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Facile Synthesis of *meso*-Tetrakis(perfluoroalkyl)porphyrins: Spectroscopic Properties and X-ray Crystal Structure of Highly Electron-Deficient 5,10,15,20-Tetrakis(heptafluoropropyl)porphyrin[†]

Stephen G. DiMagno* and R. Allen Williams

Department of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588-0304

Michael J. Therien*

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

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The synthesis, structure, optical spectrum, and electrochemistry of 5,10,15,20-tetrakis(perfluoropropyl)porphyrin, **1**, are reported. The high yield preparative method, starting from (hydroxymethyl)pyrrole precursors such as 2,2,3,3,4,4,4-heptafluoro-1-(2-pyrrolyl)-1-butanol, **2**, is general for a wide variety of *meso*-perfluoroalkyl-substituted porphyrins. The X-ray crystal structure of **1** is noteworthy in that it shows a S_4-distorted porphyrin core that appears to derive from an unusual hydrogen bonding interaction between a fluorocarbon fluorine atom and a porphyrin NH proton. A comparison of the electrochemical properties of the zinc derivative of **1** with those of [5,10,15,-20-tetrakis(pentafluorophenyl)-2,3,7,8,12,13,17,18-octabromoporphinato]zinc(II) indicates that *meso*-perfluoroalkylated porphyrins are among the most electron-deficient porphyrin ligands known. *meso*-Tetrakis(perfluoroalkyl)porphyrins and their elaborated derivatives, with their unusual electronic properties, should thus serve as useful ligands for a variety of catalytic and stoichiometric transition metal-mediated redox reactions.

Introduction

The utility of the porphyrin ligand has been demonstrated in a wide variety of metal-catalyzed redox reactions. Catalyst stability as well as catalytic activity of the metalloporphyrin in many of these metal-mediated conversions would be dramatically enhanced if suitably robust, highly electron-deficient porphyrin ligands were readily available. For example, the electrocatalytic reduction of O_2 at cofacial bis[porphinato(metal)] complexes should be able to be driven at or near the thermodynamic potential provided the metal centers could be rendered more electrophilic.[1] Likewise, appropriate cofacial metalloporphyrin catalysts based on extremely electron-deficient porphyrin ligands may also find utility in electrocatalytic water oxidation. Moreover, a substantial body of literature describing metalloporphyrin-catalyzed alkane hydroxylation[2] and alkene epoxidation[3] reactions underscores the need for and interest in such materials.

Numerous electron-withdrawing groups have been attached to the porphyrin ring; specific examples include *meso*- and/or β-modified porphyrins bearing fluoro, chloro, bromo, pentafluorophenyl, cyano, or nitro groups as well as β-derivatized species featuring trifluoromethyl moieties.[4] The degree to which these groups stabilize the porphyrin HOMO (as reflected in the oxidation potential) depends on its point of attachment to the porphyrin ring as well as upon a convolution of steric and electronic effects. Nonplanar distortions of the porphyrin ring caused by bulky electron-withdrawing substituents raise the HOMO energy, partially counteracting the gains made by additional substitution.[5] For example, the oxidation potential of 2-bromo-5,10,15,20-tetraphenylporphyrin is shifted 80 mV positive from that of 5,10,15,-20-tetraphenylporphyrin (TPP),[6] while the addition of 7 more bromine atoms is only responsible for a further shift of 220 mV.[7] Some of this leveling effect is due to the conformational changes that further substitution engenders. Another critical consideration regards the nature of the substituents fused directly to the porphyrin π-system: groups with π-electrons can interact strongly with the HOMO by electron donation, an effect that

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becomes more important as the porphyrin becomes increasingly electron-deficient.

Due to both their electron-deficient nature and their limited ability to function as π-donors, it has been recognized that perfluoroalkyl moieties fused to the porphyrin *meso*-position should drastically alter the electronic nature of the porphyrin ligand. Recent theoretical studies by Gassman suggest that porphyrins bearing four *meso* trifluoromethyl groups ($\sigma_{p^+} = 0.61$) will have a substantially lower energy HOMO than the corresponding *meso* cyano ($\sigma_{p^+} = 0.66$) substituted porphyrin:[8] this coincides with experimental evidence indicating that a ranking of the electron-withdrawing ability of substituents using Hammett σ_{p^+} values is inappropriate for ring-fused groups[6,9] and bolsters the view that *meso*-tetrakis(perfluoroalkyl)porphyrins should have unique electronic properties.

