Synthesis of Helical Conjugated Ladder Polymers

Yujia Dai and Thomas J. Katz*

Department of Chemistry, Columbia University, New York, New York 10027

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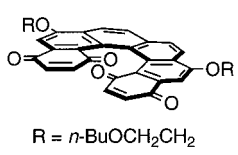
The synthesis is described of the first helical ladder polymers with unbroken pathways of conjugation that extend not only through each monomeric unit, but between them as well. The key step is the condensation of 1,2-phenylenediamine and a transition metal salt with a helicene having salicylaldehyde's functionality at both ends. This gives rise to "metal salophen" units that bind adjacent helicenes, provide conjugated links from one ring system to the next, and constrain the p-orbitals of the rings they unite to be nearly parallel. Because the helicene monomers are enantiopure, so too are the polymeric structures to which they give rise. One of the polymers (**6**) winds continuously in only one direction. Another (**4a**) winds in one direction through the helicene moieties and in the other direction through the metal−salophens. The circular dichroisms of the former at wavelengths near 600 nm are notably large. The corresponding circular dichroisms of the latter are much smaller. MALDI-TOF mass spectra provide particularly strong evidence for the structures assigned. The polymers are very soluble in a variety of organic solvents and seem to have number average molecular weights of ca. 7000.

The problem solved in this paper[1] was to find a way to prepare nonracemic[2] ladder polymers (in the cases below, enantiomerically pure polymers) that have double bonds conjugated on helical paths extending not just through each monomeric unit, but also from one to the next. The synthesis of such materials was studied because, although they should present both the electronic and optical properties of polymers with conjugation extending over long distances[3] and added features of asymmetry that achiral and racemic materials can not,[2] none were previously known. To ensure conjugation, the polymers were designed to have "classical"[4] ladder structures[4,5] —that is, "restrictive links around which rotation cannot occur without bond rupture."[6] Although ladder polymers are often too insoluble to manipulate easily,[4,5] the problem should be ameliorated in the case of helical molecules, for they are usually much more soluble than those that are planar. Notably, **1**, which was used as the starting material for this research, dissolves in benzene at room temperature to the extent of 270 g/L, and it dissolves easily in many other solvents as well.[7]

Previously, the only known formally conjugated nonracemic polymers[8] had structures in which conjugation could be weakened either by rotation about single bonds—these include polypyrroles,[9] polythiophenes,[10]



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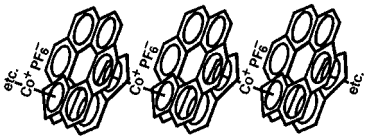

2

polyquinoxalines,[11] polyacetylenes,[12] and copolymers comprised of binaphthyls and a variety of benzene derivatives[13]—or by only partially effective delocalization through a metal linkage, in the case of the polymer **2**.[14] A way was recently described to prepare a nonracemic polythiophene in which adjacent rings are forced to lie in essentially one plane; the structure of the resulting polymer is not yet fully defined.[15]

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

(1) Part of this work was published previously as a preliminary communication: Dai, Y.; Katz, T. J.; Nichols, D. A. *Angew. Chem.* **1996**, *108*, 2230; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2109.

(2) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994.

(3) (a) *Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure*; Salaneck, W. R., Lundström, I., Rånby, B., Eds.; Oxford University Press: New York, 1993. (b) Bryce, M. R. *Chem. Soc. Rev.* **1991**, *20*, 355. (c) Ferraro, J. R.; Williams, J. M. *Introduction to Synthetic Electrical Conductors*; Academic Press: Orlando, 1987.

(4) Scherf, U.; Müllen, K. *Adv. Polym. Sci.* **1995**, *123*, 1.

(5) (a) Schlüter, A.-D. *Adv. Mater.* **1991**, *3*, 282. (b) Yu, L.; Chen, M.; Dalton, L. R. *Chem. Mater.* **1990**, *2*, 649. (c) Overberger, C. G.; Moore, J. A. *Adv. Polym. Sci.* **1970**, *7*, 113.

(6) This definition is that of Overberger and Moore (ref 5c). Schlüter's definition (ref 5a) is slightly different.

(7) (a) Willmore, N. D.; Liu, L.; Katz, T. J. *Angew. Chem.* **1992**, *104*, 1081; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1093. (b) Willmore, N. D. Ph.D. Dissertation, Columbia University, 1994.

(8) For a comprehensive review, see: Pu, L. *Acta Polym.*, submitted for publication.

(9) Elsenbaumer, R. L.; Eckhardt, H.; Iqbal, Z.; Toth, J.; Baughman, R. H. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 111.

(10) (a) Lemaire, M.; Delabouglise, D.; Garreau, R.; Guy, A.; Roncali, J. *J. Chem. Soc., Chem. Commun.* **1988**, 658. (b) Kotkar, D.; Joshi, V.; Ghosh, P. K. *J. Chem. Soc., Chem. Commun.* **1988**, 917. (c) Roncali, J.; Garreau, R.; Delabouglise, D; Garnier, F.; Lemaire, M. *Synth. Met.* **1989**, *28*, C341. (d) Andersson, M.; Ekeblad, P. O.; Hjertberg, T.; Wennerström, O.; Inganäs, O. *Polym. Commun.* **1991**, *32*, 546. (e) Bouman, M. M.; Havinga, E. E.; Janssen, R. A. J.; Meijer, E. W. *Mol. Cryst. Liq. Cryst.* **1994**, *256*, 439. (f) Bouman, M. M.; Meijer, E. W. *Adv. Mater.* **1995**, *7*, 385. (g) Bidan, G.; Guillerez, S.; Sorokin, V. *Adv. Mater.* **1996**, *8*, 157. (h) Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Christiaans, M. P. T.; Meskers, S. C. J.; Dekkers, H. P. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1996**, *118*, 4908.

(11) Ito, Y.; Ohara, T.; Shima, R.; Suginome, M. *J. Am. Chem. Soc.* **1996**, *118*, 9188 and references cited therein.

(12) (a) Aoki, T.; Shinohara, K.-i.; Kaneko, T.; Oikawa, E. *Macromolecules* **1996**, *29*, 4192. (b) Aoki, T.; Kokai, M.; Shinohara, K.; Oikawa, E. *Chem. Lett.* **1993**, 2009. (c) Kishimoto, Y.; Itou, M.; Miyatake, T.; Ikariya, T.; Noyori, R. *Macromolecules* **1995**, *28*, 6662. (d) Yashima, E.; Nimura, T.; Matsushima, T.; Okamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 9800. (e) Yashima, E.; Matsushima, T.; Okamoto, Y. *J. Am. Chem. Soc.* **1995**, *117*, 11596. (f) Yamaguchi, M.; Omata, K.; Hirama, M. *Chem. Lett.* **1992**, 2261. (g) Moore, J. S.; Gorman, C. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 1704. (h) Ciardelli, F.; Lanzillo, S.; Pieroni, O. *Macromolecules* **1974**, *7*, 174.

(13) (a) Bedworth, P. V.; Tour, J. M. *Macromolecules* **1994**, *27*, 622. (b) Hu, Q.-S.; Vitharana, D.; Liu, G.-Y.; Jain, V.; Wagaman, M. W.; Zhang, L.; Lee, T. R.; Pu, L. *Macromolecules* **1996**, *29*, 1082. (c) Hu, Q.-S.; Vitharana, D.; Liu, G.; Jain, V.; Pu, L. *Macromolecules* **1996**, *29*, 5075. (d) Ma, L.; Hu, Q.-S.; Musick, K. Y.; Vitharana, D.; Wu, C.; Kwan, C. M. S.; Pu, L. *Macromolecules* **1996**, *29*, 5083.

(14) (a) Katz, T. J.; Sudhakar, A.; Teasley, M. F.; Gilbert, A. M.; Geiger, W. E.; Robben, M. P.; Wuensch, M.; Ward, M. D. *J. Am. Chem. Soc.* **1993**, *115*, 3182. (b) Sudhakar, A.; Katz, T. J.; Yang, B.-W. *J. Am. Chem. Soc.* **1986**, *108*, 2790.

(15) Fiesel, R.; Huber, J.; Scherf, U. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2111.

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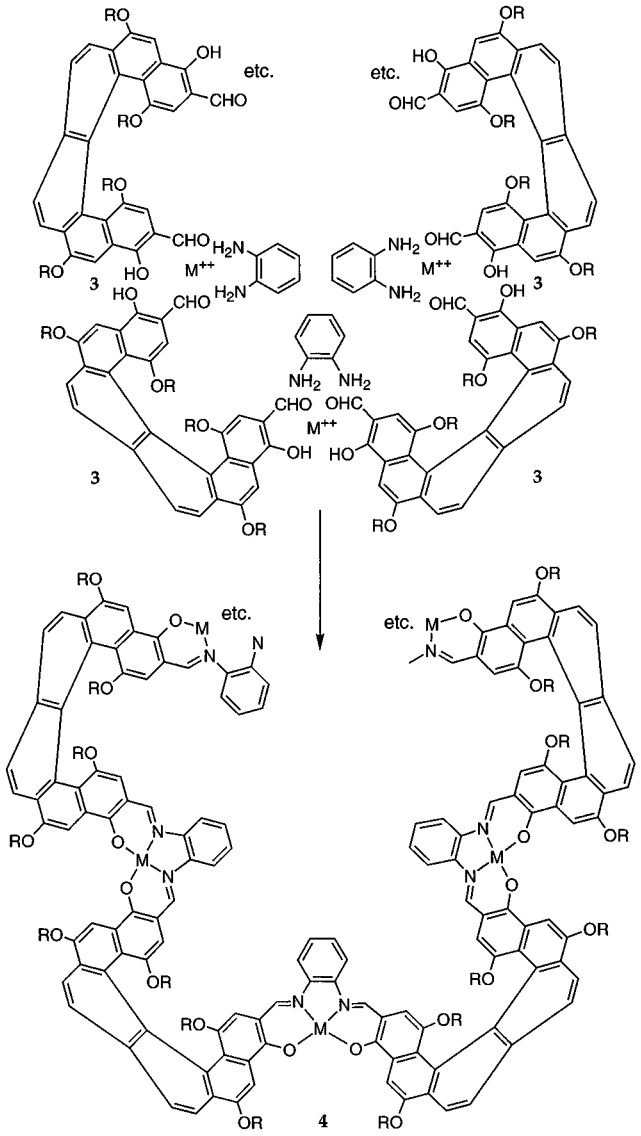
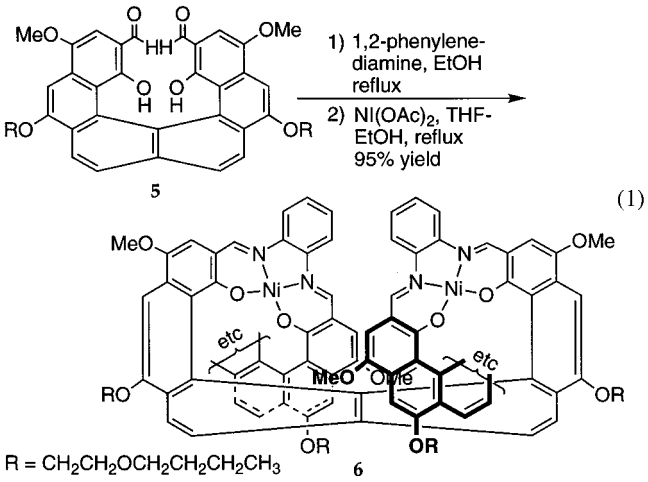
Scheme 1



The plan developed here and illustrated in Scheme 1 conjugatively links derivatives of enantiopure helical quinone **1** by means of a condensation reaction and a coordination reaction with a metal salt. The salophen ligand, which in this scheme is fused to both ends of the helicene backbone, binds strongly to a number of metal ions.[16] Moreover, its linkage (or the linkage of related Schiff base ligands) with metal ions provides the basis for polymers that have been made before.[17] The ones in Scheme 1, like other metal−coordination polymers,[18] should have paths of conjugated double bonds extending from one end of the polymer to the other because the metal ions constrain the p-orbitals of the ligand and the rings they unite to be nearly parallel.[19,20] In addition, the overlap of orbitals on the metals with those on the ligand might enhance electronic delocalization.[21]

The essential task that had to be achieved to test this idea was to find ways to convert **1** into appropriate salicylaldehydes. Described below is a synthesis of the salicylaldehyde in Scheme 1 (structure **3**) and its conversion into three metal salophen polymers (**4a**−**c**, M = Ni, Cu, and Co). In addition, and more significantly because the resulting polymeric structure winds continuously with one helicity, salicylaldehyde **5** was made in which the hydroxyl and aldehyde functions of **3** are relocated. This, when combined with 1,2-phenylenediamine and nickel acetate, gives (as in eq 1) helical polymer **6**. The electronic absorption and circular dichroic spectra of the helical salophen polymers and their precursors are compared.



Results

Although the primary goal was to synthesize **5** and **6**, a way to synthesize **3** and **4** is presented first, for only subsequently was a path to **5** found. The descriptions of the syntheses are followed by evidence for the structures. The chiroptical properties follow.

