methanol. However, the relative softness of cadmium(II) apparently disfavors attack of the hard, methanol nucleophile at cadmium. Equations 2 and 3 together suggest that the alcoholysis-and-polycondensation strategy may generally fail with precursors having hard, electropositive cations.

$$\tfrac{1}{2}\mathbf{1} + 2\mathrm{MeOH} \rightarrow \mathrm{Zn(OMe)_2} + 2\mathrm{HP(SiMe_3)_2} \tag{3}$$

Precursors **1** and **2** gave the ternary phosphides $ZnGeP_2$ and $CdGeP_2$ according to eq 4. Intermediates were precipitated from refluxing toluene solutions of **1** or **2** and $Ge(OMe)_4$ that contained $SiMe_3$ and OMe groups;[12] these were substantially removed by heating the dry solids to 300–350 °C in vacuo. Conversion to polycrystalline $ZnGeP_2$[13] and $CdGeP_2$[13] was achieved at temperatures of 800 and 600 °C, respectively, which are 200 °C below the melting points of the compounds[14] and are mild conditions.[15] However, the $ZnGeP_2$ and $CdGeP_2$ contained residual-carbon impurities of ca. 3% and 1%, respectively.[13] Efforts to decrease carbon levels by optimizing precursors and processing conditions are in progress.

$$\begin{aligned}
&\underset{\mathbf{1-2}}{\tfrac{1}{2}\{\mathrm{M[P(SiMe_3)_2]_2}\}_2} + \mathrm{Ge(OMe)_4} \xrightarrow[\text{toluene}]{-(4-x)\mathrm{MeOSiMe_3}} \\
&\quad \underset{\substack{\mathrm{M = Zn},\ x = 0.5 \\ \mathrm{M = Cd},\ x = 0.3}}{[\mathrm{MGeP_2(OMe)}_x\mathrm{(SiMe_3)}_x]} \xrightarrow[\text{solid state}]{\Delta} \mathrm{MGeP_2} + x\mathrm{MeOSiMe_3}
\end{aligned} \tag{4}$$

The $A^{II}{}_3B^{V}{}_2$ and $A^{II}B^{IV}C^{V}{}_2$ families have potential applications in photovoltaics (Zn_3P_2),[16] IR-transmitting ceramics ($ZnGeP_2$),[17] nonlinear optics ($ZnGeP_2$),[18] and variable-band-gap devices ($ZnSnP_2$).[19] Photophysical studies describing the novel properties of colloidal Cd_3P_2 have recently appeared.[20] By analogy to the sol-gel process for oxides, rational metallorganic syntheses may become useful for preparing phosphide particles, films, or monoliths.

Acknowledgment. Support was provided by Washington University and the donors of the Petroleum Research Fund, administered by the American Chemical Society. The Washington University X-ray Crystallography Facility was funded by the NSF Chemical Instrumentation Program (Grant CHE-8811456). The Washington University High-Resolution NMR Service Facility was funded in part by NIH Biomedical Research-Support Shared-Instrument Grant 1 S10 RR02004 and a gift from the Monsanto Co. We are also grateful to Dr. Charles Campana, Siemens Analytical X-Ray Instruments, Inc., for assistance with crystallography and Drs. D. Kremser and T. Huston for technical assistance.

Supplementary Material Available: Listings of the details of the data collection, final positional and equivalent isotropic thermal parameters, bond distances, bond angles, calculated hydrogen atom parameters, and anisotropic thermal parameters for **1** and a description of experimental details (10 pages); a listing of observed and calculated structure factors for **1** (12 pages). Ordering information is given on any current masthead page.

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(12) IR spectra contained prominent, characteristic absorbances for OMe and $SiMe_3$ groups. Anal. Calcd for $ZnGeP_2(OMe)_{0.5}(SiMe_3)_{0.5}$: C, 9.52; H, 2.38; Zn, 25.95. Found: C, 11.01; H, 2.04; Zn, 25.47. Calcd for $CdGeP_2(OMe)_{0.3}(SiMe_3)_{0.3}$: C, 5.16; H, 1.30; Cd, 40.40. Found: C, 5.94; H, 0.63; Cd, 40.79.