Experimental Section

Materials. All manipulations were carried out under nitrogen previously passed through an O_2 scrubbing tower (Schweizerhall R3-11 catalyst) and a drying tower (Linde 3-Å molecular sieves) unless otherwise stated. All solvents utilized in this work were obtained from Fisher Scientific (HPLC Grade). Tetrahydrofuran (THF), diethyl ether, hexane, and toluene were distilled from Na/benzophenone under N_2. Methylene chloride and pyridine were distilled under N_2 from calcium hydride. Pyrrole was distilled from CaH_2 under vacuum and stored under N_2. Heptafluoropropionaldehyde, heptafluorobutyryl chloride, p-TsOH·H_2O, triethylamine, and sodium borohydride were obtained from Aldrich and were used as received. [5,10,15,20-Tetrakis(pentafluorophenyl)-2,3,7,8,-12,13,17,18-octabromoporphinato]zinc(II) and 5,10,15,20-[tetraphenylporphinato]zinc(II) were synthesized according to literature methods. Chemical shifts for ^1H NMR spectra are relative to residual protium in the deuterated solvents ($CDCl_3$, $\delta = 7.24$ ppm). Chemical shifts for ^{13}C NMR spectra are relative to deuteriochloroform solvent ($CDCl_3$, $\delta = 77.00$ ppm). All J values are reported in hertz. Chromatographic purification (silica gel 60, 230–400 mesh, EM Science) of all newly synthesized compounds was accomplished on the benchtop. Elemental analyses were performed by M-H-W Laboratories (Phoenix, AZ). Mass spectra were performed at the Midwest Center for Mass Spectrometry at the University of Nebraska.

Instrumentation. Electronic spectra were recorded on an OLIS UV/vis/NIR spectrophotometry system that is based on the optics of a Carey 14 spectrophotometer. Cyclic voltammetric measurements were performed with a PAR 273 electrochemical analyzer and a single compartment electrochemical cell (total volume = 2 mL).

2,2,3,3,4,4,4-Heptafluoro-1-(2-pyrrolyl)-1-butanol (2). Heptafluorobutyraldehyde hydrate (9.26 g, 42.9 mmol) was placed in a 100 mL Schlenk flask, degassed, and placed under nitrogen. Pyrrole (5.95 mL, 85.8 mmol) and NaOH (4.52 g, 113 mmol) were added, and the mixture was stirred overnight, during which time it solidified. The volatiles were removed *in vacuo*, leaving a light brown solid. The solid was dissolved in 40 mL of water, and the solution was extracted (4 × 50 mL) with CH_2Cl_2. The organic layers were dried over $Na_2(SO_4)$ and then evaporated to dryness leaving 5.39 g (47%) of **2** isolated as a light yellow-brown solid, mp 69–71 °C. This material was sufficiently pure for further reactions. An analytical sample was recrystallized from toluene: colorless needles; mp 72–72.5 °C; ^1H NMR ($CDCl_3$, 360 MHz) δ 8.55 (br s, 1H), 6.87 (dt, 1H, $J_1 = 2.7$ Hz, $J_2 = 1.5$ Hz), 6.32 (m, 1H), 6.22 (dt, 1H, $J_1 = 2.7$ Hz , $J_2 = 3.5$ Hz), 5.26 (dd, 1H, $J_{HF} = 7.8$ Hz, $J_{HF'} = 16.7$ Hz), 2.42 (br s, 1H); $^{13}C\{^1H$ decoupled$\}$ NMR ($CDCl_3$, 50.3 MHz) δ 123.35, 120.08, 110.12, 108.73, 66.54 (dd, $J_{CF} = 23$ Hz, $J_{CF'} = 29$ Hz); $^{13}C\{^{19}F$ decoupled$\}$ NMR ($CDCl_3$, 125.7 MHz) δ 123.35, 120.05 (d, $J_{HC} = 190.5$ Hz), 117.74, 114.42, 110.05 (d, $J_{HC} \approx 184$ Hz), 109.32, 108.63 (d, $J_{HC} \approx 172$ Hz), 66.51 (d, $J_{HC} = 146.1$); FAB MS [m/z (rel inten)] 266.036 81 (M + 1, 1.5), 265.033 22 (M^+, 15.8). Anal. Calcd for $C_8H_6F_7NO$: C, 36.24; H, 2.28; N, 5.28. Found: C, 36.40; H, 2.46; N, 5.14.

