

Biaryl-Based Macrocyclic and Polymeric Chiral (Salophen)Ni(II) Complexes: Synthesis and Spectroscopic Study

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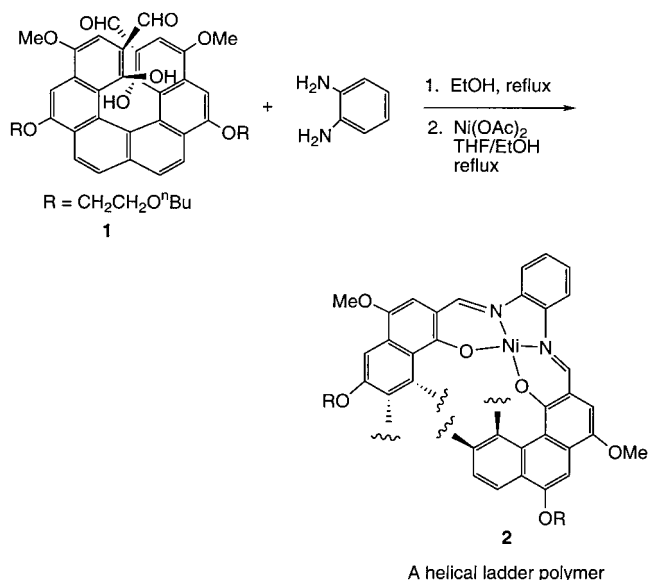
Polymeric/oligomeric and macrocyclic (salophen)Ni(II) complexes have been synthesized starting from both an achiral biphenol dialdehyde and an optically active BINOL dialdehyde. It was found that these polysalophens contain nonplanar coordination of Ni(II) units that are paramagnetic. This is different from the previously reported (salophen)Ni(II) complexes which are square planar and diamagnetic. The nonplanar (salophen)Ni(II) units make the new polymeric Ni(II) complexes different from the helical structure proposed for chiral biaryl-based polymers containing square-planar (salophen)Ni(II) units. The copolymerization of the chiral binaphthyl monomer with the achiral biphenyl monomer demonstrates that the chirality of the binaphthyl unit is not propagated along the biphenyl polymer chain.

Introduction

Transition-metal complexes based on bis(salicylaldiminato) ligands such as *N,N*-ethylenebis(salicylaldiminato) (salen) and *N,N*-disalicylidene-1,2-phenylenediaminato (salophen) have recently been found to exhibit significant nonlinear optical responses.^{1–3} The high thermal stability of these coordination compounds makes them attractive and potentially useful. Polymeric salen and salophen complexes have also been synthesized for materials applications.^{4,5} For example, (salophen)Ni(II) ladder polymer **2** was prepared by Katz and co-workers from the condensation of optically active helicene **1** with 1,2-phenylenediamine (Scheme 1).⁶ In this polymer, the (salophen)Ni(II) unit is planar, which generates a diamagnetic conjugated helical structure.

The interesting chemical and physical properties of both monomeric and polymeric transition metal salophen complexes have spurred us to construct new polymer structures for these materials. We are particularly interested in studying whether helical polymeric salophen–metal complexes can be generated from chiral biaryl molecules and how the chirality of biaryl molecules

Scheme 1. Synthesis of a Helical Polymeric (Salophen)Ni(II) Complex



influences the structure and property of the salophen polymers. Herein, our work on the use of salicylaldehydes derived from biphenyl as well as optically active binaphthyl compounds for the synthesis of novel poly[(salophen)Ni(II)] complexes is reported.

Results and Discussion

1. Synthesis of Biaryl Dialdehyde and Aryl Diamine Monomers. We have developed a new method to synthesize 3,3'-diformyl-2,2'-dihydroxyl-1,1'-biphenyl,⁷ **5**, as a monomer to polysalophens (Scheme 2). Treatment of 2,2'-biphenol with NaH and then with methoxymethyl (MOM) chloride gave **3**. The two OMOM groups of **3** directed ortho metalation⁸ in the presence of *n*-BuLi which after addition of DMF generated **4**. Hydrolysis of the MOM protecting groups of **4** gave the desired biphenol dialdehyde monomer **5**. Each step in this synthesis

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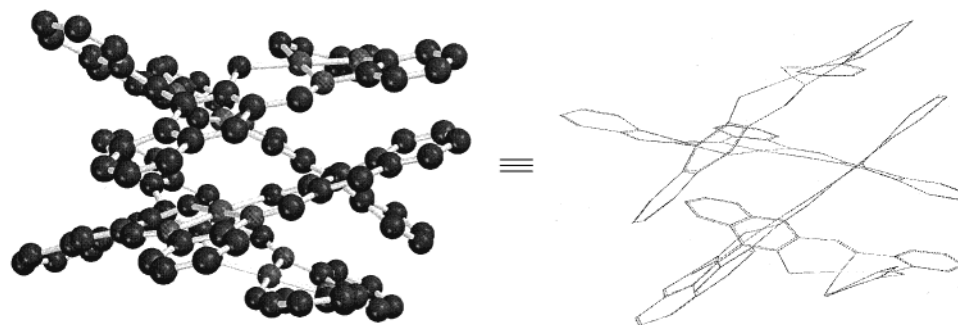
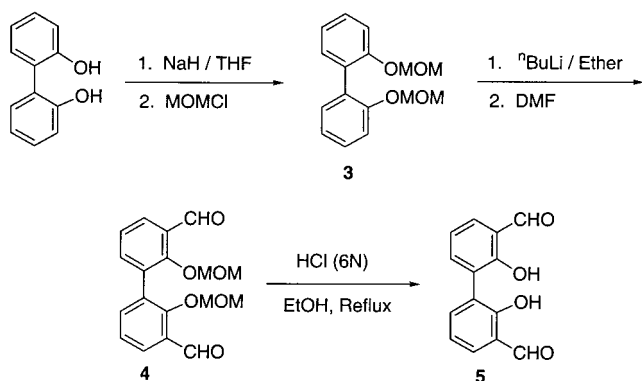


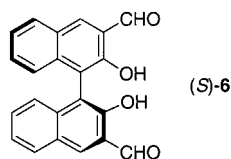
Figure 1. Proposed helical structure for poly[(salophen)Ni(II)] complex **9** containing (*S*)-1,1'-binaphthyl units.

