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Differential substituent effects of β-halogens in water-soluble porphyrins †

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The first water-soluble β-octafluorinated porphyrins, 5,10,15,20-tetrakis(4-sulfonatophenyl)-2,3,7,8,12,13,17,18-octafluoroporphyrin, **1**, and 5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)-2,3,7,8,12,13,17,18-octafluoroporphyrin, **2**, have been prepared and their aqueous aggregation, acid–base, and optical properties have been characterized. The porphyrins are tetraanionic at neutral pH (at pH = 3–11 for **1** and pH = 0–9 for **2**). Semiempirical (AM1) calculations provide evidence that somewhat unusual acidity characteristics of the fluorinated compounds (with respect to similar brominated porphyrins) can be rationalized solely on the basis of chemical hardness and electronegativity arguments. These results indicate that the large conformational differences seen in the structures of brominated and fluorinated water-soluble porphyrins have little impact upon N–H acidity. Metalation of **1** and **2** with $ZnCl_2$ yielded the zinc complexes, which were characterized by optical spectroscopy and electrochemistry.

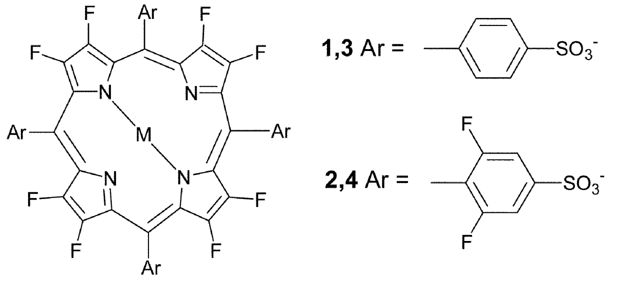
Introduction

Recently, the first reports of β-perfluorinated tetraarylporphyrins have shown that the structures and electronic properties of fluorinated derivatives differ markedly from those substituted with the heavier halogens.[1–5] β-Perfluorinated porphyrins generally exhibit more planar structures, hypsochromically shifted absorption bands, longer singlet excited state lifetimes, and greater redox stability in comparison to their β-perchlorinated or β-perbrominated counterparts. In addition, the electron-withdrawing nature of the fluorine substituents, and the resulting weak basicity of the central nitrogen atoms in the porphyrin core, have been argued to be responsible for the unusual, and in some cases unprecedented metal-centered chemistry seen in coordination compounds featuring these macrocycles. Examples include the observation of a high-spin ground state for a Co(II) porphyrin,[3] and the demonstrated ability of the Rh(I) derivative to act as a leaving group in a methyl transfer reaction.[6] Accordingly, we sought to obtain aqueous pK_a measurements of fluorinated porphyrins and compare them with previously measured pK_a values for brominated derivatives to ascertain whether N–H acidity was correlated with novel metal-centered chemistry. Here we report the syntheses and characterization of water-soluble β-fluorinated porphyrins. The results of these studies show that fluorine substituents have a larger impact on N–H acidity than bromine (or chlorine), and that this difference can be explained based upon purely electronic rather than stereoelectronic effects.

Results and discussion

The procedures employed for introducing sulfonate groups into β-fluorinated *meso*-tetraarylporphyrins were modelled after those established for other *meso*-tetraarylporphyrins.[7–11] The two porphyrin precursors, F_8TPP and F_{16}TPP, were prepared from 3,4-difluoropyrrole[12,13] and aryl aldehydes following published procedures.[1,2] After the porphyrins sulfonation in heated fuming sulfuric acid (18–20% SO_3), neutralization (aqueous NaOH), and desalting, acceptable yields (80–90%) of the (exclusively) tetrasulfonated derivatives were obtained. In contrast to many similar preparations involving non-halogenated porphyrins,[7,8] this procedure gave no detectable quantity of partially sulfonated material; the rather aggressive conditions tolerated by these electron-deficient species permit electrophilic aromatic substitution to be run to completion.

