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Synthesis and Electrochemistry of Free-Base Porphyrins Bearing Trifluoromethyl meso-Substituents

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Abstract: CF₃-substituted porphyrins have attracted increasing interest over the past decade. However, the number of examples reported in the literature remains quite limited and much remains to be done to understand the properties and reactivity of these molecules. We are now reporting on the synthesis of a series of free base porphins incorporating one, two and three CF₃ substituents, including the 5,10,15-tris(CF₃) substituted porphyrin which has never been described before. We have also carried out detailed electrochemical and spectroscopic analyses aiming at assessing the EWG properties of the CF₃ substituents compared to the widely used C₆F₅. Our studies led us to propose an interpretation of the quite unusual electrochemical signature of these molecules featuring three successive one-electron reduction waves.

Introduction

The chemistry of porphyrins has been in continuous development ever since the discovery of hematoporphyrin by Nencki and Zeleski in the 1900s.¹ The key role of the meso- and/or β substituents on the spectroscopic, chemical, photophysical and electronic properties of these aromatic macrocycles has led researchers to conceive a whole range of peripheral modification strategies. Much efforts have focused over the past decades at providing access to peripherally crowded macrocycles,² at introducing water-solubilizing groups,³ at expanding π conjugation or at introducing peripheral coordination sites.⁴ These essential works have paved the way for applications in many different fields such as in catalysis, sensing, medicine and in energy related domains.5, 6 The introduction of electronwithdrawing groups (EWG) have proved particularly useful to enhance the axial binding ability of metalloporphyrins,⁷ to tune the redox activity of porphyrins and of the metal ion inserted in their cavities^{8, 9} or to enable the synthesis/stabilization of particular porphyrin analogs.^{10, 11} Such modifications are thus of paramount importance for synthetic purposes and to promote the applications of porphyrins in (electro)catalysis,¹² sensing¹³ or in molecular magnetism.14

The most widely used electron-withdrawing substituent in porphyrin chemistry so far is the pentafluorophenyl group. The latter is easily introduced at the *meso* positions of porphyrins using acid-catalyzed Rothemund-Lindsey type of condensations¹⁵ between selected pyrrole derivatives and the commercially available 2,3,4,5,6-pentafluorobenzaldehyde. The large gain in popularity of this substituent over the past decades is due the availability of this key reactant, to the presence of five strongly electronegative fluorine atoms and also to the chemical reactivity of the para fluorine atom which can be exploited for further functionalization. It should be noted however that other

substituents, like the 4-trifluoromethylphenyl, 3,5bis(trifluoromethyl)phenyl,^{16, 17} nitro,¹⁸ cyano, halogens, 4nitrophenyl or 4-pyridiunium, have also been used, albeit to a lesser extent, to tune the electron density of porphyrins.¹⁹ In addition to their EWG character, fluorine atoms are also particularly interesting for medicinal applications.²⁰ The incorporation of fluorine atoms is for instance known to enhance the pharmacological activity of organic molecules²¹ while ¹⁹F-NMR spectroscopy may also prove extremely useful as a monitoring tool in biological media.

The CF₃ substituents is a particularly interesting/powerful EWG which has already been introduced at the β -position of porphyrins. These syntheses require the introduction of CF₃ groups prior to pyrrole formation^{22, 23} or the use of halogenated porphyrin-based intermediates.²⁴⁻²⁸ These substituents have also been introduced at the *meso* positions in corroles²⁹⁻³¹ and expanded porphyrins.³² It also includes a handful of articles reporting on the synthesis of mono,³³ bis-(5,15)³⁴⁻³⁸ and tetra-substituted^{12, 35, 39-43} porphyrin derivatives. All these products have been obtained either from reactions between trifluoroacetaldehyde and pyrrole ⁴⁴ or using a CF₃-substituted dippyromethane as an intermediate.^{45, 46}

We are now reporting on the synthesis of a series of free base *meso*-substituted porphyrins incorporating one, two and three CF₃ substituents, including the 5,10,15- tris(CF₃) substituted porphyrin which has never been reported before. We have also carried out detailed electrochemical and spectroscopic analyses aiming at assessing the EWG properties of the CF₃ substituents compared to the widely used C₆F₅.

Results and Discussion

Synthesis

Our strategy to synthesize the targeted molecules was inspired by the work of Lindsey and co-workers on porphyrins bearing different *meso*-substituents.¹⁵ The targeted free base macrocycles bearing electron-withdrawing substituents were prepared using a rational methodology involving acylation at the 1,9-positions of the trifluoromethyl-substituted dipyrromethane 1, followed by condensation with a dipyrromethane to give the corresponding *trans*- A_2B_2 -porphyrin **5** H_2 , and A_3B -porphyrins **4** H_2 (Scheme 1).47 For this purpose, the 5and 6H₂ trifluoromethyldipyrromethane (1) was isolated in a moderate vield by condensation of pyrrole and trifluoroacetaldehyde, used as its hemiacetal, in the presence of stoichiometric amounts of trifluoroacetic acid. ²⁹ Treatment of **1** with trifluoroacetic anhydride at ambient temperature afforded the targeted 1,9bis(trifluoroacetyl) derivative 2 in 98% yield.32 Standard formylation of **1** with two equivalents of Vilsmeier reagents (POCl₃/DMF) then afforded the key intermediate **3** in 67% yield.⁴⁸