(13) (a) XRD patterns matched simulated powder patterns.[13b] Anal. Found for $ZnGeP_2$: C, 3.01; H, 0.00. Anal. Found for $CdGeP_2$: C, 0.93; H, 0.00. Energy-dispersive X-ray spectroscopy showed only background levels of silicon. (b) Shay, J. L.; Wernick, J. H. *Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties, and Applications*; Pergamon: New York, 1975; pp 3–8.

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Stabilization of Mononuclear Five-Coordinate Iron(IV)

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High oxidation state middle transition metal compounds are of considerable importance, especially for the first-row metals. These rare species provide a major source of metallooxidants. In the case of iron, highly oxidized complexes are significant as reactive intermediates in many biological and biomimetic redox processes.[2] Despite this significance, high valent iron coordination chemistry is limited. Few stable, well-defined compounds of iron(IV) exist,[3] and the V and VI oxidation states are established only for the tetraoxo polyanions.[3] The coordination chemistry of high-valent middle and later first row transition metals can be expanded by the use of oxidation-resistant, strongly donating ligand complements.[4] The donor capacity and resistance to oxidative destruction of tetradentate tetraanionic ligands has been refined[4] to give the innocent macrocyclic tetraamide, $H_4[\mathbf{1}]$ (Scheme I). The resistance of the macrocycle to oxidative degradation and the strong donor capacity of the amido-*N* donors are central features of this system. The ability of amido-*N* ligands to stabilize higher oxidation states was first demonstrated by Margerum and co-workers in extensive studies of copper and nickel chemistry,[5] studies that are a foundation of the current work. Here we report the initial results of a study of the iron chemistry of $H_4[\mathbf{1}]$,

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(2) See, for example: (a) *Cytochrome P-450; Structure, Mechanism, and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1986. (b) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1404–1449. (c) *Metal Ion Activation of Dioxygen*; Spiro, T. G., Ed.; Wiley: New York, 1980. (d) *Oxygenases*; Hayashi, O., Ed.; Academic Press: New York and London, 1976. (e) *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; John Wiley & Sons: New York, 1989. (f) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981. (g) Baldwin, J. E.; Abraham, E. *Nat. Prod. Rep.* **1988**, 129–145. (h) Fox, B. G.; Lipscomb, J. D. Methane Monooxygenase: A Novel Biological Catalyst for Hydrocarbon Oxidations. In *Biological Oxidation Systems*; Reddy, C. C., Ed.; Academic Press: New York, in press. (i) Dunford, H. Peroxidases. In *Advances in Inorganic Biochemistry*; Eichorn, G. L., Marzilli, L. G., Eds.; Elsevier Biomedical: New York, 1982; Vol. 4, pp 41–68.

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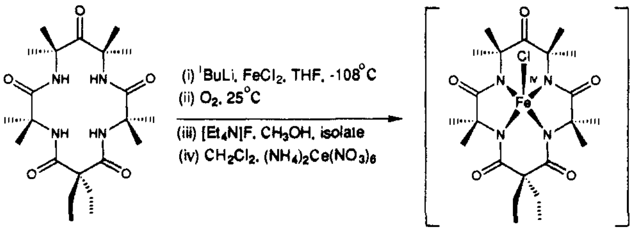
Scheme I



specifically the production of a five-coordinate iron(IV) complex, stable both in solution and as a crystalline material under ambient conditions.

