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Functionalized porphyrins from meso-poly-halogeno-alkyl-dipyrromethanes: synthesis and characterization

Porphyrines fonctionnalisées au départ de meso-poly-halogéno-alkyle-dipyrrométhanes. Synthèse et caractérisation

Paul-Gabriel Julliard, Simon Pascal, Olivier Siri, Diego Cortés-Arriagada, Luis Sanhueza∗, c, d and Gabriel Canard∗, a

Abstract. Starting from pyrrole-carbinol derivatives, a set of three optimized experimental conditions was used to prepare six dipyrromethanes (DPM) bearing meso-poly-halogeno-alkyl chains. On the one hand, the condensation of p-anisaldehyde and the DPMs bearing a perfluoroalkyl chain (CF₃, C₃F₇ or C₇F₁₅) produced, after oxidation, the expected trans-A₂B₂-porphyrins in reasonable yields. On the other hand, 5,15-diformyl-10,20-diarylporphyrin was directly obtained starting from the meso-(dichloromethyl)dipyrromethane, while traces of an unprecedented porphyrin bearing two meso-acyl fluoride groups were isolated from the use of the meso-(chlorodifluoromethyl)dipyrromethane. The straightforward formation of bis-formyl porphyrins is competitive compared to previously reported methods and has been extended to other benzaldehydes. The electron-withdrawing character of the

* Corresponding authors.
1. Introduction

The synthesis and functionalization of porphyrinoid macrocycles are still the ongoing subjects of intense research activities because these exciting compounds are applied in numerous areas such as catalysis, biology or materials science [1–5]. One of the reasons for this major interest lies in the easy preparation of meso-substituted derivatives from the simple condensation of pyrrole and aldehydes which can produce, after oxidation and depending on the experimental conditions, a huge number of polypyrrolic and aromatic macrocycles such as porphyrins, corroles, contracted and expanded porphyrins [1–8]. The physico-chemical properties of these macrocycles can be tuned by the introduction of different meso-substituents that often require the prior synthesis of oligopyrrole precursors such as the widely used meso-substituted dipyrromethanes (DPMs). Though various synthetic procedures of meso-substituted-DPMs are described [9–12], very few are devoted to or can be applied to the preparation of derivatives bearing a meso-poly-halogenoalkyl group or a meso-perfluoroalkyl chain [13–23]. These specific substituents are however of major interest because, beyond their high electron-withdrawing character, they can confer to molecules a certain lipophilicity and/or an increased metabolic stability [24,25]. Moreover meso-perfluoroalkyl chains were shown to induce an important non-planar distortion [26–29] and a high photo-stability [30] when they occupy the meso-positions of porphyrins.

To the best of our knowledge, the DPMs 3a and 3b bearing respectively a meso-CF3 group or a meso-C3F7 group are the only DPMs substituted by a meso-perfluoroalkyl chain for which synthetic procedures are described (Scheme 1). The common preparation of meso-substituted DPMs relies on the acid-catalyzed condensation of an aldehyde and pyrrole [9–12]. In boiling tetrahydrofuran (THF) and concentrated aqueous HCl (Scheme 1, route a), the condensation of stoichiometric amounts of pyrrole 1 and aldehydes 2a or 2b (as hemiacetal or as hydrate) gave for the first time the meso-perfluoroalkyl DPMs 3a and 3b with high yields (50–70% for 3a and 35–50% for 3b) [13]. Similar yields of 3b were obtained by repeating this procedure [14–17] or by replacing the acid and the refluxing solvent by p-toluene sulfonic acid (PTSA) and CHCl3, respectively (Scheme 1, route b) [18]. It was later shown that milder experimental conditions (Scheme 1, route c) also give high yields of 3a (20–40%) and 3b (35%) [19,20]. An original preparation of 3a was reported by Dmowski et al. who used the sodium dithionite coupling of 1-bromo-1-chloro-2,2,2-trifluoroethane with 1 (Scheme 1, route d) [21,22].

If this simple and inexpensive procedure gives high yields of 3a (49–58%), it can only be applied to incorporate this specific meso-substituent.

A key intermediate during the aldehyde-pyrrole condensation is the pyrrole-carbinol derivative 4 (Scheme 1). Such an intermediate bearing a heptafluoropropyl chain was prepared and dissolved with an excess of pyrrole in refluxing benzene containing PTSA (Scheme 1, route e) [23]. This stepwise strategy produced 3b with a high yield (77%). Having in mind that several 2-(polyhalogeno)acyl-pyrroles are easily prepared (or commercially available) and know-
ing that they are quantitatively reduced into the corresponding pyrrole-carbinol derivatives, we report herein how this latter strategy can be adapted, leading to a variety of meso-polyhalogenoalkyl DPMs. For this purpose, a set of three experimental conditions was selected and/or optimized to prepare the known 3a and 3b but also the unprecedented DPMs 3c–f bearing on the meso position a perfluoroheptyl (3c), a chlorodifluoromethyl (3d), a dichloromethyl (3e) or a trichloromethyl group (3f).

These DPMs were involved in the synthesis of trans-A2B2-meso-substituted porphyrins through their acid-catalyzed condensation with p-anisaldehyde. The DPMs 3a–c gave the expected porphyrins 6a–c whereas the condensation of DPMs 3d and 3e led surprisingly to porphyrins bearing two meso-fluoroacyl groups (6d) and two meso-formyl groups (6e), respectively (Table 2). Other benzaldehydes were used to illustrate the straightforward access to 5,10-bis-(formyl)-15,20-diarylporphyrin because it is really competitive compared to previously described ones that were based on multistep elegant strategies such as: (a) the Vilsmeier formylation of copper porphyrins and their subsequent demetallations [31]; (b) the palladium catalyzed formation of meso-bis-(trimethyl)silylmethylporphyrins followed by their oxidation [32]; (c) the preparations and/or derivations of protected formyl groups (dithiane or acetal moieties) before the DPM-aldehyde condensation and their deprotections after the porphyrin ring formation [33,34].

Because the physico-chemical properties of meso-perfluoro alkyl and meso-formyl porphyrins have been rarely described, those of the eight new free base porphyrins 6a–e, 7, 8 and 9 will be investigated in this contribution by a combination of photophysical, electrochemical and theoretical studies.

2. Results and discussion

2.1. Synthesis

The reaction of a slight excess of acyl-chloride or acid anhydride and pyrrole gave the 2-acyl pyrroles 5a–f according to previously reported procedures (Table 1) [27,31]. These compounds were at first reduced to the corresponding carbinol derivatives 4a–f using a slight excess of NaBH₄ (2 equiv.) in MeOH containing 2 equivalents of NaHCO₃ [35]. Because TLC analyses showed a complete conversion of the acylpyrroles 5a–f and the formation of the alcohols 4a–f with no observable side products, the pyrrole-carbinols 4a–f were not isolated (nor characterized) but were always freshly prepared and used directly in the next condensation step (Table 1).

In 2011, a pyrrole-carbinol derivative analogous to 4a but bearing an aryl group on the second α-position was condensated with pyrrole (2 equiv.) in dichloromethane (DCM) during 16 h at room temperature and using P₂O₅ (1 equiv.) as the activating agent [35]. These conditions gave very high yields of an asymmetrical meso-CF₃ DPM. Consequently, they were applied, in the present study, at the millimolar scale (condensation at 0.07 M in DCM) and using pyrrole 5a to give 3a with a yield of 60% (Table 1, entry 1). Higher concentrations or using pyrrole as the solvent did not improve the reaction yield (Table 1, entries
Table 1. Optimization of the synthesis of DPMs 3a–f