Alternatively, 2,2,3,3,4,4,4-heptafluoro-1-(2-pyrrolyl)-1-butanol could be prepared from pyrrole and heptafluorobutyryl chloride using the following two-step procedure.

2,2,3,3,4,4,4-Heptafluoro-1-(2-pyrrolyl)-1-butanol, method 2. Pyrrole (7.46 mL, 0.108 mol), triethylamine (18.1 mL, 0.129 mol), and THF (500 mL) were placed under N_2 in a 1 L round bottom flask equipped with a magnetic stirring bar. The flask was cooled in an ice bath before heptafluorobutyryl chloride (25 g, 0.108 mol) was added by syringe. A thick white precipitate formed immediately, and swirling was required to free the stir bar. The mixture was stirred for 4 h at 25 °C. The mixture was filtered by suction, and the amine salt was washed with 3 (100 mL) portions of dry ether. The filtrate was collected, and the solvents were removed by rotary evaporation leaving a brown oil. The oil was dissolved in 300 mL of 50% aqueous methanol, and the resulting solution was treated with $NaHCO_3$ (1 g) and $NaBH_4$ (8.2 g). The mixture was stirred at 25 °C for 10 h, and an additional portion of $NaBH_4$ (2 g) was added. After 2 h approximately half of the solvent was removed by rotary evaporation, water was added (250 mL), and the mixture was extracted twice with 200 mL of ether. The combined organic layers were dried over $NaSO_4$, and the solvents were evaporated leaving 2,2,3,3,4,4,4-heptafluoro-1-(2-pyrrolyl)-1-butanol (23.5 g, 0.089 mol, 82%) isolated as a light brown solid. This material was recrystallized from toluene.

5,10,15,20-Tetrakis(heptafluoropropyl)porphyrin (1). Reagent grade benzene (650 mL) was placed in a 1 L two-necked round bottom flask equipped with a recycling Dean-Stark trap and an efficient condenser, and p-TsOH·H_2O (50 mg) was added. The solution was heated at reflux, and water was removed by azeotropic distillation. After 20 min the heat source was removed and the solution was cooled under dry N_2. The trap was charged with active 4 Å molecular sieves, and the solution was again brought to reflux. Recycling of the solvent through the drying agent was continued for 20 min. Compound **2** (265 mg, 1 mmol) was dissolved in 10 mL of dry benzene and added to the dry, boiling benzene solution. The solution became pink and then gradually darkened. Heating was continued for 35 min. A vigorous boil was maintained during the course of the reaction. The reaction was quenched with DDQ (600 mg). Heating was continued for 30 min;

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Table 1. Summary of Structure Determination of 5,10,15,20-Tetrakis(heptafluoropropyl)porphyrin

formula	$C_{32}H_{10}F_{28}N_4$
formula wt	982.42
crystal class	monoclinic
space grp	C2/c (#15)
Z	4
cell constants	
a (Å)	20.778(3)
b (Å)	15.543(5)
c (Å)	11.092(2)
β (deg)	103.28(1)
V (Å^3)	3486(2)
μ (cm^{-1})	20.02
D_{calc} (g/cm^3)	1.872
F(000)	1928
radiation	Cu Kα (λ = 1.541 84 Å)
θ range (deg)	2.0 – 60.0°
scan mode	$\omega - 2\theta$
h, k, l collected	±23, +17, +12
no. reflns measured	2879
no. unique reflns	2597
no. reflns used in refinement	1659 ($F^2 > 3.0\sigma$)
no. parameters	291
data/parameter ratio	5.7
R_1	0.065
R_2	0.094
GOF	3.076

