$CaCl_2$, 1 mM $MnCl_2$, and 0.1 M NaCl. Crystals were recovered following 24 h of incubation at 4 °C.

Chemical analysis of the crystals: Crystals were dissolved in 30 mM HCl, pH 1.5, and the amount of **1** was determined spectrophotometrically. A sample from this solution was immediately mixed with a ninefold volume of acetonitrile. The precipitating protein was removed by centrifugation, and the amount of remaining soluble **2** determined by HPLC.

Electron microscopy: The electron transmission micrograph shown in Figure 4 was prepared from samples placed on a freshly discharged, 300 mesh, carbon-coated parlodion grid, stained by 1 % phosphotungstate, pH 7, and observed at 100 kV with a Philips CM-12 electron microscope.

X-ray crystallography: The imaging plate area detector Rigaku Raxis-II implemented with high-resolution blue imaging plates and equipped with a Rigaku FRC rotating anode and focusing mirrors was used for the diffraction experiments. To overcome the weak diffracting power of the crystals, the combination of the high brilliance X-ray generator and focusing mirrors was used. The detector parameters and the accurate crystal – detector distance were determined using a high-quality orthorhombic homogeneous crystal of **1**, a short time before the start of the experiment. All diffraction experiments have been performed at low temperature generated by an Oxford Cryostream device. Crystals were mounted on the loops made of a nondiffracting monofilament nylon line. Hydrocarbon oil has been used as a cryoprotectant. Small oscillation angle (0.5°) diffraction images were taken from several crystals of the approximate size of 0.1 mm in the largest dimension, using exposure time of one hour in various places of the reciprocal space. These images were indexed using HKL package of the diffraction pattern processing programs.[27]

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N-Substituted Corroles: A Novel Class of Chiral Ligands[**]

Zeev Gross[*] and Nitsa Galili

There is a steady increase of interest in porphyrin-like macrocycles, which display many novel physical and chemical properties.[1] One class of such molecules are the corroles, whose skeleton may also be viewed as the aromatic version of corrin, the moiety ligated to cobalt in the coenzyme of vitamin B_{12}.[2] Alternatively, and more commonly, corroles are considered as analogues of porphyrins that have one less carbon atom (Scheme 1); both macrocycles are aromatic and provide an inner core containing four nitrogen atoms as an equatorial coordination template for metal ions.[3]

Indeed, corroles and porphyrins share many spectroscopic and chemical features.[2] Still, corroles act as trianionic rather than dianionic ligands, their inner core is somewhat contracted, and their symmetry (C_{2v}) is lower than that of porphyrins (D_{4h}). The first two factors were found to have a remarkable effect on the stabilization of metal ions in exceptionally high oxidation states.[4] One consequence of the different symmetries is that while substitution of one of the inner NH protons in porphyrins leads to a single product, two isomers are formed in the case of corroles (N21- and N22-substituted corroles, Scheme 2).[5] In addition, since the N-substituted

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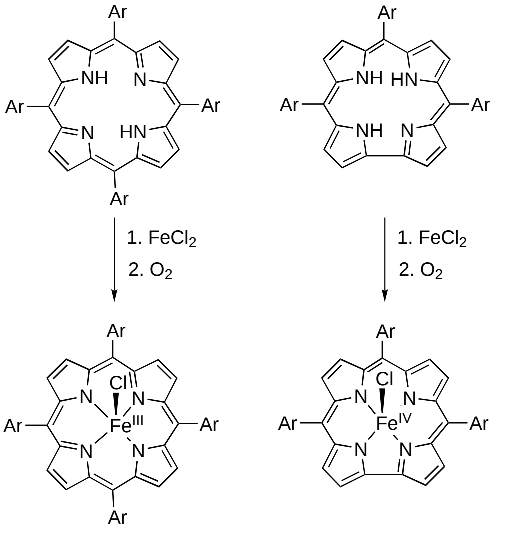
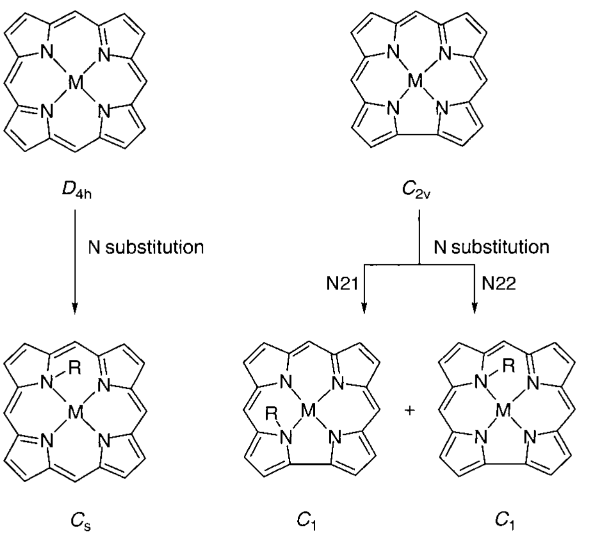