| Entry | Procedure | Reactant | [4a–f] (M) | Solvent | Acid | Pyrrole/4a–f/acid | t (h) | Product | Yield (%) |
|-------|------------|----------|------------|---------|------|------------------|------|---------|-----------|
| 1     | A          | 4a       | 0.07       | DCM     | P₂O₅ | 2:1:2            | 16   | 3a      | 60        |
| 2     | 4a         | CF₃      | 0.23       | DCM     | P₂O₅ | 2:1:2            | 16   | 3a      | 39        |
| 3     | 4a         | CF₃      | 0.58       | Pyrrole | P₂O₅ | 25:1:2           | 16   | 3a      | 0         |
| 4     | 4a         | CF₃      | 3.64       | Pyrrole | Eaton's reagent | 4:1:1 | 1       | 3a        | 0         |
| 5     | 4a         | CF₃      | 0.2        | THF     | HClₐq | 2:1:1.2          | 16   | 3a      | 26        |
| 6     | 4a         | CF₃      | 0.15       | H₂O     | HClₐq | 2:1:1.2          | 16   | 3a      | 22        |
| 7     | 4a         | CF₃      | 0.15       | H₂O     | HClₐq | 2:1:1.2          | 16   | 3a      | 20        |
| 8     | B          | 4a       | 0.15       | H₂O     | HClₐq | 2:1:1.2          | 16   | 3a      | 24 (28)²  |
| 9     | 4a         | CF₃      | 0.15       | H₂O     | HClₐq | 2:1:1.2          | 16   | 3a      | 35        |
| 10    | 4a         | CF₃      | 0.15       | H₂O     | HClₐq | 2:1:1.2          | 16   | 3a      | 20        |
| 11    | A          | 4b       | 0.07       | DCM     | P₂O₅ | 2:1:2            | 16   | 3b      | 52 (41)³  |
| 12    | B          | 4b       | 0.15       | H₂O     | HClₐq | 2:1:1.2          | 16   | 3b      | 3         |
| 13    | A          | 4c       | 0.15       | C₇F₁₅   | P₂O₅ | 2:1:2            | 16   | 3c      | 65 (87)⁴  |
| 14    | B          | 4c       | 0.15       | C₇F₁₅   | P₂O₅ | 2:1:2            | 16   | 3c      | 0         |
| 15    | A          | 4d       | 0.15       | C₁₂F₂Cl | P₂O₅ | 2:1:2            | 16   | 3d      | 0–2       |
| 16    | B          | 4d       | 0.15       | C₁₂F₂Cl | P₂O₅ | 2:1:2            | 16   | 3d      | 18 (18)⁴  |
| 17    | B          | 4e       | 0.15       | HClₐq   | 2:1:1.2          | 16   | 3e      | 60 (67)⁶  |
| 18    | A          | 4f       | 0.07       | DCM     | P₂O₅ | 2:1:2            | 16   | 3f      | 0         |
| 19    | B          | 4f       | 0.15       | HClₐq   | 2:1:1.2          | 16   | 3f      | 0         |
| 20    | 4f         | CCl₃     | 0.2        | DCM     | TFA  | 1:1:1.2          | 16   | 3f      | 0         |
| 21    | 4f         | CCl₃     | 0.2        | THF     | HClₐq | 1:1:1.2          | 2    | 3f      | 3         |
| 22    | C          | 4f       | 0.2        | THF     | HClₐq | 11:1:0.9         | 2    | 3f      | 9         |

²All reactions were performed at room temperature unless otherwise noted. ³Pyrrole polymerization occurs. ⁴Reactions at reflux. ⁵Resulting concentrations if pyrrole carbinol 4 was soluble in water. ⁶Gram-scale yields are noted in brackets. ⁷Eaton's reagent: P₂O₅ (7.7 wt%) in CF₃SO₃H. ⁸HCl in Et₂O (1 M).

2–5). This procedure (Table 1, procedure A) was extended to pyrroles 5b, c and afforded high amounts of 3b (52%) and 3c (65%) but only traces of 3d (0–2%) and no 3f (Table 1, entries 11, 13, 15 and 18). The preparation of 3b and 3c were repeated on a gram scale and gave DPMs with high yields.

To ensure better yields of 3d, new experimental conditions were applied in the preparation of 3a from 4a (used as a model compound). The utilization of refluxing THF and concentrated aqueous HCl was moderately efficient (Table 1, entry 6) but proved that the presence of water in the solvent was not detrimental to get meso-polyhalogeno alkyl DPMs. Several works have shown that meso-aryl oligopyrrole syntheses can be performed in water and using concentrated aqueous HCl as catalyst [36–38]. The application of the conditions of Dehaen et al. [39] ([HCl] = 0.18 M, [4a] = 0.15 M, 2 equiv. of pyrrole, room temperature, 4 h) afforded 3a with a yield of 22% that increases with the reaction.
time whereas higher amounts of pyrrole do not have any beneficial effect (Table 1, entries 7–10). We selected a reaction time of around one night (16 h) and applied these conditions (procedure B) to get DPMs 3b–f (Table 1, entries 12, 14, 16 and 19). This procedure failed to give DPMs 3b,c and 3f, but produced 3d and 3e with up-scalable yields of 18% and 66% respectively.

Since mild conditions did not afford the DPM 3f, and because the only example of a β-substituted DPM bearing a meso-Cl group was obtained through harsh conditions (TFA as solvent, 40 °C) [40], we used again refluxing THF and HCl (aq) during the condensation step (Table 1, entry 21). A low yield of 3f was obtained (3%) but reached 9% when using the experimental conditions described to synthesize a meso-Cl tripyrromethane from a DPM-mono-carbinol (Table 1, entry 22) [41]. Because no porphyrin could be, up to now, obtained from this particular DPM (vide infra), we have not pursued this optimization.

The DPMs 3a–f were used as building blocks in the synthesis of porphyrins (Table 2). For this purpose, we chose to apply the conditions of the acid-catalyzed condensation of the DPMs 3a,b with various aromatic aldehydes that were shown to be effective in the preparation of trans-A2B2 porphyrins bearing two meso-perfluoroalkyl groups (Table 2) [19]. The reaction of p-anisaldehyde (0.01 M) with DPMs 3a–f catalyzed by TFA (10 equiv.) or by BF3·OEt2 (0.33 equiv.) in DCM was stopped after the complete disappearance of the DPMs (TLC analysis). The two catalysts have been tested and this contribution reports only the conditions giving the highest yields.

After oxidation by DDQ (1.5 equiv.) and purification by chromatography, modest yields (4–9%) of the trans-A2B2 porphyrins 6a–c were obtained from the DPMs 3a–c although, as previously described, no scrambling occurred during the condensation step [19]. It has to be noted that, in addition to the expected porphyrin, each experiment led to the formation of several other colored chromophores but in too low yields to ensure their characterization. On the one hand, no porphyrin was detected from the reactions involving the DPM 3f bearing a sterically hindered trichloromethyl group, while on the other hand, the less chlorinated DPMs 3d and 3e gave quite unexpected results (Table 2).

Unlike the common purple spots on TLC and purple solutions observed during the purification of porphyrin 3a-c, green colored TLC spots and solutions were obtained while running the chromatography on the crude mixture from 3e. The red-shifted UV–visible absorption of the isolated compound combined with its 1H NMR spectrum featuring a downfield singlet located at 12.54 ppm were the first evidence of the exclusive formation of the bis-formyl porphyrin 6e which was further confirmed by its HRMS analysis and its IR spectrum displaying an intense carbonyl stretching band at 1672 cm⁻¹ (see the Supporting Information). The hydrolysis of the two CHCl2 groups remains unexplained because it was neither observed during the preparation of DPM 3e though being performed in acidic water, nor during its purification, which was also performed on silica gel. Suspecting that this hydrolysis would not have been quantitative, we performed another synthesis of 6e and washed the reaction mixture with water after the oxidation step. This supplementary treatment led to an identical yield of 6e. The CHCl2 groups of the intermediate porphyrinogen have probably stability close to the CHCl2 group of DPM 3e. Their hydrolysis could occur during the oxidation step as it was previously observed after the condensation of a meso-nitromethyl DPM with an aromatic aldehyde leading to meso-formyl porphyrins [42]. Such hydrolysis was also observed during the metal-assisted cyclization of a meso-CHCl2-β-substituted-a,c-biladiene into meso-formyl metallocorroles [43]. Because the simple use of DPM 3e gives straightforward access to trans-meso-bis(formyl) porphyrin, it was extended to p-cyano-, p-chloro and p-tert-butyl-benzaldehydes and led in the same way to porphyrins 7, 8 and 9 with respective yields of 9%, 2% and 12% (Table 2). The low isolated yield of 8 comes partly from its delicate purification due to its very low solubility in common organic solvents. In the same way, pure and solid 7 has only a slightly higher solubility. Consequently, a protonation–deprotonation sequence was used to ensure the complete dissolution of 7, 8 and 9 when recording their physico-chemical properties (see the experimental part).

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1No other porphyrin was detected by TLC or during the chromatographic purification.
Table 2. Syntheses of porphyrins 6a–e, 7, 8 and 9

![Image of porphyrin synthesis](image)

| DPM       | R    | Acid | Porphyrin | Ar          | R’     | Yield (%) |
|-----------|------|------|-----------|-------------|--------|-----------|
| 3a        | CF₃  | BF₃  | 6a        | p-MeO-C₆H₄  | CF₃    | 9         |
| 3b        | C₃F₇ | TFA  | 6b        | p-MeO-C₆H₄  | C₃F₇  | 4         |
| 3c        | C₇F₁₅| TFA  | 6c        | p-MeO-C₆H₄  | C₇F₁₅ | 4         |
| 3d        | CFCl₂| BF₃  | 6d        | p-MeO-C₆H₄  | CFO    | 2         |
| 3e        | CHCl₂| TFA  | 6e        | p-MeO-C₆H₄  | CHO    | 11        |
| 3f        | CHCl₂| TFA  | 7         | p-CN-C₆H₄   | CHO    | 9         |
| 3e        | CHCl₂| TFA  | 8         | p-Cl-C₆H₄   | CHO    | 2         |
| 3e        | CHCl₂| TFA  | 9         | p-Me₃C-C₆H₄ | CHO    | 12        |

R’ groups are at the 5,15 positions, Ar are at the 10,20 positions.

