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On the role of β-fluorine substitution on the extent of core deformation of porphyrin dications

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Abstract—Careful analysis of fully and partially β-fluorinated dicationic porphyrins have been performed suggesting an electronic influence of the β-fluorine atoms on the extent of the macrocycle deformation, in agreement with the crystal structure of β-octafluoro-*meso*-tetraphenylporphyrin dication. © 2002 Elsevier Science Ltd. All rights reserved.

Biological relevance of the deformations of the porphyrinic macrocycles have been proposed for several hemeproteins.[1] Non planar conformations are also often encountered with synthetic porphyrins and can play a role in the preparation of multicomponent porphyrin systems. Four different origins of the distortion have been described for the 5,10,15,20-tetraarylporphyrins: (i) the steric repulsion due to the introduction of numerous peripheral bulky substituents at the β and/or the *meso* positions, (ii) the nature of the metal, (iii) the axial ligands and (iv) the steric congestion of the porphyrin core by *N*-substitution.[2]

β-Octafluoro-*meso*-tetraarylporphyrins have recently been reported[3] owing to the henceforth possible access to 3,4-difluoropyrrole,[4] which has permitted their synthesis by condensation with arylaldehydes under the Lindsey conditions.[5] When compared to the other β-halogenotetraphenylporphyrins (X = Br or Cl), the fluorinated ones correspond to the more electron-deficient derivatives. Furthermore, in contrast with the other halogens, the size of the fluorine atom is small enough to minimize steric distortion of the free bases. This remarkable feature permits to discriminate between the steric and the electronic influences of the β-substituents on the physical properties of the porphyrins. For example, the 2,3,7,8,12,13,17,18-octafluoro - 5,10,15,20 - tetrakis(pentafluorophenyl)porphyrin (H_2F_8TPFPP) has been found to be planar[6] as well as its zinc complex.[3c]

Herein, a careful analysis of the UV–vis spectra and the proton NMR data of partially β-fluorinated porphyrin free bases and their corresponding dications have been realized. The free bases were obtained, using the Lindsey conditions, in two ways: (i) the co-condensation of benzaldehyde with a mixture of difluoropyrrole and pyrrole and (ii) the condensation of benzaldehyde with 3-fluoropyrrole.[7] After protonation, the first experiment led to **2**, **3a**, **3b** and **4**[8] (Scheme 1) with the fluorine atoms in pairs per pyrrole, whereas the second synthesis gave a mixture of isomeric **3c**[8] with one fluorine atom per pyrrole. The plots of the Soret band wavelength versus the number of fluorine atoms for the ionic and the neutral forms are presented in Fig. 1. Whereas with the free bases, a linear blue-shift of 1.8 nm per fluorine atom is observed, the Soret band of the dicationic derivatives display an unexpected linear red-shift of 1 nm per fluorine atom. The variations of the averaged ^{1}H chemical shifts of the NH protons of the porphyrin core are displayed in Fig. 2.[9] Similarly, the number of fluorine atoms induces different effects depending on the form, neutral or dicationic, of the porphyrins. In the case of the free bases, a linear shielding is observed whereas with the dicationic forms a linear deshielding of the resonances is encountered.

The free bases H_2F_8TPP and H_2F_8TPFPP have previously been described to be planar with blue-shifted Soret bands and strongly shielded chemical shifts of the

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Keywords: fluorinated porphyrins; dication porphyrins; crystal structure; saddle shaped.

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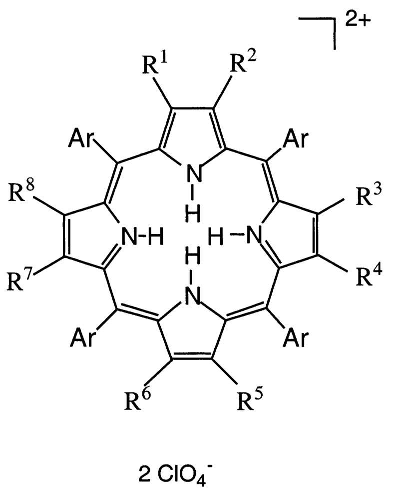

Ar = phenyl	
R^{1-8}= H	**1**: H_4TPP^{2+}
$R^{1,2}$= F; R^{3-8}= H	**2**: $H_4F_2TPP^{2+}$
R^{1-4}= F; R^{5-8}= H	**3a**: H4F4cTPP $^{2+}$
$R^{1,2,5,6}$= F; $R^{3,4,7,8}$= H	**3b**: H_4F_4tTPP $^{2+}$
$R^{1,2}$=$R^{3,4}$=$R^{5,6}$=$R^{7,8}$=H,F	**3c**: $H_4F_4TPP^{2+}$
R^{1-6}= F; $R^{7,8}$= H	**4**: $H_4F_6TPP^{2+}$
R^{1-8}= F	**5**: $H_4F_8TPP^{2+}$
Ar = pentafluorophenyl	
R^{1-8}= H	**6**: H_4TPFPP^{2+}
R^{1-8}= F	**7**: $H_4F_8TPFPP^{2+}$
Ar = mesityl	
R^{1-8}= H	**8**: H_4TMP^{2+}

Scheme 1. Structure of the investigated porphyrins.