Scheme 1. Schematic representation of the *meso*-aryl-substituted porphyrins (left) and corroles (right), and their iron complexes.

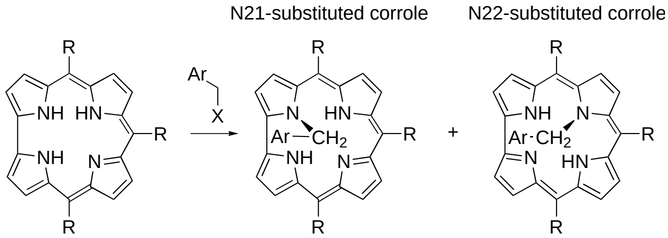


Scheme 2. The symmetry of porphyrins and corroles, and of their N-substituted derivatives.

corroles retain two inner NH groups, they may be expected to form stable complexes with divalent metal ions. This anticipation is indeed fulfilled, and stable complexes were reported with Ni^{II}, Cu^{II}, Pd^{II}, and Co^{II} as well as with the monovalent Rh^{I}.[2] However, a most crucial difference between N-substituted porphyrins and corroles was not appreciated until now. With porphyrins, the symmetry of the single product is quite low (C_s), but one mirror plane is conserved (bisecting the N-substituted pyrrole). However, as can be easily seen from Scheme 2, there is absolutely no symmetry element in N-substituted corroles; that is, their symmetry is C_1. This holds for both the N21- and the N22-substituted corroles. Still, in spite of the almost 35 years of research, it has not been recognized that N-substituted corroles are chiral.

The first corrole was reported in 1964 and the first N-substituted corrole in 1965,[5, 6] but the research activity remained quite low because reasonably simple and short syntheses of corroles were introduced only during the last few years.[7] We have recently contributed to this field in disclosing the synthesis of 5,10,15-tris(pentafluorophenyl)corrole (TpFPC-H_3, see Scheme 3) directly from pyrrole and pentafluorobenzaldehyde.[8] As one appealing feature of TpFPC-H_3 is its structural similarity to 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin—whose metal complexes are among the most active oxygenation catalysts—we have recently prepared several metal complexes of TpFPC-H_3. In what appears to be the first ever application of corroles, we have demonstrated that they are very good catalysts indeed.[9]

We now describe several N-substituted corroles in order to demonstrate the extremely easy access to these chiral metal-binding macrocycles. The starting material in all cases was TpFPC-H_3, whose reaction with either benzyl chloride or 2-(chloromethyl)pyridine leads to the *N*-benzylcorroles **1a** and **2a** and the *N*-picolylcorroles **1b** and **2b** (Scheme 3) in



R = C_6F_5
TpFPC-H_3

1a: Ar = phenyl
2a: Ar = 2-pyridyl

1b: Ar = phenyl
2b: Ar = 2-pyridyl

Scheme 3. Reaction of TpFPC-H_3 with arylmethyl halide to provide N21- and N22-substituted corroles.

high overall yields of 74% and 90%, respectively (see Experimental Section). In both cases, the N21- and N22-substituted corroles were easily separated by column chromatography (**1a**:**1b** = 1.2:1, **2a**:**2b** = 1.5:1).