As observed during the porphyrin synthesis starting from DPM 3e, the acid-catalyzed condensation of DPM 3d with p-anisaldehyde gave, after oxidation, a green spot on TLC and a green solution during the purification on silica. After purification, the red-shifted UV-visible spectrum of the isolated porphyrin 6d together with the presence of a single signal at −62.63 ppm in its ¹⁹F NMR spectrum indicated that the former CF₂Cl group borne by DPM 3d had probably disappeared in 6d. The unexpected structure of the bis-fluoro-acyl derivative 6d was elucidated thanks to its HRMS analysis and its IR spectrum featuring a carbonyl stretching band at 1796 cm⁻¹ (see the Supporting Information). Although the yield of this transformation is low (≤2%), it gave repeatedly the first example of a porphyrin-bearing meso-fluoro acyl groups. As for 6e, we are not able yet to give the causes and/or the mechanism of the peculiar hydrolysis that has been rarely observed [44] although it has been reported that C-X bonds of meso-perfluoroalkyl groups borne by DPMs or porphyrins are prone to be involved in eliminations, intramolecular cyclization or solvolysis processes [45–50].

2.2. Electrochemical analysis of porphyrins 6a–e and 9

The cyclic voltammograms (CVs) of 6a–e and 9 were recorded in DCM containing 0.1 M of [nBu₄N]PF₆ (Figure 1 and Figure S1 in the Supporting Information). The corresponding oxidation and reduction half-wave and peak potential values are listed in Table 3 together with those of the tetra-meso-CF₃ porphyrin (CF₃)₄PH₂ [51], the tetra-meso-C₃F₇...
porphyrin (C₃F₇)₄PH₂ [51], and of the porphyrin 10 analogous to 6b but where the p-anisyl groups are replaced by p-diethylphophonate-phenyl substituents [17]. Each CV features a first reversible reduction and a first irreversible oxidation centered on the porphyrin ring. For the perfluoro derivatives 6a–c, this oxidation seemed to be reversible at a scan rate of 100 mV/s but proved to be irreversible when increasing the scan rate up to 800 mV/s. Depending on the substituents, a second oxidation and/or a second reduction were also enlightened by the CVs of 6a–e.

No oxidation could be observed previously when recording the CVs of (CF₃)₄PH₂ and (C₃F₇)₄PH₂ (Table 3) [51]. The replacement of two of these chains by p-anisyl groups in 6a and 6b leads to a significant negative shift of the first reduction potential (∼−300 mV) and allows access to the data corresponding to the macrocycle oxidation (E₁/₂ ∼ 1.3 V versus SCE).

Whereas the electrochemical properties of porphyrins are substantially varying with the number of meso-perfluoroalkyl chain, they are not notably tuned by the length of these lipophilic chains because the first oxidation/reduction potential values of 6a, 6b and 6c are nearly the same (Table 3). Interestingly, the comparison between 6b and 10 shows that decreasing the electron richness of the 10,20-aryl groups shifts, as expected, the first oxidation process to higher potential values but leaves unchanged the energy of the first reduction. Therefore, varying the nature of 10,20-aryl groups has probably little influence on the energy of the LUMO of such trans-A₂B₂ porphyrins which is controlled by the

**Table 3.** Half-wave and peak potentials (V versus SCE) of porphyrins 6a–e, 9, (CF₃)₄PH₂ and (C₃F₇)₄PH₂ measured in CH₂Cl₂ containing 0.1 M of [([nBu₄]N)PF₆] (scan rate of 100 mV/s)

|          | R10,20 | R5,R15 | Reduction          | Oxidation         | ΔE (V)ᵃ |
|----------|--------|--------|--------------------|-------------------|---------|
|          |        |        | Second             | First             |         |
|          |        |        | First              | First             |         |
|          |        |        | Second             | First             |         |
| 6a       | 4-OCH₃-C₆H₄ | CF₃    | −1.33ᵇ             | −0.81 (100)ᶜ      | 1.32ᵇ   |
| 6b       | 4-OCH₃-C₆H₄ | C₃F₇   | −1.34ᵇᵈ           | −0.80 (80)ᶜ       | 1.31ᵇ   |
| 6c       | 4-OCH₃-C₆H₄ | C₇F₁₅  | −0.81 (100)ᶜ       | 1.29ᵇ           | 1.78ᵇ   |
| 6d       | 4-OCH₃-C₆H₄ | CFO     | −0.79 (107)ᶜ      | −0.54 (72)ᶜ       | 1.39ᵇ   |
| 6e       | 4-OCH₃-C₆H₄ | CHO     | −0.89 (74)ᶜ       | −0.57 (64)ᶜ       | 1.33ᵇ   |
| 9        | 4-Me₃C-C₆H₄ | CHO     | −0.90 (73)ᶜ       | −0.58 (69)ᶜ       | 1.40ᵇ   |
| 10ᵈ      | 4-PO₃Et₂-C₆H₄ | CF₃    | −0.81              | 1.43             |         |
| (CF₃)₄PHₑ | CF₃    | CF₃    | −0.48ᵈ (160)ᶜ     |                   |         |
| (C₃F₇)₄PHₑ | C₃F₇   | C₃F₇   | −0.44ᵈ (158)ᶜ     |                   |         |

ᵃHOMO–LUMO electrochemical gap calculated by ∆E = E₁/₂(ox₁) − E₁/₂(red₁) or by ∆E = E₁pa(ox₁) − E₁pa(red₁).ᵇIrreversible peak potential at a scan rate of 100 mV/s.ᶜΔEₚ = Eₚa − Eₚc in mV.ᵈA third irreversible reduction peak is placed at Eₚc = −1.56 V versus SCE.⁹From Ref. [17].⁹From Ref. [51].

![Figure 1. CVs of porphyrins 6a (—), 6d (—) and 6e (—) in DCM containing 0.1 M of [([nBu₄]N)PF₆] (scan rate of 100 mV·s⁻¹). The dotted traces emphasize the reversibility of selected redox processes.](image-url)
meso-perfluoroalkyl chains.

The important anodic shift (+240 mV) affecting the first reduction process when replacing CF₃ moieties in 6a by formyl groups in 6e cannot be explained by a field/inductive effect because the latter is stronger for CF₃ than for CHO (Hammett parameters: σ_p (CF₃) = +0.54, σ_p (CHO) = +0.42) [52]. A positive shift is also observed between the two corresponding macrocycle-centered oxidations but has a little amplitude (∼30 mV) (Table 3). As for the CF₃ porphyrins 6b and 10, modifying the aryl groups in the formyl-substituted macrocycles 6e and 9 produces only a slight modification of the first oxidation potential whereas the reduction potentials remain unchanged. It has to be noted that the solubility of 7 and 8 was too low in DCM to record accurate electrochemical data.

Supplementary anodic shifts are affecting the first reduction and potential processes when two CFO groups are appended by the porphyrin ring in 6d. Therefore, the remarkable reduced HOMO–LUMO electrochemical gaps of 6d and 6e compared to those of derivatives 6a–c result from a π-conjugation between the carbonyl groups and the aromatic porphyrin ring that are put into evidence by theoretical calculations.

2.3. Spectral properties of the porphyrins

The absorption and corrected emission spectra of porphyrins 6a–e, 7, 8 and 9 were recorded in DCM at room temperature and are shown in Figure 2 and Figure S2 in the Supporting Information. The molar absorption coefficients and absorption maxima of these seven novel compounds are gathered in Table 4 with their emission maxima (excitation at λ = 590 nm) and fluorescence quantum yields. In order to give structure–properties relationships, selected photophysical data of 10 [17], (CF₃)₄PH₂ [53] and of (C₃F₇)₄PH₂ [53] are also given in Table 4 together with those of the porphyrins 11 [19] and 12 [32] analogous to 6a and 6e but where the p-anisyl groups are replaced by simple phenyl substituents.

As reported for the meso-bis-CF₃ porphyrin 11 [19], porphyrins 6a–c exhibit absorption spectra that are distinct from that of the well known tetra-phenylporphyrin (TPP). Compared to TPP, their Soret bands are blue-shifted and broadened (fwhm 27–28 nm) but significantly red-shifted compared to those of the tetra-perfluoroalkyl derivatives (CF₃)₄PH₂ and (C₃F₇)₄PH₂.

In the same way, as shown for 11, the Q bands of 6a–c have absorption maxima close to those of TPP but with a different pattern. For example, the UV–visible spectra of the trans-A₂B₂ 6a–c feature, as 10 and 11, a noticeable increased intensity for the 0–0 component corresponding to a band at ca. 646 nm (Table 4). The length of the perfluoroalkyl chain has only a minor impact on the light-absorption and light-emission properties of 6a–c that give similar fluorescence spectra and fluorescence quantum yields of ca. 7–9%. When comparing on the one hand the analogous 6a and 11, and on the other hand the analogous dyes 6b and 10, it can be noted that enhancing the electron richness of the aromatic substituents induces a little red shift of the absorp-
The red shift of the absorption and emission bands.