pyridine (5 mL) was added, and the mixture was heated at reflux for an additional h. The solvents were removed, and the remaining residue was dissolved, to the extent possible, in 50 mL of warm hexane containing 1 mL of pyridine. The suspension was poured directly onto a short (2 × 10 cm), hexane-packed column of silica gel topped with a 2 cm pad of Celite. Elution was carried out with hexane. Collection was continued until the eluant was nearly colorless. The solvent was removed, and the resulting solid was washed with 10 mL of cold hexane and filtered to yield essentially pure **1** (90 mg) in 37% yield: ^{1}H NMR (360 MHz, $CDCl_3$) δ 9.50 (s, 8 H), −2.30 (s, 2 H); ^{19}F NMR ($CDCl_3$, TFA ext. std.) δ −79.7 (br t, 12 F), −81.2 (br s, 8 F), −118.7 (broad s, 8 F); vis ($CHCl_3$) 404.5 (5.02), 510.5 (3.97), 545 (3.88), 594 (3.67) 647 (3.93); low resolution FAB MS 982 (calcd 982). An analytical sample was recrystallized from $CHCl_3$. Anal. Calcd for $C_{32}H_{10}F_{28}N_4$: C, 39.12; H, 1.03; N, 5.70. Found: C, 39.39; H, 0.91; N, 5.53.

Control Experiments for Water Removal. The condensation reactions were performed on the same scale and in the same concentration (1 mmol of reactants, 600 mL of benzene, 50 mg of p-TsOH·H_2O) as the above procedure. The solvent and acid were predried by azeotropic distillation for all four reactions. In reactions where water removal was not employed, a simple reflux condenser was substituted for the Dean-Stark trap immediately before the reactants were added to the benzene solution. Quenching of the reaction and isolation of the product were performed as above.

X-ray Crystallography.[10] The crystal structure for 5,10,15,20-tetrakis(heptafluoropropyl)porphyrin (**1**) was solved by direct methods (SIR88).[11] Table 1 contains details of the crystal and data collection parameters. The structure was determined by Dr. Patrick Carroll at the Chemistry Department's X-ray facility at the University of Pennsylvania.

5,10,15,20-Tetrakis(heptafluoropropyl)porphyrin (1). Crystallization was induced from chloroform solution at −20 °C over a 2 day period to yield rectangular purple plates. The crystal dimensions were 0.03 × 0.18 × 0.40 mm^3. Compound **1** crystallizes in the monoclinic space group $C2/c$ (systematic absences hkl, $h + l$ = odd, and $h0l$, l = odd) with a = 20.778(3) Å, b = 15.543(5) Å, c = 11.092(2) Å, β = 103.28(1)°, V = 3486(2) Å^3, Z = 4, and d_{calc} = 1.872 g/cm^3. The cell constants were determined from a least squares fit of the setting angles for 25 accurately centered reflections. X-ray intensity data were collected on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Cu–Kα radiation (λ = 1.541 84 Å) and using the $\omega - 2\theta$ scan technique. X-ray data were processed, and the structure was solved and refined using the Enraf-Nonius MolEN package on a DEC MicroVAX 3100 computer. A total of 2879 reflections were measured over the ranges: $4 \le 2\theta \le 120°$, $-23 \le h \le 23$, $0 \le k \le 17$, $0 \le l \le 12$. Three standard reflections measured every 3500 s of X-ray exposure showed an intensity decay of 2.8% over the course of data collection. A linear decay correction was applied.

The intensity data were corrected for Lorentz and polarization effects but not for absorption. Of the reflections measured a total of 1659 unique reflections with $F^2 > 3\sigma(F^2)$ were used during subsequent structure refinement. Refinement was by full-matrix least-squares techniques based on F to minimize the quantity $\Sigma w(|F_o|-|F_c|)^2$ with $w = 1/\sigma^2(F)$. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included as constant contributions to the structure factors and were not refined. Refinement converged to R_1 = 0.065 and R_2 = 0.094.