Synthesis of Optically Active Monomer 3. Structure **1** was chosen as the starting point for the synthesis (Scheme 2) because (a) it can be prepared easily in much larger amounts than other helicenes,[7] (b) because it is very soluble in many solvents, and (c) because the manifold chemistry of quinone functions provides opportunities for a variety of transformations.[22]

(16) (a) Holm, R. H.; Everett, G. W., Jr.; Chakravorty, A. *Prog. Inorg. Chem.* **1966**, *7*, 83. (b) Mahmoud, M. R.; Ibrahim, S. A.; Ismail, N. M. *Monatsh. Chem.* **1985**, *116*, 167. (c) Stronski, I.; Zielinski, A.; Samotus, A.; Stasicka, Z.; Budesinsky, B. *Z. Analyt. Chem.* **1966**, *222*, 14. The value of nickel salophen's stability constant reported in this paper is questioned in the following: (d) Martel, A. E. In *Stability Constants of Metal−Ion Complexes, Supplement No. 1, Part II (Special Publication No. 25)*; The Chemical Society: London, 1971; p 775.

(17) (a) Chen, H.; Cronin, J. A.; Archer, R. D. *Inorg. Chem.* **1995**, *34*, 2306. (b) Chen, H.; Cronin, J. A.; Archer, R. D. *Macromolecules* **1994**, *27*, 2174. (c) Archer, R. D. *Coord. Chem. Rev.* **1993**, *128*, 49. (d) Dewar, M. J. S.; Talati, A. M. *J. Am. Chem. Soc.* **1964**, *86*, 1592.

(18) (a) Pittman, C. U., Jr.; Carraher, C. E., Jr.; Sheats, J. E.; Zeldin, M. In *Inorganic and Metal-Containing Polymeric Materials*; Sheats, J., et al., Eds.; Plenum Press: New York, 1990; p 1. (b) Manners, I. *Adv. Organomet. Chem.* **1995**, *37*, 131. (c) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21. (d) *Inorganic and Organometallic Polymers II*; Wisian-Neilson, P., Allcock, H. R., Wynne, K. J., Eds.; ACS Symposium Series 572; American Chemical Society: Washington, DC, 1994. (e) Chen, C.-T.; Suslick, K. S. *Coord. Chem. Rev.* **1993**, *128*, 293.

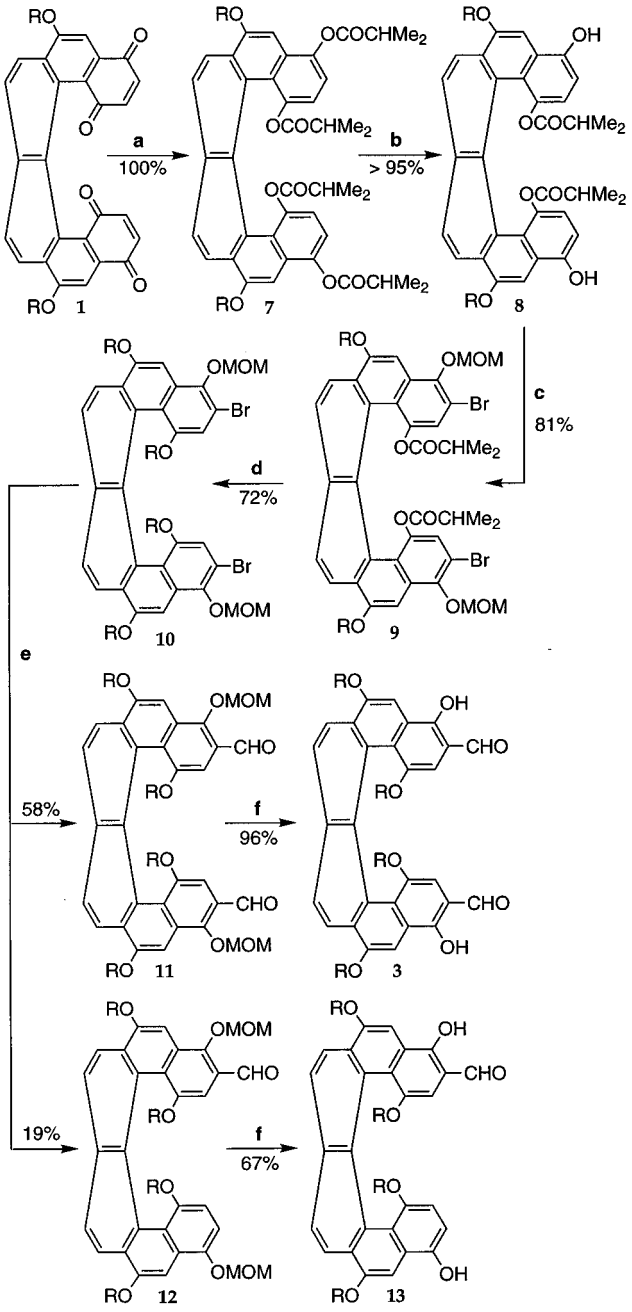
(19) Radha, A.; Seshasayee, M.; Ramalingam, K.; Aravamudan, G. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 1169 and references therein.

(20) The geometries of previously prepared metal−salophen polymers are not appropriate for conjugation to be maintained from one end to another.

(21) However, little evidence of this effect has been found when sought in other molecules. (a) Larin, G. M. *Soviet J. Coord. Chem.* **1992**, *18*, 598. (b) Brill, G.; Musso, H. *Liebigs Ann. Chem.* **1979**, 803. (c) Nazzal, A.; Mueller-Westerhoff, U. T. *Transition Met. Chem.* **1980**, *5*, 318.

(22) (a) *Methoden der Organischen Chemie (Houben Weyl)*; Grundmann, C., Ed.; Georg Thieme Verlag: Stuttgart, 1977; Vol. VII/3a, (b) *The Chemistry of Quinoid Compounds*; Patai, S., Ed.; Wiley: New York, 1977; Part 1. (c) *The Chemistry of Quinoid Compounds*; Patai, S., Rappaport, Z., Eds.; Wiley: New York, 1988; Vol. 2, Parts 1 and 2.

Scheme 2[a]



[a] Reagents and conditions: (a) Zn, $(Me_2NCH_2)_2$, $(i\text{-PrCO})_2O$, DMF; (b) K_2CO_3, MeOH, rt; (c) Br_2, CCl_4-CH_2Cl_2, 0 °C to rt, then MOMCl, $i\text{-Pr}_2NEt$, CH_2Cl_2, reflux; (d) K_2CO_3, $n\text{-BuOCH}_2CH_2OTs$, EtOH, reflux; (e) *n*-BuLi, THF, −78 °C, then DMF, −78 °C to rt; (f) H_2SO_4, HOAc, 60 °C.

Zinc and isobutyric anhydride reduce **1** and esterify the reduction product, giving tetraester **7** in essentially quantitative yield.[23] Again in nearly quantitative yield, potassium carbonate in methanol at room temperature then selectively removes the ester groups on the outer periphery of the ring. It is for this selectivity to be achieved that isobutyrates were chosen as the esters introduced in the preceding step, for while the tetraacetate analogue of **7** was easily prepared, no way could be found to selectively remove a pair of acetates from it. Neither the procedure that converts **7** into **8** nor a variety of others worked. They included the following, and they

(23) This transformation was discovered in our lab by Nikolaos D. Willmore (unpublished results).

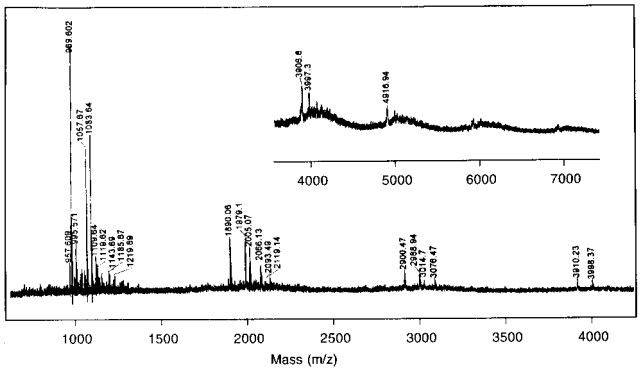


Figure 1. MALDI-TOF mass spectrum of **4a**. The matrix was 2,5-dihydroxybenzoic acid. The inset shows peaks at higher mass when the instrument was operated in linear mode. Otherwise it was operated in reflector mode.

resulted either in complex mixtures (Et_2NH in refluxing benzene for 15 h, $BuNH_2$ in benzene at room temperature for 17 h,[24] or Zn in methanol at room temperature for 21 h[25]) or in no reaction [$(i\text{-Pr})_2NH$ in benzene for 15 h at reflux or $i\text{-PrNH}_2$ in benzene for 5 h at 65 °C]. The exposed phenol functions then made it possible to selectively brominate two positions in the molecule—those ortho to the phenols—in preference to the four positions ortho to ethers. This step worked well, but only after some experimentation. Thus, Br_2 in CH_2Cl_2, either alone at −10 °C or mixed with $t\text{-BuNH}_2$ at −72 °C,[26] gave a mixture of products. However, when the solvent was 3:1 (v/v) CCl_4-CH_2Cl_2 at 0 °C, the results were good.[27] Methoxymethyl chloride (MOMCl) then protected the phenol functional groups. In the expectation that solubility would thereby be enhanced, the remaining isobutyrate esters were replaced by *n*-butoxyethyl ethers. The resulting material (**10**), when combined with *n*-butyllithium in THF at −78 °C, followed by DMF, gave the expected bis-aldehyde **11** in 58% yield, along with a 19% yield of monoaldehyde **12**. The two were separated by flash chromatography, and the MOM groups were removed by treatment with acid. In this way, bis-salicylaldehyde **3** and monosalicylaldehyde **13** were obtained.

Synthesis of the Polymers 4. Of the two procedures for preparing metal−salophen complexes,[16a] combining the bis-salicylaldimine of 1,2-phenylenediamine with metal salts[28] or combining the metal complexes of salicylaldehydes with 1,2-phenylenediamine,[29] only the former procedure succeeded,[30] giving the helical metal complexes easily and in high yields. Thus, refluxing (−)-**3** and 1,2-phenylenediamine in ethanol gave a red solution (presumably of the Schiff base), which, after further reflux with added $Ni(OAc)_2\cdot 4H_2O$ and then purification by

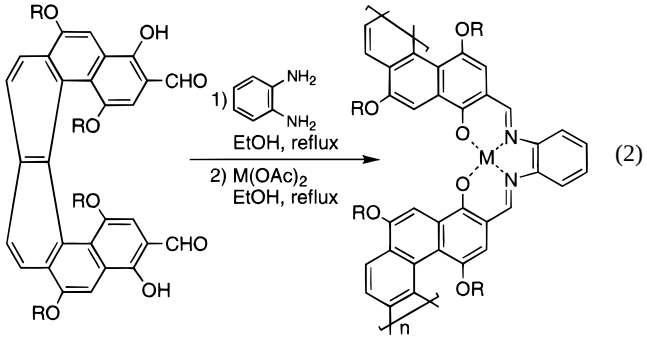
(24) Bell, K. H. *Tetrahedron Lett.* **1986**, *27*, 2263.
(25) González, A. G.; Jorge, Z. D.; López Dorta, H. *Tetrahedron Lett.* **1981**, *22*, 335.
(26) Pearson, D. E.; Wysong, R. D.; Breder, C. V. *J. Org. Chem.* **1967**, *32*, 2358.
(27) Br_2 in HOAc at room temperature also gave good results.
(28) Pfeiffer, P.; Hesse, T.; Pfitzner, H.; Scholl, W.; Thielert, H. *J. Prakt. Chem.* **1937**, *149*, 217.
(29) Pfeiffer, P.; Breith, E.; Lübbe, E.; Tsumaki, T. *Liebigs Ann. Chem.* **1933**, *503*, 84.
(30) Although the latter procedure was recommended a number of years ago (ref 16a), it failed for the synthesis of the helical nickel salophen because the required nickel complex of salicylaldehyde **3** could not be prepared. A yellow alcoholic solution of (*M*)-**3** when combined with $Ni(OAc)_2\cdot 4H_2O$ immediately turned red, but the solution remained clear, and attempts to isolate a nickel complex by extraction with CH_2Cl_2 (after aqueous workup) returned the starting material, (*M*)-**3**.