As observed when recording the electrochemical data, introducing meso-formyl groups produces a noticeable lower HOMO–LUMO optical gap. The UV-visible absorption and fluorescence bands of 6e are important red-shifted. For example, the Soret band maximum of 6e is at 430 nm and the 0–0 component of its Q bands can be found at 686 nm. Its quantum yield is as for 6a–c of ca. 8%. Replacing electron-withdrawing aryl groups in 7 and 8 by electron-donating ones in 9 and 6e produces a supplementary red shift of the absorption and emission bands.

For the unique 6d-bearing meso-fluoro acyl moieties, it can be noted that its light-absorption and emission bands are also red-shifted compared to those of 6a–c and of TPP but with a lower amplitude. Its fluorescence spectrum has also a unique pattern with a single and broadened band at 690 nm corresponding to a quantum yield of 10%.

2.4. Theoretical and structural studies of selected porphyrins

DFT and Time-dependent DFT (TD-DFT) calculations were performed to analyze the effects of the meso-substituents CF$_3$, C$_3$F$_7$, C$_7$F$_{15}$, CFO and CHO on the structural, electronic and optical properties of porphyrins 6a–e. The structures of 6a–e were fully optimized and gave values of geometrical parameters.
such as bond distances, angles and dihedral angles that are illustrative of the effect of the meso substitutions on their core structures (Figure 3 and Figure S3 in the Supporting Information). Although there were no symmetry constraints in the calculation procedures, results did provide symmetric structures. Therefore, only parameters corresponding to one-half of the porphyrin macrocycles are detailed in Figures 3 and S3. Very slight differences are observed between the bond distances and angle values of 6a–e despite the variation of the nature of 5,15 meso-substituents (Figures 3 and S3). In fact, most relevant differences in the geometrical parameters are related to the values of the calculated external dihedral angles $\alpha$ and $\beta$ which are listed in Table 5 and represented in Figure 3. These dihedral angles stand for the plane torsion regarding two adjacent pyrrole units of the porphyrin core center. As observed in Table 5, the $\alpha$ values are about 5.0° for 6a-bearing CF$_3$ moieties and increase up to 10.6° for 6b and 6c substituted respectively by the more bulky C$_3$F$_7$ and C$_7$F$_{15}$ substituents. The $\beta$ values are quite low with values in the range of $\sim$0.7°. On the other hand, the presence of CFO and CHO as highly acceptor moieties in 6d and 6e induces decreased $\alpha$ values of 7.8° and 7.2°, respectively, while significantly increased $\beta$ values of 12.4° (6d) and 8.5° (6e) are observed for these systems. These results indicate that the introduction of CHO or CFO groups on the meso-positions produce a noticeable supplementary out-of-plane distortion of the macrocycles in 6d and 6e compared to those of the alkyl appended porphyrins 6a–c.

During the final editing stages of this contribution, we were glad to get diffraction single crystals of porphyrins 6a and 6b (Figures 3(b) and (c)). As for the calculated geometries, the corresponding experimental structures feature a small out-of-plane distortion of the porphyrin 6a and 6b which is higher for 6b and correspond to a slight ruffling of the macrocycles.

The frontier molecular orbitals (FMOs) of 6a–e were also studied by DFT calculations. The energies of the two HOMOs and of the two LUMOs are listed in Table 5 and their plots are displayed in Figure 4 and Figure S4 in the Supporting Information. The calculated HOMO–LUMO gaps are in accordance with the experimental data and decrease in importance when fluoro acyl or formyl groups are borne by the 5 and 15 meso-positions. As observed during the UV–Vis absorption and electrochemical experiments, the lowest HOMO–LUMO gap is obtained for the bis-formyl derivative 6e. For 6a–e, the HOMO appears mainly to be located at the $p$-anisyl substituents, the core-N atoms and the meso-bridging carbon atoms at the 5,15 positions. Therefore, the lack of any apparent
Table 5. Calculated dihedral angles (°), experimental dihedral angles (°) and orbital energies (eV) of porphyrins 6a–e

|       | R5,15 | α (°) | β (°) | HOMO−1 (eV) | HOMO (eV) | LUMO (eV) | LUMO+1 (eV) |
|-------|-------|-------|-------|-------------|-----------|-----------|-------------|
| 6a    | CF₃   | 4.3   | 3.3   | −5.36       | −5.25     | −3.47     | −3.16       |
| 6b    | C₃F₇ | 10.6  | 13.4  | −5.37       | −5.23     | −3.49     | −3.16       |
| 6c    | C₇F₁₅| 10.6  | 0.6   | −5.38       | −5.24     | −3.50     | −3.16       |
| 6d    | CFO   | 7.8   | 12.4  | −5.44       | −5.27     | −3.69     | −3.23       |
| 6e    | CHO   | 7.2   | 8.5   | −5.40       | −5.26     | −3.78     | −3.18       |

Table 5a: Experimental dihedral angle values from the single crystal X-ray diffraction structures of 6a and 6b.

Figure 4. Plots of the calculated frontier orbitals and values of the HOMO–LUMO gaps (in eV) of 6a, 6d and 6e.

3. Conclusions

Meso-polyhalogeno alkyl dipyrromethanes were prepared by the reduction of 2-acyl pyroles and their subsequent acid-catalyzed reaction with pyrrole. Three sets of experimental conditions were optimized depending on the starting compound. This procedure lead firstly to the known DPMs 3a and 3b substituted by a trifluoromethyl group and a heptfluoropropyl chain, respectively. New derivatives were also obtained, bearing on the meso-position a perfluorohexyl (3c), a chlorodifluoromethyl (3d), a dichloromethyl (3e) or a trichloromethyl group (3f). Dipyrromethanes are useful compounds in the synthesis of various chromophores including BODIPYs, corroles or expanded porphyrins. Herein, they were used to build trans-A₂B₂ meso-substituted porphyrins through their condensation with aromatic aldehydes. The perfluoro DPMs produce the expected bis-alkylporphyrins while exciting meso-functionalized analogs were obtained from DPMs and CHO that are responsible for the concomitant lower LUMO energies and lower HOMO–LUMO gaps. The simulation of the UV–visible spectra of 6a–e was obtained from further TD-DFT calculations and is detailed in the Supporting Information together with the corresponding compositions, vertical excitation energies, oscillator strengths and hole–electron excited states’ surface distributions. For 6a–e, theory gives Soret bands between 380 and 450 nm and these are red-shifted for 6d and 6e as observed experimentally. On the contrary, few differences are obtained when comparing the locations and intensities of the calculated Q bands of 6a–e, because the different 5,15 meso substituents have only a slight impact on the corresponding electronic transitions.
bis-formyl porphyrins were prepared directly from 3e and illustrate an original and straightforward strategy to get such derivatives. Similarly, the use of 3d leads to 6d as a unique example of a porphyrin-bearing meso-fluoro acyl moieties. The electron-withdrawing character of the perfluoralkyl chains and of the π-conjugated formyl and fluoro acyl groups were investigated and enlightened thanks to photophysical and electrochemical analyses supported by theoretical calculations. These studies revealed, for example, that when appended by porphyrins, formyl and fluoro acyl functional groups give to the macrocycles reduced HOMO–LUMO electrochemical gaps and red-shifted absorption and emission properties.

4. Experimental section

4.1. Materials

All reagents were used as received. Pyrrole was distilled before use. The distillation of THF was performed on sodium/benzophenone. Flash column chromatography was performed on silica gel 60 (230–400 mesh). Visualization of DPM TLC spots was achieved by staining the TLC plates with a solution of phosphomolybdic acid (2.5 g) in ethanol and by subsequent heating.

4.2. Physical measurements

1H, 13C and 19F nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECS400 NMR spectrometer at room temperature. NMR chemical shifts are given in ppm (δ) relative to Me4Si using solvent residual peaks as internal standards (CDCl3: δ = 7.26 ppm for 1H and 77.2 for 13C; Acetone-d6: δ = 2.05 ppm for 1H and 29.8 for 13C; DMSO-d6: δ = 2.50 ppm for 1H and 39.5 for 13C). IR spectra were recorded on an Agilent Cary 630 FTIR equipped with an attenuated total reflectance (ATR) sampling. Melting points (M.P.) were measured in open capillary tubes with a STUART SMP30 melting points apparatus and are uncorrected. High resolution mass spectrometry (HRMS-ESI) analyses were performed on a QStar Elite (Applied Biosystems SCIEX) spectrometer or on a SYNAPT G2 HDMS (Waters) spectrometer by the “Spectropole” of Aix-Marseille University. These two instruments are equipped with an electrospray ionization (ESI) or a MALDI source and a TOF analyser.

