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Synthesis and characterization of partially β-fluorinated 5,10,15,20-tetraphenylporphyrins and some derivatives

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Abstract—The synthesis of partially β-fluorinated *meso*-tetraphenylporphyrins using Lindsey conditions, has been examined, starting either from 3,4-difluoro-1*H*-pyrrole or from 3-fluoro-1*H*-pyrrole. In the case of the first synthon, condensation with pyrrole and benzaldehyde afforded a mixture of porphyrins of general formula β-F_nTPP (n=0,2,4,6,8) displaying linearly correlated spectroscopic and electrochemical properties. With the second synthon, condensation with benzaldehyde produced an unresolvable mixture of β-tetrafluoroporphyrins presenting spectroscopic and electrochemical properties in coherence with those observed in the first case. Preliminarily, the synthesis and isolation of the hitherto unknown 3-fluoro-1*H*-pyrrole has been approached via several methods.

1. Introduction

The synthesis of β-halogenated metalloporphyrins and their use as oxidation catalysts of organic substrates has attracted considerable attention during the last 10 years. Nevertheless, these studies were mainly restricted to the halogens bromine and chlorine, due to relatively easy access to such complexes by direct halogenation of the parent porphyrin. Whereas iodine has received little attention as a β-substituent, the indirect introduction of fluorine at the pyrrolic β-positions has only recently been rendered possible by the development of routes to 3,4-difluoro-1*H*-pyrrole (**1**).[1] Thus, the synthesis and characterization of the first β-octafluoro-*meso*-tetraarylporphyrins, members of a new class of highly electron-deficient ligands, has been reported in 1997 by us[2a] and others.[2b] These porphyrins and their metal complexes have been found to display original features e.g. blue-shifted electronic absorption spectra as well as positively shifted redox potentials, compared to the benchmark 5,10,15,20-tetraphenylporphyrin ($TPPH_2$). Another remarkable feature for these ligands was their nearly planar structure, in opposition to the distorted one of other encumbered electron-deficient porphyrins. Many studies on variously substituted porphyrins have been devoted to a better understanding of the relationship existing between the physicochemical properties of the ligand and the σ, π and steric effects prevailing in the macrocycle.[3a] As confirmed afterwards for fluorine, it was anticipated that planar porphyrins bearing electron-withdrawing β-substituents would display inter alia, very high oxidation potentials as a consequence of the lack of destabilization of the HOMOs due to ring distortion.[3b] Nevertheless, the predicted higher resistance to oxidation was partially challenged by catalysis studies on some metalated β-octafluoroporphyrins.[4]

Assuming that the physicochemical properties of β-octafluoro-*meso*-tetraarylporphyrins are mainly governed by the strong σ-electron-withdrawing effects of the peripheral fluorine atoms, it was advisable to check this feature on partially fluorinated analogs. Since the Lindsey procedure proved to be valuable for the synthesis of β-octafluoroporphyrins bearing *meso*-tetraaryl substituents,[2] we applied it to the preparation of partially fluorinated analogs, starting either from a mixture of 3,4-difluoropyrrole and pyrrole or from the hitherto unknown 3-fluoro-1*H*-pyrrole (**2**). In this paper, we will report first our attempts to prepare **2** in pure form via several routes. In a second part, the synthesis and characterization of porphyrins of the type β-F_nTPP (n=2,4,6) will be presented.

2. Results and discussion

2.1. Routes to 3-fluoro-1*H*-pyrrole

On the contrary to 3-chloro-[5] or 3-bromo-1*H*-pyrrole,[6] 3-fluoro-1*H*-pyrrole (**2**) was unreported in literature. Nevertheless, functionalized *N*-unsubstituted 3-fluoropyrrole moieties have already been obtained through various synthetic procedures. The first examples of such compounds, **3**, have been obtained by Buhr via thermally or

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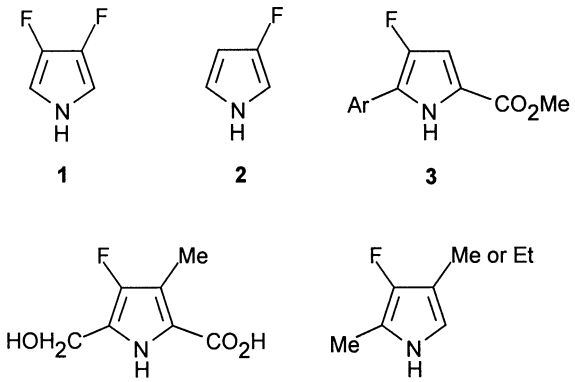
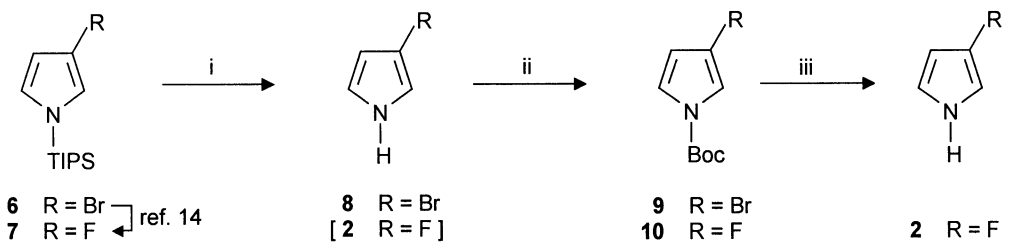
photochemically induced ring contraction of 2-azido-3,3-difluorocyclobutenes in the presence of nucleophilic arenes e.g. benzene.[7] Pyrrole **4** was prepared via a multistep sequence involving at the fluorination step a modified Schiemann reaction i.e. the photolysis of a diazonium tetrafluoroborate salt. This compound was used for the preparation in low yield of 2,7,12,17-tetrafluoro-3,8,13,18-tetramethylporphyrin.[8a] More recently, the same group prepared ring-monofluorinated analogs of *meso*-porphyrin IX and related compounds from the 4-fluoropyrroles **5** obtained by thermal decarboxylation of the corresponding 2-carboxylic acids. As previously, fluorine was introduced via the photochemical decomposition of diazonium tetrafluoroborate salts.[8b,c]



3-Alkyl or -aryl substituted-4-fluoropyrrole-2-carboxylates or -2-tosyl have been obtained in low yields, along with other products, by Michael type addition of isocyanomethylide anions to α-fluoroalkenyl sulfones and sulfoxides.[9] A high yielding route to 3-fluoro-2,5-disubstituted pyrroles, starting from α,α-difluoro-γ-iodo-γ-(electron-withdrawing group) substituted ketones has been reported.[10] Ethyl 3-fluoropyrrole-2-carboxylate has been obtained as the major product (no yield reported) in the reduction of a cyclic difluoro hemiaminal[11] and more recently, the already known ethyl 4-fluoro-3,5-dimethylpyrrole-2-carboxylate[8a] has been prepared in 40% yield by rhodium-catalyzed cyclocondensation of ethyl isocyanoacetate with 3-fluoro-2,4-pentanedione.[12]

Except ethyl 3-fluoropyrrole-2-carboxylate,[11] a possible precursor of **2** via a saponification–decarboxylation sequence, all the β-fluoropyrroles reported above were too heavily functionalized to be used in the Lindsey-type porphyrin synthesis we envisioned.[13] We finally focused our attention on 3-fluoro-1-(triisopropylsilyl)pyrrole (**7**), first prepared by Barnes and co-workers from the 3-bromo analog **6** (Scheme 1).[14] Curiously, it appeared from a literature survey that **7** was never deprotected to give access to the 3-fluoro-1*H*-pyrrole (**2**) we required for the synthesis of β-tetrafluoro-5,10,15,20-tetraphenylporphyrin (β-F_4TPPH_2) (**23**) (vide infra). For this peculiar use, the isolation of **2** was unnecessary as we briefly reported in a recent paper.[15] This compound was conveniently prepared as a 10^{-2} M solution in dichloromethane by deprotection of **7** with 1 M *n*-tetrabutylammonium fluoride in tetrahydrofuran, followed by an aqueous washing and subsequent drying. The deprotection reaction was fast and quantitative as checked by ^1H and ^{19}F NMR (Scheme 1). Nevertheless, for the sake of full characterization, we found it useful to isolate the pyrrole **2** in pure form. With this aim in view, three routes have been investigated.