Scheme 2. Synthesis of Biphenyl Dialdehyde Monomer



was about 54–68% yield. The preparation of **5** described here is a more direct synthesis than the previously reported.⁷

The synthesis of 3,3'-diformyl-2,2'-dihydroxy-1,1'-binaphthyl (**6**) from an *O*-methylated 1,1'-bi-2-naphthol (BINOL) was reported before by Brunner et al.⁹ We have modified this method by starting with a MOM protected optically active (*S*)-BINOL. This synthesis parallels the preparation of biphenol monomer **5** shown in Scheme 2. The specific optical rotation of the resulting (*S*)-**6** is $[\alpha]_D = -254$ ($c = 0.3$, CH_2Cl_2).¹⁰



We have prepared 4,5-dialkyl-substituted 1,2-phenylenediamines **8a** and **8b** in order to make their condensation polymers with the biaryl monomers soluble in organic solvent. Dibromination of 1,2-dinitrobenzene with bromine in the presence of Ag_2SO_4 and sulfuric acid gave 1,2-dibromo-4,5-dinitrobenzene (Scheme 3).¹¹ Cross-coupling of 1,2-dibromo-4,5-dinitrobenzene with terminal

alkynes in the presence of $\text{Pd}(\text{PPh}_3)_4/\text{CuI}$ produced **7a** and **7b**.¹² Catalytic hydrogenation of **7a** and **7b** with Pd (10%)/ C under hydrogen (10 psi) gave the desired monomers **8a** and **8b** in good yields.

2. Condensation of the Optically Active BINOL Dialdehyde Monomer (*S*)-6 with Aryl Diamines. In 1994, Brunner and Schiessling reported that when (*R*)-**6** was reacted with (*R,R*)-1,2-diamino-1,2-diphenylethane, a polymer was produced, but when (*S*)-**6** was reacted with (*R,R*)-1,2-diamino-1,2-diphenylethane, a macrocyclic compound was obtained.¹³ Thus, the steric structure of the condensation products.

We have examined the condensation of the optically active BINOL monomer (*S*)-**6** with the planar 1,2-phenylenediamine in an effort to generate salophen-Ni(II) polymer **9** (Figure 1).^{14,15} Polymer **9** contains chiral (*S*)-binaphthyl units as well as planar (salophen)Ni(II) units which may generate a helical structure similar to **2**.⁶ However, the reaction of (*S*)-**6** with 1,2-phenylenediamine produced a macrocycle (*S,S*)-**10** rather than a polymer in very high yield at various concentrations (Scheme 4). This is similar to the reaction of (*S*)-**6** with (*R,R*)-1,2-diamino-1,2-diphenylethane as observed by Brunner.¹³ The specific optical rotation of (*S,S*)-**10** is $[\alpha]_D = +1561$ ($c = 0.3$, CH_2Cl_2). There is a large increase in optical rotation from (*S*)-**6** to (*S,S*)-**10** accompanied with a change of the sign.

Compound (*S,S*)-**10** was converted to a nickel complex (*S,S*)-**11** by reaction with 2 equiv of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$. Unlike the previously reported (salophen)Ni(II) complexes which are square planar and diamagnetic,^{1–6,16} complex (*S,S*)-**11** is paramagnetic. The ^1H NMR spectrum of (*S,S*)-**11** does not give any signal in the normal spectral region. The mass spectrum of (*S,S*)-**11** shows that its molecular ion (also the base peak) contains two nickel atoms and two acetate groups. Because of the steric strain in the macrocycle, it is impossible for (*S,S*)-**11** to contain two planar (salophen)Ni(II) units. Therefore, a structure containing a planar (salophen)Ni(II) unit and a tetrahedral Ni(II) center is proposed for (*S,S*)-**11**. The

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Scheme 3. Preparation of Alkylated Aryl Diamines

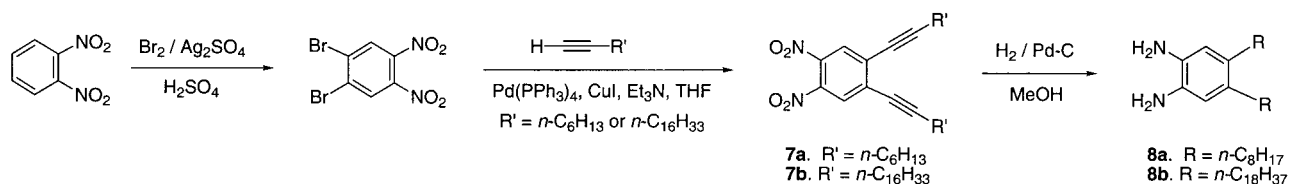
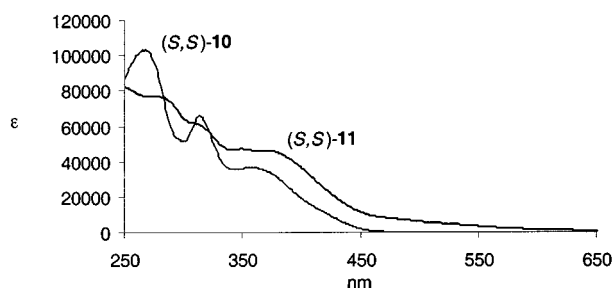
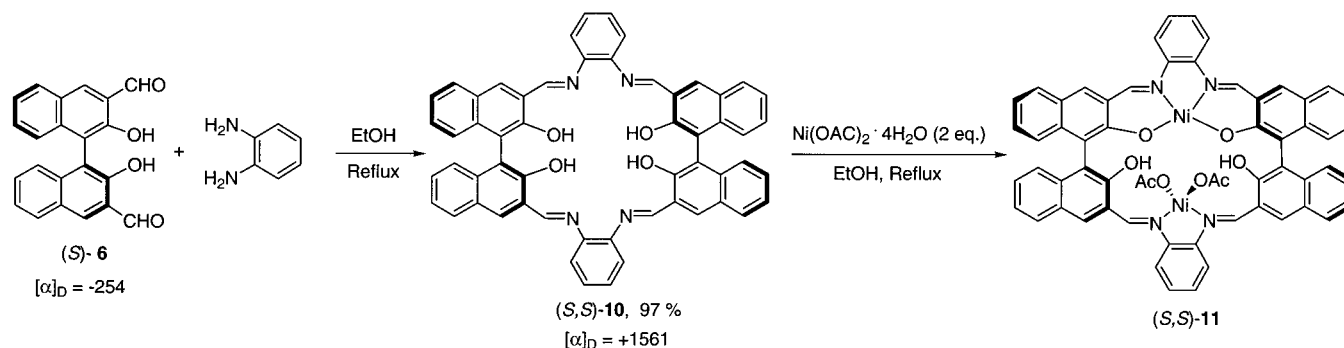
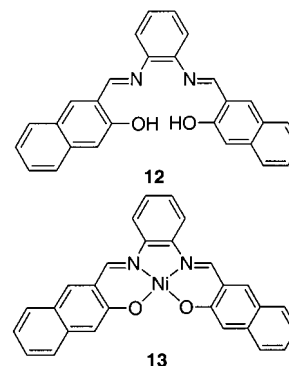
Scheme 4. Condensation of (*S*)-6 with 1,2-Phenylenediamine