 $\begin{array}{l} \label{eq:scheme 1. For 1: a) TFA, CH_2Cl_2, RT, 12 h. For 2: b) (CF_3CO)_2O, toluene, RT, 5 h. For 3: b) POCl_3, DMF, 0^{\circ}C, 1.5 h. For 4: c) NaBH_4, then 2,2^{-} dipyrrolylmethane, MsOH, CH_2Cl_2, 35 ^{\circ}C, 1.5 h, then DDQ. For 5H_2: c) NaBH_4, then 1, Yb(OTf)_3, CH_2Cl_2, 35 ^{\circ}C, 1.5 h, then DDQ. For 6H_2: c) NaBH_4, then 2,2^{-} dipyrrolylmethane, MsOH, CH_2Cl_2, 35 ^{\circ}C, 1.5 h, then DDQ. \\ \end{array}$

In this study, we also focused on *meso*-pentafluorophenylsubstituted porphyrins as reference compounds. The *bis* (**7**H₂), *tris* (**8**H₂) and *tetra* (**9**H₂) C₆F₅-substituted porphyrin derivatives were obtained using methods described in the literature (Scheme 2).^{49, 50}



Scheme 2. $CF_{3}\text{-}$ (4-6H_2) and $C_6F_5\text{-substituted}$ (7-9H_2) porphyrins investigated in this study.

The targeted trifluoromethyl *meso*-substituted porphyrins $4H_2-6H_2$ were fully characterized by ¹H-NMR spectroscopy using 1D- and 2D-NMR experiments. The number and relative intensities of the signals observed in the ¹H- and ¹⁹F-NMR spectra recorded in deuterated chloroform (1mM) at room temperature are in agreement with the proposed structures. Observation of one or two ¹⁹F signals in the spectrum of $4H_2$ and $5H_2$ is for instance fully consistent with the symmetry of these molecules leading to the chemical equivalence of both CF₃ substituents introduced at position 5 and 15 of the porphyrin ring (Figure 1). Detailed attribution of the ¹H signals are shown in Figure 1. As expected, the electron-withdrawing character of the trifluoromethyl groups is brought to light through the chemical shift window, which shortens with the number of CF₃ groups. This trend reflects a weakening of the aromatic ring current due to a decrease of the electron density on the porphyrin ring. The effect is particularly strong on the signals attributed to the inner NH resonances shifting from -3.39 to -2.71 ppm upon introducing one and three CF₃ substituents, respectively. This effect is far less marked in the aromatic region involving resonances attributed to the β and meso-hydrogen atoms. The maximum shift is observed for the meso hydrogen atoms undergoing a 0.12 ppm upfield shift between $4H_2$ and $6H_2$. The limited shift of the aromatic signals can actually be explained by the fact that these protons are subjected to two opposite effects: a weakening of the aromatic ring current leading to an upfield shift of the signals attributed to all protons located outside the ring and the EWG effect of the CF₃ substituents leading to a downfield shift of the same signals.



Figure 1. Partial ¹H- (left) and ¹⁹F- (right) NMR spectra of $4H_2$, $5H_2$ and $6H_2$ (1 mM, CDCl₃, 25 °C, 400 MHz).

These compounds were further characterized by UV-Vis absorption spectroscopy. The spectra of $4H_2$ - $6H_2$ recorded in acetone exhibit one intense Soret band centered at $\lambda_{max} = 391$ -398 nm (8.3 10³ - 25 10³ M⁻¹.mm⁻¹) and four much weaker Q bands, including shoulders (See Fig ESI15). The absence of aggregation in these conditions was revealed by the linear evolution of the intensity measured at λ_{max} as a function of concentration (see Fig. SI6). As expected, the addition of CF₃ substituents on the porphyrin core leads to significant bathochromic shifts of the absorption bands and to a decrease of the molar extinction coefficients from 18 10³ M⁻¹.mm⁻¹ for 6H₂ down to 8.9 10³ M⁻¹.mm⁻ ¹ for $4H_2$ (see Table 1). We found however no clear linear dependence of the max wavelengths with the number of CF₃ substituents. Increasing the number of CF3 has also a much stronger effect on the Q bands than on the Soret band which undergoes only a 7nm shift by increasing the number of CF₃ from 1 to 3 (4H₂ to 6H₂)

Taken together, the spectroscopic data discussed above are consistent with the conclusion that the introduction of CF₃ substituent lead to weakening of the electron density and of the aromaticity of the porphyrin ring. DFT investigations carried out on **4**H₂, **5**H₂ and **6**H₂ moreover revealed that the addition of 1, 2 or 3 CF₃ groups does not induce significant distortion of the porphyrin plane, which support the conclusion that all the shifts discussed above only result from the electronegative character of the CF₃ substituents.

Table 1. Maximum wavelength (λ_{max} in nm) and extinction coefficient values (ϵ in M⁻¹ mm⁻¹) measured for 4H₂, 5H₂ and 6H₂ in acetone and dichloromethane.

		Soret Band		Q1		Q2		Q3		Q4	
		λ _{max}	٤	λ _{max}	٤	λ _{max}	٤	λ _{max}	٤	λ _{max}	ε
Acetone	6 H ₂	391	18200	492	1100	523	820	564	480	617	560
	5 H ₂	390	8300	498	480	533	840	573	260	626	750
	4 H ₂	398	8900	504	660	538	630	583	330	636	610
DCM	6 H ₂	394	9500	494	470	528	240	567	130	619	90
	5 H ₂	393	13400	498	660	536	1180	577	290	628	1030
	4 H ₂	402	19700	505	1180	538	1060	587	410	637	1090

The EWG effect of the CF_3 groups was further studied upon assessing the ability of the inner nitrogen atoms to accept or release protons in the presence of added acid and base, respectively.