Table 1. Analysis of the Mass Spectrum of 4a in Figure 1[a]

C	H	N	Ni	O	calcd	found	diff	assignt
52	64			12	881.06			**3**
58	68	2		11	969.17	969.6	0.4	**s-b**
58	74			14	995.20	995.6	0.4	**s-x**
64	72	4		10	1057.28	1057.7	0.4	**b-b**
64	78	2		13	1083.31	1083.6	0.3	**b-x**
64	84			16	1109.34	1109.6	0.3	**x-x**
110	130	2	1	22	1890.90	1890.1	−0.8	**s-Ni-s**
116	134	4	1	21	1979.01	1979.1	0.1	**s-Ni-b**
116	140	2	1	24	2005.05	2005.1	0.0	**s-Ni-x**
122	138	6	1	20	2067.12	2066.1	−1.0	**b-Ni-b**
122	144	4	1	23	2093.16	2093.5	0.3	**b-Ni-x**
122	150	2	1	26	2119.19	2119.1	−0.1	**x-Ni-x**
168	196	4	2	32	2900.75	2900.5	−0.3	**s-Ni-Ni-s**
174	200	6	2	31	2988.86	2988.4	−0.5	**s-Ni-Ni-b**
174	206	4	2	34	3014.89	3014.7	−0.2	**s-Ni-Ni-x**
180	204	8	2	30	3076.97	3078.5	1.5	**b-Ni-Ni-b**
226	262	6	3	42	3910.59	3910.2	−0.4	**s-Ni-Ni-Ni-s**
232	266	8	3	41	3998.70	3998.4	−0.3	**s-Ni-Ni-Ni-b**
284	328	8	4	52	4920.44	4916.9	−3.5	**s-Ni-Ni-Ni-Ni-s**

[a] The mass calculated for the indicated formula is followed by the mass found, the difference between the two, and the assignment. For the symbols see the text.

n-hexane-induced precipitation from CH_2Cl_2, gave (−)-**4a**, a black solid, in 98% yield (eq 2). The same

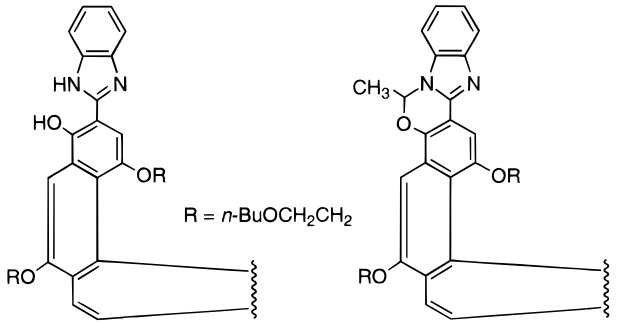


(2)

procedure, but with other metal acetates, gave the Cu-analogue **4b** and the Co-analogue **4c**. All three are very soluble in common organic solvents, including CH_2Cl_2, $CHCl_3$, and THF.

Characterization of Polymers 4a−c. The best evidence that eq 2 proceeds as shown is provided by the TOF mass spectrum of the nickel-containing product in a matrix of 2,5-dihydroxybenzoic acid after matrix-assisted laser desorption−ionization (MALDI).[31] Figure 1 shows that the spectrum consists of clusters of peaks whose first members (at *m*/*z* 1890, 2900, 3910, and 4917) are separated by 1010 Da, exactly the mass of the repeat unit ($C_{58}H_{66}N_2NiO_{10}$) of structure **4a**. Such a spectrum would be expected for a sample comprised of oligomers.

The MALDI-TOF mass spectrum identifies three different end groups. One is the salicylaldehyde function of the starting material. Another has a mass 88 Da greater and is likely to be the benzimidazole **14** formed by the condensation of the aldehyde with 1,2-phenylenediamine followed by oxidation.[32] The third, and seemingly less frequent end group, has a mass 114 Da heavier than the salicylaldehyde. We are unsure what this is but speculate that it might be **15**.[33] Table 1 shows how these three end groups—the salicylaldehyde (symbolized **s**), the benzimidazole (symbolized **b**), and the unknown group with the mass of **15** (symbolized **x**)—and the nickel salophen repeat unit in **4a** (symbolized **Ni**) account for the peaks in the mass spectrum in Figure 1.



The ^{1}H NMR, ^{13}C NMR, and IR spectra of **4a** all evidence the absence of the CHO and OH functions of the starting salicylaldehyde (**3**). The detection limits in the ^{1}H NMR spectrum are such that if free salicylaldehydes capped the polymer at both ends, the intensities of the noise and of any peaks attributable to the CHO (at δ 9.66 ppm in **3**) and OH (at δ 11.96 ppm in **3**) would imply that the number average chain had more than nine nickel atoms, more than 11 helicene rings, and a molecular weight $>10^4$. If a free salicylaldehyde capped only one end of each polymer, M_n would be half as large.

The ^{1}H NMR spectrum of polymer **4a** (displayed, as is the spectrum of **3**, in the Supporting Information) exhibits broad peaks for the resonances of the side chains, at the same positions as these appear in the spectrum of **3**, and very broad peaks for the resonances of the aromatic protons, including some at the chemical shifts of the two central rings of helicene **3** (the doublets at δ 8.6 and 8.1 ppm) and of the high-field singlet (at δ 5.93 ppm) in the spectrum of **3**, assigned to the lone aromatic hydrogen of the outermost ring. The other singlet in the spectrum of **3**, assigned to the proton on the second ring, is shifted in the spectrum of **4a** to higher frequency, seemingly by 0.4 ppm (from δ 7.71 to ca. 8.2 ppm).

The ^{13}C NMR spectrum of **4a** is very similar to that of its precursor, **3** (Figure 2). In particular, the peaks attributable to the side chains, at δ <74 ppm, are almost identical. The other signals are all considerably broader in **4a** than in **3**, but generally the chemical shifts are similar. Among the differences between the two spectra, all of which are accounted for by the differences between the structures of **4a** and **3**, are these: (1) the absence, discussed above, of a carbonyl resonance, which in the spectrum of **3** appears at 195.6 ppm; (2) the presence in the spectrum of **4a** of resonances at 162, 151, and 143 ppm similar to the three resonances at lowest field in the spectrum of the parent nickel salophen (166.4, 154.2, and 142.7 ppm), attributable to the resonances of its *C*−O, *C*H=N, and CH=N-*C*;[34] and (3) the shift to lower field of the resonance that in **3** is found at 98 ppm

(31) Hellenkamp, F.; Karas, M.; Beavis, R. C.; Chait, B. T. *Anal. Chem.* **1991**, *63*, 1193A.

(32) (a)Wright, J. B. *Chem. Rev.* **1951**, *48*, 397. (b) Preston, P. N. In *Benzimidazoles and Congeneric Tricyclic Compounds*; Preston, P. N., Ed.; Wiley: New York, 1981; Part 1, Chapter 1.

(33) Of 6*H*-benzimidazo[1,2-*c*][1,3]benzoxazines, only the parent appears to be described, and it was not synthesized from formaldehyde (Mahesh, V. K.; Maheswari, M.; Sharma, R.; Sharma, R. *Can. J. Chem.* **1985**, *63*, 632).

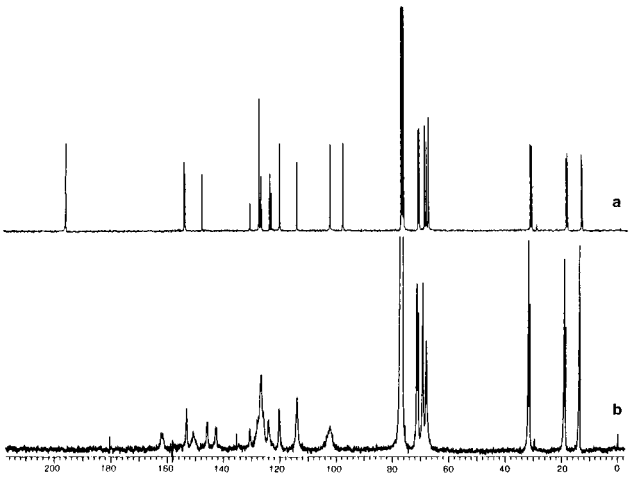
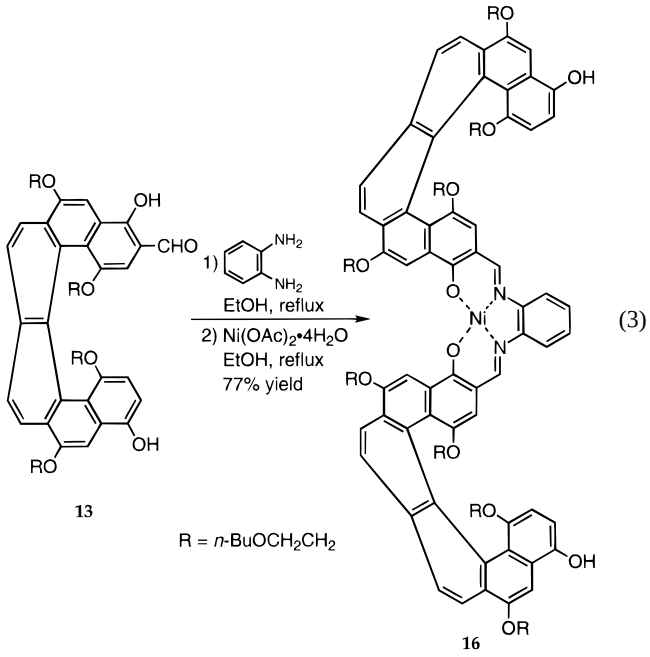


Figure 2. 75 MHz ^{13}C NMR spectra of (a) **3** and (b) **4a**, both in $CDCl_3$.

(assigned to the unsubstituted carbon in the second ring from the end, β to an alkoxyl)[35] when, as in **4a**, the resonating carbon is brought into the proximity of another ring system. The infrared spectrum of **4a** (see below) shows a peak at 1597 cm^{-1} that is similar to one, associated with the CH=N stretch, in the spectrum of the parent nickel salophen.[36] The analyses for Ni, N, and H in **4a** were largely satisfactory, but as as in the case of other highly unsaturated polymers, the analysis for carbon gave figures that were low.[37]

Although, as shown above, it was possible to analyze **4a** by mass spectrometry, the equipment available to us at first could not analyze molecular weights that high. At the time it was significant that a dimer analogue, **16**, prepared as shown in eq 3 from the monosalicylaldehyde, **13**, exhibited the expected base peak at mass M + 1 (1836).[38] It is unfortunate that the amount of this material that we could prepare easily was too little and the ^{13}C NMR spectrum too broad[39] to be analyzed and compared to that of **4a**. The ^1H NMR spectrum of **16**, although broad, is similar to that of **4a**, discussed above. The spectra are compared in the Supporting Information.

The Co- and Cu-analogues of **4a** (**4b** and **4c**) have an odd number of electrons. They must therefore be paramagnetic, and accordingly, their ^1H NMR spectra are even broader than that of **4a**, particularly in the aromatic region of the spectrum. In the spectrum of the Cu-complex (**4b**), ca. five broad peaks can be seen between δ 7.0 and 9.3 ppm, while in the spectrum of the Co-complex (**4c**), only two very broad signals at ca. δ 8.6 and 8.0 ppm were discernible in the noise. However, at δ <4.9 ppm both spectra show the expected resonances for



(3)

the side chains, although the resonances in the spectrum of **4c** are particularly broad.

Evidence that the structures of **4**−**c** and **16** are similar is provided by their IR spectra, which, as Figure 3 shows, are almost identical. The only notable difference is that, as expected, the spectrum of **16**, which unlike the other structures has two free OH groups, shows an OH stretch at 3500 cm^{-1}.

Synthesis of Optically Active Monomer 5 and Polymer 6. Salicylaldehyde **5** was synthesized as outlined in Scheme 3 starting, as in the case of salicylaldehyde **3** described above, from enantiopure helical bisquinone **1**. The key step is the addition of HBr that converts **1** into **17**, a transformation analogous to the conversion of 6-methoxy-1,4-naphthoquinone into its 2-bromo derivative by HBr in propanoic acid and air.[40] However, while the oxidant used in that procedure, air, proved unsatisfactory in the preparation of **17**, chloranil was effective. Further analogy pointing to the helicene quinone's inside carbon (C-2) as the position to which the nucleophile (Br) attaches is provided by the observation that **1** itself is converted by prolinol into a nitrogen analogue of **17**.[41] And *evidence* that the Br is attached as in structure **17** is provided by the demonstration that **17** differs from its isomer, **23**, synthesized from **8** in Scheme 2 according to eq 4.

It is notable, in view of the point (made above in connection with the synthesis in Scheme 2) that no way could be found to remove selectively two of the ester functions from the acetate-analogue of **7**, that there is no difficulty removing the outer two acetates from **18**, which differs from the previous ester only by the two added bromines. Thereby **19** is obtained. The other steps to **5** in Scheme 3 are straightforward. This product (**5**) is transformed into **6** according to eq 1, that is, in exactly the same way that **3** is transformed into **4a** (eq 2). Moreover, **6** can be purified in the same way as **4a**. The yield was 95%.

(34) Costes, J. P.; Dominguez-Vera, J. M.; Laurent, J. P. *Polyhedron* **1995**, *14*, 2179.

(35) Ewing, D. F. *Org. Magn. Reson.* **1979**, *12*, 499.

(36) The parent nickel salophen in KBr shows the peak at 1604 cm^{-1} (according to the measurement of David A. Nickols in our lab). Bands at ca. 1620 and 1220 cm^{-1} are described as characteristic of salophen and its complexes: (a) Reference 16b. (b) Nagar, R.; Sharma, R. C.; Parashar, R. K. *Spectrochim. Acta* **1990**, *46A*, 401.

(37) Carbon analyses were found to be too low: (a) by 3.3, 4.5, and 4.9% (absolute) for three such polymers in: Lamba, J. J. S.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11723. (b) By 1.7% (absolute) for two such polymers in: Goldfinger, M. B.; Swager, T. M. *J. Am. Chem. Soc.* **1994**, *116*, 7895. (c) By 2.9% (absolute) for 1 such polymer in ref 13a. (d) By 1.6, 1.8, and 2.3% (absolute) for three such polymers in ref 13d.

(38) FAB from an *m*-nitrobenzyl alcohol matrix.

(39) Possibly this is because of the large size of the molecule or because the configuration at Ni is not perfectly square-planar (see ref 16a).

