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Facile preparation of pure 5,10,15,20-tetrakis(perfluoroalkyl)porphyrins

József Rábai, Anikó Nemes, István Jalsovszky and Dénes Szabó*

Institute of Chemistry, Eötvös Loránd University, P. O. Box 32, H-1518, Budapest 112, Hungary
E-mail: rabai@elte.hu

Abstract: *A chromatography-free method for the preparation of meso-tetrakis(perfluoroalkyl)porphyrins is suggested. This method involves carbinol cyclization coupled with azeotropic water removal using clay supported acid catalyst. Product isolation techniques disclosed here are based on inherent differences in stability of porphyrins and oligomeric side products toward oxidation and in their basicity.*

Keywords: *fluorous porphyrins, TsOH/montmorillonite K10, 2-pyrryl-carbinols, $LaCl_3$ template effect*

Introduction

Porphyrins and their metal complexes play great role in biochemical reactions involving oxidation reactions by molecular oxygen [1]. They are tested as biomimetic catalysts for selective oxidation in organic chemistry [2]; photosensitizes in photodynamic therapy (PDT) [3] and in dye sensitized solar cells [4]; or used as building blocks for supramolecular chemistry and materials science [5]; and in sensors based on their inherent molecular recognition properties [6].

Synthesis of electron-deficient porphyrins is often based on fluorine or perfluoroalkyl-substitution for hydrogens in the molecules of the parent compounds [7]. Although such derivatives are among the most robust ligands tested for O_2 activation, it was clearly established that fluorous iron prophyrins are not stable in oxidative environments [8]. Although this approach has not resulted in new fluorous oxidation catalyst, it led to the development of a much broader concept of fluorous chemistry [9,10].

Motivated by the Therien paper [11], which disclosed the effective preparation of *meso-*$(C_3F_7)_4PorH_2$ ligand we turned our attention to develop chromatography-free isolations and scaling up batch sizes that could provide fluorous porphyrins at the gram scale. We soon applied the strategy of Therien [12] – using high dilution for carbinol cyclization with azeotropic water removal in the porphyrinogen formation step, which is followed by oxidation with *2,3-dichloro-4,5-dicyano-1,4-benzoquinone* (= DDQ) – but supplemented it with simple

isolation protocols.

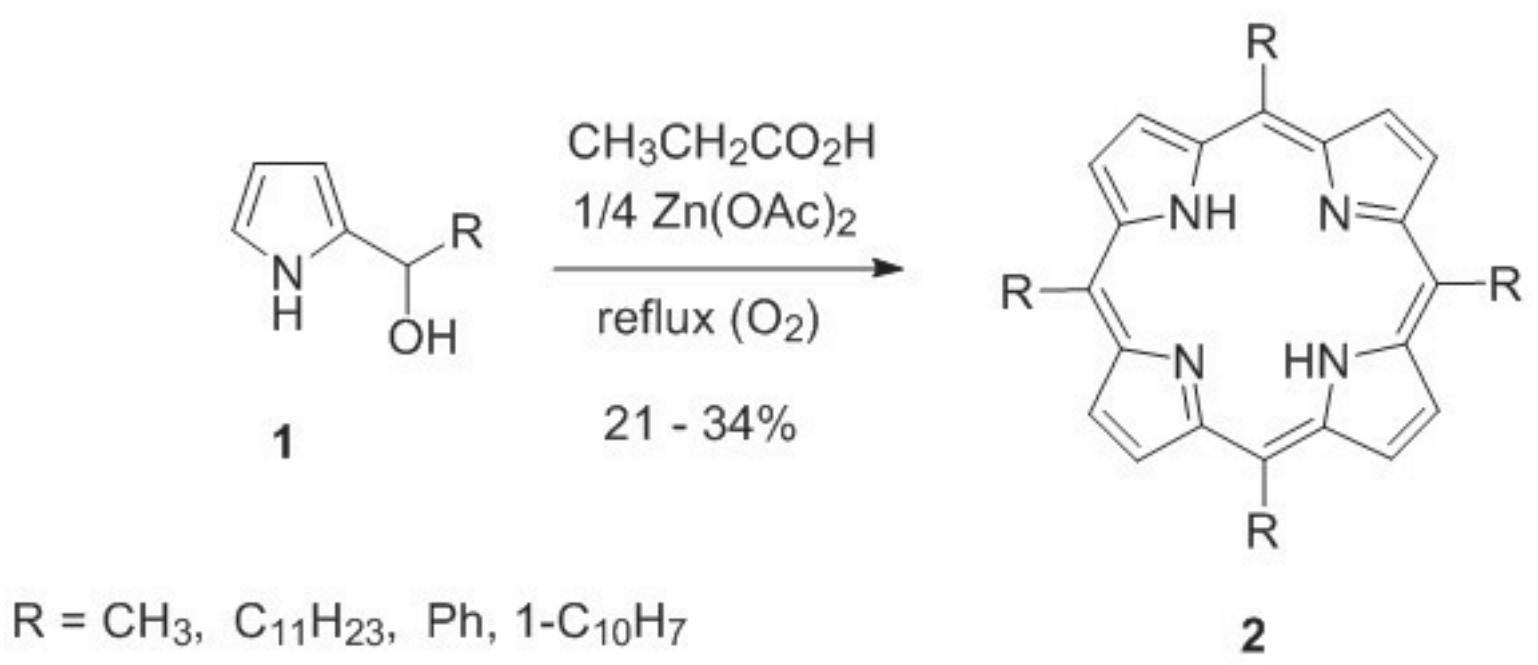
We thought that the differences in the basicity and oxidative stability of target porphyrins and their oligopyrrolene type side products could be exploited for divising effective separation protocols. Here we disclose some improved methods involving unusual work-up protocols (UWP's) (*cf. later*).

