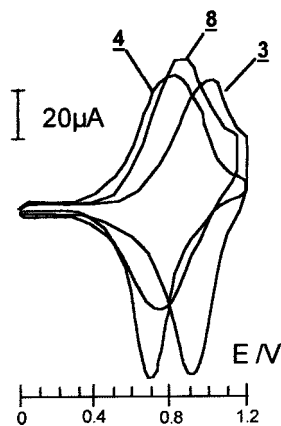
Figure 3. CVs of the films poly-**3**, poly-**4**, and poly-**8**. Experimental conditions: CH₃CN, 0.1 M TEAP, $v = 100$ mV s⁻¹ on a Pt electrode and at the polymerization charge $Q_p = 500\ \mu$C.

Figure 4. CVs realized on poly-**4** films in CH₃CN, 0.1 M TEAP prepared at different potentials E_{imp}: polymerization charge, $Q_p = 500\ \mu$C; $v = 150$ mV s⁻¹. CV a corresponds to the stable electrochemical response of polymer. Peaks b represent oxidation of nonpolymerized species.

begins at relatively low potentials (around 0.8 V), especially in the case of the *methoxy*-substituted polymers. The potential domain where good polymerization yields are obtained is also much larger than that in the case of classical salens or conducting polymers in general (e.g. polypyrrole) These bis(salens) complexes have the largest polymerizability domain observed in the case of conducting polymers. Moreover, as a related feature, the films appear to be rather resistant to high potentials, even more than in the case of the previously studied binuclear salens-type complexes, synthesized from Robson's and Mazureck's ligands.[39]

3.2.2. Behavior of the Polymers. General Features. All polymers issued from compounds **3**, **4**, and **8** exhibit a behavior generally similar to that of the poly(salens) upon electrochemical oxidation (Figure 3). However, contrariwise to the case of simple salens, there is a clear difference between the polymers according to the synthesis potential, whatever the monomer. When a given monomer is oxidized at relatively low potentials, and then cycled into a clean electrolyte, the first scans are very different from the stabilized cyclic voltammograms (CVs) (usually obtained after five to seven cycles. The stability upon prolonged cycling of these polymers is comparable to the case of simple salens.[10,29] Besides, the anodic charges recorded for these scans are higher than the cathodic ones. Thus, this cannot be attributed to the memory effect as in the case of some conducting polymers (polypyrrole, polyanilines), where mainly distortion of the voltammogram is observed, with no or little variation of the exchanged charge. (It should be noted too that no memory effect has ever been mentioned in the literature in the case of polysalens.) All this indicates that overoxidation of the films continues to take place during several further scans. This behavior is clearly illustrated in Figure 4, which displays the CVs recorded from a poly-**4** film as a function of the imposed potential E_{imp} used for the electrolyses at a fixed controlled potential (chronoamperometric mode). The most straightforward explanation for this particular behavior is therefore that low-potential films are cross-linked during the following scans: the pendant-
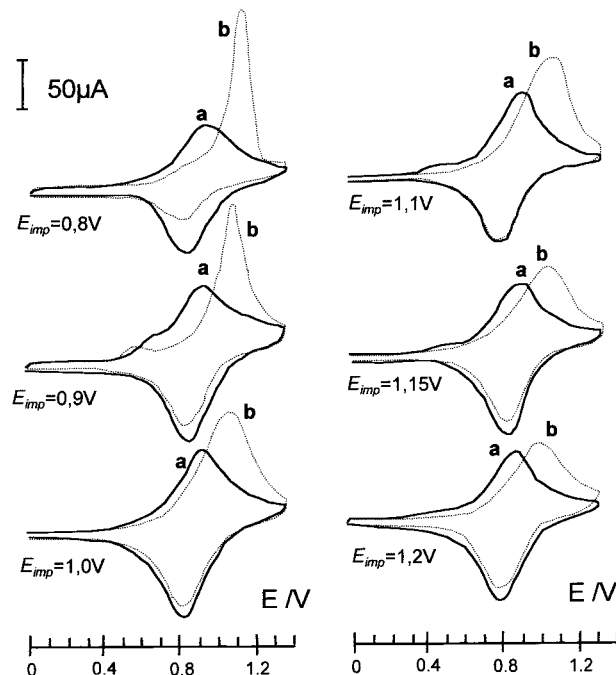
salen moieties are chemically bonded to the polymer matrix during the overoxidation process as shown in Scheme 2.