Firstly, several attempts were made to isolate **2** from the reaction mixture obtained after desilylation. Since **2** could be reasonably anticipated to be more volatile than 3,4-difluoropyrrole,[1] the use of a solvent like tetrahydrofuran was discarded, dichloromethane appearing to be the most appropriate. Deprotection of **7** with tetra-*n*-butylammonium fluoride trihydrate exclusively in this solvent led, after an aqueous work up and rotary evaporation of the solvent at −10°C, to a mixture of **2** and triisopropylsilanol. The reaction being conducted on small quantities of **7**, a classical fractional distillation was not possible. Bulb-to-bulb distillation under the water-pump vacuum led to low amounts of **2** contaminated either by remaining traces of solvent (no heating applied) or triisopropylsilanol (heating at ca. 40°C). Therefore, a part of the crude mixture was submitted to a preparative GLC (SE30 column) at low oven temperature (ca. 70°C) affording on cooling (dry ice–acetone), the pyrrole **2** as a colorless liquid turning to green–black on standing at room temperature (rt). Nevertheless, the quantity of **2** collected was too low to determine its boiling point experimentally. Calculations predicted, for this compound, a boiling point of 136.43±13.00°C at 760 mm Hg and 144.82±20.00°C for 3,4-difluoropyrrole (experimental 160–162°C[16]) vs 129.76±9.00°C for pyrrole (experimental 131°C).[17] The ^1H NMR spectrum of **2** was deceptive since the signals of the H-2 and H-5 protons overlapped, giving a multiplet, even at high sweep frequency (600 MHz) Their respective chemical shifts could be obtained from a ^1H–^{13}C heterocorrelated spectrum, the proton signal at 6.49 ppm being connected with the C-5 resonance at 115.4 ppm and that located at 6.50 ppm with the C-2 resonance at 101 ppm. The H-4 signal appeared roughly as a quartet, including the couplings with the H-2 and H-5 protons and with fluorine. ^{19}F NMR



Scheme 1. *Reagents and conditions*: (i) 1 M *n*-Bu_4NF/THF, THF or MeCN (R=Br) or 1 M *n*-Bu_4NF/MeCN, MeCN (R=Br, F), rt; (ii) Boc_2O, DMAP, MeCN, rt; (iii) flash-thermolysis, 180°C.

spectroscopy was not very informative either, giving rise to a poorly resolved complex multiplet as the signal. Finally, no obvious proton–proton or proton–fluorine coupling constant could be extracted from the observed patterns. The ^{13}C NMR spectrum was more explicit, the four carbon resonances being assigned unambiguously, displaying coupling constants in the range of those observed e.g. with fluoropyridines.[18]

A second procedure for the isolation of **2** starting from **7** was investigated (Scheme 1). Since the major problem was the predictable volatility of the desired pyrrole, we thought to convert it in situ into the heavier *N*-Boc protected 3-fluoropyrrole **10**. Two advantages were expected from this transformation. First, an easiest isolation and second, the possibility of a thermal, solvent-free deprotection of **10** leading to **2**, along with carbon dioxide and isobutylene. Such a procedure was successfully used for the synthesis of 3,4-bis(trifluoromethyl)-1*H*-pyrrole from its *N*-Boc precursor.[19] We tried the *tert*-butoxycarbonylation reaction[20] on the more readily accessible 3-bromopyrrole **8**[6] either on the isolated compound[21] or directly in situ after desilylation. The *N*-Boc protected 3-bromopyrrole **9** was obtained from the *N*-TIPS analog **6** in 52% yield after purification. Despite various reaction conditions, when the same sequence was applied to **7**, without intermediate isolation of **2**, only small amounts of *N*-Boc protected 3-fluoropyrrole **10** could be obtained with difficulty. Nevertheless and as expected, a sample of (impure) **10** was deprotected into **2** upon heating at 180°C in a sealed glass-tube, although accompanied by a substantial amount of metallic-like, blue–black deposit.

Further experiments in this way required disposal of substantial amounts of **7**. In practice, the access to this starting material did not prove to be fully satisfactory in our hands, the yield (36%) being limited by the concomitant formation of the reduction product, *N*-(triisopropylsilyl)-pyrrole, and a problematic scaling up.

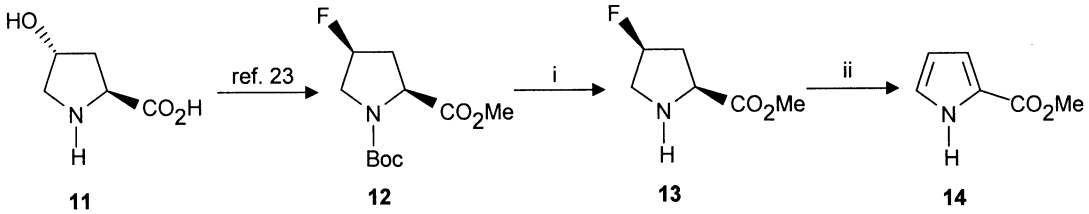
So we were conducted to examine the preparation of the hitherto unknown 4-fluoro-pyrrole-2-carboxylic acid (**18**), a compound susceptible of being thermally decarboxylated into **2**. Since substituted pyrroles could be prepared by dehydrogenation of pyrrolidines with activated manganese dioxide in refluxing tetrahydrofuran,[22] the aromatization of a 3-fluoroprolinate derivative by this method appeared to be feasible. With this aim in view, we prepared the *N*-Boc protected *cis*-fluoroproline methyl ester **12** from the *trans*-4-hydroxy-L-proline (**11**).[23] Since the treatment of **12** with manganese dioxide left the starting material unchanged, we looked for the *N*-deprotected *cis*-4-fluoroproline methyl ester (**13**). This seemingly unreported compound was obtained with some difficulty (due inter alia to its volatility) by treatment of *N*-Boc prolinate **12** with trifluoroacetic acid then displacement of the resulting trifluoroacetate with sodium carbonate.[24] Unexpectedly, the reaction of **13** with manganese dioxide led to the loss of fluorine and methyl pyrrole-2-carboxylate **14** was obtained instead of the expected methyl 4-fluoropyrrole-2-carboxylate (**17**) (Scheme 2).

Owing to this result, it was anticipated that the same process, when applied to the 4,4-difluoroproline methyl ester **16**, would lead to the desired 4-fluoropyrrole **17**. The starting material **16** was also prepared from the *trans*-4-hydroxy-L-proline **11**, via the *N*-Boc-protected 4,4-difluoroproline methyl ester (**15**).[23] *N*-Boc deprotection of **15** with trifluoroacetic acid afforded, after basic treatment, the free base **16** which was aromatized in good yield by treatment with activated manganese dioxide into methyl 4-fluoro-1*H*-pyrrole-2-carboxylate (**17**).[25] Saponification of this ester gave the corresponding acid **18** which was submitted to a flash thermolysis at 300°C in a sealed vacuum flask. Clean decarboxylation of the infusible acid was partially thwarted by extensive decomposition. Nevertheless, low amounts of 3-fluoropyrrole (**2**) could be extracted from the resulting mixture by vacuum transfer into a cooled receiver. Attempted decarboxylation at lower temperature (180°C) in the presence of copper powder was unsuccessful (Scheme 3).