Results and Discussion

Conventional porphyrin synthetic methodologies[12] are inappropriate for the fabrication of *meso*-perfluoroalkylporphyrins.[13] As Scheme 1 illustrates, formation of the key porphyrin intermediate, porphyrinogen, is under kinetic, not thermodynamic, control.[14] Particularly pertinent to the synthesis of *meso*-perfluoroalkylporphyrins is the circumvention of problems posed by the presence of the extra H_2O that is generated (twice the usual quantity) during condensation reactions employing perfluoroalkylaldehydes. The strong acid employed also raises the concentration of protonated pyrrole species, thereby increasing the likelihood that any porphyrinogen formed will undergo ring opening by reaction with water. Open chain species are eventually removed from solution by the formation of insoluble polymers. Successful syntheses of *meso*-tetrakis(perfluoroalkyl)porphyrins would thus appear to require removal of H_2O as it is formed. We undertook the synthesis of 5,10,15,20-tetrakis(heptafluoropropyl)porphyrin (**1**) from pyrrole and heptafluorobutyraldehyde to determine whether water removal would facilitate product formation. Table 2 (entries a and b) demonstrates that this in fact is a key synthetic concept.[15]

Previous workers have demonstrated quite clearly that porphyrinogen formation is a reversible process when

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(10) The atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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(13) No report of the synthesis of *meso*-tetrakis(perfluoroalkyl)porphyrins has been published in the open literature. The synthetic routes to such compounds reported in the patent literature gave no porphyrin in our hands. See: (a) Ellis, P. E., Jr.; Lyons, J. E.; Myers, H. K., Jr. Eur. Patent 0 471 561 A2, 1992. (b) Ellis, P. E., Jr.; Lyons, J. E. Eur. Patent 0 494 508 A1, 1992.

(14) Our use of the terms kinetic and thermodynamic product is consistent with: Lowry, T. H.; Richardson, S. *Mechanism and Theory in Organic Chemistry*, Harper and Row: New York, 1981. These definitions are not inconsistent with reversibility of individual steps in a complex reaction sequence, as has been observed for porphyrinogen formation.[12b] We will fully address mechanistic issues relevant to acid-catalyzed porphyrinogen-forming reactions in another publication.

(15) In contrast to typical Lindsey conditions,[12b] synthesis of highly electron-deficient porphyrins via acid-catalyzed condensation requires extremely strong acid. Reactions listed in Table 2 utilized benzene (650 mL) as solvent and p-TsOH·H_2O (50 mg) as the catalyst. When water removal was employed, it was executed by continuous azeotropic distillation of the solvent through a recycling Dean-Stark trap charged with freshly-activated 4 Å molecular sieves, as described in the Experimental Section.

Scheme 1

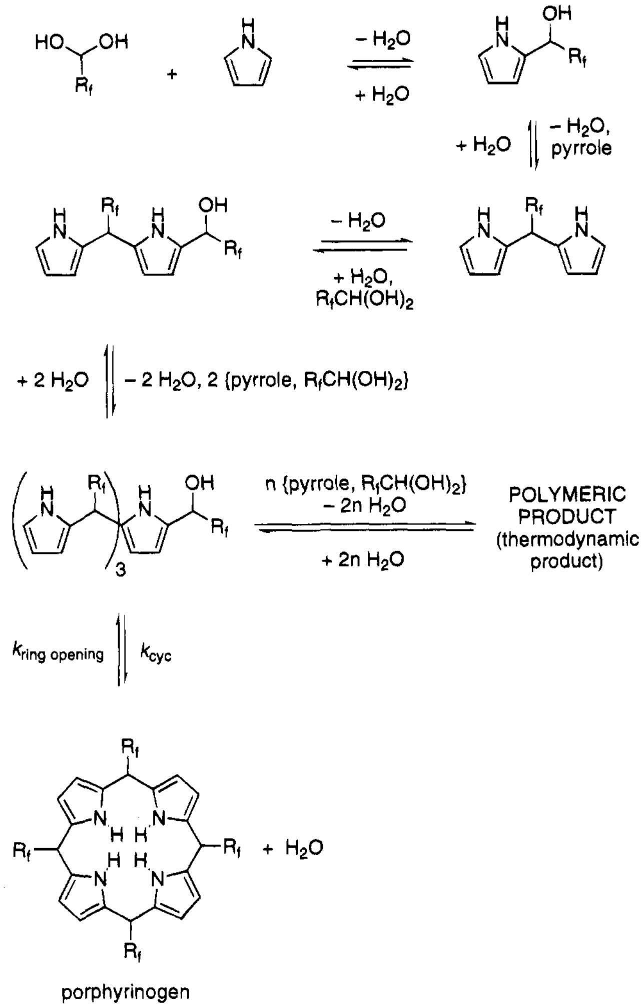

Table 2. Yield of 5,10,15,20-Tetrakis(perfluoropropyl)porphyrin (1) as a Function of Reactants and Endogenous H_2O Concentration