Metalation of **1** and **2** with $ZnCl_2$ was performed in methanol heated at reflux; favorable isolated yields (>90%) of [5,10,15,20-tetrakis(4-sulfonatophenyl)-2,3,7,8,12,13,17,18-octafluoroporphinato]zinc, **3**, and [5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)-2,3,7,8,12,13,17,18-octafluorporphinato]zinc, **4**, were obtained following ion-exchange chromatography (DOWEX®50WX8–100 resin, Na^+ salt). The structures of these compounds are shown in Fig. 1. Solubilities of > 5g L^{-1} were exhibited with these compounds in water, methanol, ethanol, and dimethyl sulfoxide.



1,2 M = 2 H
3,4 M = Zn

Fig. 1 β-Octafluorinated water-soluble porphyrins.

Because water-soluble porphyrins are amphiphilic, we investigated the aggregation behavior of the new fluorinated compounds in aqueous solution (0.1 M $NaNO_3$). Deviation from Beer's law with increasing porphyrin concentration, a key signature of supramolecular assembly, was observed spectrophotometrically in the range 10^{-5}–10^{-7} M for **1** and **3**, while no such deviation was observed for **2** and **4** in the same concentration range.[8,11,14,15] The fluorine substituents at the 2,6-aryl positions apparently provide sufficient steric bulk to reduce porphyrin–porphyrin interactions substantially. This steric argument has been invoked previously to explain the suppression of aggregation in other water-soluble *ortho*-substituted

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† Electronic supplementary information (ESI) available: electrochemical procedures, procedure for pKa determinations, Beers law deviations, calculations, Table S1 and Figs. S1 to S9. See http://www.rsc.org/suppdata/ob/b2/b209345f/

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Table 1 Properties of selected water-soluble anionic porphyrins

[a]Compd.	[b]pK_a1	[b]pK_a2	[b]pK_a3	Ref.
TPPS	4.7	4.8	—	7,8
1	0.6	3.3	10.8	[c]
2	−0.8	−0.4	9.2	[c]
Br_8TPPS	1.9	4.8	10	10
T(2,6-Cl-3-S)P	1.7	1.8	—	8
T(2,6-F-3-S)P	1.8	2.5	—	8
T(2,6-OMe-3- S)P	2.6	3.0	—	8
	1st Oxid.	[d]1st Red.		
[d]ZnTPPS	0.65	−1.27		[c]
[d]**3**	1.00	−1.08		[c]
[d]**4**	1.20	−0.89		[c]
[e]ZnTPP	0.80	−1.33		17
[e]ZnF_8TPP	1.26	−1.03		1
[e]ZnF_{28}TPP	1.70	−0.63		1

[a] Abbreviations: TPPS — 5,10,15-20-tetrakis-(4-sulfonatophenyl)-porphyrin; Br_8TPPS — 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin; T(2,6-Cl-3-S)P — 5,10,15-20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrin; T(2,6-F-3-S)P — 5,10,-15-20-tetrakis(2,6-difluoro-3-sulfonatophenyl)porphyrin; T(2,6-OMe-3-S)P — 5,10,15-20-tetrakis(2,6-dimethoxy-3-sulfonatophenyl)porphyrin; F_8TPP — 2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetraphenylporphyrin; F_{28}TPP — 2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin. [b] pK_as were determined spectrophotometrically at 25 °C and constant ionic strength (0.1 M $NaNO_3$) where possible. Solution pH was adjusted with NaOH or HNO_3. [c] This work. [d] Potentials (V) were determined by square wave voltammetry at pH 6.4 (0.1 M phosphate buffer, 0.5 M NaCl, glassy carbon working electrode) and are reported *vs.* a Ag/AgCl reference electrode. [e] in CH_2Cl_2, 0.1 M $TBAPF_6$.

$$H_4P^{(n+2)} \xrightleftharpoons{K_a1} H_3P^{(n+1)} + H^+ \quad (1)$$

$$H_3P^{(n+1)} \xrightleftharpoons{K_a2} H_2P^{n} + H^+ \quad (2)$$

$$H_2P^{n} \xrightleftharpoons{K_a3} HP^{(n-1)} + H^+ \quad (3)$$

$$HP^{(n-1)} \xrightleftharpoons{K_a4} P^{(n-2)} + H^+ \quad (4)$$

Fig. 2 Definitions of equilibrium constants.

