Electrochemistry of Nonplanar Zinc(II) Tetrakis(pentafluorophenyl)porphyrins

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The reduction potentials for the zinc derivatives of three nonplanar tetrakis(pentafluorophenyl)porphyrins, TFPPX$_8$ (X = Cl, Br, Me), have been measured by cyclic voltammetry in 0.1 M (TBA)PF$_6$/CH$_2$Cl$_2$ solution. $E^{o'}$ values (V vs AgCl/Ag): ZnTFPPCl$_8$ (2+/+ = 1.57; +/0 = 1.63; 0/− = −0.47; −/2− = −0.75); ZnTFPPBr$_8$ (2+/+ = 1.53; +/0 = 1.57; 0/− = −0.48; −/2− = 0.76); ZnTFPPMe$_8$ (2+/+ = 0.99; +/0 = 0.97; 0/− = −1.14; −/2− = −1.52 (Ep). The experimentally determined trends in the electrochemical behavior of these porphyrins are in agreement with the prediction that the $D_{4h} \rightarrow D_2$ distortion of the macrocycle destabilizes the HOMOs (a$_{1u}$, a$_{2u}$ → a, b$_1$) more than the LUMOs (e$_g$ → b$_2$, b$_3$). The instabilities of the π-radical cations, ZnTFPPX$_8^+$, relative to ZnTFPPX$_8$ and ZnTFPPX$_8^{2+}$ (K_{disp} = 12 ± 5 (X = Cl); 5 ± 3 (X = Br); 0.4 ± 1 (X = Me)), are related to the effects of electron withdrawal at the *meso* positions as well as porphyrin distortion on the relative energies of the a(a$_{1u}$) and b$_1$(a$_{2u}$) orbitals.

Introduction

Porphyrins containing redox-inactive metals typically undergo two one-electron (1e) oxidations and two 1e reductions.[1−5] The products of 1e oxidations are π-cation radicals, whose electronic structures have been studied extensively.[6−9] Here we report results of electrochemical and spectroelectrochemical experiments that show that the π-cation radicals derived from the highly distorted (nonplanar) ZnTFPPX$_8$ (X = Cl, Br, Me) complexes[10−14] are kinetically unstable, disproportionating rapidly to ZnTFPPX$_8^{2+}$ and the corresponding neutral species. We are investigating the possible reasons for these π-cation

radical instabilities, because of our interest in using porphyrins as donors or acceptors in reactions requiring 2e steps.[15]

Experimental Section

Porphyrins. ZnTPP (Aldrich) was used as received. ZnTFPP (Porphyrin Products) was purified on flash silica gel (Baker, 40 μm), eluting with CH$_2$Cl$_2$/hexane. ZnTFPPCl$_8$ was prepared from ZnTFPP and Cl$_2$(g) in refluxing CCl$_4$ under a steady stream of Ar.[16] ZnTFPPBr$_8$ was synthesized from ZnTFPP and N-bromosuccinimide in refluxing methanol.[17] Both completely halogenated porphyrins were chromatographically purified initially on neutral alumina, eluting with CHCl$_3$, and then on flash silica gel, eluting with CH$_2$Cl$_2$/hexane.

ZnTFPPMe$_8$. H$_2$TFPPMe$_8$ was synthesizd via the condensation of 3,4-dimethylpyrrole and pentafluorobenzaldehyde.[18−20] 3,4-Dimethylpyrrole was prepared from ethyl 3,4-dimethylpyrrole-2-carboxylate according to Smith and Forsyth.[21] Ethyl 3,4-dimethylpyrrole-2-carboxylate was prepared as follows:[19,22] a solution of 40 g of 2-acetoxy-3-nitrobutane in 250 mL of a 1:1 solution of isopropyl alcohol (IPA) and tetrahydrofuran (THF) was added slowly over a 1 h period to a solution of ethyl isocyanoacetate (0.8 equiv) and 1,1,3,3-tetramethylguanidine (1.7 equiv) in 500 mL of 1:1 IPA:THF. The resulting pyrrole (70% yield) was purified on silica gel, eluting with CH$_2$Cl$_2$, and sublimed in vacuo at 80 °C. Ethyl 3,4-dimethylpyrrole-2-carboxylate (20 g) was decarboxylated with 7.5 g of NaOH in 100 mL of refluxing ethylene glycol. The reaction solution was poured into water, and the pyrrole was extracted with hexane, dried over MgSO$_4$,