Results and Discussion

Synthesis of meso-tetrakis(perfluoroalkyl)porphyrins [12]

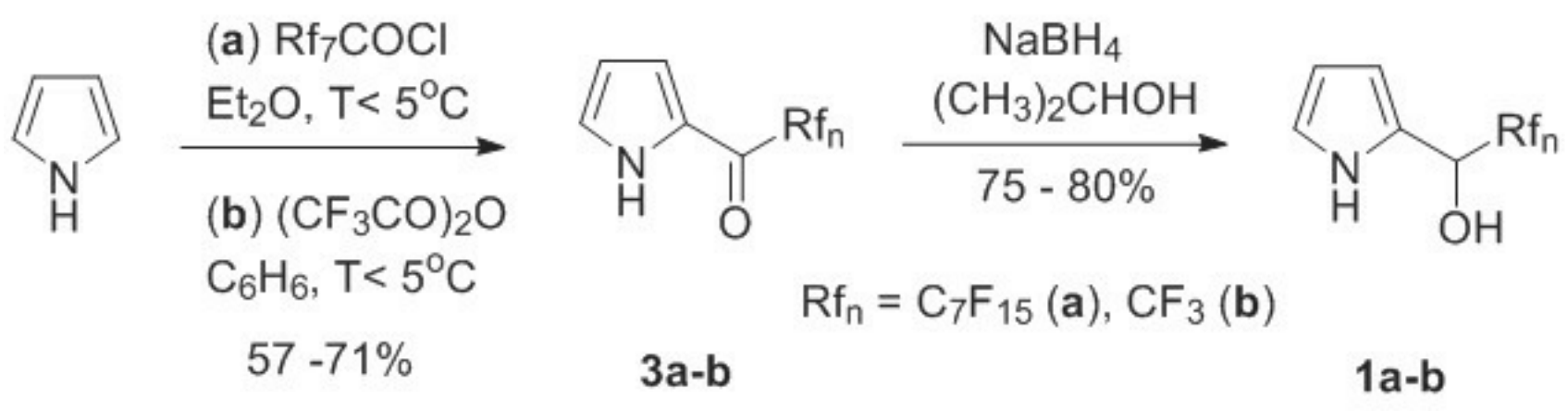
Although acid-catalyzed condensation of pyrrole and an aldehyde produces *meso*-aryl or *meso*-alkyl porphyrins in good yields, following the Adler and Longo [13], or the Lindsey protocols [14]; Vijesekara *et al*. reported that attempts to prepare *meso*-tetrakis(trifluoromethyl)porphyrin, even under harsher reaction conditions, lead only to very small quantities of this *meso*-$(CF_3)_4PorH_2$ porphyrin [15].

Our first target was *meso*-tetrakis(perfluoroheptyl)porhyrin (**2a**, R = C_7F_{15} = R_{f7}). Since no procedure was known for the synthesis of this porphyrin at the early nineties (1990'), we choosed the carbinol cyclization method of Kuroda *et al.,* since they used only alkyl- and aryl-2-pyrryl-carbinols in boiling propionic acid. The role of the added $Zn(OAc)_2$is believed to improve yields *via* Zn^{2+}-ion template effect (Scheme 1)[16].