Figure 2. UV spectra of macrocycle (*S,S*)-10 and its Ni(II) complex (*S,S*)-11.

tetrahedral Ni(II) center in (*S,S*)-11 should be paramagnetic. (Salen)Ni(II) complexes can become paramagnetic when they deviate from planarity,¹⁷ but nonplanar paramagnetic (salophen)Ni(II) complex was not reported before.¹⁶ In the mass spectrum of (*S,S*)-11, another major peak is observed for the loss of a Ni atom and two AcO groups. This should correspond to a mononuclear planar (salophen)Ni(II) fragment. However, the reaction of (*S,S*)-10 with one equivalent of Ni(OAc)₂·4H₂O failed to generate such a mononuclear diamagnetic complex.

Figure 2 shows the UV spectra of macrocycle (*S,S*)-10 and nickel complex (*S,S*)-11. The UV spectra of a salophen derivative **12** and its Ni(II) complex **13** were studied by Crawford in 1963.¹⁸ Both **12** and **13** have strong absorptions between 450 and 500 nm. However, the UV absorptions of macrocycle (*S,S*)-10 are significantly blue shifted from those of **12** with no appreciable absorption above 450 nm. This indicates that there is much less conjugation in (*S,S*)-10. We attribute the reduced conjugation of (*S,S*)-10 to the steric congestion in the macrocycle which disrupts the planarity of the two salophen units. After coordinated to Ni(II), the resulting complex (*S,S*)-11 shows increased absorption in the range of 420–600 nm. This could be due to increased conjugation

with the partial formation of a planar (salophen)-Ni(II) structure in (*S,S*)-11. It could also be attributed to additional $\pi-\pi^*$ transitions involving the metal-ligand orbitals.¹⁸



We have carried out the condensation of (*S*)-6 with the alkylated aryl diamine **8b** in the presence of Ni(OAc)₂·4H₂O. The addition of Ni(II) made it harder to form macrocycle so that an oligomer (*S*)-14 was obtained in 66% yield. The alkyl groups of **8b** allow (*S*)-14 to be soluble in organic solvents such as THF and chloroform. The molecular weight of (*S*)-14 is $M_w = 3600$ (PDI = 1.62) as determined by gel permeation chromatography (GPC) relative to polystyrene standards. Our previous study has shown that the absolute molecular weights of some binaphthyl polymers determined by laser light scattering method are often higher than those determined by using polystyrene standards.¹⁹ Thus, we estimate that the degree of polymerization for (*S*)-14 should be above 7.

Oligomer (*S*)-14 is paramagnetic since no NMR signal in the normal spectra region is observed. This indicates that there are also nonplanar coordination of Ni(II) units in this material as observed for macrocycle (*S,S*)-11. The UV spectrum of (*S*)-14 is also similar to that of (*S,S*)-11. Therefore, the structure of this oligomer should be different from that of **9** since the helical structure of **9** requires planar (salophen)Ni(II) coordination.

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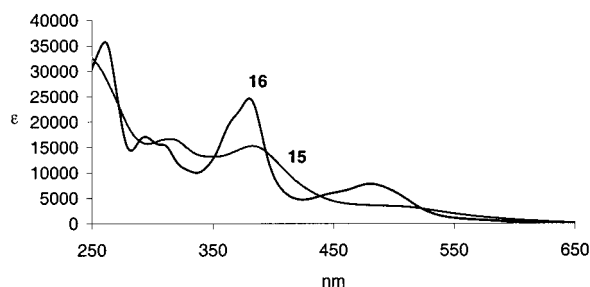
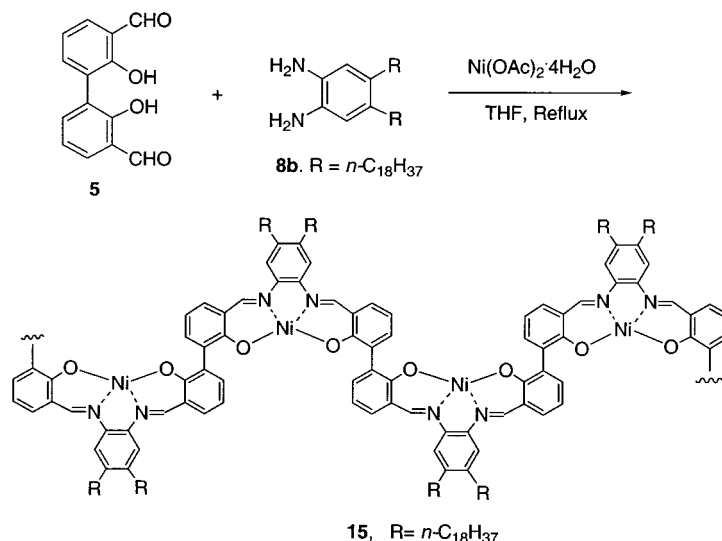
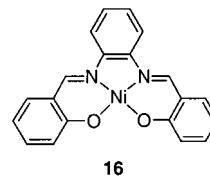
Scheme 5. Condensation of 5 with 8b in the Presence of Ni(OAc)₂·4H₂O