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(5) Several exceptions to the characteristic 1e transfers observed for porphyrins have been reported: Murray observed a net 2e oxidation of CuTPP and H$_2$TPP in toluene with perchlorate as the supporting electrolyte, and attributed the multielectron response to specific metal-binding and acid−base properties of the medium (Geng, L.; Ewing, A. G.; Jernigan, J. C.; Murray, R. W. *Anal. Chem.* **1986**, *58*, 852−860. Geng, L.; Murray, R. W. *Inorg. Chem.* **1986**, *25*, 3115−3120); Kadish observed a similar 2e wave for CoTPP in toluene (Mu, X. H.; Lin, X. Q.; Kadish, K. M. *Electroanalysis* **1989**, *1*, 113−116); and Saveant observed a 2e process that led to the formation of an isoporphyrin (with the accompaning loss of a proton) (El-Kasmi, A.; Lexa, D.; Maillard, P.; Momenteau, M.; Saveant, J-M. *J. Am. Chem. Soc.* **1991**, *113*, 1586−1595). Two groups have worked on the electrochemistry of CoTPPBr$_8$: for experiments in benzonitrile, it was found that two 1e oxidation waves merge, but the identity of the 2e oxidized product was not established (D'Souza, F.; Villard, A.; Caemelbecke, E. V.; Franzen, M.; Boschi, T.; Tagliatesta, P.; Kadish, K. M. *Inorg. Chem.* **1993**, *32*, 4042−4048); for experiments in CH$_2$Cl$_2$, two 1e oxidations were observed.[4]

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(10) Abbreviations: H$_2$TPP = 5,10,15,20-tetraphenylporphyrin; H$_2$TFPP = 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin; for TPPX$_8$ and TFPPX$_8$, X$_8$ = 2,3,7,8,12,13,17,18-octahalo (or -octaalkyl).

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and purified by passing through a pad of silica gel. The resulting pyrrole (25% yield) was used immediately in the next reaction. A solution of 0.5 g of 3,4-dimethylpyrrole and 1 equiv of pentafluorobenzaldehyde (Aldrich) in 500 mL of fresly distilled CH_2Cl_2 with 0.1 equiv of boron trifluoride etherate (Aldrich) was stirred at room temperature under Ar for 1 h. Four equivalents (per porphyrinogen) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone were added and the solution was refluxed for 30 min. $H_2TFPPMe_8$ was partially purified on a short column of neutral alumina, eluting with $CHCl_3$. $H_2TFPPMe_8$ was metalated in 10 min at room temperature in $CHCl_3$ by addition of a solution of $Zn(OAc)_2$ in methanol. Flash chromatography (silica gel), eluting with CH_2Cl_2/hexane, yielded $ZnTFPPMe_8$ as a green band (35% yield). Mass spectral analysis revealed a single peak at mass 1148.09. λ_{max} (CH_2Cl_2): nm ($\epsilon \times 10^{-3}$), 352 (35), 434 (200), 570 (20), 602 (15). ^1H NMR ($CDCl_3$, 500 MHz): δ 2.30 (s). ^{19}F NMR ($CDCl_3$, 500 MHz, vs $CFCl_3$ = 0 ppm): δ −137.7 (q, 2 F, o-Ar-F), δ −152.4 (t, 1 F, p-Ar-F), δ −162.1 (sextuplet, 2 F, m-Ar-F).

Electrochemistry. All electrochemical experiments were performed with either a Bioanalytical Systems (BAS) Model 100 electrochemical analyzer on an EG&G Princeton Applied Research Model 173 potentiostat/galvanostat driven by a Model 175 universal programmer. Cyclic voltammetry was performed at room temperature with a normal three-electrode configuration consisting of a highly polished glassy carbon disk working electrode ($A = 0.07$ cm^2) and a AgCl/Ag reference electrode containing 1.0 M KCl. The working compartment of the electrochemical cell was separated from the reference compartment by a modified Luggin capillary. All three compartments contained a 0.1 M solution of supporting electrolyte.