(40) Cameron, D. W.; Feutrill, G. I.; Griffiths, P. G. *Aust. J. Chem.* **1981**, *34*, 1513.

(41) The structure of the adduct, prepared by Willmore (ref 7b), was determined by Prof. A. L. Rheingold (unpublished results).

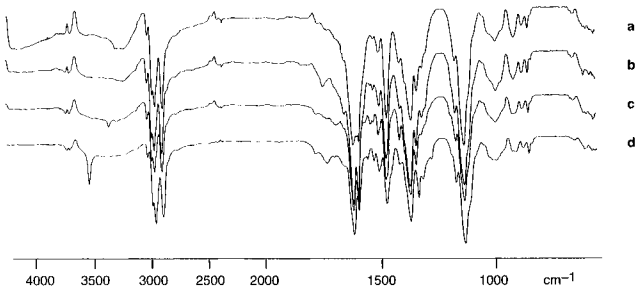
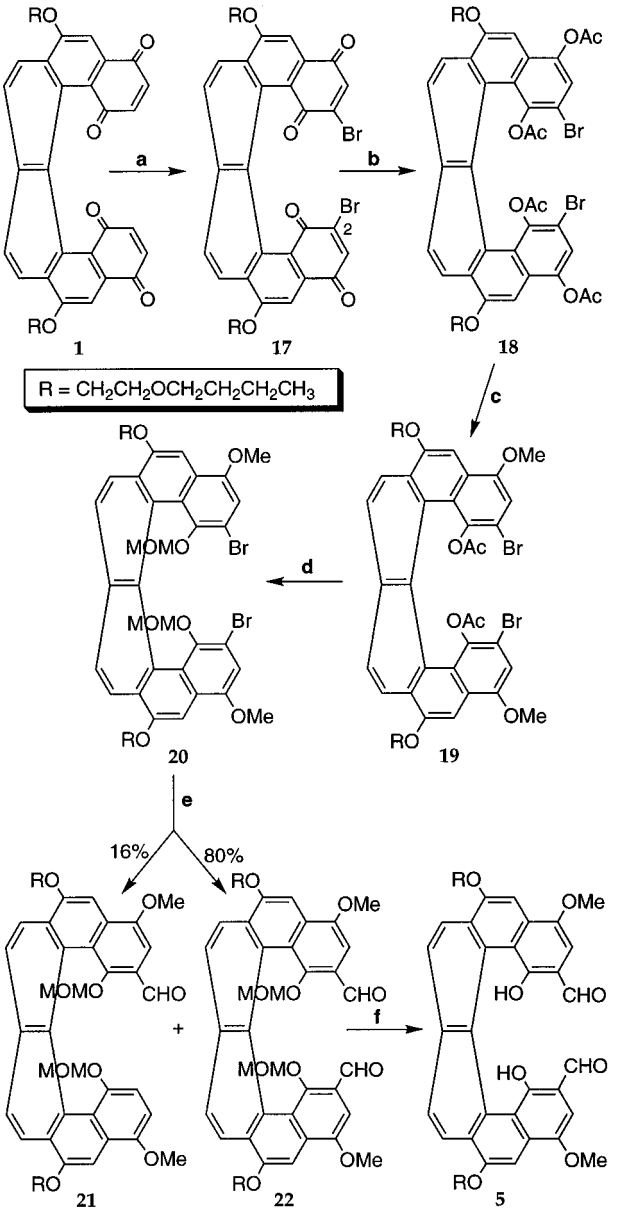


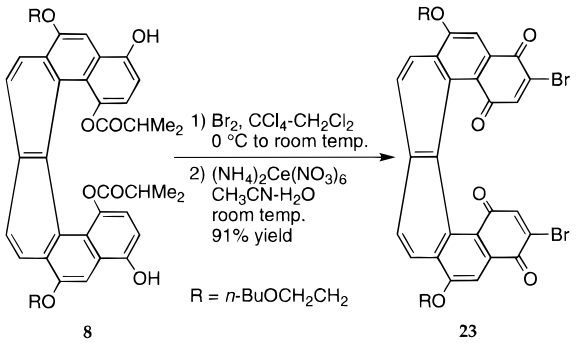
Figure 3. Infrared spectra of (a) **4c**, (b) **4b**, (c) **4a**, and (d) **16** in $CHCl_3$.

Scheme 3[a]



[a] Reagents and conditions: (a) HBr in $EtCO_2H$, then chloranil (25−30%); (b) $Na_2S_2O_4$, *n*-Bu_4NBr, H_2O−CH_2Cl_2, then Ac_2O, Et_3N, CH_2Cl_2 (78−82%); (c) K_2CO_3, MeOH, 25 °C, then MeI, K_2CO_3, acetone, reflux (81%); (d) KO-*t*-Bu, THF, 25 °C, then $MeOCH_2Cl$ (MOMCl), THF, 25 °C (92%); (e) *n*-BuLi, THF, −78 °C, then Me_2NCHO, −78 to 25 °C; (f) H_2SO_4, HOAc, H_2O, 60 °C (96%).

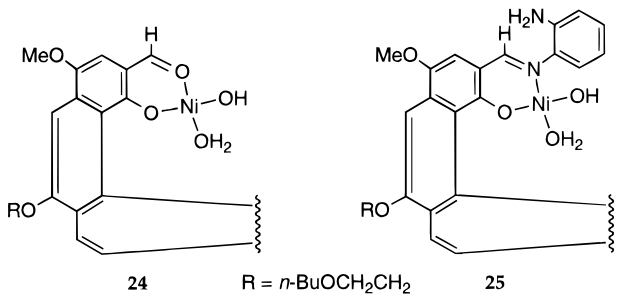
Evidence for the Structure of 6. The ^1H NMR, ^{13}C NMR, and IR spectra all show that only tiny amounts of CHOs can be present, and the IR spectrum shows that



(4)

the amounts of any OH groups are also insignificant. The MALDI-TOF mass spectrum (Figure 4 and Table 2),[31] measured using a matrix of 2,5-dihydroxybenzoic acid, consists of two peaks that repeat with decreasing intensity at intervals of 837.6 ± 0.2 Da. This figure is exactly the mass (837.6) of structure **6**'s repeating unit ($C_{48}H_{46}N_2NiO_8$). Ten such pairs can be seen in the figure, identifying oligomers up to decamers.

The mass spectrum also identifies the end-groups. The repeating motif of two peaks distinguishes two series of polymers. The simplest member of one series has the mass of **5** plus $NiO{\cdot}H_2O$, implying that one end has the *o*-hydroxybenzaldehyde functionality of **5**, whereas the other most likely looks like **24**. The second series has the additional mass (90.1) of one phenylenediamine less water. It is probably a Schiff base derivative of the aldehyde and 1,2-phenylenediamine, possibly with structure **25**, and it seems to be predominant.[42] We note incidentally that both in the MALDI mass spectrum of **6** in Figure 4 and of **4a** in Figure 1 the ions observed are those corresponding to neutral species that have lost an electron rather than added a proton.



The ^1H NMR spectrum of a $CDCl_3$ solution (displayed in the Supporting Information) shows four clearly defined broad peaks at δ 8.3−6.6, 6.4−5.0, 4.7−2.3, and 2.0−0.6 ppm, whose intensity ratios, 4.0:3.0:8.3:7.7, are appropriate for hydrogens at six aromatic positions and one CH=N, at nine aliphatics next to oxygen, and at seven other aliphatics. The positions of these resonances are, with only reasonable exceptions, shifted upfield by ca. 1 ppm from their positions in the spectra of **5** and of nickel salophen itself. The exceptions are the resonances of the outermost portions of the side chains, the propyl resonances, which are displaced from their positions in the spectrum of **5** by <0.2 ppm. Because the large shifts are

(42) This is implied by the elemental analysis for nitrogen. Anal. Calcd for $C_{378}H_{362}N_{14}Ni_8O_{68}$ (capping as in **24**, MW 6664): C, 68.12; H, 5.57; N, 2.94; Ni 6.95. Found: C, 64.51; H, 5.24; N, 3.89; Ni, 7.99. Anal. Calcd for $C_{384}H_{374}N_{16}Ni_8O_{67}$ (capping possibly as in **25**, MW 6755): C, 68.28; H, 5.58; N, 3.32; Ni, 6.95. (CHN analyses were by Desert Analytics, Tucson, AZ; the Ni analysis by Galbraith Laboratories, Knoxville, TN.) The comment in ref 37 about the carbon analyses is relevant.

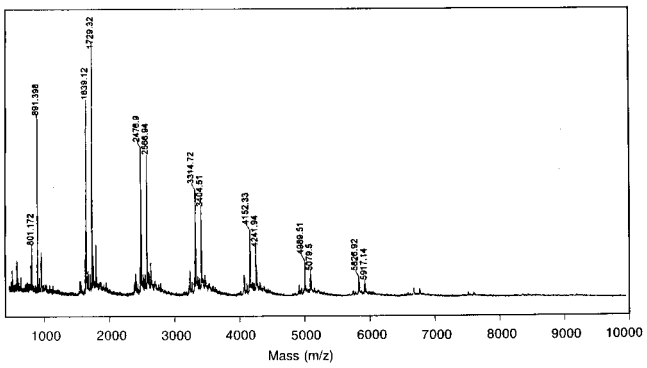


Figure 4. MALDI-TOF mass spectrum of **6**. The matrix was 2,5-dihydroxybenzoic acid, and the instrument was operated in linear mode.

Table 2. Analysis of the Mass Spectrum of 6 in Figure 4[a]

C	H	N	Ni	O	calcd	found	calcd − found	diff 1	diff 2
42	46	0	1	12	801.501	801.17	−0.3		
48	52	2	1	11	891.627	891.40	−0.2	90.23	
90	92	2	2	20	1639.082	1639.12	0.04		837.95
96	98	4	2	19	1729.208	1729.32	0.11	90.2	837.92
138	138	4	3	28	2476.663	2476.9	0.2		837.78
144	144	6	3	27	2566.789	2566.94	0.15	90.04	837.62
186	184	6	4	36	3314.244	3314.72	0.5		837.82
192	190	8	4	35	3404.370	3404.51	0.14	89.79	837.57
234	230	8	5	44	4151.825	4152.33	0.5		837.61
240	236	10	5	43	4241.950	4241.94	−0.01	89.61	837.43
282	276	10	6	52	4989.405	4989.51	0.10		837.18
288	282	12	6	51	5079.531	5079.50	−0.03	89.99	837.56
330	322	12	7	60	5826.986	5826.92	−0.07		837.41
336	328	14	7	59	5917.112	5917.14	0.03	90.22	837.64
average								90.0	837.6
standard deviation								0.2	0.2

[a] The mass calculated for the formula indicated is followed by the mass found and the difference between the two. It is followed by the difference between an entry in the found column and the one directly above (diff 1) and the difference between an entry in the found column and the one two above (diff 2).

only to higher fields, they cannot be attributed to contact with unpaired spins.[43] They are most likely due to electron currents in nearby rings. The resonances are likely to be broad because of the solution's viscosity. A small but prominent pair of resonances in the ^{1}H NMR spectrum of the oligomers, at δ 4.6 and 4.5 ppm, at lower fields than the other OCH_2 resonances and at a position characteristic of the hydrogens on one of the OCH_2 groups in precursor **5** (undoubtedly the one closest to the benzene rings), suggests that the number average molecular weight is ca. 7000.[44]

This accords with $M_n \approx 7400$ according to GPC analysis of a solution in THF and the assumption that a published correction applies that relates the weights of certain rigid rod polymers and polystyrenes.[45,46] The chromatogram, analyzed by monitoring absorption at 254 nm, is bimodal. There is a large peak, with $M_n = 29000$ (corrected, $M_w/M_n = 8.3$), and one 1/9th as large, with $M_n = 1000$ (corrected, $M_w/M_n = 1.2$).

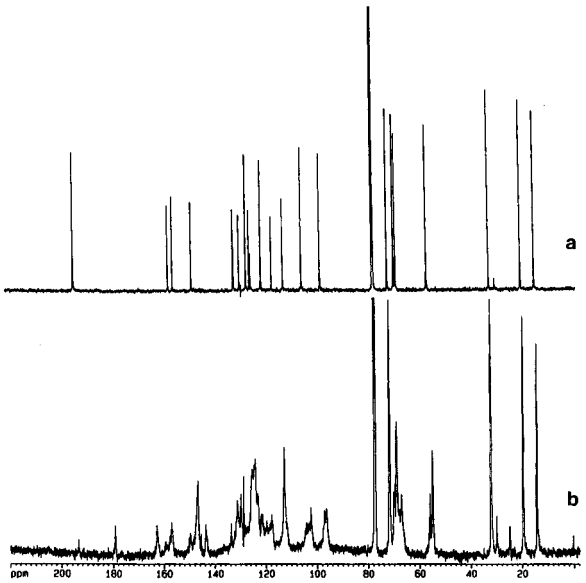


Figure 5. 125 MHz ^{13}C NMR spectra of (a) **5** and (b) **6**, both in $CDCl_3$.