reaction	precursor (s)	H_2O removal methods employed?	yield (%)
a	pyrrole, $C_3F_7CHO{\cdot}H_2O$	no	0
b	pyrrole, $C_3F_7CHO{\cdot}H_2O$	yes	2
c	**2**	no	8
d	**2**	yes	37

aryl aldehydes are condensed with pyrrole.[12b] However, it is important to recognize that this reversibility does not imply thermodynamic control. Even acid-catalyzed reactions of aryl aldehydes with pyrroles show a marked decline in the yield of porphyrinogen at long reaction times and an increase in the yield of polymeric (thermodynamic) products. Such a build up and decline of porphyrinogen may be observed on a convenient time scale simply by raising the concentration of acid catalyst used in the condensation reaction. These results clearly indicate that the porphyrinogen is a kinetically trapped intermediate. Continuous water removal facilitates trapping the porphyrinogen and should prove particularly useful in condensation reactions where the rate constants for polymerization and ring opening are large with respect to that for cyclization, as in the present case where electron-deficient aldehydes are employed (Scheme 1). If $k_{cyc} \gg k_{ring\ opening}$, as, for example, in the preparation of TPP, the decline in porphyrinogen concentration is slow, and water removal provides less dramatic improvements in yield.

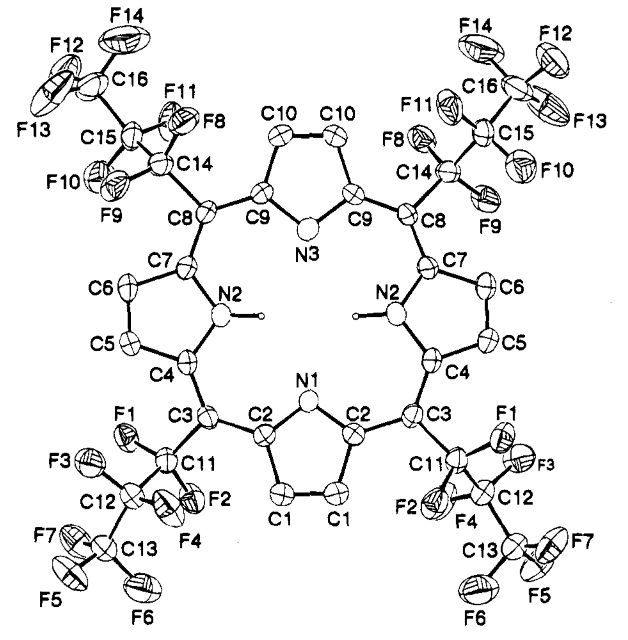

Figure 1. ORTEP view of 5,10,15,20-tetrakis(heptafluoropropyl)porphyrin with thermal ellipsoids at 30% probability.

Given that electronic properties peculiar to extremely electron-poor aldehydes result in a preferential stabilization of their hydrated forms, and the low yields of porphyrinogen obtained in the presence of water, logic dictated development of another simple precursor to *meso*-tetrakis(perfluoroalkyl)porphyrins. We have found that 2-[(perfluoroalkyl)hydroxymethyl]pyrroles can be fabricated in a one-step reaction. These materials are outstanding synthons for electron-deficient porphyrins; Table 2 shows the efficacy of 2,2,3,3,4,4,4-heptafluoro-1-(2-pyrrolyl)-1-butanol (**2**) in such a reaction.[16] Entries c and d again show the key advantage provided by H_2O removal. It is important to note the high product yield (37%) of **1** listed in entry d (Table 2);[17,18] few porphyrin syntheses utilizing monopyrroles as starting materials allow for comparable isolated product yields.[19]

Figure 1 presents the results of the single-crystal X-ray crystallographic study of compound **1**. 5,10,15,20-Tetrakis(perfluoropropyl)porphyrin shows a ruffled (S_4-distorted) structure with the porphyrin *meso*-carbons and the pyrrole C_β atoms alternately displaced 0.294 and the 0.146 Å, respectively, above and below the porphyrin least-squares plane. Consistent with the ruffled structure, four of the pyrrole C_α carbons lie in the least-squares plane while the other four are alternately displaced on average 0.185 Å. Though ruffling is generally thought to derive from ring contraction about a central metal ion or from steric crowding about the porphyrin periphery, crystal packing forces may cause a sterically unencumbered free base porphyrin to adopt

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[16] For a comparison see: Katritzky, A. R.; Law, K. W. *Magn. Reson. Chem.* **1988**, *26*, 129–133.