In addition, this behavior ceases when the synthesis potential of the films encompasses a certain value which depends on the monomer and which lies usually above 1.10−1.20 V. This overoxidation process decreases monotonically when the electrolysis potential increases, which is a further proof that the polymers still contain many reactive sites when they are prepared at relatively low potentials. It is also clear the polymers prepared at very low potentials (i.e. around 0.80 V) certainly contain a non-neglectable proportion of short chain oligomers (even maybe insoluble dimers that stick to the electrode, although higher oligomers are more likely). Their overoxidation cannot be considered as occurring the same way as the one of pendant-salen moieties. This will be discussed in the next section. A similar feature has been described with bifunctional pyrrole and pyrrole−thiophene monomers.[40,41]

Cross-linking of the Films and Ladder Polymer Formation. It is possible to investigate more quantitatively the reticulation process, by determining the overoxidation charge in relation with the synthetic charge and the evolution of the doping level through the reticulation process.

According to the classical analysis in the case of conducting polymers,[42] it is admitted that the doping

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level δ is related to the synthesis charge Q_S and the redox charge Q_R through the equation,

$$\delta = \frac{2Q_R}{Q_S - Q_R} \tag{A1}$$

provided that the synthesis yield is 100%, which is generally the case with poly(salens), and defining the doping level as the relative charge stored per monomer unit inside the polymer.

However, in the case of bifunctional monomers, those definitions need some refining. In the case where cross-linking (due to overoxidation) of the polymer takes place, an additional charge Q_{CR} necessary to the electrochemical cross-linking of the film has to be considered. In such a case, the charge used to prepare the polymer becomes a variable depending on the overoxidation advancement which occurs simultaneously with the electropolymerization.

We will call Q_S the charge used to prepare the polymer, Q_{CR} the charge necessary to overoxidize the polymer, and Q_T the sum $Q_S + Q_{CR}$, which is the total charge necessary to prepare the most completely cross-linked polymer. It should be kept in mind that all these values integrate both the synthetic charge (used for the coupling reactions) and the doping charge (used to achieve the doping of the polymer chains). Also, for an "ideal" polymerization, the less cross-linked polymer should display $Q_T = 2Q_S$ while, on the other hand, the fully cross-linked one should display $Q_T = Q_S$. In the experiments we describe and for the sake of clarity, we chose to keep Q_S controlled as a constant value (0.5 mC) and determine Q_T and Q_{CR} in relation with the imposed potential.

Similarly, we can measure the redox charges exchanged upon the dedoping process of the polymer (to avoid the cross-linking process by oxidation), in relation with its initial or final state, that is just after its synthesis at a given potential or on the contrary after full overoxidation. Admitting that the non-cross-linked units do not participate in the doping process of the polymer, we can also extract a doping level δ which depends on the state of the polymer. Let us call Λ_I the initial doping charge measured just after synthesis and Λ_F the final doping charge, measured after full overoxidation (cross-linking) of the polymer. We can relate all these charges through the definition of two doping levels, δ_I and δ_F, which represent respectively the doping levels just after synthesis and after full overoxidation:

$$\delta_I = \frac{2\Lambda_I}{Q_S - \Lambda_I} \quad \text{and} \quad \delta_F = \frac{2\Lambda_F}{Q_T - \Lambda_F} \tag{A2}$$

All the quantities Q_T, Q_{CR}, Λ_I, and Λ_F are easily determinable by coulometry, and Table 2 presents all these values, and both δ_I and δ_F, for a constant value of Q_S of 0.5 mC (about 7×10^{-2} C/cm^2) for a poly-**3** film.

On the other hand, a relevant parameter to estimate the cross-linking degree inside such polymers as ours is the following parameter Γ, defined as

$$\Gamma = \frac{(N_T - N_I)}{N_I} \tag{A3}$$

Table 2. Coulometric and Doping Level Measures Realized on Poly-3 Films Obtained at Controlled Potential E_{imp}

E_{imp}/V	Q_S	Λ_I	δ_I	Q_T	Λ_F	δ_F	Q_{CR}
0.800	500	30	0.13	1350	260	0.48	850
0.825	500	35	0.15	1310	260	0.50	810
0.850	500	40	0.17	1270	250	0.49	770
0.875	500	55	0.25	1200	270	0.58	700
0.900	500	60	0.27	1140	280	0.65	640
0.925	500	70	0.33	1070	280	0.71	570
0.950	500	90	0.44	1040	315	0.87	540
0.975	500	150	0.86	1095	340	0.90	595
1.000	500	155	0.90	1070	330	0.89	570
1.025	500	150	0.86	1075	335	0.91	575
1.050	500	160	0.94	1040	320	0.89	540
1.075	500	170	1.03	1060	340	0.94	560
1.100	500	160	0.94	890	290	0.97	390
1.125	500	155	0.90	840	290	1.05	340
1.150	500	140	0.78	850	280	0.98	350
1.175	500	140	0.78	805	270	1.01	305
1.200	500	120	0.63	800	255	0.94	300
1.225	500	120	0.63	785	245	0.91	285
1.250	500	110	*a*	740	240	0.96	240
1.275	500	105	*a*	765	240	0.91	265
1.300	500	90	*a*	740	230	0.90	240
1.400	500	85	*a*	690	210	0.88	190

a At these potentials the determination of Λ_I was too uncertain and did not give reliable values.