The protonation of porphyrins was studied in dichloromethane upon recording changes in the Soret and Q bands intensities and maximum wavelengths in the presence of trifluoroacetic acid (TFA). Initial attempts revealed that neither $4H_2$, $5H_2$ nor $6H_2$ can be protonated in DMF, which is consistent with the expected weak basicity of the inner nitrogens. However, protonation of those core N-atoms was eventually achieved in dichloromethane. The experimental data collected in these conditions in the presence of TFA are moreover in agreement with the direct formation of the doubly protonated species [PH₄]²⁺ from PH₂ with no evidence of the monoprotonated intermediate [PH₃]⁺ as revealed by the observation of a clear isosbestic point in the titration curves and by the development of a single set of signals (Soret and Q bands). The spectroscopic data collected upon addition of TFA to a solution of 4H₂ are shown in Figure 2A as an illustration of such behavior. Similar data collected with $5H_2$ and $6H_2$ are shown in the ESI section (Figure ESI17A/C). Protonation systematically led to bathochromic and hyperchromic shifts of the Soret band and to the development of only two Q bands. Most importantly, we found that the amount of TFA required to produce the bisprotonated porphyrins $[PH_4]^{2+}$ from PH_2 increase with the number of CF_3 substituents (see Figure 2C) as a result of the decrease in the basicity of the inner nitrogens.



Figure 2. Variation of the UV/Vis absorption spectra upon titration of (A) 5.87×10^{6} M DCM solution of $4H_{2}$ with TFA and (B) 9.04×10^{6} M DMF solution of $4H_{2}$ with 0,1 M solution of TBAOH in MeOH/Toluene (1cm optical path). Variation of ΔA versus (C) molar equiv. of TFA and (D) molar equiv. of TBAOH during the acid and base titration of $4H_{2}$ - $6H_{2}$ in DCM and DMF, respectively.

Accordingly, we found that the acidity of the inner NH's increase with the number of CF₃ groups. This was easily revealed upon recording changes in the Soret and Q bands intensities and maximum wavelengths in the presence of tetra-*n*-butylammonium hydroxide (TBAOH). Here again, as illustrated in Figure 2B with the curves recorded with 4H₂, all the experimental data collected in these conditions are consistent with the direct formation of the dianionic species P^{2-} from PH_2 . The formation of 4^{2-} is revealed in Figure 2B through the decrease in the intensity of the Soret and Q bands attributed to $4H_2$ at the expense of new signals developing at 439 nm and 734 nm.

Electrochemical studies

The electrochemical properties of the CF₃-substituted porphyrins $4H_2$, $5H_2$ and $6H_2$ were investigated in DMF in the presence of tetra-*n*-butylammonium hexafluorophosphate used as electrolyte. For comparison purposes, similar analyses were conducted on the reference compounds $7H_2$, $8H_2$ and $9H_2$, incorporating C₆F₅ substituents.

The CV curves recorded for $4H_2$, $5H_2$ and $6H_2$ display similar features including three successive one-electron reductions and one oxidation centered on the porphyrin ring. Detailed electrochemical data are collected in Table 2 but only the CV curves recorded with the 5,10,15-substituted compounds $4H_2$ and $8H_2$ are shown in Figure 3. CV curves recorded for $5H_2$ and $6H_2$ are provided in the ESI section (Figure ESI 1 & 2). The relative number of electrons involved in each wave was assessed from electrolysis and measurements recorded in steady state conditions at rotating disc electrodes (dashed lines in Figure 3). It should also be mentioned that similar CVs were obtained when using dichloroethane as the solvent (see Fig ESI 3).

On the anodic side, only one fully irreversible oxidation wave is observed in the accessible potential domain. Such irreversibility, frequently observed for free base porphyrins, is usually attributed to the formation of unstable cation radicals PH₂⁺⁺ readily reacting with traces of nucleophiles attacking at one of the meso position to afford isoporphyrins. RDE measurements carried out on the whole accessible potential window revealed that the intensity of the oxidation waves is significantly larger, nearly double, than that of the first reduction wave, which support the conclusion that the oxidation product is easier to oxidize than the starting porphyrin.

In agreement with the proposed attribution of the first oxidation and reduction waves to porphyrin-centered processes yielding PH₂⁺⁺ and PH₂⁺⁻, we found a similar calculated HOMO-LUMO gap (~2.1 V) for 4H₂, 5H₂ and 6H₂ (Table 2). The EWG character of the CF₃ substituents was then assessed from the *E*^{1c} and *E*^{1a} values collected for the CF₃ and C₆F₅-substituted compounds 4H₂-**9**H₂. The effect of the EWG can be seen on the CV curves depicted in Figure 4A showing the shift of the first oxidation and reduction waves with the number of substituents. These data bring to light the much larger EWG character of the CF₃ substituent compared to the C₆F₅. They are also consistent with the conclusion that two CF₃ substituents have stronger EWG effects than four C₆F₅ substituents. We also studied the way the oxidation and reduction potentials shifts with the number of substituents and compared the EWG character of CF₃ versus C₆F₅. Such comparison can be easily achieved from the electrochemical data collected in Table 1, upon taking advantage of the known dependence of electrochemical signature of porphyrins with the Hammett constants of the substituents introduced at their *meso*-positions.^{51, 52}



Figure 3. Voltamperometric curves of DMF solutions of 4H₂ and 8H₂ (1x10⁻³ M + 0.1M in TBAPF6) recorded at a vitreous carbon working electrode (full line, \emptyset = 3 mm, 0.1 V.s⁻¹) and at a rotating disk electrode(dashed lines, \emptyset = 3 mm, 0.01 V.s⁻¹, 500 rd.min⁻¹).