Figure 3. UV-vis spectra of polymer **15** and complex **16** in chloroform.

3. Condensation of the Biphenol Dialdehyde Monomer 5 with Diamines. We examined the condensation of the biphenol dialdehyde monomer **5** with diamine **8b** at various concentrations, which however, only produced a mixture of very low molecular weight materials and macrocycles. Unlike the reaction of chiral binaphthyl (*S*)-**6** with 1,2-phenylenediamine, **5** cannot react with **8b** to generate the corresponding macrocycle with high yield at even high dilutions. Because of this, Pierre and co-workers had developed a boron-templated macrocycle synthesis from the condensation of **5** with 1,2-phenylenediamine.⁷ To generate the desired polymer, we conducted the polymerization of **5** with **8b** in the presence of Ni(OAc)₂·4H₂O which indeed produced low molecular weight polymer **15** in 68% yield (Scheme 5). Diamine **8b** with two long-chain alkyl substituents gave a much more soluble material than diamine **8a** that has shorter alkyl substituents. The molecular weight of **15** is $M_w = 4900$ (PDI = 1.2) as measured by GPC. The estimated degree of polymerization is above 10. Polymer **15** is also paramagnetic with no NMR signals detected in the expected region. This indicates that either only part of the (salophen)Ni(II) units in **15** are planar or all nonplanar.

A known planar (salophen)nickel(II) complex **16** was prepared to compare with polymer **15**.²⁰ Unlike **15**, complex **16** is a diamagnetic compound and gives well-defined NMR signals. Figure 3 shows the UV spectra of polymer **15** and complex **16** in THF. The UV spectrum indicates that both of the materials contain a broad

charge-transfer band around 450–600 nm. However, the near-visible-infrared absorption spectrum (not shown in Figure 3) of **15** in chloroform (0.01 M) shows broad absorption bands in the range of 700–1200 nm ($\epsilon = 32 - 100$) due to the d–d transition of the Ni(II) center. This is consistent with the existence of nonplanar Ni(II) units in the polymer.¹⁷ The square planar diamagnetic Ni(II) complexes such as **16** do not have absorption above 700 nm in its near-visible-infrared absorption spectrum.



4. Copolymerization of the Chiral BINOL Monomer (S)-6 and the Achiral Biphenol Monomer 5 with Diamine 8b. 2,2'-Substituted 1,1'-binaphthyl molecules are chiral with restricted rotation around the 1,1'-bond.¹⁶ However, 2,2'-biphenol derivatives are achiral because the rotation barrier around the 2,2'-pivotal bond is low. To find out whether the chirality of the binaphthyl units could induce a helical chiral structure in the biphenyl-based polymer, we have conducted the co-condensation of (*S*)-**6** and **5** with **8b** in the presence of Ni(OAc)₂·4H₂O (Scheme 6). Table 1 summarizes the molecular weights of the copolymers. As shown in Table 1, the polymers with more biphenyl units have higher molecular weights than the polymers with more binaphthyl units probably because of the less steric interaction during the formation of the former materials.

The UV absorption spectra of these copolymers are compared (Figure 4). As shown in Figure 4, with the increase of the binaphthyl units in the polymers, there is significant increase in the absorptions around 250–340 nm. The circular dichroism (CD) spectra of the copolymers are also compared (Figure 5). We find that the increase in the CD maximums at 417–435 nm is linear with the increase of the chiral binaphthyl contents in the copolymers (Figure 6). This linear relationship demonstrates that there is no chiral amplification²¹ in

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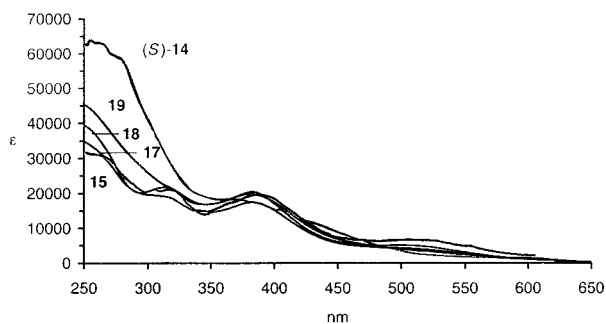


Figure 4. UV spectra of the copolymers.

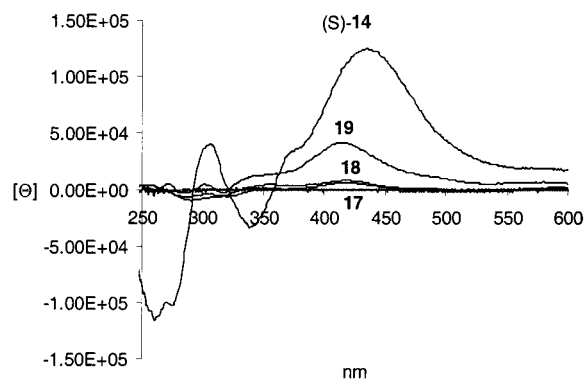


Figure 5. CD spectra of the copolymers.