Dichloromethane (Burdick and Jackson, high purity) and tetrabutylammonium hexafluorophosphate ((TBA)PF$_6$) (Southwestern Analytical) were used as received. Electrolyte solutions were passed through activated alumina prior to use. Typical reactant concentrations for cyclic voltammetry were in the range 10^{-3}–10^{-4} M.

Potentials are reported vs aqueous AgCl/Ag and are not corrected for the junction potential. Under conditions identical with those employed here, the ferrocenium/ferrocene couple has $E^{\circ\prime} = 0.48$ V.

Spectroelectrochemistry. Thin-layer UV−vis spectroelectrochemistry[23] employed an optically transparent platinum working electrode. Spectral changes were monitored either by a Tracor Northern TN-6500 diode array apparatus employing a Xe arc lamp as the light source or a Hewlett-Packard 8452A diode array spectrometer.

Results and Discussion

The cyclic voltammograms of ZnTFPP and ZnTFPPX$_8$ (X = Cl, Br, Me) are shown in Figure 1. The reduction potentials are compared with that of ZnTPP in Table 1. Halogenation of the porphyrin causes a positive shift in the reduction potentials, as well as a merging of the two 1 e oxidations into a single 2e response. The UV−vis spectral changes accompanying the oxidations of ZnTFPP are shown in Figure 2. As the potential is slowly cycled between 1.0 and 1.5 V, the initial absorptions of ZnTFPP decrease, giving rise to features at 390, 413, 625, and 695 nm. Further oxidation results in the appearance of a broad, sloping system with a maximum at 342 nm. Analogous spectral changes are observed during the oxidation of ZnTFP-PBr$_8$. As the potential is swept through the 2e wave, the two prominent absorption bands in the spectrum of ZnTFPPBr$_8$ (455, 585 nm) lose intensity, giving way to a band at 363 nm However, these changes do not occur isosbestically; absorptions at 420 and 450 nm maximize midway through the electrolysis, indicating that a radical-disproportionation reaction is occurring.[23]

The UV−vis spectra of the singly and doubly oxidized species of both ZnTFPP and ZnTFPPBr$_8$ (Figure 3) establish that the oxidations are localized on the porphyrin ring. The spectrum of each singly oxidized species is that of a π-cation radical,[6] featuring a characteristically broad, split absorption system in
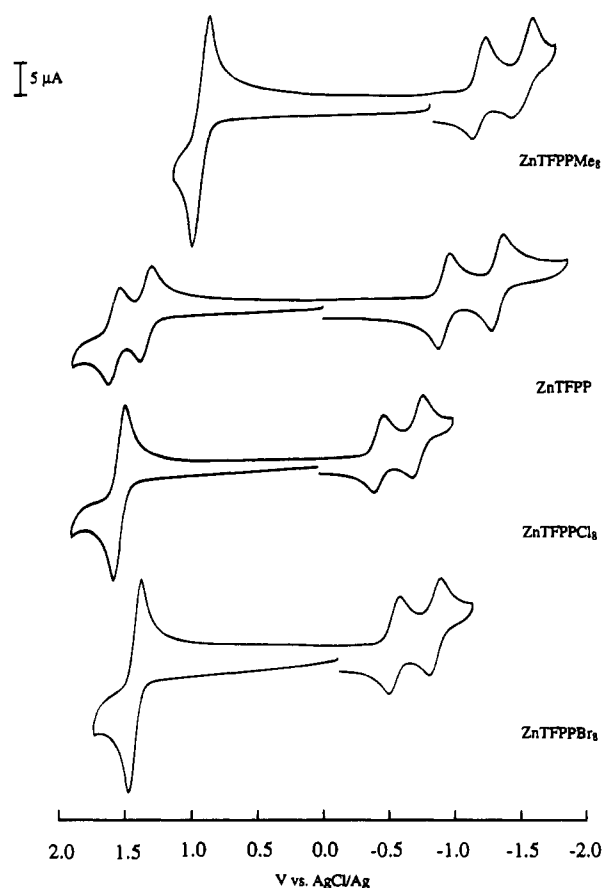
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Figure 1. Cyclic voltammograms of ZnTFPP and ZnTFPPX$_8$ (X = Me, Cl, Br) in 0.1 M (TBA)PF$_6$/CH$_2$Cl$_2$ (100 mV/s scan rate).