In all cases studied, the stability of the anion radical state 4H2+ and 8H2* at the CV time scale was revealed by the reversibility of the first one-electron reduction wave observed above -1.5 V (see in Table 2 and Fig ESI4, $\Delta E_{\rm P}$ = 60 to 65 mV at 100mV.s⁻¹, $I_{0} = \alpha(v)^{1/2}$). The exact attribution of the two subsequent reductions of $4H_2^{\bullet}$ at E^{2c} and E^{3c} proved more difficult, mainly due to the observation of three reduction waves in the whole accessible potential domain, which stands in sharp contrast with the standard electrochemical signature of porphyrins involving only two successive reduction yielding the anion radical (PH2.) and dianion (PH22-) species, respectively.53-58 Such standard signature was for instance observed with the C₆F₅-substituted reference compounds 7H₂, 8H₂ and 9H₂, which contrasts with the three reduction waves observed with the CF₃-subsituted compounds $4H_2$, $5H_2$ and $6H_2$ (see Figure 3A). As a matter of facts, more than two reduction waves can be observed on the CV curves of porphyrins i) when electroactive substituents and/or metal centers are involved *ii*) with porphyrins incorporating very strong EWG substituents like NO2 or CN or iii) when studying the electrochemistry of porphyrins in solvents featuring unusually large accessible potential windows.59-62



Figure 4. A) first reduction and first oxidation waves observed on the CV curved of DMF solution of $4H_2$, $5H_2$, $6H_2$ and $9H_2$ ($1\times10^{-3}M + 0.1M$ in TBAPF_6) recorded at a vitreous carbon working electrode ($\emptyset = 3 \text{ mm}$, $E \text{ vs } Ag^{+}/Ag (10^{-2} \text{ M})$, 0.1 V.s⁻¹). B) Plots of the oxidation and reduction potential values recorded for $4H_2$, $5H_2$ and $6H_2$ (E^{1a} , E^{1c} , E^{2c} , E^{3c} , see table 1) as a function of the number of CF₃ substituents.

As shown in table 1, the second reduction of $4H_2$, $5H_2$ and $6H_2$ was systematically observed as a fully irreversible wave shifted ~500 mV below the first one. Those reduction waves involving formation of the dianions PH22- remained irreversible at all investigated scan rates (0.1-1V/s) and their relative intensity was found to remain the same regardless of the number of CF3 substituents on the porphyrin ring (see Figure ESI 7). Previous reports by Kadish and coworkers recently established the ability of porphyrins bearing extremely strong EWG groups to undergo up to four consecutive reduction processes yielding stable trianions radicals PH2.4-.60 For all these compounds however, the potential shift measured between the first and the second reduction waves were consistently found to be much greater (nearly double) than that measured between the second and third reductions of $4H_2$, $5H_2$ and $6H_2$ (E^{2c} and E^{3c} in Table 2). The plots shown in Figure 4B also reveal that the potential values associated to the observed oxidation and reduction processes E^{1a} , E^{1c} , E^{2c} and E^{3c} decrease with similar slopes as a function of the number of CF₃ substituents. All these findings thus support the conclusion that all the observed reduction processes are centered on the porphyrin ring and that the first reduction wave (E^{1c} in in Table 2) yields a stable porphyrin-based anion radical PH2 - which is then submitted to a second one-electron reduction (E^{2c} in in Table 2) affording an unstable dianion PH22-. This latter compound is then transformed at the CV timescale via a coupled chemical step into a new species being reduced at E^{3c} (in Table 2).

Table 2. Potential values (Volt) measured by cyclic voltammetry for $4H_2$ - $9H_2$ in DMF. The number of electrons transferred and the peak-to-peak potential for each electrochemical process is shown between parentheses.

	<i>E</i> ^{3c} (n, Δ <i>E</i> _P) P²⁻/ P^{•3-}	<i>E</i> ^{2c} (n, Δ <i>E</i> _P) P⁻'/ P ²⁻	<i>E</i> ^{1c} (n, Δ <i>E</i> _P) P/ P ⁻	<i>E</i> ¹ª P/P⁺⁺	H-L gap
4 H ₂	-1.79ª (1e-, na)	-1.522 ª	-0.984 ^b (1e-, 66)	1.062 ª	2.047
5 H ₂	-2.06 ^a (1e-, na)	-1.670 ª	-1.116 ^b (1e ⁻ , 63)	0.93 ª	2.045
6 H ₂	-2.16 ª (1e-, na)	-1.861 ^a	-1.389 ^b (1e ⁻ , 60)	0.762 ª	2.151
7 H ₂	-	-1.979 ª	-1.375 ^b (1e-, 74)	0.872 ^a	2.247
8H2	-	1.785 ^b (1e-, 131)	-1.286 ^b (1e-, 73)	0.992 ^a	2.278
9 H ₂	-	-1.674 ^b (1e-, 74)	-1.187 ^b (1e-, 65)	1.085 ª	2.271

^a Peak potential; irreversible redox wave (V)

^b Half-wave potential (V)

 ΔE_p : Peak to peak potential difference (mV)

Potential values (V) are referenced versus the Fc+/Fc couple

Further investigation mostly aimed at identifying the chemical steps coupled to the formation of the dianion PH_2^{2-} . The electrochemical reduction of organic molecules is particularly well known to produce basic species capable of abstracting protons from their environment, as observed with numerous aromatic hydrocarbons and heterocyclic compounds including porphyrins, ⁶³⁻⁶⁶ or to release H₂, as suggested to occur upon reduction of various nitro-substituted organic molecules or porphyrins. ^{65, 67, 68}

First studies aimed at studying the electrochemical response of $4H_2$, $5H_2$ and $6H_2$ in the presence of added base or acid. As can be seen in the CV curves shown in Figure 5, addition of increasing amounts of TBAOH led to the disappearance of the first and second reduction waves attributed to the successive formation of PH_2^{-} and $PH_2^{2^-}$. The CV curves recorded after addition of an excess TBAOH, yielding the fully deprotonated species P^{2^-} (dashed lines in Figure 5A/B), displays one single reduction wave observed at the same potential as the third reduction wave of PH_2 (full line in Figure 5A/B). This behavior thus suggest that the chemical step coupled to the formation of $PH_2^{2^-}$ leads to the formation of the fully deprotonated species P^{2^-} . The mechanism proposed on the basis of these observations and of previous studies carried out on porphyrins⁶⁵ is detailed in Scheme 3.