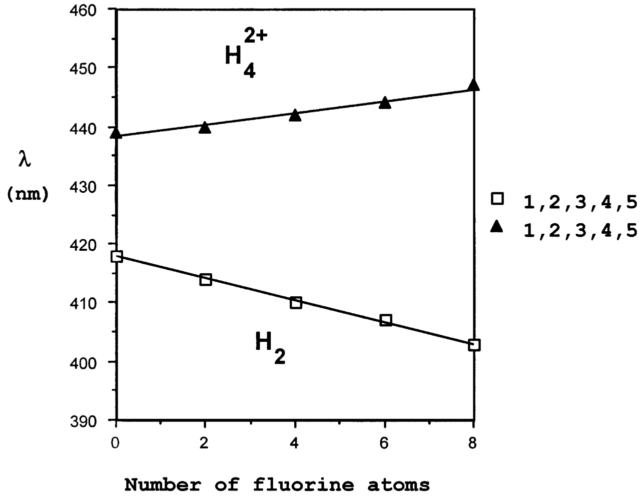

Figure 1. Plots of the Soret band wavelength of the partially β-fluorinated tetraphenylporphyrins versus the number of fluorine atoms. The upper and the lower lines correspond to the dicationic and the free base forms of the porphyrins.

NH proton.[3] The linearity observed for these two parameters versus the number of fluorine atoms highlights the gradual influence of the number of the electron-withdrawing atoms at the β-positions. In the case of the dicationic derivatives, both the red-shift of the Soret bands and the deshielding of the NH resonances can be considered as markers of the distortion of the macrocycle.[2,10] Again, the linear relationship demonstrates the progressive influence of the number of the fluorine atoms on the extent of the saddle shaped deformation of the macrocycle.

We also compared the diperchlorate salts of the dications $[H_4F_8TPFPP]^{2+}$ and $[H_4TPFPP]^{2+}$. These derivatives present a Soret band at 443 and 432 nm, respectively. The observed red-shift of 11 nm (in contrast with a blue-shift of 10 nm for the corresponding free bases) can also be associated with an increase of the distortion of the macrocycle.

The crystal structure of the complex $[H_4F_8TPP][ClO_4]_2 \cdot 2H_2O \cdot 2CH_2Cl_2$ was solved.[11] The macrocycle displays a large distortion, mainly a saddle shaped deformation which is usually observed for the dicationic forms of tetraarylporphyrins.[12] The perpendicular displacements of the porphyrin atoms from the porphyrin mean plane of the 24-atom core are displayed in Fig. 3. The averaged displacements of the carbon atoms (Δ_{24}) relative to the porphyrin mean plane (P_{24}) and the average of the angles defined between the pyrrole rings and the mean 4N-plane (P_4) are reported in Table 1. The comparison with the unsubstituted $[H_4TPP]^{2+}$,[13] of which selected values are also included in Table 1, permits us to define an increase of the macrocycle distortion associated with the β-octafluorination of the porphyrin. The averaged

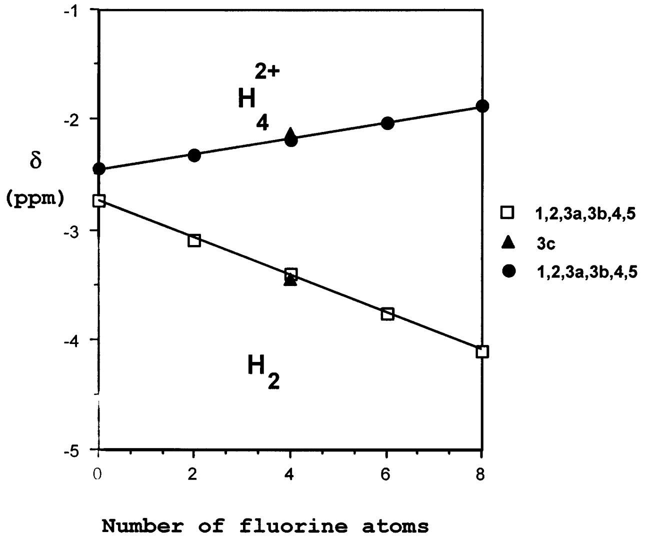

Figure 2. Plots of the variations of the averaged[9] ^1H chemical shifts of the NH protons of the porphyrin core versus the number of fluorine atoms. The upper and the lower lines correspond to the dicationic and the free base forms of the porphyrins.