where N_I is the number of salens initially polymerized in the film during the synthesis (at imposed potential E_{imp}) and N_T represents the total number of salen units polymerized after overoxidation. Both N_j values are functions of charges Q_j (j = S or T) and doping charges Λ_k (k = I or F):

$$N_I = \frac{Q_I}{(2 + \delta_I)F} = \frac{\Lambda_I}{\delta_I F}$$

and

$$N_F = \frac{Q_F}{(2 + \delta_F)F} = \frac{\Lambda_F}{\delta_F F}$$

where F is the Faraday constant.

In this way and according to eq A2, eq A3 becomes

$$\Gamma = \frac{\left(\dfrac{Q_T}{2 + \delta_F} - \dfrac{Q_S}{2 + \delta_I}\right)}{\dfrac{Q_S}{2 + \delta_I}} \tag{A4}$$

and

$$\Gamma = \frac{\left(\dfrac{\Lambda_F}{\delta_F} - \dfrac{\Lambda_I}{\delta_I}\right)}{\dfrac{\Lambda_I}{\delta_I}} \tag{A5}$$

So eqs A4 and A5 can be simplified as $\Gamma = (Q_T - Q_S)/Q_S$ and $\Gamma = (\Lambda_F - \Lambda_I)/\Lambda_I$, since δ_I is, as expected, very close to δ_T.[42] This equation shows that Γ can be determined either by the synthesis charges (Q_j) or by the doping charge values (Λ_j). So, in the following discussion, we will be precise for Γ, either $\Gamma^{(Q)}$ or $\Gamma^{(\Lambda)}$, owing to the fact that it has been calculated using the experimental values, either Q_j or Λ_j.
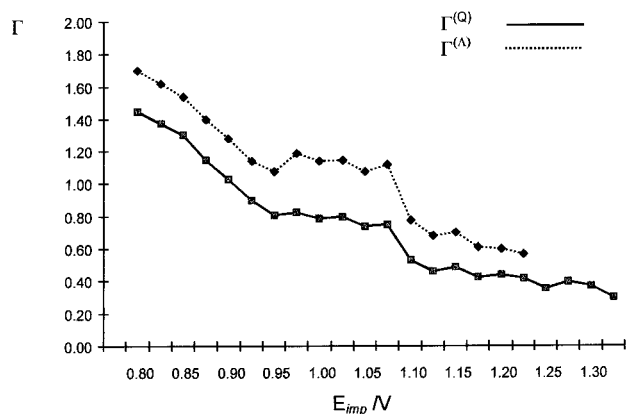
Figure 5. Plot of $\Gamma^{(Q)}$ and $\Gamma^{(\Lambda)}$ versus the imposed potential during electrosynthesis for poly-**3** (full line) and poly-**4** (dot line).

Figure 6. Plot of $\Gamma^{(Q)}$ versus the imposed potential during electrosynthesis for poly-**3** (full line), poly-**4** (dotted line), and poly-8 (dashed line).

Table 2 calls for interesting remarks: Q_T values at low potential are $>2Q_S$, as expected: this is certainly due to very short and insoluble chains (dimers, trimers, ...) that are produced (and stable) at these potentials and introduce an error on the attribution of Q_S (The equation $Q_S = (2 + \delta)FN_I$ is certainly wrong in such a case). Similar effects are also seen on δ in this region.[43] As the oxidation potential increases, these oligomers polymerize, giving birth to a more defined polymer network. Furthermore, at high potentials, Q_T is expected to be equal to Q_S because there should be no reticulation. It is also clear that the Q_{CR} quantity monotonically decreases with the increasing potential, as a proof of the production of a more and more cross-linked polymer as E_{imp} increases. Similarly, the δ_I values, initially low, which are indicative of a non-cross-linked polymer (and probably even the presence of oligomers) grow upon increasing the potential up to values close to δ_F. It should also be noticed that δ_I and δ_F values, as soon as the potential exceeds 0.9 V, are similar to the one determined for classical monofunctional salens, as could be expected.