The two first steps are the two consecutive one-electron reduction (Eq.1-2) yielding the unstable dianion $PH_2^{2^-}$ which evolves at the CV time scale into P^{2^-} with concomitant release of H_2 (eq. 3).The overall process is thus a two electron reduction yielding P^{2^-} and H_2 (eq.4).

Similar investigations were carried out using TFA as a proton source. Addition of TFA systematically led to a loss of the reversible character of the first reduction wave coming along with a two-fold increase in the peak current intensity, which suggests that the number of electrons transferred has doubled. This behavior is illustrated in Figure 6 with the diffusion-limited current recorded at a rotating disk electrode before and after addition of 2 molar equivalents of TFA to a solution of 4H₂. We also found that further addition of acid led to a progressive shift of the first reduction wave towards less negative values but without changing its relative intensity. This fully irreversible reduction is also associated to an irreversible re-oxidation wave observed on the reverse scan at $E_{\rm p} \sim -0.2$ V. The analysis of these data was carried out taking into account the acid-base experiments discussed above (see demonstrating that a full protonation of the weakly basic PH₂ species requires a large amount of TFA. The behavior observed in Figure 6 in the presence of little amount of

TFA is thus attributed to a series of reduction and protonation steps consecutive to the formation of the more basic radical anion $PH_2^{\bullet-}$ (eq. 1). According to the proposed mechanism shown in Scheme 3, the first coupled chemical process is the protonation of $PH_2^{\bullet-}$ yielding PH_3^{\bullet} (eq. 3) which is readily reduced into PH_3^{-} and then further protonated to afford the neutral species PH_4 (eq. 3). Overall, the reduction wave observed after addition of TFA involves addition of two electrons and two protons to convert PH_2 into PH_4 (eq. 6). In agreement with the proposed reaction scheme, the irreversible oxidation wave observed at *ca* –0.2 V is thus attributed to the oxidation of this later species which can ultimately afford back the initial PH_2 .



Figure 5. CV curves recorded before (full lines) and after addition (dashed line) of A) 8 or (B) 4 molar equivalents of tetra-n-butylammonium hydroxide (0.1 M in MeOH/Toluene) to 1 mM solutions of $6H_2$ and $4H_2$, respectively (GC WE \oslash 3mm, 100 mV.s⁻¹).



Figure 6. CV curves recorded before (full lines) and after addition (dashed line) of 2 molar equivalents of TFA (0.11 M in DMF) to a 0.945 mM solution of $4H_2$ (GC WE \varnothing 3mm, 100 mV.s⁻¹).Inset : voltammperogram recorded in the same conditions at a rotating disk electrode (RDE, 10 mV.s⁻¹, 500 rd.min)

$\mathbf{P}H_2 + \mathbf{e} = \mathbf{P}H_2^{\bullet-}$	(1)	$\mathbf{P}H_2 + \mathbf{e} = \mathbf{P}H_2^{\bullet-}$	(1)
$\mathbf{P}H_2^{\bullet} + e = \mathbf{P}H_2^{2^-}$	(2)	$\mathbf{P}\mathrm{H_2}^{\bullet-}$ + $\mathrm{H^+}$ = $\mathbf{P}\mathrm{H_3}^{\bullet}$	(5)
$PH_2^{2-} = P^{2-} + H_2$	(3)	$\mathbf{P}\mathrm{H}_{3}^{\bullet}$ + e = $\mathbf{P}\mathrm{H}_{3}^{-}$	(6)
\mathbf{P} H ₂ + 2e = \mathbf{P}^{2-} + H ₂	(4)	$\mathbf{PH_3}^+ \mathbf{H}^+ = \mathbf{PH_4}$	(7)
		$\mathbf{P}H_2 + 2e + 2H^+ = \mathbf{P}H_2$	4 (8)

Scheme 3. Proposed mechanisms

Spectroelectrochemistry

The stability and the spectroscopic signature of the reduced porphyrins was checked by spectro-electrochemistry (SEC) measurements carried out upon collecting time-resolved UV/Vis spectra during exhaustive reductions. The latter was carried out in a potentiostatic regime using a large surface platinum working electrode and a divided cell.

The SEC data collected with 4H₂ are displayed in

These studies revealed that the addition of CF3 substituents on the porphyrin ring leads, as expected, to an increase in the energy gap between the neutral and radical anion species by ca. 0.2 eV per –CF3 moiety, and between the radical anion species and the dianion by 0.3-0.4 eV, which is easily explained by the fact the stabilization of the radical anions and of the dianions increases with the number of CF3 substituents. Key figures reported in the ESI section demonstrate that the stabilization associated to the first electron transfer ranges from -3.39 to -3.79 eV for the mono-and tri-substituted compounds, respectively, and that the second addition of electron is slightly less favorable ranging from -2.87 to -3.24 eV. The HOMO-LUMO energy gap is constant, close to 0.15 eV for the three systems independently of their number of CF3 substituents.

. Setting the electrode potential at $E_{app} = -1.2$ V led to the progressive disappearance of the initial Soret band centered at 394 nm at the expense of a less intense signal developing at $\lambda_{max} = 422$ nm. Observation of a clean isosbestic point at 410 nm also confirms that no secondary reactions occur over the considered time range. The initial Q bands were also found to disappear at the expense of new bands developing in the visible and NIR range. The one electron reduced species $4H_2^{--}$ were found to be stable at the electrolysis time scale (~30 minutes). The latter species, produced by exhaustive electrochemical reduction at $E_{app} = -1.2$ V, was also identified by RDE measurements carried out after addition of one electrons/moles.