The chirality of each of the isomers is easily recognized by several methods, as demonstrated for **2a**. The first consequence of the chirality of **2a** is that its benzylic protons are not identical, but rather diastereotropic. This shows up in the ^1H NMR spectrum, where the benzylic protons—easily identified by their position at high field due to the diamagnetic current shift of the corrole—appear as two mutually coupled resonances (Figure 1a). Secondly, in the presence of an unichiral acid the number of NMR resonances doubles due to the formation of diastereomeric salts (Figure 1b).[10] The ^{19}F NMR spectra are also very informative, as demonstrated in traces c–e of Figure 1. The bottom spectrum is of TpFPC-H_3, the middle one of **2a**, and at the top that of **2a** in the presence of excess (1*S*)-(+)-10-camphorsulfonic acid. From the bottom to the top the number of *para*-F resonances increases from two (in the ratio of 2:1), to three, and finally to six. These are exactly the expected patterns for the C_{2v} symmetry of TpFPC-H_3, the C_1 symmetry of **2a**, and the two diastereomeric salts of **2a** with the unichiral acid.

All four N-substituted corroles can be separated into their enantiomers by HPLC on Chiralcel OD, a chiral column which has previously been used for separation of chiral porphyrins.[11] This is demonstrated for **2a** in the inset of Figure 2, which shows the HPLC profiles of the racemic

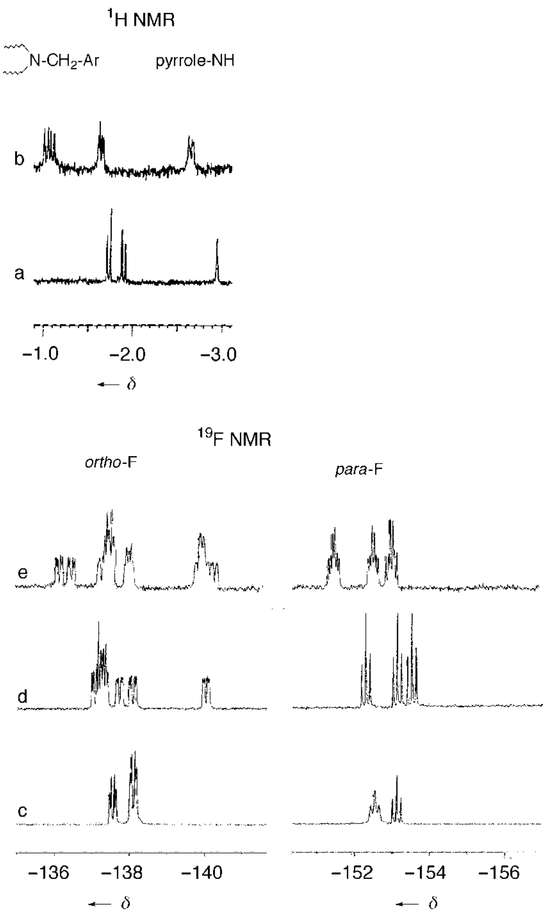


Figure 1. The high-field region of the ^{1}H NMR spectra a) of **2a** and b) of **2a** in the presence of excess (1*S*)-(+)-10-camphorsulfonic acid. A section of the ^{19}F spectra c) of TpFPC-H$_3$, d) of **2a**, and e) of **2a** in the presence of excess (1*S*)-(+)-10-camphorsulfonic acid.