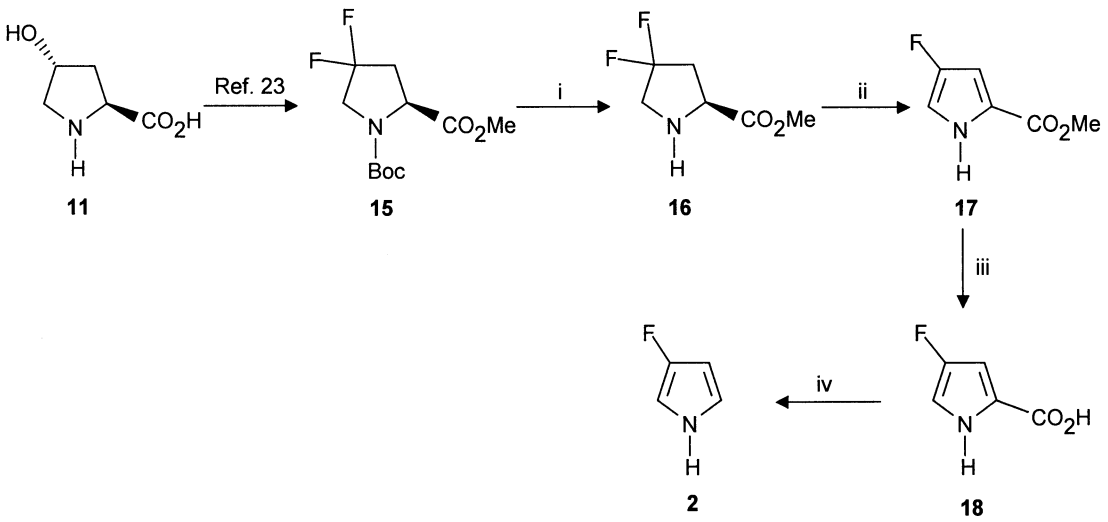
From the two last methods examined above to prepare **2**, it could be concluded that this compound is unstable, as suggested for pyrroles **5**.[8b,c] The harsh reaction conditions used for decarboxylation are probably responsible for this apparent instability. Nonetheless, 3-chloropyrrole has been reported to be unstable[5] and we verified that 3-bromopyrrole (**8**)[6] (mixed with triisopropylsilanol) decomposed quickly on standing at rt. On the other hand, (impure) samples of **2** obtained by desilylation of **7** seemed not to decompose at rt.

2.2. Synthesis from 3,4-difluoro-1*H*-pyrrole and characterization of porphyrins β-F$_n$TPP (n=2,4,6)

By condensation of a mixture of 3,4-difluoro-1*H*-pyrrole (**1**)[1] and pyrrole with benzaldehyde in dichloromethane under Lindsey conditions (each pyrrole at ca. 5.10^{-3} M, benzaldehyde 10^{-2} M and $BF_3{\cdot}Et_2O$ 10^{-3} M) followed by DDQ oxidation,[13] a mixture of porphyrins was obtained. Under our unoptimized conditions (pyrrole ratios, concentrations, etc.), variously fluorinated porphyrins were obtained, along with $TPPH_2$ as major product. A rough separation was first realized by column chromatography associated to an UV–visible monitoring, affording, by order of elution, the porphyrins β-F_8TPPH_2 (**19**), β-F_6TPPH_2 (**20**), β-F_4TPPH_2 (*opp* and *adj* isomers) (**21**) and



Scheme 2. *Reagents and conditions*: (i) TFA, CH_2Cl_2, then $NaHCO_3/H_2O$, rt; (ii) MnO_2, THF, 80°C.



Scheme 3. *Reagents and conditions*: (i) TFA, CH_2Cl_2, then $NaHCO_3/H_2O$, rt; (ii) MnO_2, THF, 80°C; (iii) 4 M KOH/H_2O, MeOH, rt; (iv) flash-thermolysis.

β-F_2TPPH_2 (**22**) in low yields and impure form. A further, more efficient separation was also effected by column chromatography, but after metalation of the free bases samples with zinc acetate. The four new partially fluorinated Zn complexes **20**(Zn)–**22**(Zn) thus obtained (Fig. 1) have been characterized by UV–visible spectroscopy (Table 1), NMR and high-resolution mass spectrometry (see Section 4). As anticipated, the UV–visible absorption spectra of the new porphyrins β-F_nTPPZn (n=2,4,6) are *hypsochromically* shifted relative to the β-unsubstituted TPPZn. Remarkably, the recorded shifts are directly proportional to the number of fluorine atoms at the periphery, both for the Soret (B) and the two Q bands. For example, the Soret band wavelength follows the linear relationship (1) (expressed in nanometers), or its energy counterpart (2) (expressed in electronvolts) (Fig. 2), where n is the number of fluorine atoms.

$$\lambda \text{ (Soret) (nm)} = 417.5 - 1.50n \quad (1)$$

$$E \text{ (Soret) (eV)} = 2.97 + 0.01097n \quad (2)$$

The already known Zn(II) complex of β-octafluoro-*meso*-tetraphenylporphyrin[2] also fits these equations.

2.3. Synthesis from 3-fluoro-1*H*-pyrrole and characterization of porphyrins β-F_4TPP

As we shortly reported in a paper on the electrochemical oxidation of preformed porphyrinogens,[15] 3-fluoro-1*H*-pyrrole (**2**) and benzaldehyde condense under Lindsey

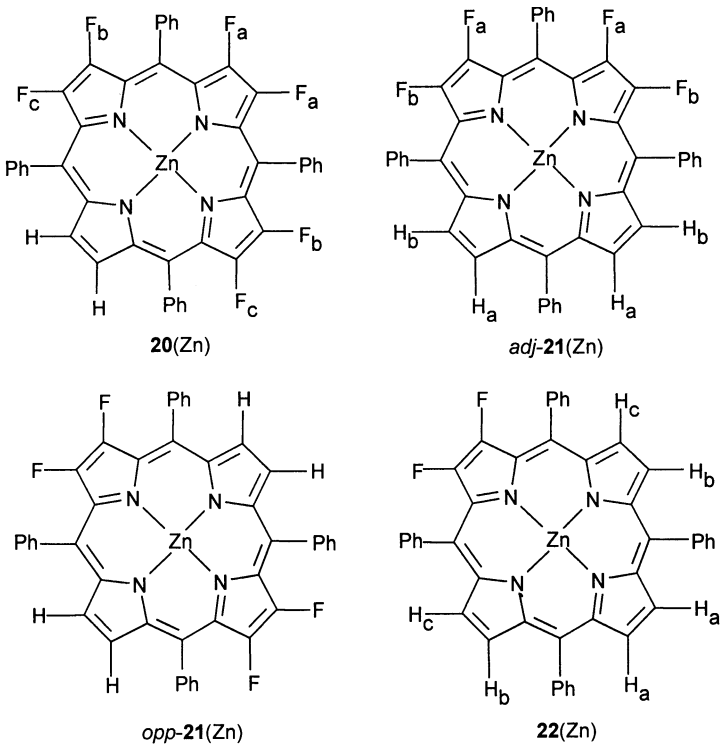


Figure 1. β-Fluoroporphyrins obtained from a mixture of 3,4-difluoropyrrole, pyrrole and benzaldehyde (β-F_8TPPZn and TPPZn are not represented).