4.3. Electronic absorption and fluorescence

UV–Vis absorption spectra were recorded in spectrophotometric grade solvents (ca. 10–6 M) on a Varian Cary 50 SCAN spectrophotometer. Ten equivalents of TFA were added to the suspension of the porphyrins 7, 8 and 9 in order to ensure their complete dissolution as protonated and non-aggregated dyes. A subsequent addition of twelve equivalents of 1Pr2NEt afforded back the non-protonated free bases soluble in solution. Emission spectra were obtained using a Horiba-Jobin Yvon Fluorolog-3 spectrofluorimeter equipped with a three-slit double-grating excitation and a spectrograph emission monochromator with dispersions of 2.1 nm-mm−1 (1200 grooves per mm). A 450 W xenon continuous wave lamp provided excitation. Fluorescence of diluted solutions was detected at right angle using 10 mm quartz cuvettes. Fluorescence quantum yields Φ were measured in diluted dichloromethane solutions with an optical density lower than 0.1 using the following equation:

$$\frac{\Phi_x}{\Phi_r} = \left( \frac{A_r(\lambda)}{A_x(\lambda)} \right) \left( \frac{n_x^2}{n_r^2} \right) \left( \frac{D_x}{D_r} \right)$$

where $A$ is the absorbance at the excitation wavelength (λ), $n$ the refractive index and $D$ the integrated intensity. “r” and “x” stand for reference and sample. The fluorescence quantum yields were measured relative to tetraphenylporphyrin (TPP) in acetonitrile (Φ = 0.15) [54]. Excitation of reference and sample compounds was performed at the same wavelength (590 nm).

4.4. Electrochemistry

Cyclic voltammetric (CV) data were acquired using a BAS 100 Potentiostat (Bioanalytical Systems) and a PC computer containing BAS100W software (v2.3). A three-electrode system with a Pt working electrode (diameter 1.6 mm), a Pt counter electrode and a leak-free Ag/AgCl reference electrode (diameter 5 mm) was used. [6But4N]PF6 (0.1 M in CH2Cl2) served as an inert electrolyte while the concentration of the electro-active compound is of ca. 5 × 10⁻⁴ M.
Cyclic voltammograms were recorded at a scan rate of 100 mV-s⁻¹. Ferrocene (0.46 V/SCE) was used as internal standard [55]. Solutions were degassed using argon and the working electrode surface (Pt) was polished before each scan recording. The solubility of porphyrins 7 and 8 in the solvent is too low to get accurate electrochemical values.

4.5. Computational details

All (TD-)DFT calculations have been performed using the Gaussian 16 program [56]. The geometry optimizations were carried out without symmetry constraints to ensure the minima energy. Calculations were performed using the CAM-B3LYP exchange functional (since this level of theory has been widely used in this type of compounds and also because this functional reproduces correctly the corresponding geometrical parameters) and the 6-311+G(d,p) basis set for all atoms [57,58]. Frequency calculations were also included to corroborate the optimized structures, showing only positive values in all vibrational modes. TD-DFT calculations were performed for the first 80 vertical excitations, in vacuum and in dichloromethane (DCM) as solvent, using the conductor-like polarizable continuum model (CPCM) [59]. Here, the BLYP functional was implemented in conjunction with the 6-311+G(d,p) basis set for all atoms. The BLYP functional was chosen because this level of theory accurately reproduces the experimental UV–Vis results [60].

4.6. Single crystal X-ray diffraction

Suitable diffracting single crystals of 6a and 6b were obtained by slow diffusion of n-pentane into concentrated solutions of the porphyrins in dichloromethane. The intensity data for compound 11a were collected on a Rigaku Oxford Diffraction SuperNova diffractometer using CuKα radiation (λ = 1.54184 Å) at 293 K. Data collection, cell refinement and data reduction were performed with CrysAlisPro (Rigaku Oxford diffraction). Using Olex2 [61], the structures were solved with shelXT [62] and shelXL [62] was used for full matrix least squares refinement. CCDC-2074306 (6a) and CCDC-2074307 (6b) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request cif.

4.7. Synthetic methods

The 2-acylpyrroles 5a (R = CF₃) [63], 5b (R = C₂F₅) [26], 5c (R = C₂F₅) [64], 5f (R = CCl₃) [65] and 5e (R = CHCl₂) [66] were prepared as previously reported.

4.7.1. 2-(Chlorodifluoroacetyl)pyrrole (5d)

This compound was prepared following a protocol adapted from the synthesis of 2-(trifluoroacetyl)pyrrole 5a [63]. A solution of chlorodifluoroacetic anhydride (4.15 mL, 23 mmol, 1.1 equiv.) in anhydrous CH₂Cl₂ (15 mL) was cooled to −15 °C under an argon atmosphere. A solution of pyrrole (1.44 mL, 20.9 mmol, 1 equiv.) in anhydrous CH₂Cl₂ (15 mL) was then added dropwise under firm stirring. The mixture was stirred at −15 °C for 1.5 h, then at room temperature during an additional hour. The organic phase was washed with water, dried over Na₂SO₄, and the solvent removed by evaporation. The resulting residue was purified by flash chromatography (CH₂Cl₂/petroleum ether 1:1) to afford 5d as a white solid (4.01 g, 22 mmol, 99%).

Rf = 0.45 (silica, CH₂Cl₂/petroleum ether 1:1).

Mp: 41.9 °C; 1H NMR (CDCl₃) δ = 10.27 (br s, 1H, NH), 7.28 (m, 1H, α-H), 7.25 (m, 1H, β-H), 6.41 (m, 1H, β-H) ppm; 19F NMR (CDCl₃) δ = −61.5 ppm; 13C (1H) NMR (CDCl₃) δ = 129.6 (CH), 124.7 (C), 112.7 (CH) ppm; IR: v⁻ = 3329 (vs, N–H), 1638 (vs, C=O) cm⁻¹; HMRs-ESI: calcld. for C₆H₆NOF₂Cl [M–H⁻] = 177.9877. Found: 177.9877.

4.7.2. 5-(Trifluoromethyl)dipyrromethane (3a)

Procedure A: to a solution of 2-(trifluoroacetylated)pyrrole 5a (500 mg, 3.07 mmol, 1 equiv.) and NaHCO₃ (514 mg, 6.13 mmol, 2 equiv.) suspended in methanol (46 mL) under firm stirring was added NaBH₄ (232 mg, 6.12 mmol, 2 equiv.) by portions. The mixture was stirred at room temperature for 30 min before removal of the solvent by evaporation. The crude product was dissolved in Et₂O. This organic phase was washed with water, dried over Na₂SO₄ and evaporated at 30 °C. The resulting residue and pyrrole (0.42 mL, 6.12 mmol, 2 equiv.) were dissolved in CH₂Cl₂ (40 mL) and under argon atmosphere. P₂O₅ (87 mg, 6.13 mmol, 2 equiv.) was then added and the mixture was stirred at room temperature for 16 h. A saturated aqueous NaHCO₃ solution (10 mL) was added, and the stirring maintained for 1 h. The
crude product was filtered and washed with DCM on a Büchner funnel equipped with sintered glass. The filtrate was dried on Na$_2$SO$_4$. The subsequent flash chromatography (CH$_2$Cl$_2$/petroleum ether 1:1, then 2:1) afforded 3a as a white solid (395 mg, 1.8 mmol, 60%).

Procedure B: to a solution of 2-(trifluororacetoyl)-pyrrole 5a (250 mg, 1.53 mmol, 1 equiv.) and NaHCO$_3$ (257 mg, 3.06 mmol, 2 equiv.) suspended in methanol (4.6 mL) under firm stirring was added NaBH$_4$ (116 mg, 3.06 mmol, 2 equiv.) by portions. The mixture was stirred at room temperature for 30 min before removal of the solvent by evaporation. The mixture was stirred at room temperature for 30 min before removal of the solvent by evaporation. The residue was finally purified by flash chromatography (CH$_2$Cl$_2$/petroleum ether 2:1) to afford 3b as a white solid (2.05 g, 6.5 mmol, 41%).

R$_f$ = 0.65 (silica, CH$_2$Cl$_2$/petroleum ether 2:1).

$^1$H NMR (CDCl$_3$) $\delta$ = 8.15 (br s, 2H, NH), 6.78 (m, 2H, $\alpha$-H), 6.25 (m, 2H, $\beta$-H), 6.22 (m, 2H, $\beta$-H), 4.85 (q, $^3J_{HF}$ = 9.0, 1H, meso-H) ppm; IR: $\nu$ = 3368 (s, N–H), 1233, 1207, 1175, 1113, 1093 (s, C–F) cm$^{-1}$. Other analytical data are consistent with literature values [13].