Table 1. Reduction Potentials of Zinc(II) Porphyrins[a]

porphyrin	$E^{\circ\prime}_{2+/0}$	$E^{\circ\prime}_{2+/+}$	$E^{\circ\prime}_{+/0}$	$E^{\circ\prime}_{0/-}$	$E^{\circ\prime}_{-/2-}$
ZnTPP[b]		1.16	0.80	−1.33	−1.66
ZnTFPP		1.58	1.37	−0.95	−1.37
ZnTFPPBr$_8$	1.55	1.53[c]	1.57[c]	−0.48	−0.76
ZnTFPPCl$_8$	1.60	1.57[c]	1.63[c]	−0.47	−0.75
ZnTFPPMe$_8$	0.98	0.99[c]	0.97[c]	−1.14	1.52[d]

[a] V vs. Ag/AgCl in 1.0 M KCl; Fc$^{+/0}$ = 0.48 V; 0.1 M (TBA)PF$_6$/CH$_2$Cl$_2$. [b] Potentials are in good agreement wtih literature values.[1] [c] Calculated from the respective K_{disp} and $E^{\circ\prime}_{2+/0}$ values, and the expressions $\ln K_{disp} = nF(E^{\circ\prime}_{+/0} − E^{\circ\prime}_{2+/+})/RT$ and $E^{\circ\prime}_{2+/0} = (E^{\circ\prime}_{+/0} + E^{\circ\prime}_{2+/+})/2$. [d] E_{pc}.

the Soret region (the low-energy band, at 700 nm, is difficult to see for ZnTFPPBr$_8$);[24,25] the principal absorption of each doubly oxidized complex, as expected for a porphyrin dication,[6] is a broad, blue-shifted band. Equilibrium constants for the disproportionation of the singly oxidized porphyrin into the neutral and doubly oxidized forms (K_{disp}) are 12 ± 5 and 5 ± 3 for ZnTFPPCl$_8$$^+$ and ZnTFPPBr$_8$$^+$, respectively.[26]

(24) The HOMO energy order is $a_{1u} > a_{2u}$. The increasing absorption intensity of $Q(0,0)$ relative to $Q(0,1)$ for the series ZnTFPPX$_8$ < CuTFPPX$_8$ < PdTFPPX$_8$ is consistent with this assignment. The relative intensities of the two Q bands are dependent on the energy difference between the a(a_{1u}) and the b$_1$(a_{2u}) orbitals;[25] the b$_1$(a_{2u}) orbital should be stabilized in the metal series relative to the a(a_{1u}), because the latter orbital has negligible amplitude at the nitrogens. The EPR spectrum of ZnTFPPBr$_8$$^+$ (recorded at −50 °C in CH$_2$Cl$_2$/(TBA)ClO$_4$) reveals a broad, structureless signal at $g = 2.015$, consistent with a $^2A(^2A_{1u})$ ground state (Hodge, J. A.; Hill, M. G. Unpublished results).