Table 1. Spectroscopic data for the free bases and their metal complexes

Compound	λ_{max} (nm)		NH shift[a] (ppm)	Ref.
	Soret band[b]	Q bands[b]		
$TPPH_2$	418	515, 549, 590, 645	−2.78	This work[c]
β-F_4TPPH_2 (**23**)	410	505, 538, 583, 637	−3.45	This work
β-Br_4β′-F_4TPPH_2 (**24**)	425	522, 561, 670	−3.00	This work
β-F_8TPPH_2	403	499, 533, 581, 639	−4.16	2
TPPZn	418	547, 584		This work[c]
β-F_2TPPZn (**22**(Zn))	414	543, 581		This work
β-F_4TPPZn (**23**(Zn))	411	540, 576		This work
opp-β-F_4TPPZn (**21**(Zn))	411	539, 578		This work
adj-β-F_4TPPZn (**21**(Zn))	412	540, 578		This work
β-F_6TPPZn (**20**(Zn))	408	537, 576		This work
β-F_8TPPZn	406	534, 572		2
β-Br_4β′-F_4TPPZn (**24**(Zn))	422	551		This work
β-F_4TPPCu (**23**(Cu))	407	531		This work
β-Br_4β′-F_4TPPCu (**24**(Cu))	419	546		This work

[a] In $CDCl_3$.
[b] In CH_2Cl_2.
[c] Values in accord with the literature data (Ref. 2b).

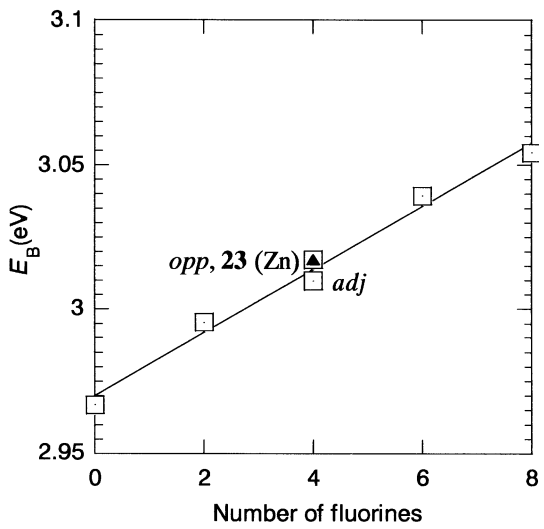
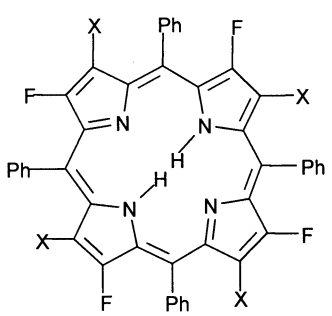
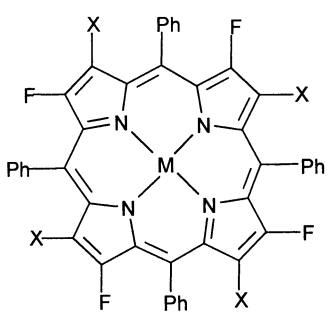


Figure 2. Plot of the energy of the Soret band, E_B of the porphyrins β-F_nTPPZn vs the number of fluorine atoms, *n* (black triangle: **23**(Zn)).

conditions to give porphyrins β-F_4TPPH_2 (**23**) (Fig. 3) in good yields, either after oxidation with DDQ (38%) or electrochemical oxidation (35%). Owing to the unsymmetrical structure of **2**, the obtainment of a mixture of isomeric tetrafluoroporphyrins was foreseeable, following the four possible arrangements depicted in Fig. 4. The isomers could not be separated by thin-layer or column chromatography and purification of the crude product was conveniently achieved by column chromatography of the dicationic porphyrins (silica gel, dichloromethane saturated with perchloric acid as eluent), affording, after neutralization, a mixture of the isomeric free porphyrins **23**. The presence of isomers was confirmed by the ^{19}F NMR spectrum of the porphyrin β-F_4TPPZn (**23**(Zn)) obtained after metalation with zinc acetate but it was not possible to determine their nature and distribution. Six unresolved singlets of variable intensities were observed. Examination of the four possible isomeric structures **a**–**d** (Fig. 3) indicated that configurations **a** and **d** would exhibit only one kind of fluorine atom vs, respectively, four and two for configurations **b** and **c**, leading to a maximum of eight ^{19}F NMR signals. A ^{19}F spectrum of **23** gave no information on the isomer distribution since only a very broad singlet was observed, due to the NH proton exchange. The aromatic part of the ^1H NMR spectrum of **23** was no more informative on the various isomers present. Furthermore, the NH resonance signal appeared as a singlet. As observed for the symmetrical analogs *opp*-**21** and *adj*-**21**, the UV–visible absorption spectra of the porphyrins β-F_4TPPH_2 (**23**) and



23 X = H
24 X = Br



23(Zn) X = H, M = Zn
23(Cu) X = H, M = Cu
24(Cu) X = Br, M = Cu
24(Zn) X = Br, M = Zn

Figure 3. β-Tetrafluoroporphyrins obtained from 3-fluoropyrrole and benzaldehyde (only one of the possible regioisomers is represented).

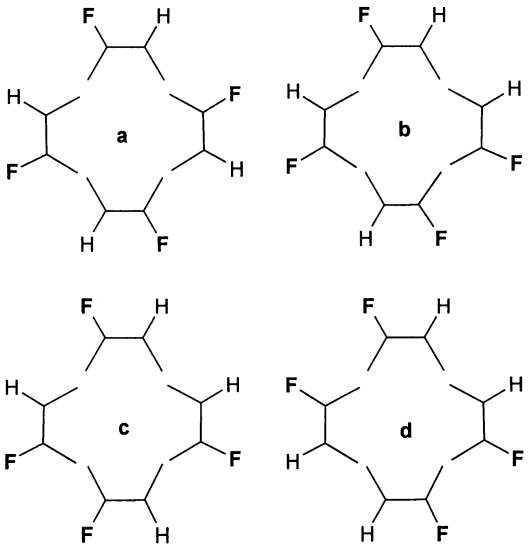


Figure 4. Possible arrangements of the isomeric β-tetrafluoroporphyrins **23** and derivatives.

β-F_4TPPZn (**23**(Zn)) are *hypsochromically* shifted relative to the β-unsubstituted $TPPH_2$ and TPPZn (Table 1), the shifts (Soret and Q bands) being also the half of those observed for the β-octafluoro analogs β-F_8TPP,[2] always in comparison to the same TPP reference compounds. Consequently, the wavelengths found for **23**(Zn) fit the least-squares lines established for the porphyrins β-F_n-TPPZn i.e. TPPZn and **19**(Zn)–**22**(Zn) (Fig. 2). It should be emphasized that the absorption spectrum of **23**(Zn) did not display shoulders or particularly broad bands and was quasi superimposable to that of its regioisomers *opp*-**21** and *adj*-**21**. The redox potentials of the free base porphyrin **23** and its Zn(II) complex **23**(Zn) have been measured by cyclic voltammetry in CH_2Cl_2 (see Section 4). Remarkably, β-tetrafluorination of $TPPH_2$ resulted in positive shifts of the oxidation and reduction potentials that are the average of the corresponding values for TTP and β-F_8TPP (H_2 and Zn):

$$E^{1/2}(\beta\text{-}F_4TPP) = [E^{1/2}(TPP) + E^{1/2}(\beta\text{-}F_8TPP)]/2$$

As mentioned above, the ^{1}H NMR spectrum of the mixture of isomeric free base porphyrins **23** only displays a singlet for the NH resonances located at δ −3.45 ppm. Again, this value is the average of the NH chemical shifts for $TPPH_2$ and β-F_8TPPH_2 i.e. −2.78 and −4.16 ppm, respectively.