Figure 5 illustrates both $\Gamma^{(Q)}$ and $\Gamma^{(\Lambda)}$ versus the potential for the poly-**3** film: results provided by coulometry show the same tendency of Γ variation as predicted by eqs A4 and A5. Ideally, the following trend should be observed: at low oxidative potentials (E_{imp}), the film has the lowest reticulation degree. Γ should be equal to 1 because the bis(salen) complexes should contain only one unit engaged in polymer chains. Then, the higher the polymerization potential is, the more Γ is expected to decrease because the film gets more and more cross-linked. So, for high E_{imp}, Γ should reach zero values. The evolution of Γ values is displayed in Figure 5. Two features are clearly discernible: (i) Both Γ values appear to be slightly overestimated, $\Gamma^{(\Lambda)}$ is still more than $\Gamma^{(Q)}$; (ii) a step is observed in a defined potential range corresponding to average potentials. The first point is probably due to leak currents which lead to an overestimation of Λ_F in the $\Gamma^{(\Lambda)}$ determination and to the fact that the polymerization yield is not exactly 100%, which leads to a similar but less important overestimation of Q_T. The second point will be discussed in the next paragraph.
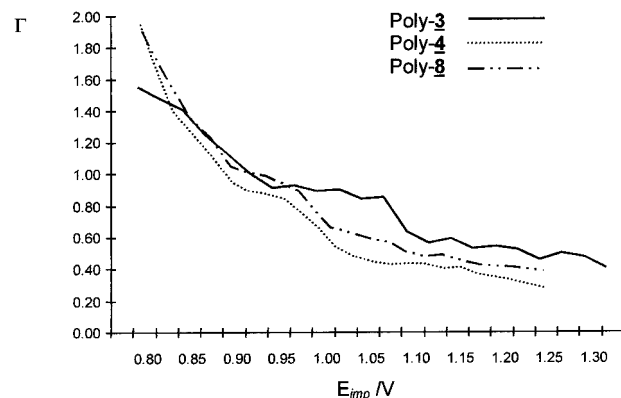
Table 3

E_{imp}	$D/cm^2\ s^{-1}$	E_{imp}	$D/cm^2\ s^{-1}$
0.80	1.6×10^{-9}	1.10	4.3×10^{-7}
0.90	2.7×10^{-9}	1.20	2.9×10^{-6}
1.00	3.1×10^{-8}	1.30	4.8×10^{-6}

Figure 6 gives the $\Gamma^{(Q)}$ curves against E_{imp} for poly-**3**, poly-**4**, and poly-**8**. We notice that only for poly-**3** do we observe a well defined plateau in a potential range varying from 0.90 to 1.10 V. This means that the cross-linking process certainly does not occur during the polymerization below 1.1 V. Concerning half-methoxylated and fullly methoxylated polymers, this tendency is limited to a shorter potential range (0.90−0.95 V) (see figure): in these cases, low E_{imp} potentials are sufficient to start the cross-linking process at the same time as the polymerization one whatever E_{imp}. This is somewhat surprising in the case of poly-**8**, since one would have expected the initial polymerization of the methoxylated salens followed by the cross-linking of the unsubstituted salens as in the case of bifunctional pyrroles and pyrrole thiophene monomers.[40,41] This probably shows that indifferent polymerization of the methoxylated and unsubstituted salens occurs in a manner almost irrelevant of the applied potential.

Kinetics of Electron Transfer. The kinetics of the electron transfer have been estimated in the polymers, from the basis of chronoamperometry experiments. As often observed with poly(salens), the electrochemical response of the film exhibits a less important capacitive current and better defined peaks, and the charge-transfer kinetics exhibit a diffusion-like dependence; that is, the current varies as a linear function of $t^{-1/2}$ in the 0−10 ms range. This is a quite common behavior with conducting polymers, since the discharge of the capacitive tailing usually takes place at much shorter times. Cottrell plots are therefore easily exploitable to determine the apparent diffusion coefficients of charge transfer. Table 1 compares these values to those of films of parent mono(salen) complexes: it is clear that the diffusion kinetics of charge carriers are improved in the case of the bis(salen) polymers. Also, the more the film contains methoxy units, the higher is the diffusion coefficient, which is in accordance with previous results.

There is a correlation between D and Γ values: Table 3 gives the different D values for $\Gamma^{(Q)}$ in the case of poly-**3**. We observe that the D values increase with the cross-

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(43) At very low potentials, where the film is probably made of low molecular weight oligomers, this is not true, but even so, the intrinsic error in the calculation remains low.

linking degree, in a proportion going from 1 to 10^3, when one compares as-grown and fully cross-linked films. This gives an indication of a more rigid and compact structure of such cross-linked polysalens and confirms that the charge transfer is much faster in fully cross-linked films.

4. Conclusion

Bis(salen) complexes allow us to tune the selective introduction of two metals in the same molecule. Despite solubility problems, a monometallic derivative can be polymerized, and the properties of the polymers were found to depend strongly on the cross-linking degree, which in turn depends on the synthesis potential. These characteristics make these polymers versatile materials; in particular, the insertion of two different metals other than nickel could open the way to new magnetic properties and will be the subject of further studies.