tetraarylporphyrins.[8] It is also supported by the observation that rhodium porphyrins bearing 2,6-difluoroaryl groups do not form Rh–Rh bonds, while those sporting phenyl groups do.[6]

Due to the symmetrical disposition of the substituents in **1** and **3**, fairly simple ^{1}H and ^{19}F NMR spectra are obtained for these compounds in MeOD and D_2O, although for **1** slow N–H tautomerism is evident from the two β-F signals ($\delta = -142.11$, -147.70) arising from the protonated and free pyrrole rings. In contrast, the 3-sulfonyl substituents in **2** and **4** reduce the symmetry of these compounds substantially, giving rise to the possibility of atropoisomism. The ^{1}H-decoupled ^{19}F NMR spectrum of **2** in D_2O shows multiple doublets for each of the two aryl ring fluorine substituents, indicating slow aryl rotation on the NMR timescale. Slow rotation of 2,6-disubstituted aryl groups in β-perfluorinated porphyrins has been observed previously.[6]

Porphyrins have a rich acid–base chemistry; five potential protonation states can be obtained for the porphyrin core, as is shown in Fig. 2. The pK_a values for the various acid–base reactions were determined by pH-dependent UV-vis spectroscopy. For **2** pK_a1 and pK_a2 could not be determined definitively because the monoprotonated species is in equilibrium with the free base and the diprotonated species at low pH.

The data summarized in Table 1 exhibit a trend consistent with expectations based upon electronic substituent effect arguments; all pK_a values for **1** and **2** are reduced substantially from those reported for the benchmark TPPS. However, when one compares the acidities of **1** and **2** to those of the corresponding β-brominated derivatives (Table 1), some interesting nonlinear substituent effects are apparent. Compounds **1** and **2** are less basic *and* less acidic than the corresponding β-brominated derivatives. To determine if the fluorinated compounds' greater resistance to nitrogen ionization originates in electronic, conformational, or solvent effects, we performed semiempirical (AM1)[16] calculations of the fluorinated, brominated and unsubstituted porphyrins listed in Table 2.

Optimized planar or saddled geometries were obtained for all compounds in their various protonation states. Table 2 summarizes the relative energies for the halogenated compounds in comparison to the non-halogenated porphyrin analogues for each of the gas phase acidities (eqns. 1–4) depicted in Fig. 2. The AM1 gas phase data are largely consistent with the experimental solution results; for each porphyrin, fluorination induces a larger increase in relative acidity for eqn. 1 and eqn. 2 than does bromination. However, for eqn. 3 and eqn. 4, the substituent effects of fluorine and bromine are comparable. It is important to note that these effects are independent of the steric demand at the porphyrin periphery. Thus, solvent and conformational arguments need not be invoked; electronic effects alone suffice to explain the differing acidity trends for the fluorinated and brominated compounds.

To support this interpretation, we investigated the effect of constrained saddled conformations upon the relative acidities of porphine, β-octafluorinated and β-octabrominated porphine. The saddled geometries were obtained using dihedral constraints exclusively, following methods reported previously.[18,19] Otherwise, the structures were fully optimized. The

Table 2 Semi-empirical (AM1) calculations of relative gas phase acidities[a]

Compd	rel. Δ*H* (eqn. 1)	rel. Δ*H* (eqn. 2)	rel. Δ*H* (eqn. 3)	rel. Δ*H* (eqn. 4)
P	0.000	0.000	0.000	0.000
[b]F_8P	−18.721	−22.395	−27.192	−27.067
[b]Br_8P	−8.431	−14.697	−23.884	−27.551
TPP	0.000	0.000	0.000	0.000
[b]F_8TPP	−11.921	−21.580	−14.616	−20.541
[b]Br_8PP (β-Br)	−5.446	−14.647	−12.963	−20.099
T(2,6F)PP	0.000	0.000	0.000	0.000
[b]T(2,6F)PF_8P	−11.706	−14.492	−22.092	−21.600
[b]T(2,6F)PBr_8P	−3.952	−6.239	−19.680	−22.489
[c]P[*Con*]	2.002	2.836	−1.621	−1.810
[c]F_8P[*Con*]	2.043	2.545	−1.399	−1.126
[c]Br_8P[*Con*]	1.868	2.810	−1.352	−1.080