As expected from the CV data discussed above, further reduction of $4H_2^{\bullet}$ at $E_{app} = -1.53$ V led to irreversible changes in the UV/Vis spectrum. The latter had little effects on the Soret Band but led to the disappearance of the signals at 626 and 814 nm at the expense of a broad absorption bands centered at 733 nm. The irreversible nature of the transformation associated to this second electron transfer was confirmed by failure to regenerate the initial porphyrin $4H_2$ by reoxydation. In support of the mechanism proposed in Scheme 3, we found that the broad band centered at 733 nm is similar to that observed upon formation of the deprotonated species 4^{2-} .



Figure 7. UV/vis spectra recorded during (A) the first (E_{app} = -1.2 V) and (B) the second (E_{app} = -1.53 V) exhaustive one-electron of **4**H₂ (8.5x10⁻⁵ M) in DMF (0.1m TBAPF₆) (working electrode: Pt, 10 mL, I = 1 mm, t ≈ 30 min).

DFT calculations

The structures of $4H_2-6H_2$ were optimized by density functional theory (DFT) at the M062X/6-31+G(d,p) level of theory, using the self-consistent reaction field (SCRF) polarizable continuum model (PCM) to account for solvation in N,N-dimethylformamide. DFT calculations were performed using the Gaussian 16 Revision B.01 series of programs.

These studies revealed that the addition of CF₃ substituents on the porphyrin ring leads, as expected, to an increase in the energy gap between the neutral and radical anion species by ca. 0.2 eV per –CF₃ moiety, and between the radical anion species and the dianion by 0.3-0.4 eV, which is easily explained by the fact the stabilization of the radical anions and of the dianions increases with the number of CF₃ substituents. Key figures reported in the ESI section demonstrate that the stabilization associated to the first electron transfer ranges from -3.39 to -3.79 eV for the monoand tri-substituted compounds, respectively, and that the second addition of electron is slightly less favorable ranging from -2.87 to -3.24 eV. The HOMO-LUMO energy gap is constant, close to 0.15 eV for the three systems independently of their number of CF₃ substituents.

DFT calculations were also carried out to get structural information on the CF₃-substituted porphyrins and to gain insights into the effect (energy, structure) of protonation and deprotonation of the inner nitrogen atoms of PH_2 to yield PH_3^+ ; PH_4^{+2} and $PH^$ and \mathbf{P}^{2} , respectively. The relative energies of all these species are shown in Figure ESI 36/37. Optimizations carried out on the neutral PH₂ molecules first confirmed that the planarity of the porphyrin ring is not affected by the number of CF₃ groups, a result which is consistent with their small size and low bulkiness. Significant distortion was however observed upon protonation and deprotonation of the inner nitrogens (Figure 8). We found that deviation from planarity is enhanced upon protonation, with an average value of 14 degrees for $4H_{3^+}$, $5H_{3^+}$ and $6H_{3^+}$ and 22.8 degrees for $4H_4^{2+}$, $5H_4^{2+}$ and $6H_4^{2+}$. In all case, the out-of-plane distortion leads to an increase of the hydrogen...hydrogen diagonal distance from 2.15 Å to 2.50 Å (see Figure ESI 38).



Figure 8. Optimized structures at the M06-2X/6-31G+(d,p) level of theory for the series of monosubstituted porphyrins with various protonation states.

Most importantly, these DFT data allow to compare the relative energies and stabilities of the five protonation states of each CF₃-substituted porphyrins. It also allowed provide support for the hypothesis formulated on the ground of the CV data, by demonstrating that the elimination of H₂ from the doubly reduced species $4H_2^{2^2} - 4^{2^2} + H_2$ is energetically favorable by about 4.97 eV (114.5 kcal.mol⁻¹).

Conclusion

We have reported the synthesis of a series of free base porphins incorporating one, two and three CF_3 substituents, including the 5,10,15-tris(CF_3) substituted porphyrin which has never been described before. We have also carried out detailed

electrochemical and spectroscopic analyses aiming at assessing the EWG properties of the CF₃ substituents compared to the widely used C₆F₅. Our studies led us to propose an interpretation of the quite unusual electrochemical signature of these molecules featuring three successive one-electron reduction. In particular, the spectroscopic, electrochemical and spectroelectrochemical data supported by DFT calculations support the conclusion that the second irreversible reduction affords unstable dianions which are not stable at the CV time scale and evolve with elimination of dihydrogen.

Experimental Section

Synthesis and characterization

All reagents were obtained commercially unless otherwise noted. All reactions were performed in oven-dried glassware under an argon atmosphere. All solvents were dried and distilled by standard procedures. Flash column chromatography separations were achieved on silica gel (VWR 40-63 μ m).

¹H-NMR and ¹⁹F-NMR spectra were recorded at room temperature on a Bruker Avance 300 or a Bruker Ascend 400 spectrometer. ¹H chemical shifts were referenced to residual solvent peaks. Coupling constants values (*J*) are given in hertz and chemical shifts (δ) in ppm. The abbreviations used are: s = singlet, d = doublet, t = triplet, m = multiplet and br = broad.

UV/Vis spectra were recorded on a MCS 500 or MCS 601 UV/NIR Zeiss spectrophotometer using all-quartz immersion probes (Hellma Inc.). Mass spectrometry measurements were carried out at the "Centre Commun de Spectrométrie de Masse - Lyon 1" mass spectrometry facility with a MicrOTOFQ II (Bruker) using electrospray ionization (ESI).

Electrochemistry

Acetonitrile (Acros Organics, extra-dry with molecular sieves, water < 0.005%), dimethylformamide (Sigma Aldrich, extra-dry with molecular sieves, water < 0.01%) were degassed using Freeze-Pump-Thaw procedure and were used for the spectroelectrochemical studies. The electrolyte tetra-*n*-butylammonium perchlorate (TBAP, Fluka puriss.) was purchased and used without further purification.