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(26) Disproportionation equilibrium constants for the 1e oxidized complexes were determined from the spectroelectrochemical data; see ref 23.
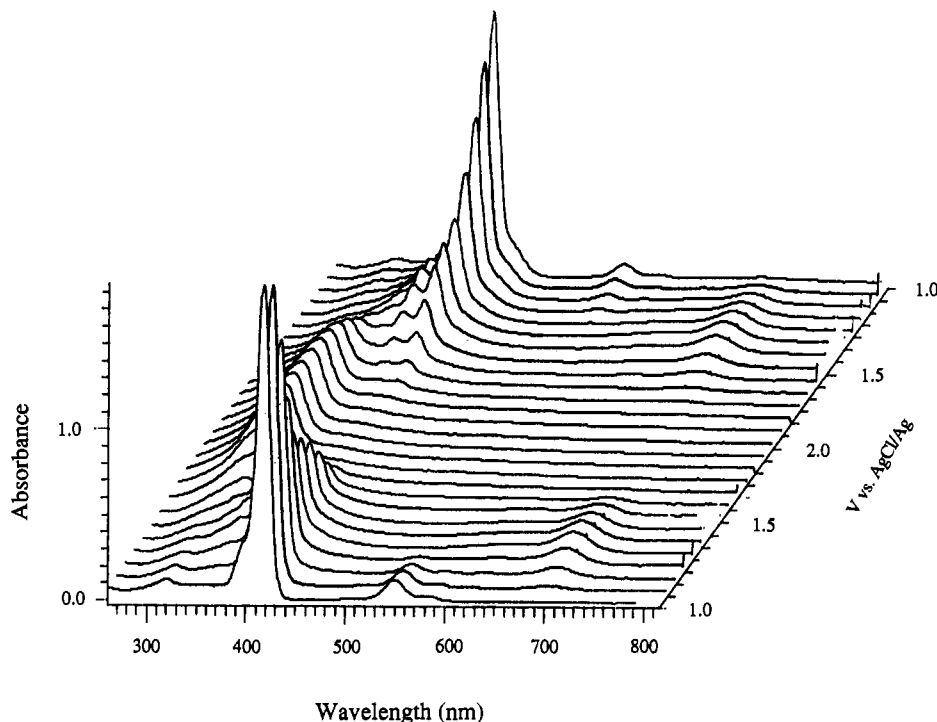
Figure 2. Changes in the absorption spectrum of ZnTFPP in 0.1 M (TBA)PF$_6$/CH$_2$Cl$_2$ recorded during a slow (4 mV/s) cyclic potential sweep.
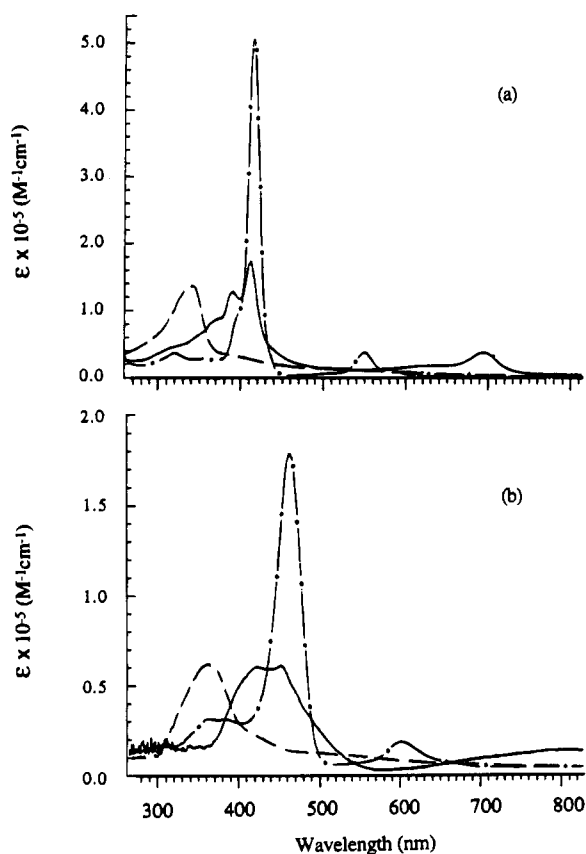

Figure 3. (a) Electronic spectra of ZnTFPP (— · —), ZnTFPP$^+$ (—), and ZnTFPP^{2+} (— — —) in 0.1 M (TBA)PF$_6$/CH$_2$Cl$_2$. (b) Electronic spectra of ZnTFPPBr$_8$ (— · —), ZnTFPPBr$_8^+$ (—), and ZnTFPPBr$_8^{2+}$ (— — —) in 0.1 M (TBA)PF$_6$/CH$_2$Cl$_2$. The spectrum of ZnTFPPBr$_8^+$ was extracted from the measured value of K_{disp}.[26]