[a] All energies in kcal mol^{-1}. [b] Reported energy is relative to that of the β-H_8 derivative. [c] Reported energy is relative to that of the unconstrained derivative. The saddling distortion was induced by dihedral constraints (20°) as is described in the ESI.

constrained saddled geometry had a consistent and extremely modest effect upon the calculated gas phase acidities (Table 2). These calculations support the notion that out-of-plane ring deformation plays only a minor role in porphyrin N–H acidity.

Simple electronegativity and chemical hardness concepts provide a compact explanation for the observation that compounds **1** and **2** are less basic and less acidic than the corresponding β-brominated derivatives.[20] Aside from hydrogen, fluorine forms the hardest σ-bonds to carbon (hardness is directly related to the HOMO–LUMO energy gap). Because the difference in the ionization potentials of F (17.422 eV) and Br (11.814 eV) greatly exceeds that of their electron affinities (F = 3.448 eV; Br = 3.363 eV),[21] it is expected that the filled σ-orbitals in the neutral porphyrin would be more stabilized by F than Br, and thus be less basic. The AM1 results provide support for this interpretation; the highest-lying porphyrin σ-orbital (which involves the nitrogen lone pairs) has an eigenvalue of −11.55 eV for H_2F_8P and −11.2 eV for H_2Br_8P. The corresponding σ-LUMOs lie at +0.99 eV and +0.33 eV for H_2F_8P and H_2Br_8P, respectively. The calculated difference in σ-HOMO energy disappears as the porphyrin becomes negatively charged; for the anionic $[HF_8P]^-$ the σ-HOMO energy is −7.67 eV, while it is −7.69 eV for $[HBr_8P]^-$.

The electrochemistry of the zinc complexes **3** and **4** was investigated by cyclic, differential pulse, and square wave voltammetry; the potentials for the quasi-reversible oxidation and reduction processes are given in Table 1. The magnitudes of the redox potential shifts caused by β-fluorination of water-soluble TPPS are slightly smaller than those measured for the non-ionic derivatives in CH_2Cl_2[1] (Table 1), presumably because charge on the porphyrin ring is better solvated by water than by CH_2Cl_2. Nevertheless, the electrochemical results indicate that β-fluorination has a profoundly stabilizing effect upon the ligand orbitals, and that much of the interesting metal-centered chemistry observed for the organic soluble fluorinated porphyrins may be transferable to aqueous solution.

Conclusion

The acidity and electrochemical data for the β-octafluorinated water-soluble porphyrins indicate that **2** is the most electron-deficient *meso*-tetra(sulfonatophenyl) derivative yet reported. The electronegativity and chemical hardness arguments outlined above should be readily transferable to fluorinated derivatives of cationic derivatives, such as *meso*-tetrakis-(*N*-alkyl-4-pyridinium)porphyrins. Since the cationic porphyrins are generally more acidic than the anionic derivatives,[22] fluorine substitution is a simple approach to extend the current range of accessible acidities and redox potentials for water-soluble porphyrins.

Experimental

Instrumentation and materials

2,3,7,8,12,13,17,18-Octafluoro-5,10,15,20-tetraphenylporphyrin was prepared according to literature methods.[1] Reagents were supplied from Aldrich, Fisher, Fluka, or Cambridge Isotope Laboratories and used as received unless otherwise indicated. NMR spectra were obtained using a Bruker 500 MHz spectrometer at the University of Nebraska-Lincoln. ^1H NMR spectra were collected in $CDCl_3$, D_2O or CD_3OD using the residual protons in the solvent as a chemical shift standard. ^{19}F NMR spectra were collected at 470 MHz in the same solvents using hexafluorobenzene as an internal chemical shift reference ($\delta = -164.9$ ppm). All J values are given in Hertz. Absorption spectra were obtained using a modified (OLIS-14) Cary-14 UV-vis-NIR spectrophotometer. A Fisher Scientific Accumet pH meter with a combination electrode (Ag/AgCl reference, gel-filled) was employed for pH determinations. Mass spectra were collected at the Nebraska Center for Mass Spectroscopy. Combustion analyses were conducted by QTI, Whitehouse NJ.