Cyclic voltammetry (CV) and voltammetry with rotating disc electrodes (RDE) were recorded using a SP300 Bilogic potentiostat. The analytical studies were conducted under an argon atmosphere (glove box or argon stream) in a standard one-compartment, three-electrode electrochemical cell. Tetra-*n*-butylammonium was used as supporting electrolytes (0.1 M). An automatic ohmic drop compensation procedure was systematically performed when using cyclic voltammetry. Vitreous carbon ($\emptyset = 3$ mm) working electrodes (CH Instruments) were polished with 1 mm diamond paste before each recording. Voltamperometry with a rotating disk electrode (RDE) was carried out with a radiometer (CTV101 radiometer analytical) equipment at a rotation rate of 500 rad min⁻¹ using a glassy carbon RDE tip ($\emptyset = 3$ mm).

Spectroelectrochemical measurements were carried out at room temperature under an argon atmosphere (glove box or argon stream) in a standard one-compartment, three-electrode electrochemical cell with a biologic SP300 potentiostat coupled to an MCS 500 or MCS 601 UV/NIR Zeiss spectrophotometer using 1 or 10 mm all-quartz Helmma immersion probes. Electrolyses were conducted at room temperature using platinum plates (10 cm²) working electrodes and a large piece of carbon felt as a counter-electrode isolated from the electrolytic solution through an ionic bridge. Ag/AgNO₃ (CH Instruments, 10^{-2} M + TBAP 10^{-1} M in CH₃CN) was used as a reference electrode.

5-Trifluoromethyldipyrromethane (1)

To a stirred solution of freshly distilled pyrrole (3.35 g, 50 mmol) and trifluoroacetaldehyde ethyl hemiacetal (3.60 g, 25 mmol) in dichloromethane (150 mL) was added trifluoroacetic acid (2.85, 25 mmol). The reaction was stirred for 12 h at room temperature and then treated with water (50 mL). The mixture was washed with aqueous saturated NaHCO₃ (50 mL) and the combined organic layers were dried over MgSO₄, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (CH₂Cl₂/heptane: 2/8) gave 1 (1.34 g, 25%) as a white solid. ¹H NMR (CDCl₃, 300 MHz): δ = 4.84 (q, 1H, J_{HF} = 8.9 Hz), 6.23 (m, 2H), 6.26 (br m, 2H), 6.76 (m, 2H), 8.06 (br s, 2H) ppm. ¹⁹F NMR (CDCl₃, 282 MHz): δ = -68.6 (d, 3F, J_{FH} = 8.9 Hz) ppm. These values are consistent with those reported in the literature.⁴⁵

1,9-Bis(trifluoroacetyl)-5-trifluoromethyldipyrromethane (2)

To a stirred solution of 1 (2.14 g, 10 mmol) in toluene (60 mL) was added trifluoroacetic anhydride (10.5 g, 50 mmol). The reaction mixture was stirred for 5 h at room temperature, treated with aqueous saturated NaHCO₃ (50 mL) and extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over MgSO₄, filtered and concentrated under reduced pressure. Recrystallization in dichloromethane (30 mL) gave 2 (3.98 g, 98%) as a white solid. ¹H NMR (CD₃COCD₃, 300 MHz): δ = 5.63 (q, 1H, J_{HF} = 8.8 Hz), 6.64 (d, 2H, J = 3.9 Hz), 7.26 (m, 2H), 11.88 (br s, 2H) ppm. ¹⁹F NMR (CD₃COCD₃, 282 MHz): δ = -68.7 (d, 3F, J_{FH} = 8.9 Hz), -73.3 (d, 6F, J_{FH} = 1.8 Hz) ppm. These values are consistent with those reported in the literature.⁴⁵

1,9-Diformyl-5-trifluoromethyldipyrromethane (3)

To stirred and cooled (0°C) DMF (10 mL) was added phosphorus oxychloride (3.1 g, 20 mmol). The mixture was stirred for 15 min before introduction of 1 (2.03 g, 9.4 mmol) in DMF (10 mL). The reaction was stirred for 1.5 h at 0°C and then treated with aqueous saturated AcONa (10 mL). After 4 h at room temperature, the mixture was extracted with AcOEt (3 × 10 mL). The combined organic layers were washed with brine (10 mL), water (10 mL), dried over MgSO₄, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (CH₂Cl₂/AcOEt: 8/1) gave **3** (1.70 g, 67%) as a white solid. ¹H NMR (CD₃COCD₃, 300 MHz): δ = 5.44 (q, 1H, J_{HF} = 9.1 Hz), 6.48 (d m, 2H, J = 3.8 Hz), 7.01 (d, 2H, J = 3.8 Hz), 9.52 (s, 2H), 11.31 (br s, 2H) ppm. ¹⁹F NMR (CD₃COCD₃, 282 MHz): δ = -68.9 (d, 3F, J_{FH} = 9.1 Hz) ppm. These values are consistent with those reported in the literature.⁶⁶