2.4. Preparation of the β-Br_4β′-F_4TPPZn complex

Once the mixture of β-tetrafluoroporphyrins **23** had been prepared, it was appealing to introduce bromine atoms on the free β-positions to have access to mixed β-halo-porphyrins. After several attempts, we found convenient to use the copper complex β-F_4TPPCu (**23**(Cu)) as a substrate for the introduction of bromine, mainly for an easy demetalation. The bromination of the complex **23**(Cu) was performed with bromine in a chloroform/dichloromethane mixture in analogy to the octabromination of the complex TPPCu,[26] leading to the complex β-Br_4β′-F_4TPPCu (mixture of isomers) in 70% yield. The latter was demetalated in dichloromethane with sulfuric acid, affording the free base β-Br_4β′-F_4TPPH_2 in 65% yield after purification (mixture of isomers). Further metalation with zinc acetate afforded quantitatively the zinc complex β-Br_4β′-F_4TPPZn, always as an inseparable mixture of isomers (Scheme 4).

The effects of β-bromination of *meso*-tetraarylporphyrins on their physicochemical properties have been widely studied. They are an admixture of steric and electronic effects in which the bulkiness of bromine appears to play a prevailing role by distorting the macrocycle, at least beyond a minimum number of bromine atoms.[27] The new mixed haloporphyrins have been characterized by UV–visible spectroscopy (Table 1), the spectra displaying no shoulders or excessive band widths, indicating close spectroscopic properties for these isomers despite somewhat heterogeneous structures. As anticipated, the introduction of four bromine atoms in the free base or metalated fluoroporphyrins β-F_4TPP induces a *red* shift of their whole spectra. For the Soret band, this shift varies from 11 (Zn complex) to 15 nm (free base).

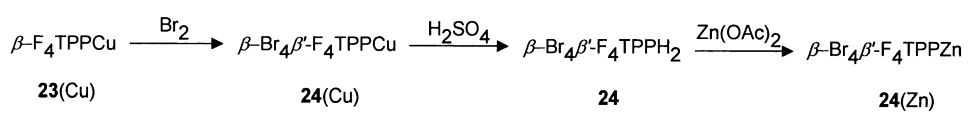
3. Conclusion

In conclusion, we have shown that 3-fluoro-1*H*-pyrrole prepared in situ from 3-fluoro-1-(triisopropylsilyl)pyrrole may be validly used for the preparation of β-tetrafluoro-5,10,15,20-tetraphenylporphyrins. Although obtained as an unresolved mixture, these porphyrins display homogeneous spectroscopic and electrochemical properties, linearly correlated to those observed with the other terms of the series β-F_nTPP (n=0,2,4,6,8) prepared from 3,4-difluoro-1*H*-pyrrole. This remarkable coherence is clearly a direct consequence of the strong electron-withdrawing character of fluorine which overwhelms other structural effects e.g. macrocycle distortion.

4. Experimental

4.1. General

Methylene chloride was distilled from CaH_2 prior to use. Benzaldehyde was distilled under argon immediately prior to use. The remaining reagents were used as received from commercial sources. Manganese(IV) oxide, precipitated active, was purchased from Merck. After work up, solvent removal was effected by rotary evaporation under the water-pump vacuum unless otherwise specified. Column chromatography was performed on silica gel 60 (230–400 mesh) with the indicated solvents. Thin layer chromatography



Scheme 4.

(TLC) was carried out on precoated silica gel $60F_{254}$ plates and compounds were visualized by UV fluorescence or the specified staining reagents. Preparative GLC was performed using a Varian Aerograph Model 920 apparatus equipped with a SE-30 column. UV–visible spectra were obtained using an Uvikon 941 spectrometer. NMR spectra were obtained in $CDCl_3$ at rt, either at the University de Rennes 1 (Bruker DPX 200, AC 300P or DMX 500 spectrometers) or at the Ecole Normale Supérieure (Bruker AC 250 or DRX 400 spectrometers). ^1H NMR chemical shifts (δ) are reported in ppm using the residual chloroform as a chemical shift reference (7.24 ppm). ^{19}F NMR chemical shifts are given relative to $CFCl_3$ as reference. ^{13}C NMR chemical shifts are reported using $^{13}CDCl_3$ as a reference (77.0 ppm). Splitting patterns are abbreviated as follows: s, singlet, d, doublet, t, triplet, q, quartet, quint, quintuplet and m, multiplet. Cyclic voltammograms were obtained using a PAR M 263 apparatus. EI and CI mass spectra were recorded on a Jeol JMS-700 spectrometer.

4.2. *N*-protected fluoropyrroles routes

4.2.1. 3-Fluoro-1*H*-pyrrole (2) from 7. To a stirred solution of **7** (174 mg, 0.72 mmol)[14] in CH_2Cl_2 (1 mL) was added a solution of tetra-*n*-butylammonium fluoride trihydrate (238 mg, 0.75 mmol) in CH_2Cl_2 (1 mL) at rt. After disappearance of the starting material (ca. 10 min by TLC, petroleum ether as eluent, R_f (**7**)=0.48, revelation: iodine vapor), CH_2Cl_2 (5 mL) was added to the mixture which was washed with water (2×3 mL) then brine (3 mL). The organic layer was dried ($MgSO_4$) and filtered. Evaporation of the solvent at −10°C afforded a fluid oil (250 mg) composed from ca. 44% of **2** and 56% of triisopropylsilanol. Distillation bulb-to-bulb at rt under the water-pump pressure (ca. 20 mm Hg) afforded in the condenser at −70°C a small amount of liquid composed of **2** and residual CH_2Cl_2 as the major component. By heating the mixture at ca. 40°C, a liquid containing **2** and triisopropylsilanol in the ratio 27:1 (evaluation by ^1H NMR) was obtained.

3-*Fluoro*-1*H*-*pyrrole* (**2**). ^1H NMR (250.13 MHz, $CDCl_3$) δ 5.97 (apparent q, 1H, J=2.5 Hz, H-4), ~6.50 (m [7 lines: 6.531, 6.521, 6.514, 6.504, 6.493, 6.483, 6.471 ppm], 2H, H-2, H-5), 7.70 (v br t, J~54 Hz, NH); ^{19}F NMR (235.36 MHz, $CDCl_3$) δ −168.47 (m); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 97.19 (d, J=17.3 Hz, C-4), 100.99 (6) (d, J=29.6 Hz, C-2), 115.35 (d, J=6.7 Hz, C-5), 152.51 (d, J=236.9 Hz, CF); HRMS(EI) m/z 85.0306 (M calcd for C_4H_4FN: 85.0327) (^{13}C NMR and high-resolution mass spectra have been obtained on a sample of **2** prepared by thermal decarboxylation of **18**).

4.2.2. 3-Bromo-1-(*tert*-butoxycarbonyl)pyrrole (9). To a stirred solution of **6**[6] (400 mg, 1.32 mmol) in THF (4 mL) under argon was added tetra-*n*-butylammonium fluoride (1.4 mL, 1 M in THF) at rt. After 10 min, ether (15 mL) was added and the organic layer washed with water (10 mL), brine (10 mL) and dried over $MgSO_4$. Removal of the solvent at rt afforded a colorless viscous oil [the same compound was obtained when operating in CH_3CN using a ca. 1 M solution of tetra-*n*-butylammonium fluoride trihydrate in CH_3CN] which was immediately dissolved in dry acetonitrile (3 mL). DMAP (19.2 mg, 0.157 mmol) and di-*tert*-butyl dicarbonate (0.35 g, 1.60 mmol) were added. Evolution of gas started and after 20 min, TLC (cyclohexane, UV) revealed the presence of **9** (R_f=0.33; R_f(**6**)=0.66; R_f(**8**)=0.12). Stirring was continued for 1 h and to the mixture was added ether (15 mL) then 1 M aqueous $KHSO_4$ (6.5 mL). The organic layer was washed with 1 M aqueous $KHSO_4$ (5×3 mL), water (5 mL), 1 M aqueous $NaHCO_3$ (3 mL) and then brine (3×5 mL). After drying ($MgSO_4$) and filtration, removal of the solvent at rt afforded an oil which was purified by flash column chromatography (eluent: cyclohexane/ethyl acetate 95:5) to give the pyrrole **9** (170 mg, 52% vs **6**. TLC: R_f=0.55) as a fluid, colorless oil: ^1H NMR (250.13 MHz, $CDCl_3$) δ 1.56 (s, 9H, Me), 6.19 (dd, 1H, J=3.3, 1.6 Hz, H-4), 7.14 (dd, 1H, J=3.3, 2.5 Hz, H-5 or H-2), 7.21 (approx dd [unsym. t], 1H, J=2.2, 1.7 Hz, H-2 or H-5); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 27.88 (Me), 84.38 (CHMe$_3$), 100.50 (CBr), 114.59 (C-4), 119.40, 120.43 (C-2, C-5), 147.73 (CO); MS (CI, NH_3): m/z 246 $[M^{79}Br+H]^+$, 248 $[M^{81}Br+H]^+$.