2,3,7,8,12,13,17,18-Octafluoro-5,10,15,20-tetrakis(2,6-difluorophenyl)porphyrin, $F_{16}TPP$

2,6-Difluorobenzaldehyde (0.76 mL, 7.1 mmol), 3,4-difluoropyrrole (0.66 g, 6.4 mmol) and anhydrous CH_2Cl_2 (500 mL) were placed (under N_2) in a 1 L round-bottom flask equipped with a magnetic stir bar. Boron trifluoride etherate (1 mL, 7.8 mmol) was injected into the mixture and the resulting solution was stirred for 30 min. DDQ (2.0 g, 8.8 mmol) and pyridine (10 mL) were added. The mixture was stirred for an additional 12 h and filtered through a short silica gel column (CH_2Cl_2 eluent). Following solvent evaporation, the crude solid was chromatographed on silica gel (warmed 10:1 hexanes–$CHCl_3$) and recrystallized by layering hexane on a $CHCl_3$ solution. Yield (705 mg, 45%); (Found: C, 58.32; H, 1.18; N, 6.07. Calc. for $C_{44}H_{14}F_{16}N_4$: C, 58.55; H, 1.56; N, 6.21%); λ_{max} ($CHCl_3$)/nm 396 (ε/dm^3 mol^{-1} cm^{-1} 186 000), 495 (20 400), 525 (3 700), 580 (5 700), 636 (1 700); δ_F (470 MHz; $CDCl_3$) −111.1 (8F, t, *J* 6.1, β-F), −144.9 (4F, s, *o*-F), −149.8 (4F, s, *o*-F); δ_H (500 MHz, $CDCl_3$) 7.78 (4H, tt, *J* 15 and 6, *p*-H), 7.33 (8H, dd, *J* 8 and 7, *m*-H), −4.13 (2H, s, NH); *m*/*z* (high res. FAB) 902.0963 (calcd $C_{44}H_{15}N_4F_{16}$: 903.1018).

2,3,7,8,12,13,17,18-Octafluoro-5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin tetrasodium salt 1

F_8TPP (50 mg, 0.066 mmol) was dissolved in fuming H_2SO_4 (18–20% free SO_3, 0.5 mL) and heated at 80 °C for 45 minutes. The vessel was capped with a $CaSO_4$ drying tube. The mixture was cooled to room temperature prior to the careful addition of H_2O (20 mL). Upon neutralization with 1 M aqueous NaOH, the solution color changed from green to red. The solvent was removed *in vacuo* and the remaining solid was taken up in CH_3OH and filtered to remove Na_2SO_4. This desalting step was repeated twice. The desalted compound was precipitated from CH_3OH by layering dry diethyl ether on top of the solution. The precipitate was filtered and dried *in vacuo*. Yield (65 mg, 87%); (Found: C, 38.64; H, 2.38; N, 4.10. Calc. for $C_{44}H_{18}F_8N_4Na_4O_{12}S_4\cdot 11\ H_2O$: C, 38.72; H, 2.90; N, 4.10%); λ_{max} (CH_3OH)/nm 408 (ε/dm^3 mol^{-1} cm^{-1} 190 000), 500 (13 000), 531 (5 500), 581 (4 100), 638 (3 400); δ_F (470 MHz; CD_3OD) −142.11 (4F, s, β-F); −147.70 (4F, s, β-F); δ_H (500 MHz, CD_3OD) 8.21 (8H, d, *J* 8, *m*-H); 8.17 (8H, d, *J* 8, *o*-H); *m*/*z* (FAB neg. ion) 1099 (calc. $[M - 2H + Na^+]^-$ 1099), 1121 (calcd $[M - 3H + 2Na^+]^-$ 1121).