In the ^{13}C NMR spectrum (Figure 5, measured using a solution in $CDCl_3$), most of the peaks are similar to those in the spectrum (also displayed in Figure 5) of the precursor **5**. Peaks that are attributable to parts of the salophen structure are also seen, at δ 163 and 143 ppm, as in the spectrum of **4a**, mentioned above. The peak assigned to the *C*H=N in **4a**, at 152 ppm, seems in **6** to be at 147 ppm, not unreasonable considering that in **6**, although not in **4a**, this carbon should be in the shielding region of the outer rings of the helicene to which it is attached.[47] The peaks in the aromatic region of the spectrum are broad and multiple, expected both because the material is a mixture of oligomers and because in any one oligomer some carbons are nearer the ends while others are nearer the middle.

The infrared spectrum, determined using a sample in KBr, shows a peak at 1596 cm^{-1}, similar to one discussed above in the spectra of **4a** and the parent nickel salophen, attributed to the CH=N stretch.[36]

UV and CD Spectra. The UV and CD spectra of the precursors of the two polymers, the bis-salicylaldehydes **3** and **5**, and of the nickel salophen polymers themselves (**4a** and **6**) are displayed in Figures 6 and 7. The CD spectrum of the nickel dimer **16** and its precursor **13** are displayed in Figure 8. The CD and UV spectra of the copper and cobalt polymers (**4b** and **4c**) are shown in Figure 9.

Discussion

The two nickel salophen polymers **4a** and **6** were prepared from opposite enantiomers of **1**, **4a** from (*P*)-**1** and **6** from (*M*)-**1**. Accordingly, it seems appropriate, as seen in Figure 6, that the circular dichroisms (CDs) of their bis-salicylaldehyde precursors (**3** and **5**) are almost all of opposite sign. However, the CD spectra of the nickel salophen polymers themselves appear remarkably

(43) (a) Eaton, D. R.; Phillips, W. D.; Caldwell, D. J. *J. Am. Chem. Soc.* **1963**, *85*, 397. (b) Reference 16a.

(44) If the distinction of the OCH_2s that give rise to this resonance in the oligomers is their location on the outer end of the caps, where they are not flanked by an adjoining helicene (and there is one such group on the cap at each end), the intensity (0.24 protons/[6]helicene unit) implies that the average chain contains 8.3 helicene units. If both $ArOCH_2$ groups at each end gave rise to this resonance, the average molecule would be twice as large. M_n would be ca. 14 000.

(45) Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem.* **1994**, *106*, 1445; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1360.

(46) Also see (a) ref 13d. (b) Yamamoto, T.; Takagi, T.; Kizu, K.; Maruyama, T.; Kubota, K.; Kanbara, H.; Kurihara, T.; Kaino, T. *J. Chem. Soc., Chem. Commun.* **1993**, 797.

(47) Similarly, the aldehyde carbon in **5** (193.7 ppm) is somewhat more shielded than in **3** (195.6 ppm).

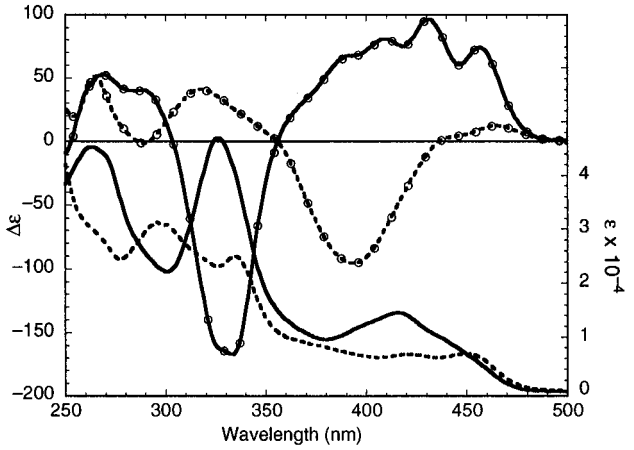


Figure 6. UV (ordinate on the right) and CD (ordinate on the left) spectra of bis-salicylaldehydes **3** (- - -, 1.6×10^{-5} M, in $CHCl_3$) and **5** (—, 2.4×10^{-5} M, in CH_2Cl_2). The CD spectra are marked by circles.

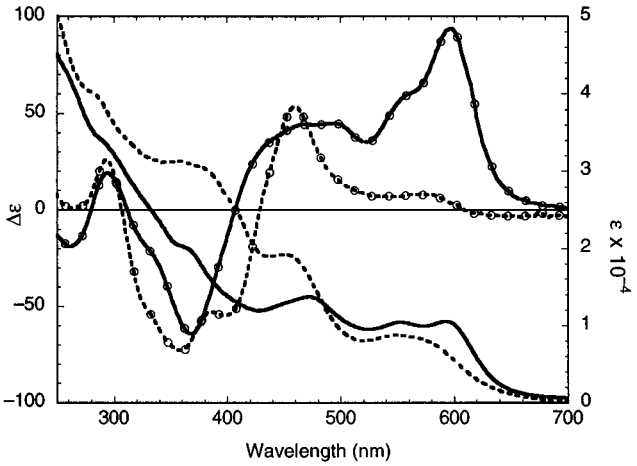


Figure 7. UV (ordinate on the right) and CD (ordinate on the left) spectra of polymers **4a** (- - -, average of two spectra: 5.6×10^{-6} M and 4.0×10^{-5} M, in $CHCl_3$) and **6** (—, 3.1×10^{-5} M, in CH_2Cl_2). The CD spectra are marked by circles.

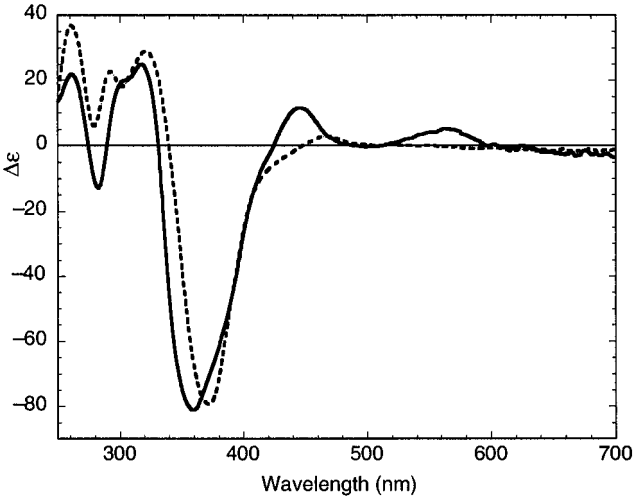


Figure 8. CD spectra of nickel dimer **16** (—, 9.6×10^{-6} M, in $CHCl_3$) and its precursor, **13** (- - -, 1.8×10^{-5} M, in $CHCl_3$).

similar (Figure 7). In particular, the signs of the CD peaks at longest wavelength are the same. This is appropriate, for according to the analysis of Bosnich[48] and Di Bella *et al.*[49] and the analogies provided by the spectra

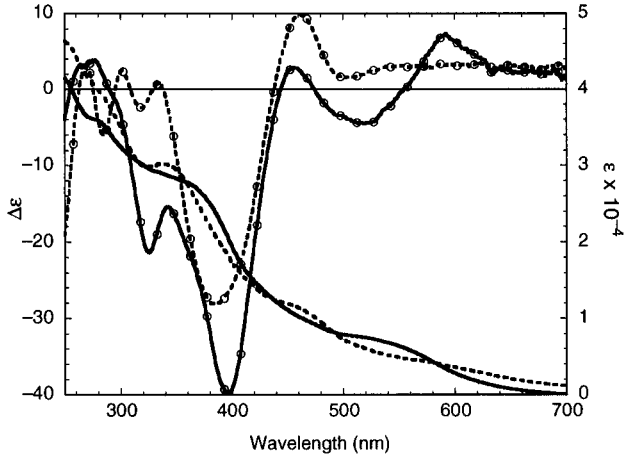
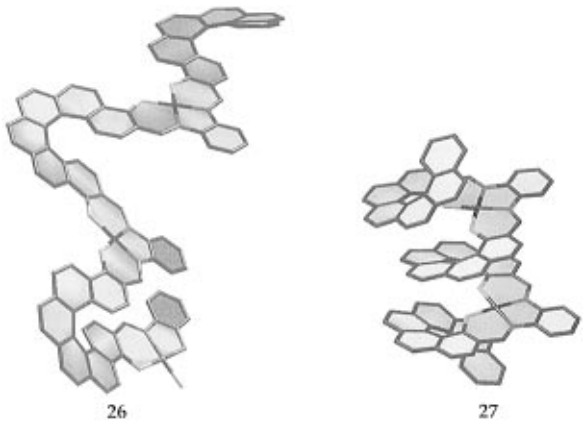


Figure 9. UV (ordinate on the right) and CD (ordinate on the left) spectra of Cu—polymer **4b** (—, 1.6×10^{-5} M, in $CHCl_3$) and Co-polymer **4c** (- - -, 1.9×10^{-5} M, in CH_2Cl_2). The CD spectra are marked by circles.

of nickel salophen[16b,48,50] and of related nickel—Schiff base complexes,[34,48,51] these peaks are associated with the nickel salophen portion of the molecules. As structures **26** and **27** make clear—these are three-dimensional representations of **4a** and **6**, respectively, with side chains removed to increase clarity—in **6** (≡ **27**) the helix winds to the right both in the helicene and the salophen portions of the molecule, but in **4a** (≡ **26**), when the helicene moiety winds to the left, the salophen winds to the right. Thus, in both **4a** and **6** the helix winds through the salophen to the right.



The magnitudes of the two polymers' circular dichroisms at longest wavelengths differ significantly. These CDs are recorded in Figure 7 on the basis of the molar concentrations of the polymers' monomeric subunits calculated under the assumption that the molecular weights are infinite. The CDs in Figure 7 of the polymer that winds in one direction (**6**) are much larger than those of the one that winds alternately to the left and to the right (**4a**). They are also ca. 30 times as large as those of simpler nickel Schiff base complexes studied previously.[34,48,51a,b] Although the positions of the UV—vis

(48) Bosnich, B. *J. Am. Chem. Soc.* **1968**, *90*, 627.
(49) Di Bella, S.; Fragalà, I.; Ledoux, I.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 9481.
(50) Crawford, S. M. *Spectrochim. Acta* **1963**, *19*, 255.
(51) (a) Pasini, A.; Gullotti, M.; Ugo, R. *J. Chem. Soc., Dalton Trans.* **1977**, 346. (b) Downing, R. S.; Urbach, F. L. *J. Am. Chem. Soc.* **1970**, *92*, 5861. (c) Di Bella, S.; Fragalà, I.; Ledoux, I.; Diaz-Garcia, M. A.; Lacroix, P. G.; Marks, T. J. *Chem. Mater.* **1994**, *6*, 881.

absorption maxima at longest wavelength (594 nm in the spectra of **6** and ca. 578 nm in the spectra of **4a**) are similar to those in the spectra of nickel salophen (absorption maxima at ca. 580 nm in $CHCl_3$,[50] 572 nm in DMF[16b]) and in the spectra of other nickel−Schiff base complexes,[34,48,49,51] in all of which they have been assigned to d-d transitions, the intensities are ca. 60 times larger. Accordingly, we assign the peaks to "metal-to-ligand" charge-transfer bands that, because the energies of the HOMOs are raised by conjugation either with the other helicene rings or with the electron-donating substituents, have been shifted to longer wavelength by 98−114 nm from the position (480 nm) in the spectrum of the parent nickel salophen.[48,49]

The CDs at shorter wavelengths, likely to be associated with $\pi \rightarrow \pi^*$ transitions of the helicene skeleton, appear similar in the precursor bis-salicylaldehyde and the nickel salophen arising from it. This is seen in Figure 8, which compares the CD spectra of the nickel salophen dimer **16** and its precursor, **13**. (For the dimer, the concentration was measured as the molarity of the helicene moiety—that is, half the molarity of the dimer.) The corresponding polymer's CD spectrum (that of **4a** in Figure 7) is somewhat similar to that of the dimer and to that of the precursor of the polymer, **3**. However, at wavelengths below ca. 425 nm, the spectra of the copper and cobalt polymers **4b** and **4c** (Figure 9) resemble, even more than the nickel analogue, the CD spectrum of this bis-salicylaldehyde precursor (Figure 6). Otherwise, the CD spectra of the copper and cobalt materials are similar to the spectrum of the nickel analogue, **4a**, just as the electronic spectra of other cobalt−, nickel−, and copper−Schiff base complexes are similar.[52] The CD spectrum (Figure 7) of **6**, the nickel salophen polymer that winds continuously in only one direction, appears to be similar to the spectrum of the polymer's precursor (**5** in Figure 6), but displaced to longer wavelengths by ca. 34 nm, presumably by the increased conjugation.

In the CD spectra of the two bis-salicylaldehyde precursors (Figure 6), whose helical skeletons wind in opposite direction, the peaks at longest wavelength are likely to be associated with the salicylaldehydes' $n \rightarrow \pi^*$ transitions. Those peaks are of the same sign in both spectra, which is appropriate, for when viewed from a point along the axis of a helicene, the orientation of a salicylaldehyde fused to the helicene's positions 1 and 2 is the reverse of a salicylaldehyde fused to positions 4 and 3. But the orientation of the two salicylaldehydes would be the same if the transposition were accompanied by an inversion of the helix's chirality.

Conclusions

Helical conjugated polymers can be made by condensing helicene bis-salicylaldehydes with 1,2-phenylenediamine and nickel, copper, and cobalt acetates. The circular dichroisms of absorptions associated with the metal−ligand moieties are very large.