Table 1. Molecular Weights of the Copolymers

| polymer | percentage of the chiral binaphthyl (%) | M_w | M_n | PDI |
|---------|---|-------|-------|-----|
| 15 | 0 | 4900 | 4000 | 1.2 |
| 17 | 5 | 5400 | 3400 | 1.6 |
| 18 | 10 | 4400 | 3900 | 1.1 |
| 19 | 40 | 3400 | 2600 | 1.3 |
| (S)-14 | 100 | 3600 | 2200 | 1.6 |

these poly(salophen-Ni) complex. The chirality of the binaphthyl units cannot propagate along the biphenyl polymer chain. This is consistent with the existence of nonplanar Ni(II) coordination in the polymers which makes them different from the proposed helical structure of **9**. Thus, the chiral binaphthyl units cannot induce a main chain helix in the polymer of the achiral biphenyl. The red-shift from 417 to 435 nm in the CD maximums going from copolymer **17** to the chiral binaphthyl polymer (S)-**14** is probably due to the increased conjugation of the (salophen)Ni(II) units from **20** to **22** (Figure 7).

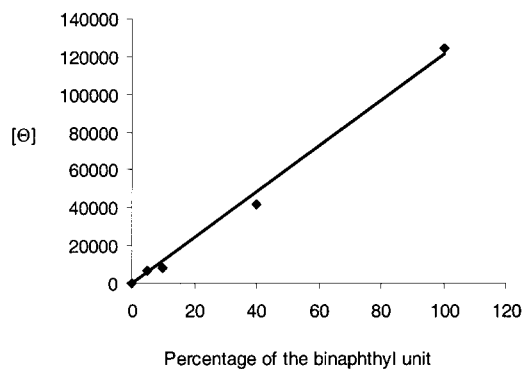


Figure 6. Plot of the molar ellipticity (at $\lambda = 417\text{--}435$ nm) of the copolymers versus the percentage of the chiral binaphthyl unit.

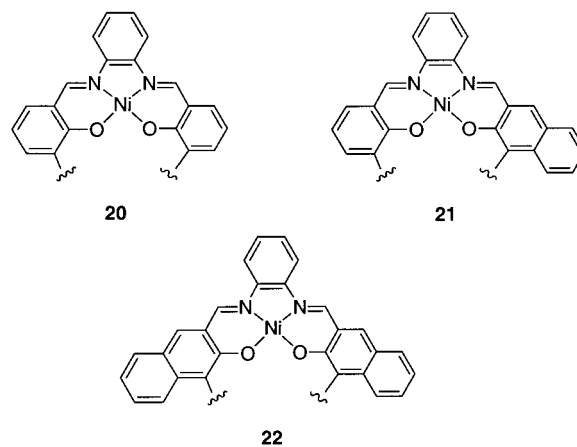
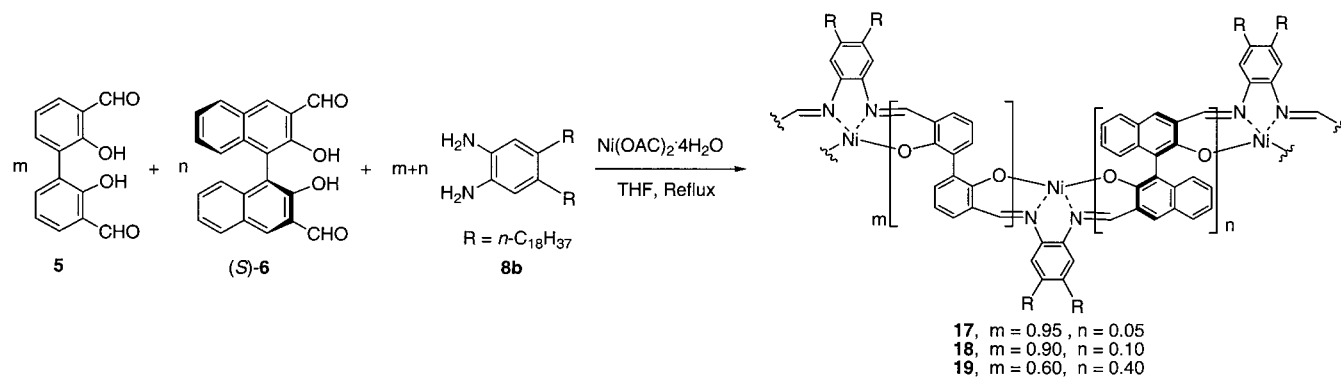


Figure 7. (Salophen)Ni(II) units **20–22** that may be present in the copolymers.

Summary

Polymeric/oligomeric and macrocyclic (salophen)Ni(II) complexes have been synthesized starting from both an achiral biphenol dialdehyde and an optically active BINOL dialdehyde. It was found that these polysalophens contain paramagnetic nonplanar Ni(II) coordination. This is different from the previously reported (salophen)Ni(II) complexes which are square planar and diamagnetic. The nonplanar Ni(II) coordination makes the new polymeric Ni(II) complexes deviated from a helical structure proposed for chiral biaryl-based polymers containing square planar (salophen)Ni(II) units. Copolymerization of the chiral binaphthyl monomer with the achiral

Scheme 6 Copolymerization of (S)-**6** and **5** with **8b** in the Presence of Ni(OAc)₂·4H₂O



biphenyl monomer demonstrates that the chirality of the binaphthyl unit is not propagated along the biphenyl polymer chain. This is consistent with the nonhelical chain structure of these (salophen)Ni(II) polymers. The nonlinear optical property of these polymers and macrocycles is under investigation.

Experimental Section

Unless otherwise noted, all materials obtained from commercial suppliers were used without further purification. Tetrahydrofuran, diethyl ether, and toluene were distilled from sodium benzophenone ketyl immediately prior to use. Hexane was distilled over calcium chloride. Dichloromethane was distilled over calcium hydride. Ethanol was distilled over Mg turnings. Thin-layer chromatography was performed on pre-coated silica gel plates. Silica gel (70–230 and 230–400 mesh) was used for column chromatography.