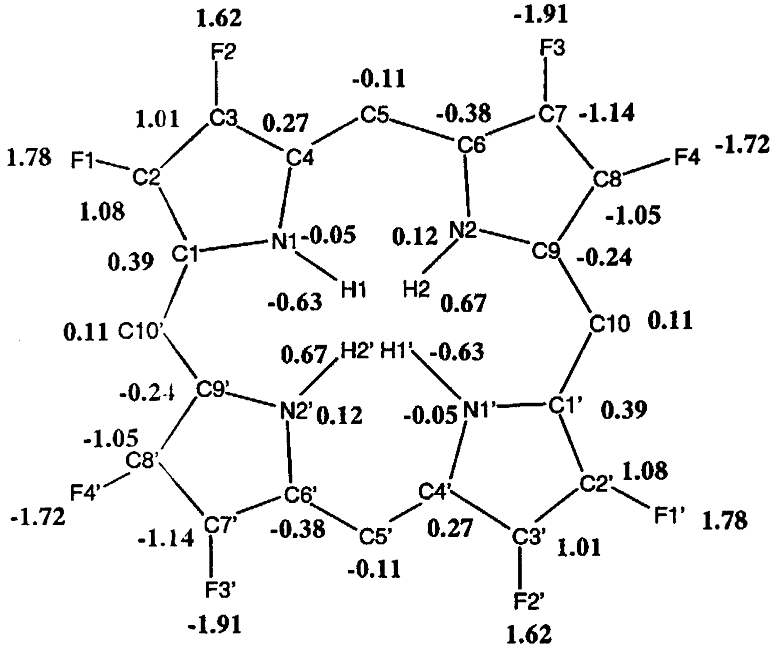

Figure 3. Formal diagram of the porphyrin diacid core of $[H_4F_8TPP](ClO_4)_2$. The perpendicular displacements (in units of Å) of the porphyrin core atoms from the 24-atoms mean plane are displayed.

Table 1. Selected parameters characterizing the extent of the macrocycle deformation of some porphyrin dications

Porphyrin dications	Δ_{24}	ΔC_b	Pyrrole tilt angle (°)
$[H_4F_8TPP]^{2+}$	0.50	1.07	33.3
$[H_4TPP]^{2+}$[a]	0.44	0.98	28.5
$[H_4TMP]^{2+}$[b]	0.31	0.66	20.5

[a] See Ref. 13.

[b] From Ref. 12e.

displacements of the β-carbons (ΔC_b) versus the mean plane of the porphyrin (P_{24}) are 1.07 Å for $[H_4F_8TPP]^{2+}$ and 0.98 Å for $[H_4TPP]^{2+}$.[13] Also particularly relevant for an analysis of the extent of the saddle shaped conformation are the angles defined by the pyrrole rings and the porphyrin mean plane (P_4). The averaged values are 33.3° for $[H_4F_8TPP]^{2+}$ and 29.5° for $[H_4TPP]^{2+}$.[13] Although the steric hindrance of the β-substituents and the *meso*-groups contribute to the deformation of the macrocycle, steric repulsion alone cannot account for all the reported data. For example, the formally more crowded $[H_4TMP]^{2+}$ is in fact less distorted than $[H_4TPP]^{2+}$.[12e] Although crystal packing forces might be responsible for some deformation of the porphyrin macrocycles,[2] the present structure suggests an influence of the fluorine atoms on the increased distortion of the macrocycle, in good agreement with the visible spectra and the ^1H NMR data.

Acknowledgements

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8. Previously reported procedures were used for the synthesis of the corresponding free bases of porphyrins **5** and **7** from 3,4-difluoropyrrole,[3a,c] porphyrin **3c** from 3-

fluoropyrrole[3b,7] and partially fluorinated porphyrin free bases **2**, **3a**, **3b** and **4**.[7] All the dication complexes were obtained by addition of perchloric acid. **CAUTION**: no problems have been reported for the preparation of perchlorate salts of porphyrin diacids, nevertheless compounds should be handled in milligram quantities.