$[Et_4N][FeCl(\eta^4\text{-}\mathbf{1})]$ was synthesized as follows (Scheme I): $H_4[\mathbf{1}]$ (70 mg) was dissolved in dry, deoxygenated THF (24 mL), and a stoichiometric amount of *tert*-butyllithium (0.41 mL, 1.7 M in pentane, 4 equiv, Aldrich) was added to the frozen solution under nitrogen. $FeCl_2$ (anhydrous, 29 mg, 1.2 equiv, Alfa) was added under nitrogen when the THF solution thawed (−108 °C). As the stirred suspension warmed to 20 °C, a dark green precipitate (presumably an iron(II) complex) collected on the flask walls. After stirring at 20 °C (30 min), air was admitted through a calcium chloride drying tube and an orange precipitate rapidly developed as the green precipitate disappeared (presumably as the result of oxidation of the iron(II) complex by oxygen to iron(III)). This precipitate was stirred (30 min), and then the THF was removed under reduced pressure to yield an orange solid. The solid was washed with CH_2Cl_2, dissolved in CH_3OH, and filtered through Celite. $[Et_4N]F{\cdot}xH_2O$ (116 mg, Aldrich) was added, and the CH_3OH was removed under reduced pressure. The resulting orange-brown residue was dissolved in CH_2Cl_2 (20 mL) and filtered through a Celite pad. $(NH_4)_2Ce(NO_3)_6$ (0.1 g, Aldrich) was added to the orange CH_2Cl_2 solution, immediately producing a dark brown solution. After stirring (15 min), the reaction mixture was dried over anhydrous Na_2SO_4 (0.2 g) and passed through a Celite pad, the mother liquor was collected, and the volume was reduced to 3 mL. Diethyl ether was layered on the CH_2Cl_2 solution, and dark brown X-ray quality crystals of $[Et_4N][FeCl(\eta^4\text{-}\mathbf{1})]$ formed upon diffusion of the two solvents at 4 °C (21.5 mg, 18.8% yield).

The compound, $[Et_4N][FeCl(\eta^4\text{-}\mathbf{1})]$, has the crystal structure shown in Figure 1.[6,7] The structure is best described as a distorted square pyramid: the four amide nitrogens lie in a plane (±0.01 Å), with the Fe atom sitting 0.42 Å above the plane. Although the Cambridge Crystallographic Database lists over 500 structures for five-coordinate iron, five-coordinate iron(IV) has been established in the solid state only for the dinuclear μ-carbido complex $[(TPP)Fe]_2C$.[8] Two structures of five-coordinate complexes with noninnocent dithiolene/dithiolate ligands have been reported.[9]

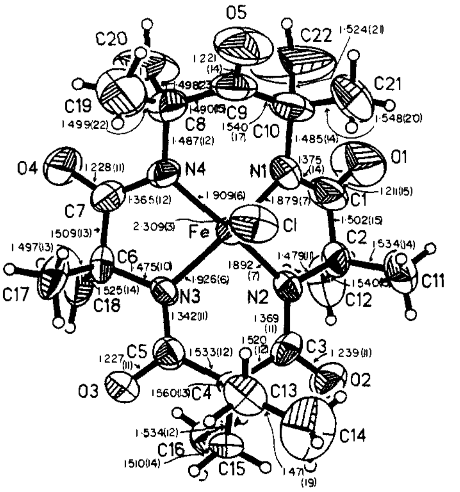


Figure 1. Molecular structure of $[FeCl(\eta^4\text{-}\mathbf{1})]^-$; ORTEP drawing with all non-hydrogen atoms drawn to encompass 50% of electron density.

Cyclic voltammetry of $[Et_4N]_2[Fe^{III}Cl(\eta^4\text{-}\mathbf{1})]$ shows a reversible $Fe^{IV/III}$ couple at $E_f = -65$ mV vs Fc^+/Fc in CH_2Cl_2 (ca. 645 mV vs NHE[4d]) with $[Bu_4N][ClO_4]$ (0.1 M) as supporting electrolyte. This formal potential can be compared with the $Fe^{IV/III}$ couple for the six-coordinate difluoro(tetraphenylporphyrinato)iron system which occurs at +160 mV vs Fc^+/Fc in acetonitrile.[10] The considerable stabilization of the iron(IV) oxidation state in $[Et_4N][FeCl(\eta^4\text{-}\mathbf{1})]$ can be attributed to the strong donor capacity of $[\eta^4\text{-}\mathbf{1}]^{4-}$.