4.7.4. 5-(Perfluoroheptyl)dipyromethane (3c)

Procedure A: scale up: to a solution of 2-(perfluoro-octanoyl)pyrrole 5c (2.01 g, 4.31 mmol, 1 equiv.) and NaHCO$_3$ (722 mg, 8.60 mmol, 2 equiv.) suspended in methanol (16 mL) under firm stirring was added NaBH$_4$ (325 mg, 8.59 mmol, 2 equiv.) by portions. The mixture was stirred at room temperature for 30 min before removal of the solvent by evaporation. The crude product was dissolved in Et$_2$O. The organic phase was washed with water, dried over Na$_2$SO$_4$ and was evaporated at 30 ºC. The resulting residue and pyrrole (0.6 mL, 8.62 mmol, 2 equiv.) were dissolved in CH$_2$Cl$_2$ (65 mL) under argon. P$_2$O$_5$ (1.22 g, 8.65 mmol, 2 equiv.) was then added and the mixture was stirred at room temperature for 16 h. NaHCO$_3$ (3.47 g, 41.3 mmol, 2.6 equiv.) was added and the stirring maintained for 1 h. The mixture was filtrated and washed with DCM on a Büchner funnel equipped with sintered glass. The filtrate was dried on Na$_2$SO$_4$ before removal of the solvent by evaporation. The residue was finally purified by flash chromatography (CH$_2$Cl$_2$/petroleum ether 2:1) to afford 3c as a light purple solid (1.92 g, 3.73 mmol, 87%).

R$_f$ = 0.60 (silica, CH$_2$Cl$_2$/petroleum ether).

$^1$H NMR (CDCl$_3$) $\delta$ = 8.15 (br s, 2H, NH), 6.78 (m, 2H, $\alpha$-H), 6.25 (m, 2H, $\beta$-H), 6.20 (m, 2H, $\beta$-H), 4.96 (t, $^3J_{HF}$ = 16.8, 2H, meso-H) ppm; $^{19}$F NMR (CDCl$_3$) $\delta$ = −80.7 (CF$_3$), −112.2, −120.5, −121.5, −121.9, −122.6, −126.0 ppm; $^{13}$C ($^1$H) NMR (CDCl$_3$) $\delta$ = 122.3 (C), 119.0 (CH), 109.7 (CH), 109.1 (CH), 108.3 (C), 41.2 (t, $^2J_{C–F}$ = 23.0, C) ppm, other carbon atoms could not be assigned due the low intensity of the
perfluorinated chain peaks [67] and because of the rapid degradation of the compound in solution; IR: \(v^- = 3405\) (br, N–H), 1235, 1198, 1143, 1095 (vs, C–F) cm\(^{-1}\); HRMS-ESI: calcd for C\(_{16}\)H\(_8\)F\(_{15}\)N\(_2\) [M–H]: 513.0453. Found: 513.0461.

### 4.7.5. 5-(Chlorodifluoromethyl)dipyrromethane (3d)

**Procedure B:** to a solution of 2-(chlorodifluoroacetyl)pyrrole 5d (100 mg, 0.56 mmol, 1 equiv.) and NaHCO\(_3\) (94 mg, 1.12 mmol, 2 equiv.) suspended in methanol (1.7 mL) under firm stirring was added NaBH\(_4\) (42 mg, 1.1 mmol, 2 equiv.) by portions. The mixture was stirred at room temperature for 30 min before removal of the solvent by evaporation. The crude product was dissolved with Et\(_2\)O. This organic phase was washed with water, dried over Na\(_2\)SO\(_4\) and evaporated to dryness. The resulting solid was then dissolved in pyrrole (0.78 mL, 1.1 mmol, 2 equiv.) before the addition of an aqueous HCl solution (0.18 M, 2 mL). The mixture was stirred at room temperature for 16 h. The mixture was then extracted with CH\(_2\)Cl\(_2\). The organic phase was washed with water, dried on Na\(_2\)SO\(_4\) and evaporated to dryness. The final purification by flash chromatography (CH\(_2\)Cl\(_2\)/petroleum ether 2:1) afforded 3d as a white solid (23 mg, 0.1 mmol, 18%).

**Scale up:** the same procedure at a ten-fold larger scale starting from 5d (2.72 g, 15.3 mmol) afforded 3d as a white solid (237 g, 10.3 mmol, 67%).

R\(_F\) = 0.4 (silica, CH\(_2\)Cl\(_2\)/petroleum ether 2:1). **Mp:** > 60 °C (degradation) \(^1\)H NMR (CDCl\(_3\)) \(\delta = 8.26\) (br s, 2H, NH), 6.75 (m, 2H, \(\alpha\)-H), 6.25 (m, 2H, \(\beta\)-H), 6.21 (m, 3H, \(\beta\)-H and CHCl\(_3\)), 4.83 (d, \(J_{\text{H,H}} = 3.5, 1H, \text{meso-H}\) ppm); \(^{13}\)C \(^1\)H NMR (CDCl\(_3\)) \(\delta = 126.8\) (C), 118.3 (CH), 108.8 (CH), 108.7 (CH), 74.9 (CH), 49.0 (CH) ppm; IR: \(v^- = 3344\) (vs, N–H), 742 (vs, C–Cl) cm\(^{-1}\); HRMS-ESI: calcd. for C\(_{16}\)H\(_8\)Cl\(_2\)N\(_2\) [M–H]: 227.0148. Found: 227.0151.

### 4.7.6. 5-(Dichloromethyl)dipyrromethane (3e)

**Procedure B:** to a solution of 2-(dichloroacetyl)pyrrole 5e (272 mg, 1.53 mmol, 1 equiv.) and NaHCO\(_3\) (257 mg, 3.06 mmol, 2 equiv.) suspended in methanol (4.6 mL) under firm stirring was added NaBH\(_4\) (116 mg, 3.06 mmol, 2 equiv.) by portions. The mixture was stirred at room temperature for 30 min before removal of the solvent by evaporation. The crude product was dissolved in Et\(_2\)O. This organic phase was washed with water, dried over Na\(_2\)SO\(_4\) and evaporated at 30 °C. The resulting solid was then dissolved in pyrrole (0.21 mL, 3.06 mmol, 2 equiv.) before the addition of an aqueous HCl solution (0.18 M, 5 mL). The mixture was stirred at room temperature for 16 h. The mixture was then extracted with CH\(_2\)Cl\(_2\). The organic phase was washed with water, dried on Na\(_2\)SO\(_4\) and evaporated to dryness. The final purification by flash chromatography (CH\(_2\)Cl\(_2\)/petroleum ether 2:1) afforded 3e as a gray solid (212 mg, 0.9 mmol, 60%).

**Scale up:** the same procedure at a ten-fold larger scale starting from 5e (2.72 g, 15.3 mmol) afforded 3e as a white solid (237 g, 10.3 mmol, 67%).

R\(_F\) = 0.65 (silica, CH\(_2\)Cl\(_2\)/petroleum ether 2:1). **Mp:** 75–80 °C; \(^1\)H NMR (CDCl\(_3\)) \(\delta = 8.19\) (br s, 2H, NH), 6.79 (m, 2H, \(\alpha\)-H), 6.27 (m, 2H, \(\beta\)-H), 6.22 (m, 3H, \(\beta\)-H and CHCl\(_3\)), 4.96 (t, \(J_{\text{H,F}} = 11.1, 1H, \text{meso-H}\) ppm); \(^{19}\)F NMR (CDCl\(_3\)) \(\delta = -53.3\) (d, \(J_{\text{F,F}} = 11.1\) ppm); \(^{13}\)C \(^1\)H NMR (CDCl\(_3\)) \(\delta = 118.7\) (CH), 117.8 (C), 109.6 (t, \(J_{\text{C,F}} = 1.4, \text{CH}\), 109.1 (CH), 108.3 (CH), 49.8 (t, \(J_{\text{C,F}} = 26.0\), C) ppm; IR: \(v^- = 3351\) (vs, N–H) cm\(^{-1}\); HRMS-ESI: calcd. for C\(_{16}\)H\(_8\)Cl\(_2\)F\(_2\)N\(_2\) [M–H]: 299.0350. Found: 299.0351.

### 4.7.7. 5-(Trichloromethyl)dipyrromethane (3f)

**Procedure C:** to a solution of 2-(trichloroacetyl)pyrrole 5f (1.63 g, 7.7 mmol, 1 equiv.) and NaHCO\(_3\) (1.28 g, 15.3 mmol, 2 equiv.) suspended in methanol (23 mL) under firm stirring was added NaBH\(_4\) (581 mg, 15.3 mmol, 2 equiv.) by portions. The mixture was stirred at room temperature for 30 min before removal of the solvent by evaporation. The crude product was dissolved in Et\(_2\)O. This organic phase was washed with water, dried over Na\(_2\)SO\(_4\) and evaporated at 30 °C. The resulting solid and pyrrole (6.0 mL, 86 mmol, 11 equiv.) were dissolved in distilled THF (40 mL) under argon atmosphere before the addition of a solution of HCl in Et\(_2\)O (1 M, 6.9 mL, 6.9 mmol, 0.9 equiv.). The mixture was stirred at 85 °C for 2 h, quenched with a saturated aqueous NaHCO\(_3\) solution. The mixture was extracted by diethyl ether. The organic phase was washed with water, dried over Na\(_2\)SO\(_4\) and evaporated to dryness. The final purification by flash chromatography (CH\(_2\)Cl\(_2\)/petroleum ether 2:1) afforded 3f as a white solid (181 mg, 0.68 mmol, 9%).