3-Bromo-1H-pyrrole (**8**). ^1H NMR (250.13 MHz, $CDCl_3$) δ 6.21 (m, 1H, H-4), 6.69 (q, 1H, J=2.86 Hz, H-2 or H-5), 6.75 (approx q, H-5 or H-2).

4.2.3. 3-Fluoro-1-(*tert*-butoxycarbonyl)pyrrole (10). To a stirred solution of **7** (300 mg, 0.61 mmol)[14] in acetonitrile (5 mL) was added at rt a 1 M solution of tetra-*n*-butylammonium fluoride trihydrate in acetonitrile (1.5 mL). After 30 min, DMAP (20 mg, 0.164 mmol) and di-*tert*-butyl dicarbonate were added. Evolution of gas commenced within 1–2 min. Stirring was continued for 4 h after which ether (20 mL) then 1 M aqueous $KHSO_4$ (6 mL) were added. After partitioning, the organic layer was washed with 1 M aqueous $KHSO_4$ (3×5 mL), water (5 mL), 1 M aqueous $NaHCO_3$ (5 mL) and brine (3×5 mL). After drying ($MgSO_4$), removal of the solvent at rt afforded an oil (210 mg), mixture of **10** (18%), **2** (55%) and triisopropylsilyl fluoride (27%) (estimation by ^{19}F NMR). Flash column chromatography (eluent: cyclohexane/ethyl acetate 95:5; TLC: R_f(**7**)~0.40, revelation: phosphomolybdique reagent then heat) afforded the pyrrole **10** as an impure oil (21 mg, 18%): ^1H NMR (250.13 MHz, $CDCl_3$) δ 1.56 (s, 9H, Me), 6.03 (approx dd, 1H, J=3.4, 1.8 Hz, H-4), 6.92 (approx q, 1H, J=2.2 Hz, H-2 or H-5), 7.02 (approx q, 1H, J=3.6 Hz, H-5 or H-2). ^{19}F NMR (235.36 MHz, $CDCl_3$) δ-160.97 (t, J=4.0 Hz); MS (GC/EI): m/z 185 (M^+).

4.3. Fluoroprolines routes

4.3.1. Methyl (2*S*,4*S*)-4-fluoro-2-prolinate (13). To a stirred solution of methyl (2*S*,4*S*)-*N*-*tert*-butoxycarbonyl-4-fluoro-2-prolinate (**12**)[23] (200 mg, 0.81 mmol) in CH_2Cl_2 (10 mL) was added trifluoroacetic acid (TFA) (0.9 mL) at rt. After ca. 2 h, TLC analysis showed complete consumption of the starting material (eluent: cyclohexane/ethyl acetate 75:25, revelation: TFA vapor, ninhydrin/EtOH spray then heat, R_f(**12**)=0.28, R_f(**13**, $CF_3CO_2^-$)~0). Evaporation of the solvent and excess TFA under reduced pressure (water-pump then oil-pump) at rt afforded the trifluoroacetate salt of **13** as a colorless oil (280 mg): MS (CI, NH_3) 148 (MH^+).

To a stirred solution of the above trifluoroacetate (97.4 mg, 0.37 mmol) in CH_2Cl_2 (2 mL) was added water (0.2 mL) then powdered anhydrous sodium carbonate (70 mg, 0.66 mmol) at rt. After 15 min of stirring, an additional sodium carbonate (300 mg) was added. After ca. 1 h of drying, the liquid was collected with a Pasteur pipette and evaporated at −10°C affording **13** as a colorless, fluid oil (37.7 mg, 69%) (*caution*: volatile product!): ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 2.21 (m, 1H, H-3), 2.34 (m, 1H, H-3′), 2.41 (br s, 1H, NH), 2.87 (ddd, 1H, J=37.6, 13.4, 3.3 Hz, H-5), 3.37 (dd, 1H, J=22.0, 13.4 Hz, H-5′), 3.73 (s, 3H, Me), 3.79 (dd, 1H, J=7.9, 5.8 Hz, H-2), 5.12 (dq, 1H, J=53.8, 2.8 Hz, H-4); ^{19}F NMR (235.36 MHz, $CDCl_3$) δ −174.39 (m); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 37.72 (d, J=21.6 Hz, C-3), 52.33 (s, CH_3), 53.91 (d, J=22.8 Hz, C-5), 58.78 (s, C-2), 93.67 (d, J=175.0 Hz, CF), 174.51 (s, CO); HRMS (CI, CH_4): m/z 148.0780 (MH^+ calcd for $C_6H_{11}FNO_2$: 148.0774).

4.3.2. Methyl pyrrole-2-carboxylate (14). To a stirred solution of **13** (33.8 mg, 0.23 mmol) in THF (1.5 mL) was added manganese oxide (160 mg, 1.84 mmol). The suspension was refluxed for 3 h and diluted after cooling with THF (5 mL), then filtered through a pad of Celite which was rinsed with THF. Evaporation of the solvent under reduced pressure afforded the pyrrole **14** as an off-white crystalline solid (19.5 mg, 68% crude): ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 3.83 (s, 3H, Me), 6.25 (apparent q, 1H, J=3.5 Hz, H-5), 6.90 (m, 1H, H-3 or H-4), 6.94 (m, 1H, H-4 or H-3), 9.14 (br s, 1H, NH); MS (EI): m/z 125 (M^+).

4.3.3. Methyl (2*S*)-4,4-difluoro-2-prolinate (16). To a stirred solution of methyl (2*S*)-*N*-*tert*-butoxycarbonyl-4,4-difluoro-2-prolinate[23] (**15**) (500 mg, 1.88 mmol) in CH_2Cl_2 (30 mL) was added TFA (2 mL) at rt. The mixture was stirred overnight (TLC analysis: cyclohexane/ethyl acetate 75:25, revelation: TFA vapor, ninhydrin/EtOH spray then heat, R_f(**15**)=0.48, R_f(**16**, $CF_3CO_2^-$)~0) and the solvent and excess TFA evaporated under reduced pressure at rt to give the trifluoroacetate salt of **16** as an oil. Saturated aqueous $NaHCO_3$ (3 mL) was added under stirring (*caution*: effervescence!) then ether (15 mL). After 15 min of stirring, the aqueous phase was extracted with ether (2×10 mL). The combined organic phases were dried (Na_2SO_4). After filtration, removal of the solvent under reduced pressure at rt (*caution*: volatile product!) afforded **16** as a slightly yellow to brown, fluid oil (270 mg, 87%): $[\alpha]_D^{20}$=−16.9° (c=1.11, $CHCl_3$). Attempted purification by bulb-to-bulb distillation at 40°C under 0.05 mm Hg afforded as small amount of more pure **16** as a colorless liquid: $[\alpha]_D^{20}$=−17.1° (c=1.04, $CHCl_3$); ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 2.37 (apparent qd, 1H, J=14.3, 6.4 Hz, H-3), 2.54 (apparent qd, 1H, J=14.3, 8.8 Hz, H-3′), 2.65 (br s, 1H, NH), 3.15 (apparent q, 1H, J=12.8 Hz, H-5), 3.31 (apparent q, 1H, J=12.5 Hz, H-5′), 3.74 (s, 3H, Me), 3.96 (dd, 1H, J=8.8, 6.4 Hz, H-2); ^{19}F NMR (376.49 MHz, $CDCl_3$) δ −99.74 (center of an AB type pattern): δ (F_A) −99.37 (dquint, 1F, ^2J=233.4 Hz, F_A), δ (F_B) −100.11 (dquint, 1F, ^2J=233.4 Hz, F_B); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 38.82 (t, J=26.0 Hz, C-3), 52.42 (s, CH_3), 53.69 (t, J=29.0 Hz, C-5), 57.88 (t, J=4.5 Hz, C-2), 130.04 (t, J=250.0 Hz, CF_2), 173.08 (s, CO); HRMS (CI, CH_4): m/z 166.0679 (MH^+ calcd for $C_6H_{10}F_2NO_2$: 166.0681).