Zero-field Mössbauer spectra of $[Et_4N][FeCl(\eta^4\text{-}\mathbf{1})]$ in acetonitrile consist of a single doublet. The quadrupole splitting, ΔE_Q, is nearly independent of temperature. The spectrum obtained at 150 K, shown in Figure 2, has $\Delta E_Q = 0.87$ mm s^{-1}, and the isomer shift is $\delta_{Fe} = -0.03$ mm s^{-1}.[11] Spectra measured at 4.2 K in fields greater than 0.5 T show well-resolved magnetic hyperfine interactions (internal field, −20.5 T), proving that the ground state has electronic spin $S > 0$.[12] The isomer shift is an excellent indicator of the oxidation state. The value obtained here, $\delta_{Fe} = +0.01$ mm s^{-1} at 4.2 K, compares very well with those of ferryl $S = 1$ hemes ($\delta_{Fe} = 0.03$–0.11 mm s^{-1} at 4.2 K), lending firm support for an iron(IV) oxidation state.[13]

Beginning with Kimura and Kodama's report in 1979,[14a] a number of research groups[14,15] have studied the chemistry of macrocyclic transition-metal complexes with amido-*N* ligands.[14] The first macrocyclic tetraamido-*N* complex was reported by Margerum and Rybka[15a] in an important contribution that, among other things, demonstrated that metal insertion is possible for such

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(6) Crystal data: The structure was solved by Crystalytics Company. Single crystals of $[Et_4N][FeCl(\eta^4\text{-}\mathbf{1})]$ at 20 ± 1 °C are orthorhombic, space group $Pna2_1$-C_{2v}^9 (No. 33) with $a = 15.341$ (3) Å, $b = 15.261$ (3) Å, $c = 14.920$ (4) Å, $\alpha = 90.00°$, $\beta = 90.00°$, $\gamma = 90.00°$, $V = 3493$ (2) Å^3, and $Z = 4$ ($d_{calcd} = 1.248$ g cm^{-3}; μ_a(Mo K$\bar{\alpha}$) = 0.55 mm^{-1}). A total of 2920 independent reflections having 2θ(Mo K$\bar{\alpha}$) < 48.3° (the equivalent of 0.7 limiting Cu K$\bar{\alpha}$ spheres) were collected by using full (0.90° wide) ω scans and graphite-monochromated Mo K$\bar{\alpha}$ radiation. The structural parameters have been refined to a convergence of R_1 (unweighted, based on F) = 0.051 for 1796 independent reflections having $2\theta_{MoK\bar{\alpha}} < 48.3°$ and $I > 3\sigma(I)$.

(7) $[Et_4N][FeCl(\eta^4\text{-}\mathbf{1})]$ contains a moderately nonplanar amido-*N* ligand (amide O1C1N1: $\bar{\tau} = -16.9°$, $\chi_N = 7.3°$, $\chi_C = -3.2°$). The twist angle τ and the pyramidalization terms χ_C and χ_N are obtained from three of the four torsion angles associated with the six atoms of each amido-*N* unit: ω_1 (C–N–C–C), ω_2 (Fe–N–C–O), and ω_3 (C–N–C–O). The Dunitz terms are then defined as follows: $\tau = (\omega_1 + \omega_2)/2$; $\chi_N = (\omega_2 - \omega_3 + \pi) \bmod 2\pi$; $\chi_C = (\omega_1 - \omega_3 + \pi) \bmod 2\pi$. Here we use the modified twist angle, $\bar{\tau}$: $\bar{\tau} = (\tau) \bmod \pi$. (a) Dunitz, J. D.; Winkler, F. K. *J. Mol. Biol.* **1971**, *59*, 169–182. (b) Dunitz, J. D.; Winkler, F. K. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 251–263. (c) Warshel, A.; Levitt, M.; Lifson, S. *J. Mol. Spectrosc.* **1970**, *33*, 84–99. (d) Collins, T. J.; Coots, R. J.; Furutani, T. T.; Keech, J. T.; Peake, G. T.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1986**, *108*, 5333–5339. (e) Collins, T. J.; Workman, J. M. *Angew. Chem., Int. Ed. Engl.* **1989**, 912–914 and references therein. (f) Reference 4b. $[Et_4N][FeCl(\eta^4\text{-}\mathbf{1})]$ belongs to the ring-constrained class of nonplanar amido-*N* ligands. The other major class of nonplanar amido-*N* ligands involves cases where the nonplanar form is thermodynamically favored over planar analogues accessible by isomerization at the metal center.

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(10) Hickman, D. L.; Nanthakumar, A.; Goff, H. M. *J. Am. Chem. Soc.* **1988**, *110*, 6384–6390.