R\(_F\) = 0.45 (silica, CH\(_2\)Cl\(_2\)/petroleum ether 2:1). **Mp:** > 70 °C (decomposition); \(^1\)H NMR (CDCl\(_3\)) \(\delta = 8.38\) (br s, 2H, NH), 6.78 (s, 2H, \(\alpha\)-H), 6.41 (s, 2H, \(\beta\)-H), 6.23 (s, 2H, \(\beta\)-H), 5.16 (s, 1H, \(\text{meso-H}\) ppm); \(^{13}\)C  

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4.7.8. 5,15-Bis(trifluoromethyl)-10,20-bis-(4-methoxyphenyl)porphyrin (6a)

Under argon, to a solution of 5-(trifluoromethyl)dipyrromethane 3a (643 mg, 3 mmol, 1 equiv) and 4-methoxybenzaldehyde (0.36 mL, 3 mmol, 1 equiv) in CH$_2$Cl$_2$ (300 mL) was added BF$_3$·OEt$_2$ (2.5 M, 0.4 mL, 1 mmol, 0.33 equiv). The mixture was stirred at room temperature for 4 h before DDQ (570 mg, 2.25 mmol, 1.5 equiv) was added and the stirring maintained for 10 min. The mixture was passed over a short silica gel plug (CH$_2$Cl$_2$/petroleum ether 1:2). The following purification by flash chromatography (CH$_2$Cl$_2$/petroleum ether 1:4) afforded 6a as a dark purple solid (88 mg, 0.13 mmol, 9%).

R$_f$ = 0.15 (silica, CH$_2$Cl$_2$/petroleum ether 1:4). $^1$H NMR (CDCl$_3$) $\delta$ = 9.59 (m, 4H, $\beta$-H), 8.93 (d, $^3$J$_{H,H}$ = 5.0, 4H, $\beta$-H), 8.06 (d, $^3$J$_{H,H}$ = 8.4, 4H, Ar–H), 7.31 (d, $^3$J$_{H,H}$ = 8.4, 4H, Ar–H), 4.13 (s, 6H, CH$_2$). The mixture was stirred for 16 h. The mixture was passed over a short silica gel plug (CH$_2$Cl$_2$/petroleum ether 1:2). The following purification by flash chromatography (CH$_2$Cl$_2$/petroleum ether 1:4) afforded 6a as a dark purple solid (29 mg, 0.03 mmol, 4.5%).

R$_f$ = 0.25 (silica, CH$_2$Cl$_2$/petroleum ether 1:4). $^1$H NMR (CDCl$_3$) $\delta$ = 9.45 (br s, 4H, $\beta$-H), 8.94 (d, $^3$J$_{H,H}$ = 5.1, 4H, $\beta$-H), 8.07 (d, $^3$J$_{H,H}$ = 7.1, 4H, Ar–H), 7.31 (d, $^3$J$_{H,H}$ = 8.6, 4H, Ar–H), 4.13 (s, 6H, CH$_3$), −2.53 (br s, 2H, NH) ppm; $^{19}$F NMR (CDCl$_3$) $\delta$ = −76.1 (CF$_3$), −81.8, −119.9 ppm; $^{13}$C $^1$H NMR spectra could not be obtained due to the poor solubility in deuterated solvents; IR: v$_{\text{max}}$ = 3271.6 (w, N–H) cm$^{-1}$; UV–Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (ε) = 414 (189,000), 514 (9910), 551 (11,430), 595 (4640), 646 nm (10,655 mol$^{-1}$·L·cm$^{-1}$); Fluorescence (CH$_2$Cl$_2$): $\lambda_{\text{ex}}$ = 590 nm, $\lambda_{\text{em}}$ = 656, 719 nm; HRMS-ESI: calcd. for C$_{38}$H$_{25}$F$_{30}$N$_2$O$_2$ [M–H]$^-$: 857.1603. Found: 857.1602.

4.7.9. 5,15-Bis(perfluoroheptyl)-10,20-bis-(4-methoxyphenyl)porphyrin (6b)

A solution of 5-(perfluoroheptyl)dipyrromethane 3b (471 mg, 1.5 mmol, 1 equiv) and 4-methoxybenzaldehyde (0.18 mL, 1.5 mmol, 1 equiv) in CH$_2$Cl$_2$ (300 mL) was stirred under argon before the addition of TFA (1.16 mL, 15.1 mmol, 10 equiv). The mixture was stirred at room temperature for 4 h before DDQ (570 mg, 2.25 mmol, 1.5 equiv) was added and the stirring maintained for 16 h. The mixture was passed over a short silica gel plug (CH$_2$Cl$_2$/petroleum ether 1:2). The following purification by flash chromatography (CH$_2$Cl$_2$/petroleum ether 1:4) afforded 6b as a dark purple solid (37 mg, 0.03 mmol, 4%).

R$_f$ = 0.4 (silica, CH$_2$Cl$_2$/petroleum ether 1:4). $^1$H NMR (CDCl$_3$) $\delta$ = 9.45 (br s, 4H, $\beta$-H), 8.94 (d, $^3$J$_{H,H}$ = 5.1, 4H, $\beta$-H), 8.07 (br s, 4H, Ar–H), 7.31 (d, $^3$J$_{H,H}$ = 8.4, 4H, Ar–H), 4.13 (s, 6H, CH$_3$), −2.52 (br s, 2H, NH) ppm; $^{19}$F NMR (CDCl$_3$) $\delta$ = −80.5 (CF$_3$), −81.1, −115.1, −120.7, −121.4, −122.3, −125.9 ppm; $^{13}$C $^1$H NMR spectra could not be obtained due to the poor solubility in deuterated solvents; IR: v$_{\text{max}}$ = 2958, 2922, 2854 (s, C$_\beta$–H) cm$^{-1}$; UV–Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (ε) = 415 (198,140), 514 (10,420), 552 (12,680), 596 (5070), 647 nm (10,655 mol$^{-1}$·L·cm$^{-1}$); Fluorescence (CH$_2$Cl$_2$): $\lambda_{\text{ex}}$ = 590 nm, $\lambda_{\text{em}}$ = 655, 720 nm; HRMS-ESI: calcd. for C$_{40}$H$_{23}$F$_{36}$N$_2$O$_2$ [M–H]$^-$: 1257.1347. Found: 1257.1349.

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4.7.11. 5,15-Bis(fluoroacyl)-10,20-bis-(4-methoxyphenyl)porphyrin (6d)

A solution of 5-(chlorodifluoromethyl)dipyrromethane 3d (345 mg, 1.5 mmol, 1 equiv.) and 4-methoxybenzaldehyde (0.18 mL, 1.5 mmol, 1 equiv.) in CH₂Cl₂ (150 mL) was stirred under argon before the addition of BF₃·O(Et)₂ (2.5 M, 0.2 mL, 0.5 mmol, 0.33 equiv.). The mixture was stirred at room temperature for 4 h before DDQ (510 mg, 4.5 mmol, 1.5 equiv.) was added and the stirring maintained for 10 min. The crude product was passed over a short silica gel plug (CH₂Cl₂). The following purification by flash chromatography (CH₂Cl₂/petroleum ether 1:1 then 2:1) afforded 6d as a dark purple solid (7 mg, 15 μmol, <2%).

Rf = 0.6 (silica, CH₂Cl₂/petroleum ether 2:1).

¹H NMR (CDCl₃) δ = 9.61 (m, 4H, β-H), 9.01 (d, 3J_H,H = 4.9, 4H, β-H), 8.09 (d, 3J_H,H = 8.5, 4H, Ar-H), 7.34 (d, 3J_H,H = 8.5, 4H, Ar-H), 4.13 (s, 6H, CH₃), −2.68 (br s, 2H, NH) ppm;¹³C [¹H] NMR spectra could not be obtained due to little quantity; IR: ν⁻ = 3291, 3067, 2921, (w, N–H), 1671 (vs, C=O) cm⁻¹; UV–Vis (CH₂Cl₂): λmax (ε) = 419 (204,600), 521 (9650), 564 (11,780), 663 nm (11,290 mol⁻¹·L·cm⁻¹); Fluorescence (CH₂Cl₂): λex = 590 nm, λem = 690 nm; HRMS-ESI: calcd. for C₃₆H₂₅N₄O₄F₂ [M+H]+: 615.1838. Found: 615.1838.