The cyclic voltammogram of ZnTFPPMe$_8$ is similar to those of the perhalogenated porphyrins; two 1e reductions and one 2e oxidation are observed (Figure 1). Methylation of ZnTFPP results in a porphyrin that is easier to oxidize and harder to

reduce. Slow cycling of the potential between 0.75 and 1.25 V yields spectral changes (Figure 4) comparable to the oxidation processes seen for ZnTFPPBr$_8$ and ZnTFPPCl$_8$. The initial absorptions of ZnTFPPMe$_8$ (434, 570, 602 nm) decrease and ultimately yield the spectrum of ZnTFPPMe$_8^{2+}$ (327 nm). Again, absorptions (650−750 nm) attributable to a cation radical are observed midway through the electrolysis. K_{disp} for ZnTFPPMe$_8^+$ is 0.4 ± 1.[26]

Crystal structures of tetraphenylporphyrins substituted with both alkyl groups and halogens in the β-pyrrole positions reveal a 2-fold distortion that reduces the molecular symmetry to D_2: there is a saddling (in which the pyrrole β-carbons are alternately above and below the mean porphyrin plane) and a smaller ruffling (in which the *meso* carbons are above and below the mean plane) (Figure 5).[11−14,20] The distortion reduces the repulsions attributable to the short interatomic contacts between the β-substituents and the ortho-carbons of the phenyl groups by twisting the phenyl ring from an approximately perpendicular orientation to a more nearly coplanar one (a difference of about 15°). The distortion can be quantified as the average displacement of the *meso*- and β-atoms from an average plane defined by the four N atoms (the N atoms are not coplanar: a tetrahedral distortion (±0.082 Å) is observed): ZnTFPPBr$_8$ C_{meso}, ±0.021 Å, C_β ±0.971 Å. Comparing the structures of CuTFPPX$_8$, we observe that displacements from planarity for X = Cl are about 70% of those for X = Br.[11,13] It is likely that the structure of ZnTFPPMe$_8$ is similar to that of ZnTFPPBr$_8$, because the distortions of ZnTPPMe$_8$[20] and ZnTFPPBr$_8$[12] are nearly the same.

Theoretical and experimental work on tetraphenylporphyrins has shown that a $D_{4h} \rightarrow D_2$ distortion destabilizes the HOMOs (a$_{1u}$, a$_{2u}$ in D_{4h} to a, b$_1$ in D_2) more than the LUMOs (e$_g$ in D_{4h} to b$_2$, b$_3$ in D_2), whereas electron-withdrawing substituents stabilize the HOMOs and the LUMOs to roughly the same extent.[4,20,27−33] The electrochemical data summarized in Table 1 are consistent with this pattern: relative to the flat ZnTFPP
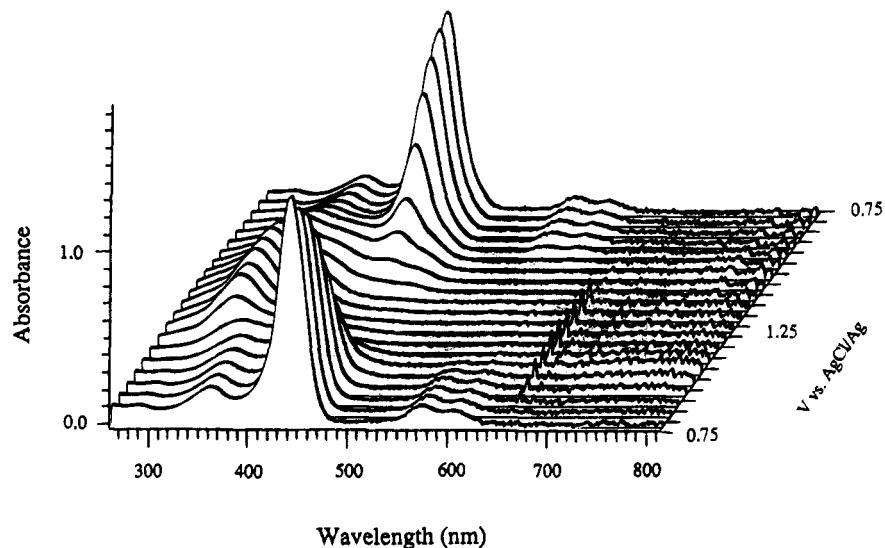
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Wavelength (nm)