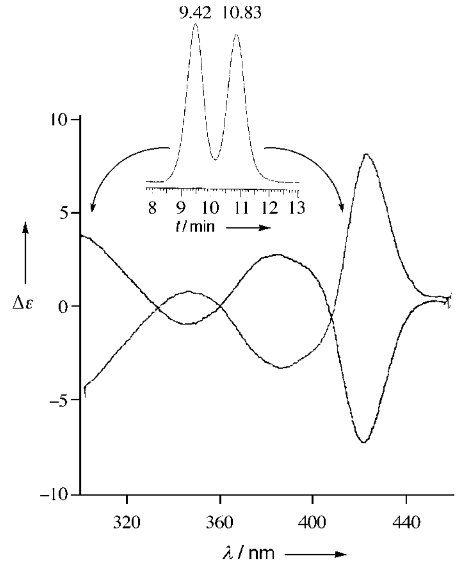
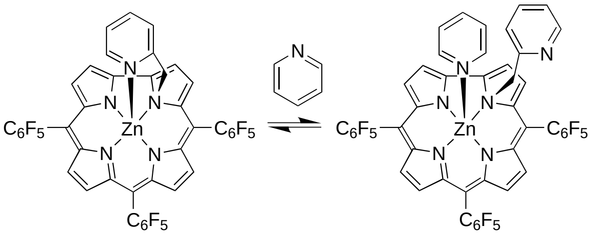


Figure 2. The CD spectra of the separated enantiomers of **2a**. Inset: the HPLC profile of the racemic mixture of **2a**.

mixture. Also shown in Figure 2 are the CD spectra of the separated enantiomers of **2a**, obtained with greater than 98% *ee*.

There are several major advantages of chiral corroles over other related chiral ligands. The chiral corroles are prepared in two very simple steps, requiring only pyrrole, aldehyde, and arylmethyl halide. This is in sharp contrast to the main methodology for the preparation of chiral porphyrins, which consists of many synthetic steps and relies on the covalent attachment of chiral molecules.[12] The latter limitation holds also for the chiral *N,N'*-bis(salicylidene)ethylenediamine dianions (salens),[13] which are excellent catalysts for various catalytic transformations. In addition, one important factor in asymmetric catalysis by metal complexes of chiral ligands is the proximity of the chiral moieties to the metal center. This has been suggested to be the principal rationale for the general superiority of the metal complexes of chiral salens over those of chiral porphyrins in inducing asymmetry.[12] Now, in the complexes of chiral corroles, the chirality is even closer than in those of salens. Finally, the potential variety in terms of the N substituents is very large and allows for extremely easy design for specific purposes.

As a first step toward such goals we have prepared the zinc(II) complex of **2a** by the reaction of **2a** with zinc acetate in pyridine. The product initially obtained contained a molecule of pyridine coordinated to the metal, whereas after column chromatography this pyridine molecule was displaced and the metal was coordinated to the pyridine moiety of the picolyl substituent. This process could be reversed by addition of external pyridine (Scheme 4), and was easily followed by NMR spectroscopy (Figure 3). Most important, the external



Scheme 4. Addition of pyridine to the zinc complex of **2a** obtained after column chromatography.

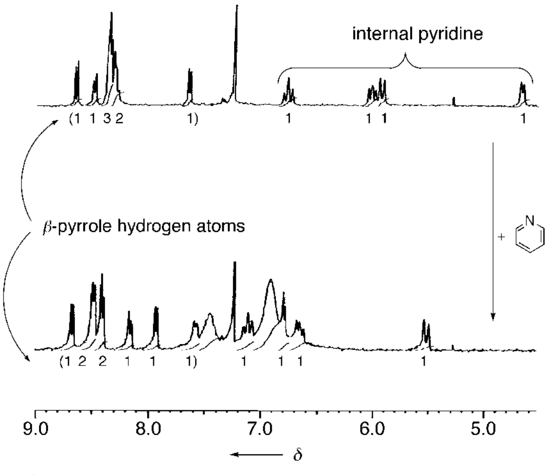


Figure 3. The ^{1}H NMR spectra of the zinc complex of **2a** without (top) and with external pyridine (bottom); see also Scheme 4.

pyridine is almost certainly bound to the same site as the internal picolyl, as indicated by the large downfield shift ($\Delta\delta = 2.33$ ppm) of the benzylic protons upon coordination. In a similar experiment with the zinc(II) complex of **1a**, the benzylic protons are essentially not affected. Such a combination of a Lewis acidic metal and the nucleophilic pyridine in a chiral environment creates an excellent reaction center.