NMR spectra were recorded on Varian-300 MHz spectrometer. Mass spectra were recorded either at electron ionization or at FAB mode using *m*-nitrobenzyl alcohol (NBA) as the matrix. Elemental analyses were performed by using a Perkin-Elmer Series II CHNS/O Analyzer. The UV–vis and visible–near-infrared spectra were recorded with Cary 5E UV–vis–NIR spectrophotometer. The CD spectra were recorded with a JASCO J-720 spectropolarimeter. Optical rotations were measured on a JASCO DIP-1000 polarimeter at 589 nm.

Preparation and Characterization of 2,2'-Bis(methoxymethoxy)biphenyl, 3. Under nitrogen, 2,2'-biphenol (3.72 g, 20 mmol) was added to a suspension of NaH (1.15 g, 48 mmol) in THF (40 mL) at 0 °C with stirring. The resulting solution was stirred at 0 °C for 10 min, and then methoxymethyl chloride (3.65 mL, 48 mmol) was slowly added. The mixture was allowed to warm to room temperature and stirred overnight to afford a creamlike mixture. Water was added to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (30 mL × 3). The combined organic extracts were washed with brine, and dried over Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel. Elution with hexane/ethyl acetate (5:1) gave compound **3** as a colorless oil in 54% yield (2.84 g): *R*_f = 0.4 (hexane/ethyl acetate = 5:1); ¹H NMR (300 MHz, CDCl₃) δ 3.24 (s, 6H), 4.97 (s, 4H), 6.97 (m, 2H), 7.10–7.25 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 55.83, 95.20, 115.57, 121.79, 128.65, 129.15, 131.48, 154.88.

Preparation and Characterization of 2,2'-Bis(methoxymethoxy)-1,1'-binaphthyl.²² The preparation procedure was the same as that of **3** by using (*S*)-1,1'-binaphthol (BINOL) as the starting material. After workup, the crude product was purified by column chromatography on silica gel. Elution with hexane/ethyl acetate (5:1) gave (*S*)-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl as a colorless crystal in 85% yield: *R*_f = 0.39, (hexane/ethyl acetate = 3:1); ¹H NMR (300 MHz, CDCl₃) δ 3.15 (s, 6H), 4.98 (d, *J* = 6.6 Hz, 2H), 5.09 (d, *J* = 6.6 Hz, 2H), 7.14–7.26 (m, 6H), 7.35 (ddd, *J* = 1.8, 8.4 Hz, 2H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.96 (d, *J* = 9.0 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 55.78, 95.13, 117.22, 121.24, 124.02, 125.50, 126.25, 127.82, 129.35, 129.83, 133.97, 152.60.

Preparation and Characterization of 3,3'-Diformyl-2,2'-bis(methoxymethoxy)biphenyl, 4. Under nitrogen, *n*-butyllithium (2.5 M in hexane, 9.0 mL, 22 mmol) was added to a solution of **3** (1.73 g, 6.6 mmol) in ether (100 mL) at room temperature. The mixture was stirred for 2 h, which produced a gray suspension. After the mixture was cooled to 0 °C, DMF (1.85 mL, 24 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. Saturated NH₄Cl (50 mL) was then added to quench the reaction. The organic layer was separated, and the aqueous phase was extracted with ethyl acetate (50 mL × 3). The combined organic phase was washed with water and brine and

dried over Na₂SO₄. Concentration with a rotary evaporator and subsequent chromatography on silica gel eluted with hexane/ethyl acetate (5:1) afforded **4** as colorless crystals in 57% yield (1.19 g): *R*_f = 0.13 (hexane/ethyl acetate = 5:1); ¹H NMR (300 MHz, CDCl₃) δ 3.15 (s, 6H), 4.81 (s, 4H), 7.37 (dd, *J* = 0.9, 8.4 Hz, 2H), 7.67 (dd, *J* = 1.8, 7.5 Hz, 2H), 7.93 (dd, *J* = 1.8, 7.8 Hz), 10.43 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 57.63, 101.19, 124.98, 129.18, 130.28, 132.73, 138.00, 158.19, 190.34.

Preparation and Characterization of (S)-3,3'-Diformyl-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl. The preparation procedure was the same as that of **4** with the use of (*S*)-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl as the starting material. After workup, the crude product was purified by column chromatography on silica gel eluted with hexane:ethyl acetate (4:1). (*S*)-3,3'-Diformyl-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl was obtained as a sticky yellow oil in 68% yield: *R*_f = 0.17 (hexane/ethyl acetate = 4:1); ¹H NMR (300 MHz, CDCl₃) δ 2.87 (s, 6H), 4.69 (d, *J* = 6.6 Hz, 2H), 4.73 (d, *J* = 6.3 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 2H), 7.42 (ddd, *J* = 0.9, 7.5, 8.1 Hz, 2H), 7.52 (ddd, *J* = 0.9, 6.9, 7.8 Hz, 2H), 8.08 (d, *J* = 8.1 Hz, 2H), 8.62 (s, 2H), 10.55 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 57.00, 100.60, 125.89, 126.08, 126.26, 128.84, 129.61, 130.05, 130.28, 132.29, 136.68, 154.02, 190.64.