Experimental Section

THF was distilled from sodium/benzophenone ketyl and CH_2Cl_2 and Et_3N from CaH_2. TMEDA was dried over KOH. Anhydrous DMF, purchased from Aldrich Chemical Co., was dried under argon over 4 Å molecular sieves. Anhydrous diisopropylethylamine, HBr (30%) in acetic acid, and 1 M KO-*t*-Bu in THF were used as purchased from Aldrich. The matrix for all FAB mass spectra was *m*-nitrobenzyl alcohol. Flash chromatography was performed on 32−63 μm silica gel from ICN Pharmaceuticals. Specific rotations were measured at room temperature using solutions in $CHCl_3$.

Reductive Esterification of (*M*)-1. Preparation of (*M*)-7.[23] Hexahelicene bisquinone (*M*)-(−)-**1** (1.00 g, 1.61 mmol)[7] was added to a stirred mixture under argon of Zn powder (3.20 g, 48.9 mmol), dry DMF (6.5 mL), TMEDA (1.94 mL, 12.8 mmol), and isobutyric anhydride (2.15 mL, 13.0 mmol) in a flame-dried two-necked round-bottomed flask that was cooled to 0 °C. After being stirred at 0 °C for 1 h and then at room temperature for 15 h, the mixture was diluted with 10 mL of THF and filtered through a pad of Celite (which was then washed with THF). The solution was then stirred for 1 h with a mixture of water (1.5 mL) and triethylamine (2 mL) and, after 10 more mL of water had been added, was extracted with CH_2Cl_2 (3 × 20 mL). Washing with 10 mL of saturated Na_2CO_3 solution, 10 mL of dil HCl, 10 mL of H_2O, and 10 mL of brine, drying with Na_2SO_4, and evaporation, gave 1.45 g of a yellow solid (100% yield): mp 216−217 °C (benzene−hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, 2 H, J = 8.3 Hz), 8.01 (d, 2 H, 8.3 Hz), 7.15 (s, 2 H), 6.91 (d, 2 H, J = 8.2 Hz), 6.28 (d, 2 H, J = 8.3 Hz), 4.44 (m, 4 H), 4.04 (m, 4 H), 3.69 (t, 4 H, J = 6.2 Hz), 3.05 (m, 2 H), 1.67 (m, 4 H), 1.49 (m, 16 H), 1.22 (m, 2 H), 0.98 (t, 6 H, J = 7.3 Hz), 0.75 (d, 6 H, J = 7.0 Hz), 0.30 (d, 4 H, J = 7.0 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 174.5, 153.6, 144.0, 143.1, 131.4, 127.3, 127.1, 126.5, 125.6, 124.2, 120.9, 120.4, 118.8, 116.0, 97.1, 71.5, 69.1, 68.3, 34.3, 32.4, 31.9, 19.4, 19.2, 18.8, 17.4, 14.0 ppm; IR (KBr) 2931, 2859, 1750, 1619, 1605, 1456, 1293, 1125 cm^{-1}; HRMS (FAB) calcd for $C_{54}H_{64}O_{12}$ 904.4398, found 904.4367.

Hydrolysis of Half of 7's Esters. Preparation of (*M*)-8. A mixture of 300 mg of (*M*)-**7** (0.332 mmol) and 100 mg of K_2CO_3 (0.73 mmol) in 15 mL of methanol under argon was stirred at room temperature for 3 h. As TLC analysis showed the reaction to be complete, the mixture was acidified with dilute HCl to pH 2−3 and poured into 15 mL of water. Extraction with CH_2Cl_2 (3 × 15 mL), washing with brine, drying with Na_2SO_4, and removal of solvent *in vacuo* left 251 mg of a brown-yellow solid (a 99% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, 2 H, J = 8.4 Hz), 8.00 (d, 2 H, J = 8.4 Hz), 7.35 (s, 2 H), 6.70 (br, 2 H, OH), 5.85 (d, 2 H, J = 8.4 Hz), 5.77 (d, 2 H, J = 8.4 Hz), 4.41 (m, 2 H), 4.25 (m, 2 H), 4.00 (m, 4 H), 3.70 (t, 4 H, J = 6.7 Hz),1.68 (m, 4 H), 1.47 (m, 4 H), 1.19 (m, 2 H), 0.98 (t, 6 H, J = 7.4 Hz), 0.72 (d, 6 H, J = 7.0 Hz), 0.24 (d, 6 H, J = 7.0 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.6, 152.4, 148.7, 139.6, 131.0, 126.9, 126.1, 125.5, 124.4, 124.1, 120.3, 115.5, 110.0, 98.1, 71.5, 69.3, 68.1, 32.5, 31.8, 19.3, 18.9, 17.6, 13.9 ppm; IR (KBr) 3418, 2963, 2931, 2868, 1764, 1606, 1417, 1240, 1205, 1059, 919 cm^{-1}.

Bromination of 8. Preparation of (*M*)-9. A solution of 111 mg of Br_2 (0.69 mmol) in 3 mL of CCl_4 contained in a dropping funnel capped with a drying tube was added in drops during ca. 20 min to 254 mg of (*M*)-**8** (0.332 mmol) dissolved in 10 mL of 3:1 (v/v) CCl_4−CH_2Cl_2 that was cooled to 0 °C by an ice bath. The mixture was stirred at room temperature for 1 h. Then 2 mL of saturated aqueous $NaHSO_3$ was added, and after the mixture had been stirred for a few minutes, 5 mL of water was added. Extraction with CH_2Cl_2 (3 × 15 mL), washing with water and brine, drying with $MgSO_4$, and evaporation of the solvent gave a brown-yellow solid, which was placed in a 25 mL flask. This was evacuated and filled with argon, and then 6 mL of dry CH_2Cl_2 was added, followed by 696 μL of *i*-Pr_2NEt (3.98 mmol) and 250 μL of MOMCl (3.32 mmol). After refluxing under argon for 20 h, the mixture was cooled, washed with saturated aqueous Na_2CO_3, water, and brine, and dried with $MgSO_4$. The solvent was removed *in vacuo* and the residue flash chromatographed, eluting with *n*-hexane−EtOAc (3:1). Obtained were 268 mg of an orange solid (an 81% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, 2 H, J = 8.2 Hz), 8.02 (d, 2 H, J = 8.2 Hz), 7.60 (s, 2 H), 6.37 (s, 2 H), 5.37 (d, 2 H, J = 5.8 Hz), 5.31 (d, 2 H, J = 5.8 Hz), 4.54 (m, 2 H), 4.48 (m, 2 H), 4.05 (m, 4 H), 3.80 (s, 6 H), 3.68 (t, 2

(52) (a) Electronic spectra of cobalt, nickel, and copper salophens: refs 16b, 49, and 50. (b) CD spectra of nickel and cobalt Schiff-base complexes: refs 51a,b. (c) CD spectra of nickel and copper Schiff-base complexes: refs 51a, b and 53.

(53) Downing, R. S.; Urbach, F. L. *J. Am. Chem. Soc.* **1969**, *91*, 5977.

H, J = 6.8 Hz), 1.67 (m,4 H), 1.47 (m, 4 H), 1.17 (m, 2 H), 0.98 (t, 6 H, J = 8.0 Hz), 0.72 (d, 6 H, J = 7.0 Hz), 0.27 (d, 6 H, J = 7.0 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 154.0, 147.4, 142.8, 131.3, 129.5, 126.65, 126.58, 125.6, 120.5, 120.0, 119.0, 112.4, 100.6, 98.5, 71.3, 68.9, 68.4, 58.3, 32.4, 31.8, 19.2, 18.5, 17.3, 13.9 ppm; IR ($CHCl_3$) 2937, 2864, 1753, 1607, 1445, 1345, 1272, 111, 944 cm^{-1}; HRMS (FAB) calcd for $C_{50}H_{58}O_{12}Br_2$ 1008.2290, found 1008.2300.

Conversion of the Esters in 9 to Ethers. Preparation of (*M*)-10. A 100 mL dry flask containing 800 mg of (*M*)-**9** (0.792 mmol) and 383 mg of K_2CO_3 (2.77 mmol) was evacuated and filled with argon. A solution of 862 mg of $TsOCH_2CH_2OBu$ (3.17 mmol) in 40 mL of ethanol was cannulated into the flask, and the mixture was refluxed under argon for 27 h. The solvent was removed, and 20 mL of H_2O was added to the residue. After extraction with EtOAc (3 × 20 mL), washing with brine, and drying with $MgSO_4$, the solvent was rotovaped and the residue purified by flash chromatography, eluting with 3:1 (v/v) *n*-hexane-EtOAc. Obtained were 609 mg (a 72% yield) of a viscous yellow oil: ^{1}H NMR (400 MHz, acetone-d_6) δ 8.49 (d, 2 H, J = 8.4 Hz), 8.13 (d, 2 H, J = 8.4 Hz), 7.51 (s, 2 H), 6.12 (s, 2 H), 5.33 (d, 2 H, J = 6.2 Hz), 5.29 (d, 2 H, J = 6.2 Hz), 5.56 (m, 4 H), 4.05 (m, 4 H), 3.81 (s, 6 H), 3.67 (t, 4 H, J = 6.5 Hz), 3.17 (m, 2 H), 3.01 (m, 4 H), 2.82 (m, 2 H), 2.70−2.59 (m, 4 H), 1.63 (m, 4 H), 1.46 (m, 4 H), 1.06 (m, 4 H), 0.94 (m, 10 H), 0.65 (t, 6 H, J = 7.3 Hz) ppm; ^{13}C NMR (75 MHz, acetone-d_6) δ 154.9, 152.0, 144.1, 131.6, 130.7, 129.7, 128.7, 127.0, 125.7, 120.6, 117.7, 113.7, 107.5, 101.4, 98.8, 71.7, 71.3, 69.8, 69.4, 68.5 (4C), 58.2, 32.7, 32.320.0, 19.6, 14.2, 14.0 ppm; IR ($CHCl_3$) 2923, 2868, 1605, 1574, 1347, 1284, 1116 cm^{-1}, 953; HRMS (FAB) calcd for $C_{54}H_{70}O_{12}Br_2$ 1068.3230, found 1068.3220.

Formylation of (*M*)-10. *n*-BuLi in hexane (168 μL, 2.5 M, 0.419 mmol) was added to a flame-dried 25 mL round-bottomed flask, cooled to −78 °C, that contained a stirred solution of 204 mg (0.191 mmol) of (*M*)-**10** in 6 mL of THF. After it had stirred at −78 °C for 30 min, 0.3 mL dry DMF was added, and stirring was continued at −78 °C for 10 min more and at room temperature for 2.5 h. After 3 mL of saturated aqueous NH_4Cl had been added, extraction with ether (2 × 15 mL), washing with 2 N HCl, water, and brine, drying with $MgSO_4$, and removal of the solvent left a residue that was flash chromatographed, eluting with *n*-hexane−EtOAc (1.5:1). A small amount of an impurity eluted first, followed by two fractions that were collected.

The first fraction, (*M*)-**12**: 34 mg (19% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (s, 1 H), 8.52 (d, 1 H, J = 8.4 Hz), 8.49 (d, 1 H, J = 8.4 Hz), 8.06 (d, 1 H, J = 8.4 Hz), 8.01 (d, 1 H, J = 8.4 Hz), 7.52 (s, 1 H), 7.46 (s, 1 H), 6.72 (d, 1 H, J = 8.6 Hz), 6.24 (s, 1 H), 5.76 (d, 1 H, J = 8.6 Hz), 5.29 (m, 4 H), 4.52 (m, 4 H), 4.07 (m, 4 H), 3.72 (s, 3 H), 3.70 (m, 4 H), 3.60 (s, 3 H), 3.22 (m, 1 H), 3.02 (m, 2 H), 2.91−2.55 (m, 9 H), 1.68 (m, 4 H), 1.47 (m, 4 H), 1.12 (m, 4 H), 0.98 (m, 10 H), 0.71 (m, 6 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.7, 154.2, 153.1, 151.5, 151.2, 149.4, 146.0, 130.6, 128.1, 128.0, 127.7, 127.2, 126.3, 126.0, 125.8, 125.37, 125.31, 125.1, 122.7, 120.2, 119.5, 117.8, 111.0, 103.8, 102.4, 98.5, 97.6, 97.5, 96.0, 71.6, 71.5, 71.05, 71.00, 69.25, 69.16, 68.37, 68.26, 68.0, 67.7, 67.6, 67.5, 58.1, 56.1, 31.9, 31.5, 31.4, 19.3, 18.9, 18.8, 14.0, 13.7 ppm; IR ($CHCl_3$) 2941, 2850, 1673. 1610, 1592, 1456, 1356, 1298, 1112, 962 cm^{-1}; HRMS (FAB) calcd for $C_{55}H_{72}O_{13}$ 940.4973, found 940.4988.