2,3,7,8,12,13,17,18-Octafluoro-5,10,15,20-tetrakis(3-sulfonato-2,6-difluorophenyl)porphyrin tetrasodium salt, 2

A solution of $F_{16}TPP$ (52 mg, 0.058 mmol) in fuming H_2SO_4 (18–20% free SO_3, 0.5 mL) was heated at 90 °C for 4 h. The remaining steps in the experimental procedure were identical to those described for **1**. Yield (66 mg, 86%); (Found: C, 34.47; H, 1.19; N, 3.51. Calc. for $C_{44}H_{10}F_{16}N_4Na_6O_{16}S_5\cdot 5\ H_2O$: C, 34.66; H, 1.19; N, 3.67%); λ_{max} (CH_3OH)/nm 409 (ε/dm^3 mol^{-1} cm^{-1} 160 000), 496 (1 400), 530 (2 700), 580 (3 600), 635 (1 000); δ_F (470 MHz; CD_3OD) −108.1 (4F, br s, *o*-F [adj. to -SO_3^-]), −108.9 (4F, m, *o*-F), −145.98 (4F, s, β-F), −151.1 (4F, s, β-F); δ_H (500 MHz; CD_3OD) 8.37 (4H, dd, *J* 15 and 9, *p*-H), 7.49 (4H, m, *m*-H); *m*/*z* (high res. FAB) 1310.8569 (Calc. $C_{44}H_{11}N_4O_{12}F_{16}S_4Na_4^+$ 1310.8592).

General procedure for zinc insertion

A CH_3OH solution of the fluorinated water-soluble porphyrin (50–100 mg) and excess (5 equiv.) $ZnCl_2$ was heated at reflux for 12 h. The solvent was removed and the remainder was dissolved in a minimum amount of H_2O, loaded onto a column containing DOWEX®50WX8–100 ion exchange resin (Na^+ salt), and eluted with H_2O until the column discharge was colorless. The water was removed *in vacuo* and the metalated porphyrins were desalted and precipitated from CH_3OH, as was described above for **1** and **2**.

[2,3,7,8,12,13,17,18-Octafluoro-5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrinato]zinc tetrasodium salt, 3

Yield: (97%); (Found: C, 37.92; H, 2.15; N, 4.05. Calc. for $C_{44}H_{16}F_8N_4Na_4O_{12}S_4Zn\cdot 10\ H_2O$: C, 37.47; H, 2.57; N, 3.97%); λ_{max} (water, pH 7)/nm 410 (ε/dm^3 mol^{-1} cm^{-1} 109 000), 509 (880), 545 (5 000), 583 (2 040); δ_F (470 MHz, CD_3OD) −144.9 (8F, s, β-F); δ_H (500 MHz, CD_3OD) 8.17 (8H, d, *J* 8, *m*-H), 8.09 (8H, d, *J* 8, *o*-H); *m*/*z* (FAB neg. ion) 1161 (Calc. $[M - 2H + Na^+]^-$ 1161).

[2,3,7,8,12,13,17,18-Octafluoro-5,10,15,20-tetrakis(3-sulfonato-2,6-difluorophenyl)porphyrinato]zinc tetrasodium salt, 4

Yield: (95%); λ_{max} (water, pH 7)/nm 410 (ε/dm^3 mol^{-1} cm^{-1} 96 700), 503 (830), 542 (6 300), 577 (701); δ_F (470 MHz; CD_3OD) −108.0 (4F, s, *o*-F), −108.7 (4F, s, *o*-F), −149.5 (s, 8F, β-F); δ_H (500 MHz, CD_3OD) 8.33 (4H, dd, *J* 15 and 5, *p*-H), 7.44 (4H, m, *m*-H); *m*/*z* (high res FAB) 1372.7723 (Calc. for $[C_{44}H_9F_{16}N_4Na_4O_{12}S_4{}^{64}Zn]^+$ 1372.7722).

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