[17] Water removal was carried out by azeotropic distillation, as described in the Experimental Section.

[18] This approach is completely general; a variety of *meso*-tetrakis-(R_f)porphyrins [$R_f = CF_3$ and $(CF_2)_n\ CF_3$ ($n > 2$)] have been synthesized in an analogous manner.

[19] The high yield of **1** is surprising, considering that elevated temperatures might be expected to favor extended conformations for the polypyrrylmethane intermediates.

Table 3. Porphyrin Electrochemistry.[a] Electronic Modulation of [Porphinato]zinc(II) Complexes as a Function of Porphyrin Peripheral Substituents

compd	$E_{1/2}$ (mV) ZnP/ZnP$^+$	$E_{1/2}$ (mV) ZnP/ZnP$^-$
[5,10,15,20-tetraphenylporphinato]zinc(II)	790	−1390
[2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(pentafluorophenyl)porphinato]zinc(II)	1560	−470
[5,10,15,20-(heptafluoropropyl)porphinato]zinc(II)	1460	−720

[a] Experimental conditions: [porphyrin] = 5 mM; [TBAPF$_6$] = 0.1 M; solvent = benzonitrile; scan rate = 0.10 V/s; reference electrode = Ag wire; working electrode = Pt disk; $E_{1/2}$ values reported are relative to SCE; the ferrocene/ferrocenium redox couple (0.43 V vs SCE) was used as the internal standard.

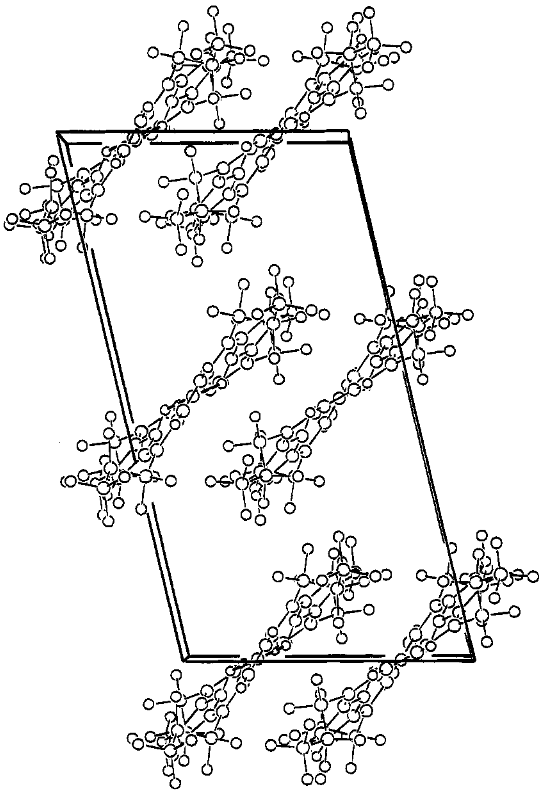

Figure 2. CHARON view of the unit cell viewed parallel to the *b*-axis.

such a structure in the solid state.[20] It is important to note, however, that in the structure of **1** the porphyrins are stacked in the unit cell such that the perfluoroalkyl side chains of one molecule lie over the nitrogen-containing core of its neighbor (Figure 2). This suggests an alternative explanation for the S$_4$ distortion, namely that it may in fact derive largely from an F−H intermolecular hydrogen bond between a porphyrin central ring proton and a F atom of the perfluoropropyl side chain of its neighbor. The N$_2$⋯F$_{4'}$ distance of 3.09 Å found in **1**'s unit cell is virtually identical to N⋯F contacts found in other structures where hydrogen bonding involving fluorocarbon fluorine atoms has been implicated.[21] Such C−F⋯H intermolecular hydrogen bonding is consistent with previous experimental results showing that C−F moieties can act as weak proton acceptors, especially when steric and/or packing forces or a lack of other proton acceptors preclude the possibility of H-bonding between heteroatoms (such as in enzyme−substrate complexes).[21] The observed ability of the porphyrin nitrogens to act as proton donors further evinces the electron-deficient nature of this ligand.