(11) δ_{Fe} values for Fe(III) complexes range from 0.2 to 0.6 mm s^{-1}. In a preliminary study of $[Et_4N]_2[Fe^{III}Cl(\eta^4\text{-}\mathbf{1})]$, $\delta_{Fe} \approx 0.25$ mm s^{-1} at 4.2 K was observed.

(12) The 300-MHz ^1H NMR spectrum of $[Et_4N][FeCl(\eta^4\text{-}\mathbf{1})]$ in $CDCl_3$ at 20 °C exhibits broad paramagnetically shifted features spread over a range of 50 ppm. The NMR of the ^1H and other nuclei are the subject of ongoing studies.

(13) See Table I in the following: Schulz, C. E.; Rutter, R.; Sage, J. T.; Debrunner, P. G.; Hager, L. P. *Biochemistry* **1984**, *23*, 4743–4754.

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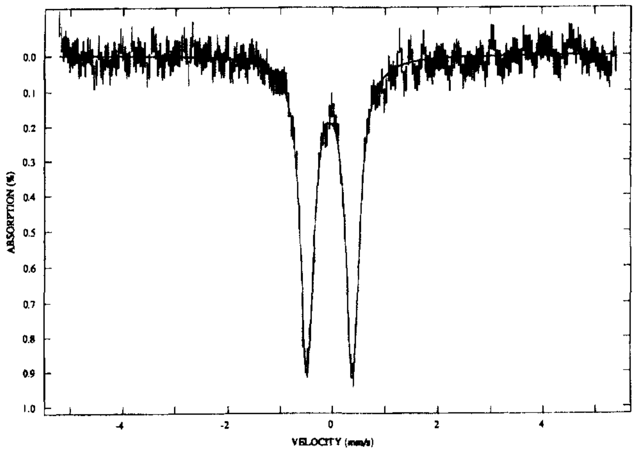

Figure 2. Mössbauer spectrum of $[Et_4N][FeCl(\eta^4-1)]$ in acetonitrile recorded at 150 K in zero field. The solid line results from fitting two Lorentzians (full width 0.30 mm s^{-1}) to the data.

a system. The weakly oxidizing copper(III) complex of Margerum's macrocycle slowly undergoes oxidative ligand decomposition.[15b] Iron(IV) species can be isolated with $[\eta^4-1]^{4-}$ because the macrocyclic tetraamide is resistant to oxidative destruction. We are continuing to expand the coordination chemistry of these ligand systems and the reaction chemistry of derivative complexes.

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Supplementary Material Available: Tables of data collection information, atom coordinates, Gaussian amplitudes, and bond lengths and angles for $[FeCl(C_{22}H_{34}N_4O_5)][N(C_2H_5)_4]$ (27 pages); a listing of structure factor amplitudes for $[FeCl(C_{22}H_{34}N_4O_5)][N(C_2H_5)_4]$ (9 pages). Ordering information is given on any current masthead page.

Photoinduced Conformational Ruffling of Distorted Porphyrin. Optical Resolution and Photochemical Behavior of Chiral "Single-Armed" Porphyrin Complexes

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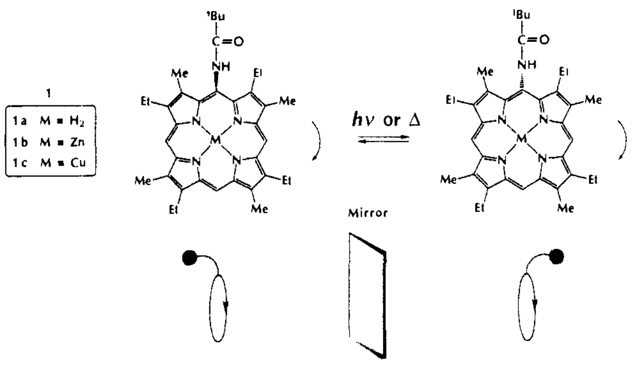
Photoinduced molecular motions of tetrapyrrole macrocycles continue to be of general interest. Whitten and co-workers have reported the photoinduced atropisomerization of the metal complexes of picket-fence porphyrins.[1] We report herein the flipping phenomena of the meso substituent of porphyrin, as studied by the thermal and photoinduced racemization profiles of the optical antipodes of a chiral "single-armed" porphyrin and its metal complexes (**1**).