4.3.4. Methyl 4-fluoro-pyrrole-2-carboxylate (17). To a stirred solution of **16** (169 mg, 1.02 mmol) in THF (15 mL) was added activated manganese dioxide (746 mg, 8.58 mmol). The suspension was refluxed for 3 h then filtered after cooling through a pad of Celite which was rinsed with THF. Evaporation of the solvent under reduced pressure gave an off-white crystalline solid (134.4 mg). Flash column chromatography (CH_2Cl_2 as eluent; TLC: R_f(**17**)=0.38, UV revelation) afforded the pyrrole **17** as a white microcrystalline solid (106.5 mg, 73%): mp 94.2–95.4°C; ^{1}H NMR ($CDCl_3$, 250.13 MHz) δ 3.83 (s, 3H, Me), 6.58 (apparent t [poorly resolved], 1H, J~2.0 Hz, H-3), 6.71 (apparent td, 1H, J=3.4, 1.8 Hz, H-5), 8.98 (br s, 1H, NH); ^{19}F NMR (235.36 MHz, CDC_3) δ −163.01 (m); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 51.69 (s, CH_3), 101.95 (d, J=15.8 Hz, C-3 or C-5), 107.36 (d, J=28.4 Hz, C-5 or C-3), 118.80 (d, J=6.3 Hz, C-2), 151.85 (d, J=241.70 Hz, C-4), 161.35 (d, J=3.1 Hz, CO). Anal. calcd for $C_6H_6FNO_2$: C, 50.35; H, 4.22; N, 9.78. Found: C, 49.98; H, 4.21; N, 9.52.

4.3.5. 4-Fluoro-pyrrole-2-carboxylic acid (18). To a stirred solution of **17** (300 mg, 2.1 mmol) in methanol (17 mL) was added 4 M aqueous KOH (35 mL) at rt. Stirring was continued overnight then methanol was evaporated at rt. The residual liquid was acidified (aqueous HCl) and extracted with ether (4×30 mL). The organic phase was washed with water (2×30 mL) then brine (30 mL). After drying (Na_2SO_4) and filtration, removal of the solvent under reduced pressure afforded the acid **18** as an amorphous off-white solid (251 mg, 93%): ^{1}H NMR (250.13 MHz, acetone-d_6) δ 6.57 (m [poorly resolved], 1H, H-3), 6.91 (apparent td, 1H, J=3.4, 1.8 Hz, H-5), 10.73 (br s, 1H, CO_2H);^{19}F NMR (235.36 MHz, acetone-d_6) δ −164.50 (m); ^{13}C NMR (62.89 MHz, acetone-d_6) δ 101.83 (d, J=15.8 Hz, C-3 or C-5), 108.32 (d, J=28.1 Hz, C-5 or C-3), 120.21 (d, J=6.2 Hz, C-2), 152.59 (d, J=238.1 Hz, C-4), 161.67 (d, J=3.0 Hz, CO_2H). Anal. calcd for $C_5H_4FNO_2$: C, 46.52; H, 3.12; N, 10.85. Found: C, 46.61; H, 3.12; N, 10.58. MS (EI): m/z 129 (M^+).

4.4. Porphyrin synthesis

4.4.1. From 3,4-difluoro-1*H*-pyrrole (porphyrins β-F$_n$TPP, 19–22). To a stirred solution of 3,4-difluoro-1*H*-pyrrole[1] (**1**) (37.1 mg, 0.36 mmol), pyrrole (24.1 mg, 0.36 mmol) and benzaldehyde (76.4 mg, 0.72 mmol) in CH_2Cl_2 (72 mL) under argon at rt, $BF_3.Et_2O$ (60 μL) was added via a syringe. After 1 h, DDQ (120 mg, 0.53 mmol) was added and stirring was maintained for an additional hour. After evaporation of the solvent, a rough separation of the porphyrins was performed under their dicationic form by column chromatography, eluting with CH_2Cl_2 saturated with perchloric acid. The organic layer was washed with water until neutral and dried over $MgSO_4$. After removal of the solvent, the residue was treated with zinc(II) acetate according to the procedure of Bhyrappa and Krishnan.[28] Column chromatography on silica gel with CH_2Cl_2 as eluent and UV–visible monitoring, afforded by order of elution, small amounts (yields not determined) of the porphyrins β-F_8TPPZn, β-F_6TPPZn, *opp*-β-F_4TPPZn and *adj*-β-F_4TPPZn, β-F_2TPPZn.

β-F₆TPPZn (**20**(*Zn*)). ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 7.76 (m, 12H, *m*-H and *p*-H), 8.07 (m, 8H, *o*-H), 8.83 (s, 2H, β-H); ^{19}F NMR (188.31 MHz, $CDCl_3$) δ −143.02 (d, 2F, *J*=4.8 Hz, F_b or F_c), −143.07 (s, 2F, F_a), −143.42 (d, 2F, *J*=4.8 Hz, F_c or F_b); UV–visible (CH_2Cl_2) λ_{max} (nm) (rel. int.) 408 (100), 537 (4.9), 576 (1.1); HRMS (FAB): *m/z* 784.1061 (M^+ calcd for $C_{44}H_{22}F_6N_4^{64}Zn$: 784.1040).

opp-β-F₄TPPZn (*opp*-**21**(*Zn*)). ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 7.77 (m, 12H, *m*-H and *p*-H), 8.11 (m, 8H, *o*-H), 8.83 (s, 4H, β-H); ^{19}F NMR (188.31 MHz, $CDCl_3$) δ −143.98 (s); UV–visible (CH_2Cl_2) λ_{max} (nm) (rel. int.) 411 (100), 539 (6.3), 578 (3.0); HRMS (FAB): *m/z* 748.1249 (M^+ calcd for $C_{44}H_{24}F_4N_4^{64}Zn$: 748.1229).

adj-β-F₄TPPZn (*adj*-**21**(*Zn*)). ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 7.80 (m, 12H, *m*-H and *p*-H), 8.16 (m, 8H, *o*-H), 8.83 (d, 2H, *J*=4.8 Hz, H_a or H_b), 8.93 (d, 2H, *J*=4.8 Hz, H_b or H_a); ^{19}F NMR (188.31 MHz, $CDCl_3$) δ −143.69 (d, 2F, *J*=5.0 Hz, F_a or F_b), −143.96 (d, 2F, *J*=5.0 Hz, F_b or F_a); UV–visible (CH_2Cl_2) λ_{max} (nm) (rel. int.) 412 (100), 540 (6.6), 578 (3.1).