Preparation and Characterization of 3,3'-Diformyl-2,2'-dihydroxy-1,1'-biphenyl, 5. After compound **4** (1.0 g, 3.0 mmol) was dissolved in a minimum amount of CH₂Cl₂, ethanol (15 mL) and HCl (6 N, 15 mL) were added successively, and the mixture was heated at reflux for about 10 h. The resulting yellow solution was concentrated with a rotary evaporator. Water (30 mL) was then added, and the solution was extracted with CH₂Cl₂ (30 mL × 3). The combined extract was dried over Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (6:1) to give **5** as yellow needle crystals in 68% yield (0.50 g): *R*_f = 0.26, (hexane/ethyl acetate = 6:1). The ¹H and ¹³C NMR spectra of **5** match the reported data.^{7a}

Preparation and Characterization of (S)-3,3'-Diformyl-2,2'-dihydroxy-1,1'-binaphthyl, (S)-6. The preparation procedure was the same as that of **5** by starting with (*S*)-3,3'-diformyl-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl. After workup, the crude product was purified by recrystallization from CH₂Cl₂/EtOH. This gave (*S*)-**6** as a yellow solid in 90% yield: *R*_f = 0.35 (hexane/ethyl acetate = 4:1). The ¹H NMR data of **5** match the reported data.¹⁰

Preparation and Characterization of 4,5-Di(1'-octynyl)-1,2-dinitrobenzene, 7a. In a drybox, 1,2-dibromo-4,5-dinitrobenzene (2.0 g, 6.1 mmol), cuprous iodide (0.12 g, 0.61 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.35 mg, 0.31 mmol) were mixed in a Schlenk flask. Triethylamine (4.0 mL, 28.8 mmol), 1-octyne (1.35 g, 12.2 mmol), and THF (80 mL) were added successively under nitrogen. The mixture was further deoxygenated by freeze–pump–thaw three times (–196 to +25 °C) and was then stirred at room temperature for 96 h until TLC showed the disappearance of the starting material. The mixture was filtered, and the precipitate was washed with ether. The filtrates were combined and concentrated by rotary evaporation. The brown oil residue was then redissolved in ether (50 mL), washed with water and brine, and dried over Na₂SO₄. Concentration with a rotary evaporator and subsequent chromatography on silica gel eluted with hexane/ethyl acetate (97:3) afforded **7a** as a light-yellow solid in 78% yield (1.84 g): *R*_f = 0.33 (hexane/ethyl acetate = 97:3); ¹H NMR (300 MHz, CDCl₃) δ 0.91 (t, 6H, *J* = 7.2 Hz), 1.30–1.35 (m, 8H), 1.47–1.50 (m, 4H), 1.62–1.67 (m, 4H), 2.51 (t, 4H, *J* = 7.2 Hz), 7.85 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 14.24, 20.00, 22.73, 28.42, 28.78, 31.52, 77.35, 102.80, 128.12, 132.07, 140.87; MS (EI) for C₂₂H₂₈N₂O₄ *m/z* (relative intensity) 384 (M⁺, 90).

Preparation and Characterization of 4,5-Di(1'-octadecynyl)-1,2-dinitrobenzene, 7b. The preparation procedure was the same as that of **7a** by starting with 1-octadecyne. After workup, the crude product was purified by chromatography on silica gel eluted with hexane/ethyl acetate (97:3). This afforded **7b** as a light-yellow solid in 90% yield: *R*_f = 0.50 (hexane/ethyl acetate = 97:3); ¹H NMR (300 MHz, CDCl₃) δ

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0.88 (t, 6 H, $J = 6.6$ Hz), 1.30 (b s, 48 H), 1.47 (m, 4 H), 1.64 (m, 4 H), 2.50 (t, 4H, $J = 7.2$ Hz), 7.85 (s, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.10, 19.81, 22.69, 28.27, 28.93, 29.17, 29.35, 131.86, 140.70; MS (FAB) m/z (relative intensity) 665 ($\text{M} + \text{H}^+$, 100). Anal. Calcd. for $\text{C}_{42}\text{H}_{68}\text{N}_2\text{O}_4$: C, 75.86; H, 10.31; N, 4.21. Found: C, 75.67; H, 10.36; N, 3.97.

Preparation and Characterization of 1,2-Diamino-4,5-dioctylbenzene, 8a. A solution of **7a** (0.77 g, 2.0 mmol) in MeOH (50 mL) was stirred under hydrogen (10 psi) in the presence of Pd (10%)/C (85 mg) at room temperature. After 24 h, TLC indicated the consumption of all the starting material. The reaction mixture was then filtered carefully through a pad of Celite and washed with diethyl ether. After removal of the solvent, **8a** (0.52 g, 78%) was obtained as a yellow powder which was pure enough for the subsequent reaction: $R_f = 0.18$ (hexane/ethyl acetate/MeOH = 5:5:1); ^1H NMR (300 MHz, CDCl_3) δ 0.89 (t, $J = 6.9$ Hz, 6 H), 1.29 (m, 20 H), 1.51 (m, 4 H), 2.45 (t, $J = 8.1$ Hz, 4 H), 3.21 (bs, 4 H), 6.51 (s, 2 H).

Preparation and Characterization of 1,2-Diamino-4,5-dioctadecylbenzene, 8b. The preparation procedure was the same as **8a** by hydrogenation of **7b**. After workup, the crude product was purified by flash chromatography on silica gel eluted with hexane/ethyl acetate (2:1) to afford compound **8b** as a light-yellow solid in 86% yield: $R_f = 0.50$ (hexane/ethyl acetate = 2:1); ^1H NMR (300 MHz, CDCl_3) δ 0.88 (t, 6 H, $J = 6.9$ Hz), 1.25 (b s, 60 H), 1.48 (m, 4 H), 2.44 (t, 4H, $J = 8.4$ Hz), 6.50 (s, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.18, 22.69, 29.35, 29.70 (broad intense signal), 31.74, 31.92, 32.08, 117.81, 118.93, 132.41; MS (CI) for $\text{C}_{42}\text{H}_{80}\text{N}_2$ m/z (relative intensity) 613 ($\text{M} + \text{H}^+$, 100).