Compound **2**: ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = -2.71$ (s, 1H, NH), −2.35 (s, 1H, NH), −2.13 (s, 2H, NH); 8.02 (m, 12H, *m*-H and *p*-H), 8.60 (m, 6H, *o*-H); 8.69 (d, β-H), 8.73 (d, β-H), 8.78 (s, β-H); ^{19}F NMR (188 MHz, $CDCl_3$, 25°C): $\delta = -145.45$ (s, 2F, β-F); UV–vis (CH_2Cl_2): $\lambda_{\max}$ (log ε) = 440 (5.48), 660 nm (4.54).

Compound **3a**: ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = -2.36$ (s, 2H, NH), −2.02 (s, 2H, NH), 8.65 (d, 2H, β-H), 8.71 (d, 2H, β-H), 8.02 (m, 12H, *m*-H and *p*-H), 8.60 (m, 8H, *o*-H).

Compound **3b**: ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = -2.58$ (s, 2H, NH), −1.80 (s, 2H, NH), 8.02 (m, 12H, *m*-H and *p*-H), 8.60 (m, 8H, *o*-H), 8.62 (s, 4H, β-H). **3a**,**3b**: ^{19}F NMR (188 MHz, $CDCl_3$, 25°C): $\delta = -145.05$ (s, 4F, β-F); UV–vis (CH_2Cl_2): $\lambda_{\max}$ (log ε) = 442 (5.54), 665 nm (4.63).

Compound **3c**: ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = -2.13$ (s, 4H, NH), 8.03 (m, 16H, β-H, *m*-H and *p*-H), 8.57 (m, 8H, *o*-H); ^{19}F NMR (188 MHz, $CDCl_3$, 25°C): $\delta = -125.17$ to −125.68 (6 s, 4F, β-F); UV–vis (CH_2Cl_2): $\lambda_{\max}$ (log ε) = 443 (5.50), 663 nm (4.60).

Compound **4**: ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = -2.22$ (s, 2H, NH), −2.00 (s, 1H, NH), −1.69 (s, 1H, NH), 8.03 (m, 12H, *m*-H and *p*-H), 8.56 (m, 8H, *o*-H), 8.52 (s, 2H, β-H); ^{19}F NMR (188 MHz, $CDCl_3$, 25°C): $\delta = -144.63$ (s, 2F, β-F), −144.64 (d, 2F, β-F), −144.69 (d, 2F, β-F); UV–vis (CH_2Cl_2): $\lambda_{\max}$ (rel. int.) = 444 (100), 672 nm (13.1).

Compound **5**: ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = -1.88$ (s, 4H, NH), 8.02 (m, 12H, *m*-H and *p*-H), 8.57 (m, 8H, *o*-H); ^{19}F NMR (188 MHz, $CDCl_3$, 25°C): $\delta = -144.28$ (s, 8F, β-F); UV–vis (CH_2Cl_2): $\lambda_{\max}$ (log ε) = 447 (5.34), 676 nm (4.62).

9. The NH resonances values are reported in Ref. 8. Large variations depending on the nature of the pyrrole ring (fluorinated or hydrogenated) bearing the NH proton and on the symmetry of porphyrins are observed. However, the averaged values are clearly representative of the overall electrodeficiency of the substituted porphyrins.
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11. A suitable crystal was obtained by slow evaporation of a dichloromethane solution. Several attempts to obtain crystal without any water molecules were unsuccessful. Crystal structure analyses were measured on a Nonius Kappa CCD using graphite monochromatized MoKα radiation ($\lambda = 0.71073$ Å) at 110 K. $C_{44}H_{24}F_8N_4 \cdot 2ClO_4 \cdot 2CH_2Cl_2 \cdot 2H_2O$, $M_r = 1165.36$, monoclinic, space group $C2/c$, $Z = 4$, $a = 22.6252(4)$, $b = 8.2738(2)$, $c = 27.3874(3)$ Å, $\beta = 112.557(1)°$, $V = 4734.6(2)$ Å^3, $\rho_{\text{calc}} = 1.635$ g cm^{-3}, $\mu = 4.59$ cm^{-1}, $F(000) = 2360$. A total of 27346 reflections were measured, 5389 independent reflections (4482 with $I > 2.0\sigma(I)$). The structure was refined by the full-matrix least-square techniques with the resulting $R = 0.044$, $R_w = 0.111$ and $S_w = 0.94$. CCDC reference number 152532.
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13. The averaged values reported herein for the $[H_4TPP]^{2+}$ correspond to the two crystallographic structures obtained with two perchlorate anions as counterion.[12e,f] Two other structures have been reported with different counterions[12a,d] leading nevertheless to similar averaged values.