β-F₂TPPZn (**22**(*Zn*)). ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 7.76 (m, 12H, *m*-H and *p*-H), 8.14 and 8.21 (m, 8H, *o*-H), 8.84 (d, 2H, *J*=4.8 Hz, H_b or H_c), 8.94 (d, 2H, *J*=4.8 Hz, H_c or H_b), 8.95 (s, 2H, H_a); ^{19}F NMR (188.31 MHz, $CDCl_3$) δ −144.52 (s); UV–visible (CH_2Cl_2) λ_{max} (nm) (rel. int.) 414 (100), 543 (6.5), 581 (3.1); HRMS (FAB): *m/z* 712.1431 (M^+ calcd for $C_{44}H_{26}F_2N_4^{64}Zn$: 712.1417).

4.4.2. From 3-fluoro-1*H*-pyrrole (porphyrins β-F₄TPP, 23). To a stirred solution of 3-fluoro-1-(triisopropylsilyl)-pyrrole[14] (**7**) (120 mg, 0.5 mmol) in CH_2Cl_2 (1.2 mL) under argon was added a 1 M solution of tetra-*n*-butylammonium fluoride in THF (0.5 mL, 0.5 mmol) at rt. After 5 min, CH_2Cl_2 (50 mL) was added. The solution was washed with water (3×10 mL) and dried ($MgSO_4$). After filtration, to this solution under argon was added benzaldehyde (53 mg, 0.5 mmol). The mixture was stirred at rt while $BF_3{\cdot}Et_2O$ (21 μL, 0.16 mmol) was added via a syringe. After 1 h, DDQ (85 mg, 0.37 mmol) was added and the reaction stirred for an additional hour. After evaporation of the solvent, the porphyrins were purified under their dicationic form by column chromatography on silica gel, eluting with CH_2Cl_2 saturated with perchloric acid. The organic layer was washed with water until neutral and dried over $MgSO_4$. After removal of the solvent in vacuo, the mixture of porphyrins **23** was obtained as a purple solid (32 mg, 38%): ^{1}H NMR (200.13 MHz, $CDCl_3$) δ −3.45 (br s, 2H, NH), 7.64–7.80 (m, 12H, *m*-H, *p*-H), 8.00–8.10 (m, 8H, *o*-H), 8.10–8.22 (m, 4H, β-H); ^{19}F NMR (188.31 MHz, $CDCl_3$) δ −124.96 (br s); UV–visible (CH_2Cl_2) λ_{max} (nm) ($\varepsilon\times10^{-5}$) 410 (2.478), 505 (0.188), 538 (0.065), 583 (0.064), 637 (0.054); CV (CH_2Cl_2/TBAPF$_6$) $E^{1/2}$ (V)=1.17, −1.08, −1.35.

4.4.3. [2,7,12,17-Tetrafluoro-5,10,15,20-tetraphenylporphinato]zinc (23(Zn)) or copper (23(Cu)). To a stirred solution of porphyrins **23** (13.7 mg, 0.02 mmol) in 15 mL of CH_2Cl_2/CH_3OH (2:1) was added a 5-fold excess of $Zn(OAc)_2{\cdot}4H_2O$ or $Cu(OAc)_2$. The reaction was monitored by UV–visible spectroscopy. When metalation was complete, the solvents were evaporated in vacuo and the porphyrins **23**(Zn) or **23**(Cu) were purified by column chromatography on silica gel using CH_2Cl_2 as eluent.

Zn(II) porphyrins **23**(*Zn*). ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 7.62–7.82 (m, 12H, *m*-H and *p*-H), 7.97–8.14 (m, 8H, *o*-H), 8.16–8.32 (m, 4H, β-H); ^{19}F NMR (188.31 MHz, $CDCl_3$) δ −124.16 (s), −124.34 (s), −124.41 (s, minor peak), −124.52 (s), −124.62 (s), −124.82 (s, major peak); UV–visible (CH_2Cl_2) λ_{max} (nm) ($\varepsilon\times10^{-5}$) 411 (4.011), 540 (0.172), 576 (0.036); CV (CH_2Cl_2/TBAPF$_6$) $E^{1/2}$ (V)=1.20, 0.96, −1.26, −1.63.

Cu(II) porphyrins **23**(*Cu*). UV–visible (CH_2Cl_2) λ_{max} (nm) (rel. int.) 407 (100), 531 (4.7).

4.4.4. [2,7,12,17-Tetrabromo-3,8,13,18-tetrafluoro-5,10,15,20-tetraphenylporphinato]copper (24(Cu)), free base (24) and Zn(II) complex (24(Zn)). To a stirred solution of porphyrins **23**(Cu) in 25 mL of $CHCl_3/CCl_4$ (1:1), was added slowly bromine (160 μL) in the same solvent (7 mL), at rt. After 4 h of stirring, a solution of pyridine (400 μL) in $CHCl_3/CCl_4$ (1:1) was added dropwise (*caution*: exothermic reaction!). The mixture was stirred overnight and quenched with a 20% aqueous $Na_2S_2O_5$ solution (30 mL). After decantation, the organic phase was dried over $MgSO_4$. After filtration and evaporation of the solvents, the copper complex **24**(Cu) was purified by column chromatography on silica gel using $CHCl_3$ as eluent.

Cu(II) porphyrins **24**(*Cu*). UV–visible (CH_2Cl_2) λ_{max} (nm) (rel. int.) 419 (100), 546 (7.0).

Demetalation procedure and Zn insertion. The brominated copper complex **24**(Cu) was dissolved in chloroform (20 mL) and concentrated sulfuric acid (4 mL) was added cautiously to the stirred solution. When demetalation was complete (UV–visible monitoring), the mixture was neutralized by addition of 4N aqueous NaOH. After separating layers, the organic phase was dried ($MgSO_4$), filtered and evaporated. The free base **24** was purified by column chromatography (CH_2Cl_2 as eluent). Zinc insertion was carried out with $Zn(OAc)_2{\cdot}4H_2O$ in a CH_2Cl_2/CH_3OH mixture as for **23**.

2,7,12,17-Tetrabromo-3,8,13,18-tetrafluoro-5,10,15,20-tetraphenylporphyrin (**24**). ^{1}H NMR (200.13 MHz, $CDCl_3$) δ-3.00 (br s, 2H, NH), 7.75 (m, 12H, *m*-H and *p*-H), 8.07 (m, 8H, *o*-H); ^{19}F NMR (188.13 MHz, $CDCl_3$) δ −118.10 (br s, 4F), −121.74 (br s, 4F); UV–visible (CH_2Cl_2) λ_{max} (nm) ($\varepsilon\times10^{-5}$) 425 (1.661), 522 (0.126), 561 (0.081), 670 (0.057); CV (CH_2Cl_2/TBAPF$_6$): $E^{1/2}$ (V)=1.57, 1.09, −0.78, −0.89.

[2,7,12,17-Tetrabromo-3,8,13,18-tetrafluoro-5,10,15,20-tetraphenylporphinato]zinc (**24**(*Zn*)). ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 7.59 (m, 12H, *m*-H and *p*-H), 7.90 (m, 8H, *o*-H); ^{19}F NMR (282.40 MHz, $CDCl_3/CD_3OD$ (4:1)) δ −118.21 (s, major peak); −118.34, −118.36, −118.41, −120.90 and −120.94 (s, minor peaks); UV–visible (CH_2Cl_2) λ_{max} (nm) ($\varepsilon\times10^{-5}$) 422 (2.082), 551 (0.121); CV (CH_2Cl_2/TBAPF$_6$): $E^{1/2}$ (V)=1.16, 1.03,

−1.25, −1.53. HRMS (FAB, *m*-NBA)): *m/z* 1061.7665 (M^+ calcd for $C_{44}H_{20}{}^{79}Br_4F_4{}^{66}Zn$: 1061.7630).

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