The second fraction, (*M*)-**11**: 108 mg (58% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 (s, 2 H), 8.51 (d, 2 H, J = 8.4 Hz), 8.07 (d, 2 H, J = 8.4 Hz), 7.47 (s, 2 H), 6.23 (s, 2 H), 5.31 (d, 2 H, J = 6.0 Hz), 5.25 (d, 2 H, 6.0 Hz), 4.52 (m, 4 H), 4.06 (m, 4 H), 3.72 (s, 6 H), 3.69 (t, 4 H, J = 6.8 Hz), 3.21 (m, 2 H), 2.98 (m, 4 H), 2.77 (m, 2 H), 2.55−2.68 (m, 4 H), 1.68 (m, 4 H), 1.47 (m, 4 H), 1.08 (m, 4 H), 0.98 (m, 10 H), 0.69 (t, 6 H, J = 7.2 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 154.2, 151.7, 151.1, 133.2, 130.7, 127.9, 127.8, 127.2, 126.3, 125.6, 122.4, 120.1, 102.5, 98.8, 97.9, 71.6, 71.1, 69.1, 68.5, 67.8, 67.7, 58.2, 31.9, 31.4, 19.4, 18.9, 14.0, 13.8 ppm; IR ($CHCl_3$) 2955, 2927, 2871, 1675, 1586, 1451, 1385, 1297, 1124, 1063, 951 cm^{-1}; HRMS (FAB) calcd for $C_{56}H_{72}O_{14}$ 968.4922, found 968.4903.

Preparation of Monosalicylaldehyde (*M*)-13. One drop of concd H_2SO_4 was added to a solution of 23 mg (0.024 mmol) (*M*)-**12** in 2 mL of 3:1 (v/v) HOAc−H_2O, and the mixture under argon was stirred at 60 °C for 2 h. After it had been cooled, the mixture was poured slowly in 10 mL of saturated aqueous Na_2CO_3, extracted with CH_2Cl_2 (3 × 5 mL), which was then washed with brine, dried with $MgSO_4$, and evaporated. The crude product was purified by preparative TLC on silica gel, eluting with 1.5: 1 *n*-hexane−EtOAc. The yield was 14 mg (67%): ^{1}HNMR (400 MHz, $CDCl_3$) δ 11.88 (s, 1 H, OH), 9.57 (s, 1 H, CHO), 8.53 (d, 1 H, J = 8.4 Hz), 8.52 (d, 1 H, J = 8.4 Hz), 8.09 (d, 1 H, J = 8.4 Hz), 8.02 (d, 1 H, J = 8.4 Hz), 7.64 (s, 1 H), 7.45 (s, 1 H), 6.40 (d, 1 H, J = 8.4 Hz), 5.81 (s, 1 H), 5.69 (d, 1 H, J = 8.4 Hz), 5.47 (br, 1 H, OH), 4.07 (m, 4 H), 3.70 (m, 4 H) ppm; $[\alpha]_D$ = −1140°.

Preparation of Bis-salicylaldehyde (*M*)-3. Concd H_2SO_4 (five small drops) was added to a solution of 108 mg of (*M*)-**11** (0.112 mmol) dissolved in 8 mL of 3:1 (v/v) AcOH−H_2O, and the mixture under argon was stirred at 60 °C for 2 h. After it had been cooled, the mixture was slowly poured into 50 mL of saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3 × 10 mL), which was then washed with brine, dried with $MgSO_4$, and evaporated, giving 94 mg of a yellow sticky material (a 96% yield): $[\alpha]_D$ = −1150°; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.96 (s, 2 H, OH), 9.66 (s, 2 H, CHO), 8.60 (d, 2 H, J = 8.5 Hz), δ 8.14 (d, 2 H, J = 8.5 Hz), 7.71 (s, 2 H), 5.93 (s, 2 H), 4.57 (m, 4 H), 4.09 (m, 4 H), 3.71 (t, 4 H, J = 6.6 Hz), 3.11 (m, 2 H), 2.96 (m, 2 H), 2.84 (m, 2 H), 2.79−2.40 (m, 6 H), 2.59 (m, 2 H), 1.70 (m, 4 H), 1.50 (m, 4 H), 1.13 (m, 4 H), 1.00 (m, 10 H), 0.72 (t, 6 H, J = 7.3 Hz) ppm; ^{13}C (75 MHz, $CDCl_3$) δ 195.6 (CO), 154.1, 153.8, 147.8, 130.7, 127.6, 127.0, 126.6, 123.8, 123.2, 123.2, 114.3, 102.7, 98.0, 71.4, 71.0, 69.1, 68.5, 67.8, 67.7, 31.9, 31.4, 19.3, 18.9, 13.9, 13.7 ppm; IR ($CHCl_3$) 2950, 2932, 2869, 1642, 1597, 1452, 1372, 1309, 1115, 904 cm^{-1}; HRMS (FAB) calcd for $C_{52}H_{64}O_{12}$ 880.4398, found 880.4394.

Preparation of Ni-dimer (−)-16. After 12 mg of (*M*)-**13** (14 μmol), 0.76 mg of 1,2-phenylenediamine (7.0 μmol), and 1 mL of ethanol under argon had been refluxed for 6 h, 5.3 mg of Ni $(OAc)_2 \cdot 4H_2O$ (21 μmol) in 0.5 mL of ethanol was added to the dark red solution, which was then stirred for 3 h. The solvent was removed *in vacuo*. The product (10 mg, a 77% yield) was precipitated by adding *n*-hexane to the residue dissolved in 0.5 mL of CH_2Cl_2: $[\alpha]_D$ = −550°; IR ($CHCl_3$) 2927, 2864, 1602, 1450, 1356, 1320, 1116 cm^{-1}; MS (FAB) 1836 (M^+ + H).

Preparation of Ni-Polymer (+)-4a. After 53 mg of (*M*)-**3** (60 μmol), 6.5 mg 1,2-phenylenediamine (60 μmol), and 1.5 mL of ethanol under argon had been refluxed for 6 h (red solution), a solution of 15 mg of Ni $(OAc)_2 \cdot 4H_2O$ (60 μmol) in 1 mL of ethanol was added, whereupon the color immediately turned rust-brown. The mixture was refluxed for 4 h. After it had cooled, ethanol was removed *in vacuo*. The product, a black solid (60 mg, a 98% yield) was precipitated by adding *n*-hexane to the residue dissolved in 1 mL of CH_2Cl_2: $[\alpha]_D$ = +1560°; IR ($CHCl_3$) 2927, 2864, 1597, 1576, 1450, 1351, 1116 cm^{-1}; Anal. Calcd for $(C_{58}H_{66}O_{10}N_2Ni)_n$: C, 68.98; H, 6.59; N, 2.77; Ni, 5.81. Found: C, 67.30; H, 6.45; N, 3.17; Ni, 6.01.

Preparation of Cu−Polymer 4b. The preparation, from (*M*)-**3** (11 mg, 12 μmol), 1,2-phenylenediamine (1.4 mg, 12 μmol), and $Cu(OAc)_2 \cdot H_2O$ (2.5 mg, 12 μmol), followed the same procedure as for Ni−polymer. The yield of brown-red solid was 12 mg, 92%: IR ($CHCl_3$) 2927, 2864, 1602, 1576, 1450, 1351, 1116 cm^{-1}.

Preparation of Co−Polymer 4c. The preparation, from (*M*)-**3** (9 mg, 10 μmol) and $Co(OAc)_2 \cdot 4\ H_2O$ (2.5 mg, 10 μmol), followed the same procedure as for Ni−polymer. The yield of brown solid was 10 mg, 100%: IR ($CHCl_3$) 2933, 2866, 1604, 1579, 1458, 1352, 1120 cm^{-1}.

Bromination of Helical Bis-Quinone 1. Preparation of (*P*)-17. HBr (30%) in HOAc (550 μL, 2.76 mmol) was added in drops to a stirred solution at −25 °C of 500 mg (0.806 mmol) of **(*P*)-(+)-1** in 25 mL of propanoic acid contained in a 100 mL round-bottomed flask capped with a drying tube. After it had been stirred further at −25 °C for 30 min, the mixture was poured into 100 mL of aqueous phosphate buffer (pH = 7.0)

and extracted with CH_2Cl_2 (3 × 20 mL). The extract was washed twice with water, and then 500 mg (0.407 mmol) of tetrachloro-1,4-benzoquinone was added. The mixture was shaken for ca. 5 min, and then washed thoroughly with saturated aqueous $NaHCO_3$, an emulsion that formed being broken by filtration through a pad of Celite. Washing with brine, drying with $MgSO_4$, evaporation, and flash chromatography on silica gel, eluting with toluene/dry THF (39:1), gave 237 mg (a yield of 38%) of dark red solid: IR (KBr) 2931, 2866, 1656, 1595, 1513, 1303, 1257, 1227, 1135, 1006, 767 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, 2 H, J = 8.6 Hz), 7.99 (d, 2 H, J = 8.6 Hz), 7.54 (s, 2 H), 7.35 (s, 2 H), 4.59 (m, 2 H), 4.49 (m, 2 H), 4.01 (m, 4 H), 3.65 (t, 4 H, J = 6.6 Hz), 1.67 (m, 4 H), 1.45 (m, 4 H), 0.97 (t, 6 H, J = 7.4 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.3, 178.9, 159.1, 140.3, 137.8, 133.4, 133.2, 131.4, 128.9, 127.8, 126.6, 125.6, 122.4, 102.1, 71.5, 68.9, 68.8, 31.8, 19.3, 14.0 ppm.

Bromination of 8. Preparation of 23. The bromination was carried out as described for the preparation of **9**, but using 100 mg (0.131 mmol) of **8** in 3 mL of CCl_4−CH_2Cl_2 and 44 mg (0.28 mmol) of Br_2 in 1.5 mL of CCl_4. A solution of the resulting dibromo diol in 10 mL of CH_3CN, contained in an open flask, was stirred at room temperature with 574 mg (1.05 mmol) of $(NH_4)_2Ce(NO_3)_6$ in 1.5 mL of H_2O. Water (20 mL) was added, and extration with CH_2Cl_2 (15 mL and 10 mL, with filtration through celite to break emulsions), drying ($MgSO_4$), and evaporation gave 93 mg (a 91% yield) of a red solid, whose ^1H NMR spectrum differs from that of **17** (see the Supporting Information). The spectrum shows an impurity to be present to the extent of ca. 16%, which may be an analogue of a pinacol isolated previously in the oxidation of a 4,13-dihydroxy[6]-helicene:[54] ^1H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, 2 H, J = 8.7 Hz), 7.99 (d, 2 H, J = 8.6 Hz), 7.62 (s, 2 H), 7.17 (s, 2 H), 4.59 (m, 2 H), 4.49 (m, 2 H), 4.01 (m, 4 H), 3.65 (t, 4 H, J = 6.6 Hz), 1.66 (m, 4 H), 1.45 (m, 4 H), 0.97 (t, 6 H, J = 7.4 Hz) ppm.

Reductive Acetylation of 17. Preparation of *(P)*-18. A 35 mL round-bottomed flask containing 189 mg (0.243 mmol) of **(*P*)-17** and 338 mg (1.94 mmol) of $Na_2S_2O_4$ was evacuated and filled with argon. After 5 mL of H_2O (previously boiled and then cooled under argon) and 9 mL of dry CH_2Cl_2 were added, the mixture was shaken vigorously until the color turned yellow. The organic phase was separated, and the aqueous phase was quickly extracted with a small amount of CH_2Cl_2. The combined organic phases were dried for ca. 5 min over $MgSO_4$, and after it had been filtered, the drying reagent was washed with ca. 2 mL of CH_2Cl_2. The organic solution was deaerated by freezing, pumping, and thawing, and then 1.05 mL of Ac_2O was added, followed by 1.30 mL of dry Et_3N. After 8 h of reflux, followed by cooling to room temperature, 5 mL of H_2O and 1 mL of Et_3N were added, and the mixture was stirred at room temperature for 1 h. Extraction with CH_2Cl_2, washing with saturated aqueous $NaHCO_3$ and brine, drying with $MgSO_4$, stripping, and flash chromatography, eluting with *n*-hexane−EtOAc (3:2), gave 218 mg (a yield of 82%) of yellow solid: IR (KBr) 2932, 2862, 1766, 1561, 1450, 1424, 1367, 1282, 1171, 1123, 1012, 892 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 8.59 (d, 2 H, J = 8.5 Hz), 8.26 (d, 2 H, J = 8.5 Hz), 7.49 (s, 2 H), 7.40 (s, 2 H), 4.68 (m, 2 H), 4.54 (m, 2 H), 4.03 (t, 4 H, J = 4.4 Hz), 3.65 (t, 4 H, J = 6.5 Hz), 2.51 (H, 6 H), 1.61 (m, 4 H), 1.45 (m, 4 H), 1.06 (s, 6 H), 0.93 (t, 6 H, J = 7.4 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 166.5, 153.9, 143.2, 141.2, 131.5, 127.3, 126.8, 126.7, 126.2, 123.4, 122.7, 121.3, 120.6, 109.8, 97.4, 71.4, 69.0, 68.4, 31.8, 21.2, 19.3, 19.2, 13.9 ppm; HRMS calcd for $C_{46}H_{46}O_{12}Br_2Na$ (M + Na) 971.1253, found 971.1271 (PEG + NaCl as reference).