In summary, we have demonstrated the easy access to chiral N-substituted corroles in only two synthetic steps, starting from simple and commercially available starting materials. The major advantages of these macrocycles are the close distance of the chiral center to a coordinated metal and the large variability in terms of possible N substituents. We trust that the results of these investigations will have a far-reaching impact on metal-catalyzed asymmetric transformations of prochiral hydrocarbons, a field in the forehead of scientific and industrial interests.[14]

Experimental Section

1a, **b**: Heating of a solution of TpFPC-H_3 (46 mg, 58 μmol) and benzyl bromide (70 μL, 0.58 mmol) in dry toluene (25 mL) in the presence of dry K_2CO_3 (0.16 g) for 4 h, followed by column chromatography on basic alumina (100:2 hexane:EtOAc), resulted in the isolation of 17 mg (33 %) of **1b** (eluted first) and 21 mg (41 %) of **1a**.

1a: UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$) = 412 (126.9), 572 (25.7), 612 nm (18.5); ^{1}H NMR ($CDCl_3$): $\delta = 8.80$ (dd, $J_1 = 4.28$, $J_2 = 2.14$ Hz, 1 H), 8.72 (br d, $J = 4.28$ Hz, 1 H), 8.59 (m, 3 H), 8.39 (d, $J = 4.28$ Hz, 1 H), 8.27 (d, $J = 4.28$ Hz, 1 H), 7.60 (d, $J = 4.28$ Hz, 1 H), 6.82 (t, $J = 7.5$ Hz, 1 H), 6.64 (t, $J = 7.5$ Hz, 2 H), 5.04 (d, $J = 7.5$ Hz, 2 H), −2.03 (d, $J = 13.92$ Hz, 1 H), −2.34 (d, $J = 14.99$ Hz, 1 H), −3.07 (br s, 2 H); ^{19}F NMR ($CDCl_3$): $\delta = -137.15$ (dd, $J_1 = 27.6$, $J_2 = 10.2$ Hz, 1 F), −137.52 (dt, $J_1 = 27.0$, $J_2 = 9.8$ Hz, 2 F), −137.95 (dd, $J_1 = 27.6$, $J_2 = 9.8$ Hz, 1 F), −139.70 (d, $J = 22.8$, 1 F), −152.10 (t, $J = 22.0$ Hz, 1 F), −153.05 (t, $J = 22.4$ Hz, 1 F), −153.43 (t, $J = 22.0$ Hz, 1 F), −161.7 (m, 2 F), −162.2 (m, 4 F).

1b: UV/Vis (CH_2Cl_2): $\lambda_{max} = 428$ (Soret), 520, 560, 590, 648 nm; ^{1}H NMR ($CDCl_3$): $\delta = 9.11$ (t, $J = 4.28$ Hz, 2 H), 8.72 (d, $J = 4.28$ Hz, 1 H), 8.64 (d, $J = 4.28$ Hz, 1 H), 8.59 (br s, 1 H), 8.44 (d, $J = 5.35$ Hz, 1 H), 8.28 (d, $J = 4.28$ Hz, 1 H), 7.96 (d, $J = 5.35$ Hz, 1 H), 6.67 (t, $J = 7.5$ Hz, 1 H), 6.44 (t, $J = 7.5$ Hz, 2 H), 4.35 (d, $J = 7.5$ Hz, 2 H), −2.99 (br s, 2 H), −3.48 (d, $J = 14.99$ Hz, 1 H), −4.09 (d, $J = 13.92$ Hz, 1 H); ^{19}F NMR ($CDCl_3$): $\delta = -137.43$ (dt, $J_1 = 24.87$, $J_2 = 9.04$ Hz, 2 F), −137.92 (dd, $J_1 = 27.13$, $J_2 = 9.04$ Hz, 1 F), −138.6 (br t, $J = 27.13$ Hz, 2 F), −139.47 (br d, $J = 22.61$ Hz, 1 F), −152.22 (t, $J = 22.61$ Hz, 1 F), −152.64 (t, $J = 20.35$ Hz, 1 F), −153.10 (t, $J = 20.35$ Hz, 1 F), −161.9 (m, 6 F); HR-MS (positive ion mode): *m*/*z*: 887.123 (calcd for $C_{44}H_{18}N_4F_{15}$: 887.129).