Figure 4. Changes in the absorption spectrum of ZnTFPPMe₈ in 0.1 M (TBA)PF₆/CH₂Cl₂ recorded during a slow (4 mV/s) cyclic potential sweep.
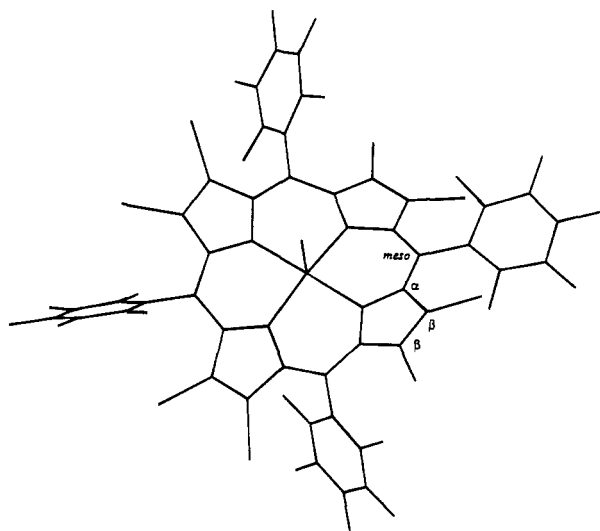

Figure 5. View of the structure of ZnTFPPBr₈, including an axially coordinated oxygen from a solvent molecule (Br atoms are at the β-positions).[12]

complex, ZnTFPPCl₈ and ZnTFPPBr₈ are, respectively, 0.47 and 0.48 V easier to reduce, but only 0.26 and 0.20 V harder to oxidize. The smaller gap between $E°'_{+/0}$ and $E°'_{0/-}$ for ZnTFPPBr₈ is consistent with the macrocycle being somewhat more distorted than ZnTFPPCl₈.[11,13] In the case of ZnTFPPMe₈, the macrocycle is 0.4 V easier to oxidize and only 0.19 V harder to reduce than ZnTFPP.

Electronic structure calculations show that the electron-density patterns of the D_{4h} HOMOs and LUMOs are maintained in the D_2 system.[27] The relative ordering of the a(a₁ᵤ) and b₁(a₂ᵤ)

orbitals is particularly sensitive to *meso* substitution,[34,35] in accord with calculations and EPR spin-density mappings that indicate that the a(a₁ᵤ) orbital localizes electron density predominantly on C_α, whereas a b₁(a₂ᵤ) electron is concentrated on the *meso* position.[6,27,35] Absorption, emission,[25] and EPR spectra[36] demonstrate that the ground state of ZnTPP⁺ is ²A₂ᵤ, whereas that of ZnTFPP⁺ or ZnTFPPBr₈⁺ is ²A₁ᵤ or ²A(²A₁ᵤ).[24] An electron-withdrawing group at the *meso*-position lowers the energy of the b₁(a₂ᵤ) orbital relative to the a(a₁ᵤ). Since neither orbital places a significant amount of density at the β-positions, the HOMO for porphyrins with perfluorophenyl groups in the *meso* position is a or a₁ᵤ.

We have found that *both* perfluorophenyl substitution at the *meso*-position and macrocyclic nonplanarity are required for π-cation radical disproportionation; the electronic nature of the β-substituent appears to be unimportant. Depopulation of the a(a₁ᵤ) orbital lowers the electronic barrier to saddling of the porphyrin structure, particularly if there are electron-withdrawing groups at the *meso*-position. We propose that the requirement for a net 2e oxidation is then met in a porphyrin whose structure is distorted toward the geometrical configuration of the ground state of the doubly oxidized species.

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