4.7.12. 5,15-Bis(formyl)-10,20-bis-(4-methoxyphenyl)porphyrin (6e)

A solution of 5-(dichloromethyl)dipyrromethane 3e (230 mg, 1.5 mmol, 1 equiv.) and 4-methoxybenzaldehyde (0.12 mL, 1 mmol, 1 equiv.) in CH₂Cl₂ (200 mL) was stirred under argon before the addition of TFA (0.77 mL, 10 mmol, 10 equiv.). The mixture was stirred at room temperature for 4 h before DDQ (340 mg, 1.5 mmol, 1.5 equiv.) was added and the stirring maintained for 16 h. The mixture was passed over a short silica gel plug (CH₂Cl₂/AcOEt 9:1). The following purification by flash chromatography (CH₂Cl₂, then CH₂Cl₂/AcOEt 2.5%) afforded 6e as a dark purple solid (31 mg, 0.05 mmol, 11%).

Rf = 0.6 (silica, CH₂Cl₂/AcOEt 97.5:2.5). ¹H NMR (CDCl₃) δ = 12.53 (s, 2H, CHO), 10.01 (d, 3J_H,H = 4.8, 4H, β-H), 9.01 (d, 3J_H,H = 4.8, 4H, β-H), 8.08 (d, 3J_H,H = 8.5, 4H, Ar-H), 7.33 (d, 3J_H,H = 8.5, 4H, Ar-H), 4.13 (s, 6H, CH₃), −2.30 (br s, 2H, NH) ppm;¹³C [¹H] NMR spectra could not be obtained due to the poor solubility in deuterated solvents; IR: ν⁻ = 3316 (w, N–H), 2957, 2921, 2852 (m, Cβ-H), 1672 (vs, C=O) cm⁻¹; UV–Vis (CH₂Cl₂): λmax (ε) = 430 (193,270), 510 (4040), 538 (6900), 587 (17,130), 686 nm (14,880 mol⁻¹·L·cm⁻¹); Fluorescence (CH₂Cl₂): λex = 590 nm, λem = 707, 771 nm; HRMS-ESI: calcd. for C₃₆H₂₅N₄O₂ [M+H]+: 569.1721. Found: 569.1716.

4.7.13. 5,15-Bis(formyl)-10,20-bis-(4-cyanophenyl)porphyrin (7)

A solution of 5-(dichloromethyl)dipyrromethane 3e (345 mg, 1.5 mmol, 1 equiv.) and 4-cyanobenzaldehyde (197 mg, 1.5 mmol, 1 equiv.) in CH₂Cl₂ (300 mL) was stirred under argon before the addition of TFA (1.15 mL, 15 mmol, 10 equiv.). The mixture was stirred at room temperature for 2 h before DDQ (570 mg, 2.25 mmol, 1.5 equiv.) was added and the stirring maintained for 10 min. The mixture was passed over a short silica gel plug (CH₂Cl₂/AcOEt 9:1). The following purification by flash chromatography (CH₂Cl₂, then CH₂Cl₂/AcOEt 2.5%) afforded 7 as a dark purple solid (39 mg, 0.07 mmol, 9%).

Rf = 0.5 (silica, CH₂Cl₂/AcOEt 97.5:2.5). ¹H NMR (DMSO-d₆, 85 °C) δ = 12.56 (s, 2H, CHO), 10.19 (d, 3J_H,H = 5.1, 4H, β-H), 8.95 (d, 3J_H,H = 5.1, 4H, β-H), 8.43 (d, 3J_H,H = 8.0, 4H, Ar-H), 8.31 (d, 3J_H,H = 8.0, 4H, Ar-H), −2.40 (br s, 2H, NH) ppm;¹³C [¹H] NMR spectra could not be obtained due to the poor solubility in deuterated solvents; IR: ν⁻ = 3316 (w, N–H), 1671 (vs, C=O) cm⁻¹; UV–Vis (CH₂Cl₂): λmax (ε) = 427 (102,970), 508 (2250), 535 (3840), 579 (8460), 680 nm (7470 mol⁻¹·L·cm⁻¹); Fluorescence (CH₂Cl₂): λex = 590 nm, λem = 688, 757 nm; HRMS-ESI: calcd. for C₃₆H₂₁N₆O₂ [M+H]+: 569.1721. Found: 569.1716.

4.7.14. 5,15-Bis(formyl)-10,20-bis-(4-chlorophenyl)porphyrin (8)

A solution of 5-(dichloromethyl)dipyrromethane 3e (345 mg, 1.5 mmol, 1 equiv.) and 4-chlorobenzaldehyde (0.21 mL, 1.5 mmol, 1 equiv.) in CH₂Cl₂ (300 mL) was stirred under argon before the addition of TFA (1.15 mL, 15 mmol, 10 equiv.). The mixture was stirred at room temperature for 2 h before DDQ (570 mg, 2.25 mmol, 1.5 equiv.) was added and the stirring maintained for 10 min. The mixture was passed over a short silica gel plug (CH₂Cl₂/AcOEt 9:1). The following purification by
flash chromatography (CH$_2$Cl$_2$) afforded 8 as a dark purple solid (8 mg, 13 µmol, < 2%).

R$_F$ = 0.7 (silica, CH$_2$Cl$_2$). $^1$H NMR (CDCl$_3$) $\delta$ = 12.54 (s, 2H, CHO), 10.04 (4H, $\beta$-H), 8.97 (d, $J_{HH}$ = 4.9, 4H, $\beta$-H), 8.11 (d, $J_{HH}$ = 7.9, 4H, Ar–H), 7.79 (d, $J_{HH}$ = 7.9, 4H, Ar–H), −2.38 (br s, 2H, NH) ppm; $^{13}$C ($^1$H) NMR spectra could not be obtained due to the poor solubility in deuterated solvents; IR: $\nu$ = 1671 (vs, C=O) cm$^{-1}$; UV–Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (c) = 427 (116,900), 535 (3630), 583 (10,310), 682 nm (9140 mol$^{-1}$·L·cm$^{-1}$); Fluorescence (CH$_2$Cl$_2$): $\lambda_{ex}$ = 590 nm, $\lambda_{em}$ = 692, 763 nm; HRMS-ESI: calc'd. for C$_{34}$H$_21$Cl$_2$N$_4$O$_2$ [M+H]$^+$: 587.1036. Found: 587.1038.

4.7.15. 5,15-Bis(formyl)-10,20-bis-(4-tert-butylphenyl)porphyrin (9)

A solution of 5-(dichloromethyl)dipyrromethane 3e (173 mg, 0.75 mmol, 1 equiv.) and 4-tert-butylbenzaldehyde (0.13 mL, 0.75 mmol, 1 equiv.) in CH$_2$Cl$_2$ (150 mL) was stirred under argon before the addition of TFA (0.58 mL, 7.5 mmol, 10 equiv.). The mixture was stirred at room temperature for 2 h before DDQ (285 mg, 1.13 mmol, 1.5 equiv.) was added and the stirring maintained for 10 min. The mixture was passed over a short silica gel plug (CH$_2$Cl$_2$/AcOEt 9:1). The following purification by flash chromatography (CH$_2$Cl$_2$, then CH$_2$Cl$_2$/AcOEt 2.5%) afforded 9 as a dark purple solid (29 mg, 0.045 mmol, 12%).

R$_F$ = 0.8 (silica, CH$_2$Cl$_2$). $^1$H NMR (CDCl$_3$) $\delta$ = 12.51 (s, 2H, CHO), 9.98 (d, $J_{HH}$ = 4.8, 4H, $\beta$-H), 9.00 (d, $J_{HH}$ = 4.8, 4H, $\beta$-H), 8.09 (d, $J_{HH}$ = 8.1, 4H, Ar–H), 7.81 (d, $J_{HH}$ = 8.1, 4H, Ar–H), 1.64 (s, 18H, tertbutyl-H), −2.37 (br s, 2H, NH) ppm; $^{13}$C ($^1$H) NMR spectra could not be obtained due to the poor solubility in deuterated solvents; IR: $\nu$ = 3302 (vw, N–H), 2962 (w, C=H), 1671 (vs, C=O) cm$^{-1}$; UV–Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (c) = 427 (206,460), 539 (6160), 585 (17,490), 684 nm (15,410 mol$^{-1}$·L·cm$^{-1}$); Fluorescence (CH$_2$Cl$_2$): $\lambda_{ex}$ = 590 nm, $\lambda_{em}$ = 692, 767 nm; HRMS-ESI: calc'd. for C$_{42}$H$_{39}$N$_4$O$_2$ [M+H]$^+$: 631.3068. Found: 631.3068.

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Supplementary data

Supporting information for this article is available on the journal’s website under https://doi.org/10.5802/crchim.97 or from the author.

The document contains $^1$H, $^{19}$F and $^{13}$C NMR spectra, additional cyclic voltammograms, absorption and emission spectra, additional theoretical details.

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