Scheme I



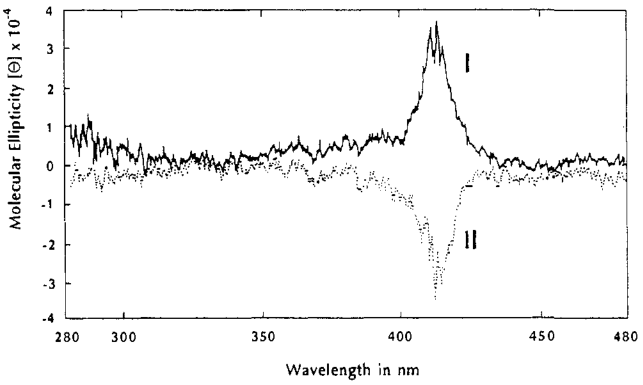


Figure 1. CD spectra of the antipodes of (α-PivNHEtioP)Zn (**1b**) in hexane/EtOH/$CHCl_3$ (70/20/10 v/v). I and II correspond to antipodes I and II in the text, respectively. Spectra were measured by using a quartz cell of 1-cm path length.

The "single-armed" porphyrin (**1**),[2] derived from etioporphyrin I (**2**), is considered to be distorted from planarity due to steric repulsion between the meso substituent and neighboring β substituents at the periphery (Scheme I).[3] Since **2** has enantiotopic faces (C_{4h} symmetry), the "single-armed" porphyrin (**1**) should be chiral due to the presence of the "amide arm" on either of the two enantiotopic faces of the porphyrin plane. In fact, the zinc complex **1b** (zinc α-(pivaloylamino)etioporphyrin I, (α-PivNHEtioP)Zn) showed two completely resolved peaks with comparable peak areas (fraction I, retention time 10.9 min; fraction II, retention time 36.5 min) when chromatographed on silica gel coated with cellulose tris(3,5-dimethylphenylcarbamate) with hexane/EtOH/$CHCl_3$ (70/20/10 v/v) as eluent.[4] The compounds corresponding to these two peaks, fractionated, were both identical with the original zinc porphyrin (**1b**) in terms of the absorption and ^1H NMR spectra, while the circular dichroism spectra were perfect mirror images of each other (Figure 1). Thus, the optical antipodes of **1b** were successfully resolved. The antipodes of the copper porphyrin (**1c**) were also resolved perfectly under the same conditions, while those of the free-base porphyrin (**1a**) were only partially resolved (60% enantiomeric purity). The HPLC analysis of **1a** exhibited two peaks (retention times 8.4 and

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(1) (a) Freitag, R. A.; Mercer-Smith, J. A.; Whitten, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 1226. (b) Freitag, R. A.; Whitten, D. G. *J. Phys. Chem.* **1983**, *87*, 3918.

(2) **1a** was prepared by the condensation of α-NH_2EtioPH_2 with pivaloyl chloride. Treatments of **1a** with metal acetates gave the corresponding metal complexes in quantitative yields. Detailed spectral data of **1a-c** are shown in the supplementary material.

(3) Comparison of the spectral data for **1a** and **1b** with those for etioporphyrin I and its zinc complex shows bathochromic shifts for the electronic absorptions (5-11 nm) and upfield shifts for the ^1H NMR signals of the meso protons (0.1-0.2 ppm). Such spectal profiles have been claimed to be due to the lack of coplanarity of the porphyrin disk: (a) Abraham, R. J.; Jackson, A. H.; Kenner, G. W.; Warburton, D. *J. Chem. Soc.* **1960**, 853. (b) Burbidge, P. A.; Collier, G. L.; Jackson, A. H.; Kenner, G. W. *J. Chem. Soc. B* **1967**, 930. (c) Gong, L.-C.; Dolphin, D. *Can. J. Chem.* **1985**, *63*, 401.

(4) Conditions: flow rate 1.0 mL min^{-1}, room temperature, monitored at 410 nm, the eluates collected in flasks cooled at −78 °C. The chromatographic conditions have been established for the resolution of the antipodes of chiral N-alkylated porphyrins: Kubo, H.; Aida, T.; Inoue, S.; Okamoto, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1015.

0002-7863/90/1512-5639$02.50/0