Porphyrin 4H₂

To a stirred solution of 2 (116 mg, 0.286 mmol) in THF (8.6 mL) and MeOH (2.9 mL) was added NaBH₄ (540.2 mg, 14.3 mmol) portion-wise over 10 min. The reaction mixture was stirred for 20 min, treated with aqueous saturated NH₄Cl (60 mL) and extracted with AcOEt (3 × 20 mL). The combined organic layers were washed with water (60 mL), dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was dissolved in CH₂Cl₂ (120 mL), and 1 (61 mg, 0.286 mmol) was added. The reaction mixture was degassed and heated to 35 °C before addition of Yb(OTf)3 (234 mg, 0.38 mmol). The reaction mixture was stirred for 1.5 h at this temperature, and cooled to RT before sequential addition of DDQ (195 mg, 0.858 mmol) and Et₃N (0.26 mL, 1.85 mmol). The reaction mixture was filtered through a pad of silica gel (CH₂Cl₂ elution) and the solvent was removed under reduced pressure. Purification by flash chromatography on silica gel (CH₂Cl₂/pentane: 1/5) gave 4H₂ (4.4 mg, 3%) as a brown solid. ¹H NMR (CDCl₃, 400 MHz): δ = -2.70 (s, 2H), 9.41 (d, 2H, J = 4.9 Hz), 9.69 (m, 2H), 9.76 (m, 4H), 11.27 (s, 1H) ppm. ¹⁹F NMR (CDCl₃, 376 MHz): δ = -35.0 (s, 3F), -37.8 (s, 6F) ppm. ¹³C NMR (CDCl₃, 100 MHz): 109.24 (s), 127.53 (q, ¹*J*_{C-F}= 275 Hz), 127.87 (q, ¹*J*_{C-F}= 275 Hz), 131.04 (q, ⁵J_{C-F}= 6 Hz), 132.12 (q, ⁵J_{C-F}= 6 Hz), 132.65 (q, ⁵J_{C-F}= 6 Hz), 134.12 (s), 143.97 (s),144.13 (s), 144.93 (s), 145.17 (s) ppm. The $C\text{-}CF_3$ peaks are expected to be quartets, and the can't be distinguished from the baseline. HRMS (ESI): calcd for C23H12F9N4 [M+H]+ 515.0918, found 515.0903.

Porphyrin $5H_2$

To a stirred solution of 3 (77 mg, 0.286 mmol) in THF (8.6 mL) and MeOH (2.9 mL) was added NaBH_4 (540 mg, 14.3 mmol) portion-wise over 10 min. The reaction mixture was stirred for 20 min, treated with aqueous saturated NH₄Cl (60 mL) and extracted with AcOEt (3 × 20 mL). The combined organic layers were washed with water (60 mL), dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was dissolved in CH₂Cl₂ (120 mL), and 1 (61 mg, 0.286 mmol) was added. The reaction mixture was degassed and heated to 35 °C before addition of Yb(OTf)₃ (234 mg, 0.38 mmol). The reaction mixture was stirred for 1.5 h at this temperature, and cooled to RT before sequential addition of DDQ (195 mg, 0.858 mmol) and Et₃N (0.26 mL, 1.85 mmol). The reaction mixture was filtered through a pad of silica gel (CH₂Cl₂ elution) and the solvent was removed under reduced pressure. Purification by flash chromatography on silica gel (CH₂Cl₂/pentane: 1/5) gave 5H₂ (10.2 mg, 8%) as a brown solid. ¹H NMR (CDCl₃, 400 MHz): δ = -2.90 (s, 2H), 9.52 (d, 4H, J = 4.8 Hz), 9.79 (m, 4H), 11.42 (s, 2H) ppm. ¹⁹F NMR (CDCl₃, 376 MHz): δ = -38.2 (s, 6F) ppm. ¹³C NMR (CDCl₃, 100 MHz): 107.31 (s), 130.37 (q, ⁵J_{C-F}= 6 Hz), 134.22 (s), 145.08 (s), 145.53 (s) ppm. The CF₃ and C-CF₃ peaks are expected to be quartets, and the can't be distinguished from the baseline. HRMS (ESI): calcd for C22H13F6N4 [M+H]+ 447.1044, found 447.1050.

Porphyrin 6H₂

To a stirred solution of 3 (200 mg, 0.286 mmol) in THF (8.6 mL) and MeOH (2.9 mL) was added NaBH₄ (540.2 mg, 14.3 mmol) portion-wise over 10 min. The reaction mixture was stirred for 20 min, treated with aqueous saturated NH₄Cl (60 mL) and extracted with AcOEt (3 × 20 mL). The combined organic layers were washed with water (60 mL), dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was dissolved in CH₂Cl₂ (120 mL), and 2,2'-dipyrrolylmethane (42 mg, 0.286 mmol) was added. The reaction mixture was degassed and heated to 35 $^\circ\text{C}$ before addition of Yb(OTf)_3 (234 mg, 0.38 mmol). The reaction mixture was stirred for 1.5 h at this temperature, and cooled to RT before sequential addition of DDQ (195 mg, 0.858 mmol) and Et₃N (0.26 mL, 1.85 mmol). The reaction mixture was filtered through a pad of silica gel (CH₂Cl₂ elution) and the solvent was removed under reduced pressure. Purification by flash chromatography on silica gel (CH₂Cl₂/pentane: 1/5) gave 6H₂ (6.5 mg, 6%) as a brown solid. ¹H NMR (CDCl₃, 400 MHz): δ = -3.39 (s, 2H), 9.48 (br s, 4H), 9.54 (d, 2H, J = 4.9 Hz), 9.82 (m, 2H), 10.34 (s, 1H), 10.38 (s, 2H) ppm. ¹⁹F NMR (CDCl₃, 376 MHz): δ = -36.7 (s, 3F) ppm. ¹³C NMR (CDCI₃, 100 MHz): 106.19 (s), 106.97 (s), 128.71 (q, ¹J_{C-F}= 275 Hz) 129.84 (q, ⁵J_{C-F}= 6 Hz), 131.73 (s), 131.89 (s), 134.01 (s),144.79 (s), 145.79 (s), 145.85 (s), 146.11 (q, ³J_{C-F}= 40 Hz), 146.35 (s) ppm. HRMS (ESI): calcd for C₂₁H₁₄F₃N₄ [M+H]⁺ 379.1171, found 379.1163.

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