2a, **b**: Application of the same procedure as for **1a**, **b**, but with 2-(chloromethyl)pyridine hydrochloride instead of benzyl bromide, resulted in the formation of a 1.5:1 mixture of **2a** and **2b** in 90 % yield. Recrystallization from CH_2Cl_2/hexane afforded 20 mg of **2a** and 10 mg of **2b**.

2a: UV/Vis (CH_2Cl_2):λ_{max} ($\varepsilon \times 10^{-3}$) = 412 (133.4), 572 (27.1), 612 nm (12.6); ^{1}H NMR ($CDCl_3$): $\delta = 8.84$ (d, $J = 4.88$ Hz, 1 H), 8.64 (br s, 1 H), 8.52 (m, 3 H), 8.33 (d, $J = 4.88$ Hz, 1 H), 8.29 (d, $J = 4.88$ Hz, 1 H), 7.74 (d, $J = 4.88$ Hz, 1 H), 7.52 (d, $J = 3.66$ Hz, 1 H), 7.14 (t, $J = 7.32$ Hz, 1 H), 6.72 (t, $J = 7.32$ Hz, 1 H), 5.37 (d, $J = 7.32$ Hz, 1 H), −1.70 (d, $J = 15.87$ Hz, 1 H), −1.88 (d, $J = 15.87$ Hz, 1 H), −2.92 (br s, 2 H); ^{19}F NMR ($CDCl_3$): $\delta = -137.22$ (m, 3 F), −137.73 (d, $J = 22.61$ Hz, 1 F), −138.07 (dd, $J_1 = 22.61$, $J_2 = 9.04$ Hz, 1 F), −140.01 (d, $J = 22.61$ Hz, 1 F), −152.25 (t, $J = 22.61$ Hz, 1 F), −153.09 (t, $J = 22.61$ Hz, 1 F), −153.48 (t, $J = 22.61$ Hz, 1 F), −162.1 (m, 6 F).

2b: UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$) = 428 (146.1), 520 (6.7), 560 (11.7), 596, 650 nm; ^{1}H NMR ($CDCl_3$): $\delta = 9.12$ (t, $J = 4.66$ Hz, 2 H), 8.70 (d, $J = 4.66$ Hz, 1 H), 8.63 (d, $J = 4.66$ Hz, 1 H), 8.58 (d, $J = 4.66$ Hz, 1 H), 8.44 (d, $J = 4.66$ Hz, 1 H), 8.29 (d, $J = 4.66$ Hz, 1 H), 7.97 (d, $J = 4.66$ Hz, 1 H), 7.49 (d, $J = 5.59$ Hz, 1 H), 6.93 (dt, $J_1 = 8.39$, $J_2 = 1.86$ Hz, 1 H), 6.56 (dt, $J_1 = 5.59$, $J_2 = 2.80$ Hz, 1 H), 4.73 (d, $J = 7.45$ Hz, 1 H), −3.12 (br s, 2 H), −3.28 (d, $J = 15.84$ Hz, 1 H), −3.94 (d, $J = 15.84$ Hz, 1 H); ^{19}F NMR ($CDCl_3$): $\delta = -137.56$ (t, $J = 27.13$ Hz, 3 F), −138.64 (d, $J = 22.61$ Hz, 1 F), −138.88 (d, $J = 22.61$ Hz, 1 F), −139.72 (d, $J = 22.61$ Hz, 1 F), −152.23 (t, $J = 22.61$ Hz, 1 F), −152.68 (t, $J = 22.61$ Hz, 1 F), −153.24 (t, $J = 22.61$ Hz, 1 F), −161.9 (m, 6 F).

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