Preparation and Characterization of Macrocycle (S,S)-10. Under nitrogen, a mixture of 1,2-phenylenediamine (43.2 mg, 0.4 mmol) and (*S,S*)-**6** (136.8 mg, 0.4 mmol) in absolute ethanol (10 mL) was refluxed for about 10 h to yield a yellow precipitate. The crude product was filtered at room temperature and washed with ice-cold ethanol to afford pure **10** as a yellow solid in 97% yield (160 mg): ^1H NMR (300 MHz, CDCl_3) δ 7.10–7.17 (m, 8H), 7.24 (d, $J = 4.2$ Hz, 8 H), 7.35 (m, 4 H), 7.84 (m, 4 H), 8.06 (s, 4 H), 8.76 (s, 4 H), 12.48 (s, 4 H); ^{13}C NMR (75 MHz, CDCl_3) δ 116.86, 119.51, 121.42, 123.22, 124.46, 127.45, 127.71, 128.64, 129.04, 134.91, 135.87, 143.75, 154.87, 163.40; MS (CI) m/z (relative intensity) 829 ($\text{M} + \text{H}^+$, 100); UV–vis λ_{max} (CHCl_3) nm 358 ($\epsilon = 3.65 \times 10^4$), 314 ($\epsilon = 6.58 \times 10^4$), 268 ($\epsilon = 1.03 \times 10^5$). Anal. Calcd for $\text{C}_{56}\text{H}_{36}\text{N}_4\text{O}_4 \cdot \text{H}_2\text{O}$: C, 79.42; H, 4.52; N, 6.61. Found: C, 79.90; H, 4.53; N, 6.57.

Preparation and Characterization of Macrocyclic Ni(II) Complex (S,S)-11. Under nitrogen, a mixture of (*S,S*)-**10** (60 mg, 0.07 mmol) and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (40 mg, 0.14 mmol) in absolute ethanol (10 mL) was refluxed for about 10 h to yield a brown precipitate. The crude product was filtered at room temperature and washed with ice-cold ethanol to afford (*S,S*)-**11** as a brown solid: MS (CI) for $\text{C}_{60}\text{H}_{40}\text{O}_8\text{N}_4\text{Ni}_2$ m/z (relative intensity) 1061.1 ($\text{M} + \text{H}^+$, 100), 885.5 ($\text{M} - \text{Ni} - 2\text{OAc} + \text{H}^+$, 60); UV–vis λ_{max} (CHCl_3) nm 369 ($\epsilon = 4.64 \times 10^4$), 349 ($\epsilon = 4.73 \times 10^4$), 310 ($\epsilon = 6.15 \times 10^4$), 277 ($\epsilon = 7.69 \times 10^4$).

Preparation and Characterization of Polymer 15. Under nitrogen, a solution of **8b** (61.2 mg, 0.1 mmol) in THF (2.0 mL) was slowly added to a mixture of **5** (24.2 mg, 0.1 mmol) and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (24.8 mg, 0.1 mmol) in THF (1.0 mL) over 10 h via a syringe pump at 70 °C. An additional 40 h reflux resulted in a dark red solution. After removal of the solvent, the brown residue was redissolved in a minimum amount of THF and precipitated with absolute ethanol. This dissolution and precipitation was repeated to give polymer **15** as a dark red solid in 68% yield (60 mg) after drying under vacuum: UV–vis λ_{max} (THF) nm 500 ($\epsilon = 5.10 \times 10^3$), 382 ($\epsilon = 2.05 \times 10^4$), 314 ($\epsilon = 2.17 \times 10^4$), 251 (3.93×10^4).

Preparation and Characterization of Polymer (S)-14. The preparation procedure was the same as that of **15** by using (*S*)-**6** as the monomer. Polymer (*S*)-**14** was isolated as a brown solid in 66% yield (64 mg) after drying under vacuum: UV–vis λ_{max} (THF) nm 370 ($\epsilon = 1.81 \times 10^4$), 260 ($\epsilon = 6.34 \times 10^4$); CD $[\Theta]_D$ (4.57×10^{-5} M, THF) 1.25 $\times 10^5$ (435 nm), -3.42×10^4 (340 nm), 4.16×10^4 (306 nm), -1.15×10^5 (260 nm).

Preparation and Characterization of Copolymer 17. Under nitrogen, a solution of **8b** (61.2 mg, 0.1 mmol) in THF (2.0 mL) was slowly added to a mixture of **5** (23.0 mg, 0.095 mmol), (*S*)-**6** (1.7 mg, 0.005 mmol) and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (24.8 mg, 0.1 mmol) in THF (1.0 mL) by syringe pump over 10 h at 70 °C. An additional 40 h reflux resulted in a dark red solution. After removal of solvent, the brown residue was redissolved in a minimum amount of THF and precipitated with absolute ethanol twice. Copolymer **17** was isolated as a dark red solid in 65% yield (57 mg) after drying under vacuum: UV–vis λ_{max} (THF) nm 514 ($\epsilon = 6.75 \times 10^3$), 387 ($\epsilon = 1.97 \times 10^4$), 317 (2.08×10^4), 259 (3.09×10^4). CD $[\Theta]_D$ (4.57×10^{-5} M, THF) 6.49 $\times 10^3$ (417 nm, the predominate signal).

Preparation and Characterization of Copolymer 18. The preparation procedure was the same as that of **17** except that **5** (21.8 mg, 0.09 mmol) and (*S*)-**6** (3.42 mg, 0.01 mmol) were used. Copolymer **18** was isolated as a brown solid in 65% yield (60 mg) after drying under vacuum. UV–vis λ_{max} (THF) nm 500 ($\epsilon = 5.11 \times 10^3$), 383 ($\epsilon = 1.75 \times 10^4$), 310 (1.93×10^4), 251 (3.93×10^4). CD $[\Theta]_D$ (4.57×10^{-5} M, THF) 8.23 $\times 10^3$ (417 nm, the predominate signal).

Preparation and Characterization of Co-Polymer 19. The preparation procedure was the same as that of **17** except that **5** (14.6 mg, 0.06 mmol) and (*S*)-**6** (13.7 mg, 0.04 mmol) were used. Copolymer **19** was isolated as a brown solid in 65% yield (61 mg) after drying under vacuum: UV–vis λ_{max} (THF) nm 381 ($\epsilon = 1.98 \times 10^4$), 254 (4.44×10^4); CD $[\Theta]_D$ (4.57×10^{-5} M, THF) 4.17 $\times 10^4$ (415 nm, the predominate signal).

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