Cleavage of Half the Esters in 18. Preparation of (*P*)-19. A mixture of 296 mg (0.312 mmol) of **(*P*)-18** , 95 mg (0.69 mmol) of K_2CO_3, and 15 mL of MeOH was deaerated by applying two freeze−pump−thaw cycles, and it was then stirred under argon at room temperature for 3 h. The brown-yellow mixture was acidified with 2 N HCl to pH = 2, and after 15 mL more H_2O had been added, the mixture was extracted with CH_2Cl_2 (3 × 15 mL), washed with brine, and dried with $MgSO_4$. The solvent was stripped, 151 mg (1.09 mmol) of K_2CO_3 and 7 mL of acetone were added to the residue, followed by 130 μL (2.09 mmol) of MeI, and the mixture was refluxed under argon for 15 h. The residue remaining after the acetone had been stripped was extracted with 5 mL of H_2O and 10 mL of CH_2Cl_2, and the aqueous phase was extracted with additional CH_2Cl_2. The combined organic phases were washed with brine and dried with $MgSO_4$. Stripping and flash chromatography, eluting with *n*-hexane−EtOAc (2:1), gave 226 mg (a yield of 81%) of yellow solid: $[\alpha]_D$ = +1390° (c = 0.86g/100 mL in $CHCl_3$); IR ($CHCl_3$) 2936, 2873, 1757, 1613, 1589, 1459, 1367, 1295, 1133, 1081, 897 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, 2 H, J = 8.5 Hz), 8.02 (d, 2 H, J = 8.5 Hz), 7.65 (s, 2 H), 8.83 (s, 2 H), 4.60 (m, 2 H), 4.47 (m, 2 H), 4.04 (m, 10H), 3.66 (t, 4 H, J = 6.6 Hz), 1.65 (m, 4 H), 1.44 (m, 4 H), 1.02 (s, 6 H), 0.96 (t, 6 H, J = 7.4 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 153.2, 152.4, 137.4, 131.0, 126.7, 126.3, 126.0, 125.1, 123.7, 120.9, 120.3, 110.1, 109.2, 98.3, 71.2, 69.1, 68.4, 56.0, 31.8, 19.2, 19.1, 13.9 ppm; HRMS calcd for $C_{44}H_{46}O_{10}Br_2Na$ (M + Na) 915.1355, found 915.1364.

Preparation of MOM Ether (*P*)-20. A flame-dried 25 mL round-bottomed flask containing 163 mg (0.182 mmol) of **(*P*)-19** was evacuated and filled with argon. Dry THF (4.4 mL) was added, followed by KO-*t*-Bu in THF (401 μL, 1 M, 0.401 mmol). The mixture, which immediately turned red, was stirred at room temperature for 8 min, and then 170 μL MOMCl (2.19 mmol) was added. The solution turned yellow within 1 min. It was stirred at room temperature for 2.5 h. After 10 mL of H_2O had been added, extraction with CH_2Cl_2 (3 × 10 mL), washing with brine, drying with $MgSO_4$, and flash chromatography, eluting with *n*-hexane−EtOAc (3:1), gave 150 mg (a 92% yield) of yellow viscous oil: IR (KBr) 2932, 2866, 1612, 1579, 1457, 1441, 1289, 1159, 1131, 940 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, 2 H, J = 8.4 Hz), 8.00 (d, 2 H, J = 8.4 Hz), 7.58 (s, 2 H), 6.79 (s, 2 H), 4.60 (m, 2 H), 4.43 (m, 2 H), 4.04 (m, 10H), 3.68 (t, 4 H, J = 6.6 Hz), 3.29 (d, 2 H, J = 6.0 Hz), 3.06 (d, 2 H, J = 6.0 Hz), 2.55 (s, 6 H), 1.67 (m, 4 H), 1.47 (m, 4 H), 0.97 (t, 6 H, J = 7.40 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 151.0, 144.8, 131.0, 127.1, 125.8, 125.6, 125.3, 124.0, 120.7, 120.4, 110.1, 109.9, 98.5, 97.8, 71.4, 69.3, 68.2, 56.9, 56.0, 31.9, 19.3, 14.0 ppm; HRMS calcd for $C_{44}H_{50}O_{10}Br_2$ 896.1771, found 896.1737.

Formylation of 20. A 25 mL flame-dried round-bottomed flask containing 113 mg (0.126 mmol) of **(*P*)-20** was evacuated and filled with argon. Dry THF (3 mL) was added, and the resulting bright yellow solution was cooled to −78 °C. *n*-BuLi in hexane (210 μL, 2.5 M, 0.525 mmol) was added in drops, whereupon the color immediately turned orange-yellow. The mixture was stirred at −78 °C for 50 min, and then 200 μL (2.52 mmol) of dry DMF was added. Stirring was continued, first at −78 °C for 15 min and then at room temperature for 2.5 h. Saturated aqueous NH_4Cl (2 mL) was added, whereupon the color of the mixture turned back to bright yellow. Extraction with CH_2Cl_2 (3 × 10 mL), washing with brine, drying with $MgSO_4$, and, after removal of solvent, flash chromatography, eluting with *n*-hexane−EtOAc (1.8:1) gave, first, a small amount of impurities and then two yellow fractions.

The first fraction, **(*P*)-21**: 16 mg, 16% yield; $[\alpha]_D$ = +1340° (c = 0.8g/100 mL in $CHCl_3$); IR ($CHCl_3$) 2935, 2870, 1658, 1598, 1455, 1381, 1293, 1113, 1076, 1048, 961 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.57 (d, 1H, J = 8.4 Hz), 8.52 (d, 1H, J = 8.4 Hz), 8.07 (d, 1H, J = 8.4 Hz), 8.01 (d, 1H, J = 8.4 Hz), 7.62 (s, 1H), 7.61 (s, 1H), 6.98 (s, 1H), 6.48 (d, 1H, J = 8.5 Hz), 6.10 (d, 1H, J = 8.5 Hz), 4.60 (m, 2 H), 4.48 (m, 2 H), 4.06 (m, 4 H), 4.03 (s, 3 H), 3.95 (s, 3 H), 3.83 (d, 1H, J = 6.6 Hz), 3.70 (m, 4 H), 3.53 (d, 1H, J = 6.6 Hz), 3.20 (d, 1H, J = 6.2 Hz), 2.99 (d, 1H, J = 6.2 Hz), 2.64 (s, 6 H), 1.69 (m, 4 H), 1.48 (m, 4 H), 0.98 (t, 6 H, J = 7.3 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.7, 155.6, 154.0, 152.6, 150.8, 149.8, 146.8, 131.2,130.0, 128.2, 126.5, 125.5, 125.4, 125.1, 124.8, 124.5, 123.4, 120.7, 120.0, 119.3, 118.6, 108.3, 106.1, 100.5, 99.1, 98.5, 98.1, 94.6, 71.5, 71.4, 69.3, 69.2, 68.5, 68.4, 56.8, 56.1 (twice as intense as the other methoxyl resonances and probably including two that overlap), 55.3, 31.9, 19.4, 14.0 ppm. The

(54) Yang, B.; Liu, L.; Katz, T. J.; Liberko, C. A.; Miller, L. L. *J. Am. Chem. Soc.* **1991**, *113*, 8993, footnote 11.

one missing resonance for an aromatic carbon is presumed to overlap one of the peaks that is observed. HRMS (FAB) calcd for $C_{45}H_{52}O_{11}$ 768.3510, found 768.3523.

The second fraction, **(*P*)-22**: 80 mg, yellow viscous oil, 80% yield; $[\alpha]_D = +1840°$ (c = 1.10g/100 mL in $CHCl_3$); IR ($CHCl_3$) 2931, 2872, 1667, 1608, 1457, 1390, 1300, 1121, 1080, 955 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 2 H, CHO), 8.58 (d, 2 H, J = 8.4 Hz), 8.08 (d, 2 H, J = 8.4 Hz), 7.63 (s, 2 H), 6.93 (s, 2 H), 4.64 (m, 2 H), 4.50 (m, 2 H), 4.07 (t, 4 H, J = 4.7 Hz), 4.00 (s, 6 H), 3.70 (t, 4 H, J = 6.6 Hz), 3.33 (d, 2 H, J = 6.1 Hz), 3.09 (d, 2 H, J = 6.1 Hz), 2.63 (s, 6 H), 1.69 (m, 4 H), 1.48 (m, 4 H), 0.99 (s, 6 H, J = 7.3 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.2, 155.4, 153.2, 151.3, 131.9, 130.5, 128.2, 126.3, 125.1, 123.6, 123.4, 120.9, 119.3, 101.2, 99.2, 98.6, 71.5, 69.2, 68.6, 56.9, 56.0, 31.8, 19.4, 14.0 ppm; HRMS (FAB) calcd for $C_{46}H_{52}O_{12}Na$ (M + Na) 819.3356, found 819.3329.

Preparation of Bis-Salicylaldehyde (*P*)-5. Concd H_2SO_4 (4 drops) was added to a stirred solution under argon of 80 mg of **(*P*)-22** (0.100 mmol) dissolved in 5 mL of AcOH-H_2O (3:1 v/v). Stirring was continued at 55−60 °C for 2 h. After it had been cooled to room temperature, the reaction mixture was slowly poured into 30 mL of saturated aqueous $NaHCO_3$, extracted with CH_2Cl_2 (4 × 10 mL), washed with brine, and dried with $MgSO_4$. Evaporation of the solvent gave 67 mg of yellow solid (a 96% yield) whose ^1H NMR spectrum showed no evidence of more than the tiniest traces of impurities: $[\alpha]_D = +4430°$ (c = 0.0705g/100 mL in CH_2Cl_2); IR (KBr) 2931, 2862, 1604, 1510, 1422, 1320, 1232, 1155, 1126, 1076, 836 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.21 (s, 2 H, OH), 9.41 (s, 2 H, CHO), 8.49 (d, 2 H, J = 8.5 Hz), 8.04 (d, 2 H, J = 8.5 Hz), 7.52 (s, 2 H), 6.47 (s, 2 H), 4.62 (m, 2 H), 4.47 (m, 2 H), 4.06 (t, 4 H, J = 3.9 Hz), 3.95 (s, 6 H), 3.69 (t, 4 H, J = 6.6 Hz), 1.69 (m, 4 H), 1.49 (m, 4 H), 0.98 (t, 6 H, J = 7.4 Hz) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7, 156.9, 155.1, 147.8, 131.6, 131.4, 129.2, 126.6, 125.3, 124.8, 120.7, 116.5, 112.2, 104.9, 97.6, 71.4, 69.0, 68.2, 56.2, 31.8, 19.3, 13.9 ppm; HRMS (FAB) calcd for $C_{42}H_{44}O_{10}$ 708.2935, found 708.2925.

Preparation of Ni−Polymer 6. A 10 mL round-bottomed flask containing 37 mg (0.052 mmol) of **5** was evacuated and filled with argon. A solution was added of 5.65 mg (0.0523 mol) 1,2-phenylenediamine in 2 mL of ethanol, and the mixture was refluxed. The bis-salicylaldehyde gradually dissolved, and the mixture became clear and turned red. Refluxing overnight (12 h) precipitated a great deal of red material on the wall of the flask. The ethanol was rotovaped to ca. 0.5 mL, and then 1.5 mL of dry THF was added. The solids all then dissolved. More 1,2-phenylenediamine (ca. 0.5 mg, 4.6 μmol) was added, and after the mixture had refluxed for 2 h, a solution was added of 13 mg (0.052 mmol) of $Ni(OAc)_2 \cdot 4\ H_2O$ in 0.6 mL of ethanol. The color immediately turned very dark. The mixture was refluxed under argon for another 12 h, and after it had cooled to room temperature, the solvent was removed in vacuo. The residue was dissolved in 1.5 mL of CH_2Cl_2 and precipitated with *n*-hexane. After centrifugation and decantation, the residue was redissolved in 2 mL of THF and precipitated with *n*-hexane. The precipitation was repeated, giving 42 mg of dark red solid (a 95% yield): IR (KBr) 2929, 2863, 1596, 1581, 1543, 1510, 1420, 1361, 1242, 1206, 1129, 826 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) there are four broad groups of resonances, at δ 8.3−6.6, 6.4−5.0, 4.7−2.3, and 2.0−0.6 ppm, whose intensities are in the ratio 4.0:3.0:8.3:7.7. This compares with the following ratios of protons in the structure: seven aromatic and imine, nine aliphatics next to oxygen, and seven other aliphatics. There are tiny peaks at δ 9.28 and 10.87 ppm. The ratio of the intensities of the resonance at δ 9.28 and all the other resonances is 0.08:46, implying, since the infinite polymer would have formula $(C_{48}H_{46}NiN_2O_8)_n$, that there is one CHO group for every 25 salophen units.

Further purification, by dissolving the material in ca. 3 mL of CH_2Cl_2 and precipitating it with *n*-hexane, gave ca. 26 mg of a solid that looked black, gave red solutions, and showed CD and UV spectra that were identical to those of the sample prior to this last reprecipitation. Anal. Calcd for ($C_{48}H_{46}N_2NiO_8$): C, 68.83; H, 5.54; N, 3.34; Ni, 7.01. Found: C, 64.51; H, 5.24; N, 3.89 (by Desert Analytics); Ni, 7.99 (by Galbraith Laboratories): $[\alpha]_D$ +4900° (c = 0.086 mg/100 mL, CH_2Cl_2).

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Supporting Information Available: Graphs showing the ^1H and ^{13}C NMR spectra of intermediates and products shown in Schemes 2 and 3, the ^1H NMR spectra of **3**, **4a−c**, **5**, **6**, **16**, and **23**, and the IR spectrum of **6** (34 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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