As expected, **1** shows a variety of unusual properties that derive from its four pendant perfluoroalkyl groups. It is soluble in solvents ranging from aqueous methanol to pentane. Its electronic absorption spectrum shows a Soret band at 404.5 nm, significantly blue shifted from the analogous transition observed for both TPP and the 5,10,15,20-tetraalkylporphyrins. It is metalated with Zn under extremely mild conditions (THF, Et$_3$N, ZnCl$_2$, room temperature). Furthermore, electrochemical studies (Table 3) indicate that the HOMO of [5,10,15,20-tetrakis(heptafluoropropyl)porphinato]zinc(II) [**1**(Zn)] is stabilized to a greater extent than any simple [5,10,15,20-(substituted)porphinato]zinc(II) species yet synthesized. Moreover **1**(Zn), which lacks any *β*-substituents, already manifests an oxidation potential similar to that observed for the perhalogenated tetrakis(perfluoraryl)porphyrins such as [2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(pentafluorophenyl)porphinato]zinc(II) (OBPFP) (Table 3). It is also important to note the effect of substitution on the potential of the first reduction. The perfluoroalkyl substitutents in **1**(Zn) lower the porphyrin HOMO and LUMO energies to the same extent compared to TPP-(Zn). However, for OBPFP the stabilization is much greater for the LUMO. While some of this difference is attributable to the distortion of the porphyrin ring,[5] the same type of effect can be observed with sterically undemanding cyano groups.[6] The results highlight that electron-withdrawing groups without *π*-orbitals are the preferred substituents to lower the HOMO energy in an aromatic system while concomitantly maintaining a constant *π*−*π** gap.

Summary and Conclusion

With the advent of the tetrakis(perfluoroalkyl)porphyrin ligand system, a number of new research opportunities are available. For example, the property that most closely correlates with catalyst activity in the [porphinato]Fe-catalyzed hydroxylation of alkanes with molecular oxygen is the metal (III/II) redox couple; further tuning of this potential beyond what the 2,3,7,8,12,13,17,18-octahalo-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin ligands afford has heretofore been impossible.[2e] Additionally, pendant porphyrin perfluoroalkyl groups open up possibilities to do chemistry in a number of unique solvents such as supercritical CO$_2$.[22] The enhanced solubility of these compounds in aqueous solvent mixtures may enable electrocatalytic reactions, such as the reduction of dioxygen, to be performed in homogeneous solution. Furthermore, since synthetic routes into

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[20] (a) TPP, for example, crystallizes in both planar and ruffled conformations. See: Hamor, M. J.; Hamor, T. A.; Hoard, J. L. *J. Am Chem. Soc.* **1964**, *86*, 1938−1942. Silvers, S. J.; Tulinsky, A. *J. Am Chem. Soc.* **1967**, *89*, 3331−3337.

[21] Murray-Rust, P.; Stallings, W. C.; Monti, C. T.; Preston, R. K.; Glusker, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 3206−3214.

[22] For an application of the solubility of fluorocarbons in supercritical CO$_2$ see: DeSimone, J. M.; Guan, Z.; Elsbernd, C. S. *Science (Washington, D.C.)* **1992**, *257*, 945−947.

3,4-dihalopyrroles and 3,4-bis(trifluoromethyl)pyrroles are established[23] as well as methodology to halogenate porphyrins and subsequently further derivatize them,[2,3,24] it may be possible to develop new families of highly elaborated electron-deficient porphyrins. Due to the facile, high-yield preparation and unique electronic properties of **1**, it is quite likely that an important new ligand system has been defined for organotransition metal chemistry.

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[24] (a) DiMagno, S. G.; Lin, V. S.-Y.; Therien, M. J. *J. Am Chem. Soc.* **1993**, *115*, 2513–2515. (b) DiMagno, S. G.; Lin, V. S.-Y.; Therien, M. J. *J. Org. Chem.* **1993**, *58*, 5983–5993. (c) Lin, V. S.-Y.; DiMagno, S. G.; Therien, M. J. *Science (Washington, D.C.)* **1994**, *264*, 1105–1111.