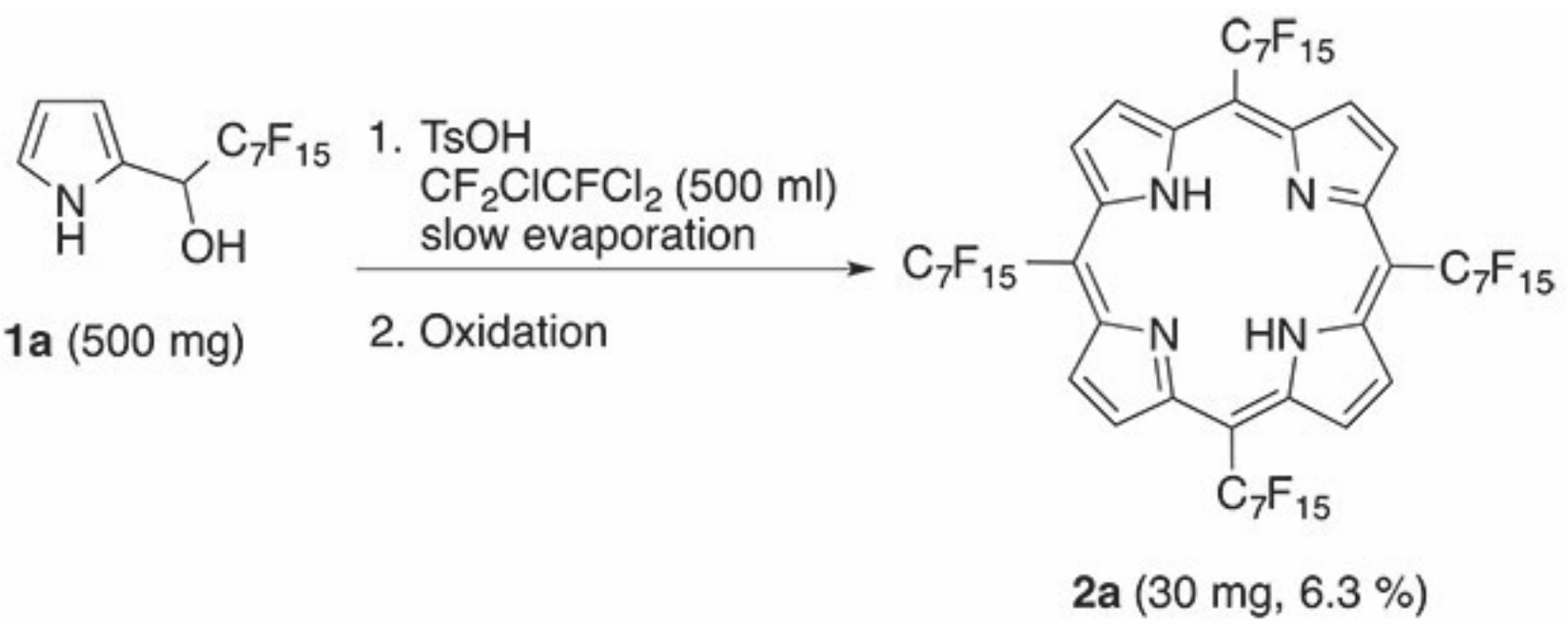
Scheme 1. *Carbinol based synthesis of meso-alkyl- or aryl-porphyrins.*

To reveal the suitability of this method for the synthesis of *meso-(*perfluoroalkyl)porphyrins we made first *F-alkyl*-carbinols (**1a,b**) by $NaBH_4$ reduction of precursor *F-alkyl*-pyrryl-ketones (**3a,b**), which could be prepared in good yield by our optimized procedures based on literature precedences (Scheme 2) [17].



Scheme 2. *Improved synthesis of F-alkyl-(2-pyrryl)-carbinols.*

Then we tested **1a** using same conditions (Scheme 1), but it failed to afford any *meso*-$(R_{f7})_4PorH_2$(**2a**). Next we changed propionic acid to a *fluorous* solvent (R-113) and refluxed a 1:1 mixture of **1a** and $TsOH*H_2O$. No formation of **2a** was detected by UV-V is until in a serendipitious experemint ½ volume of the solvent escaped due to a brake of cooling water supply. This test experiment on work up (Et_2O-CF_3CO_2H-CH_3OH = UWP-1) gave noticable amount of the target *fluorous* porphyrin **2a** (Scheme 3).

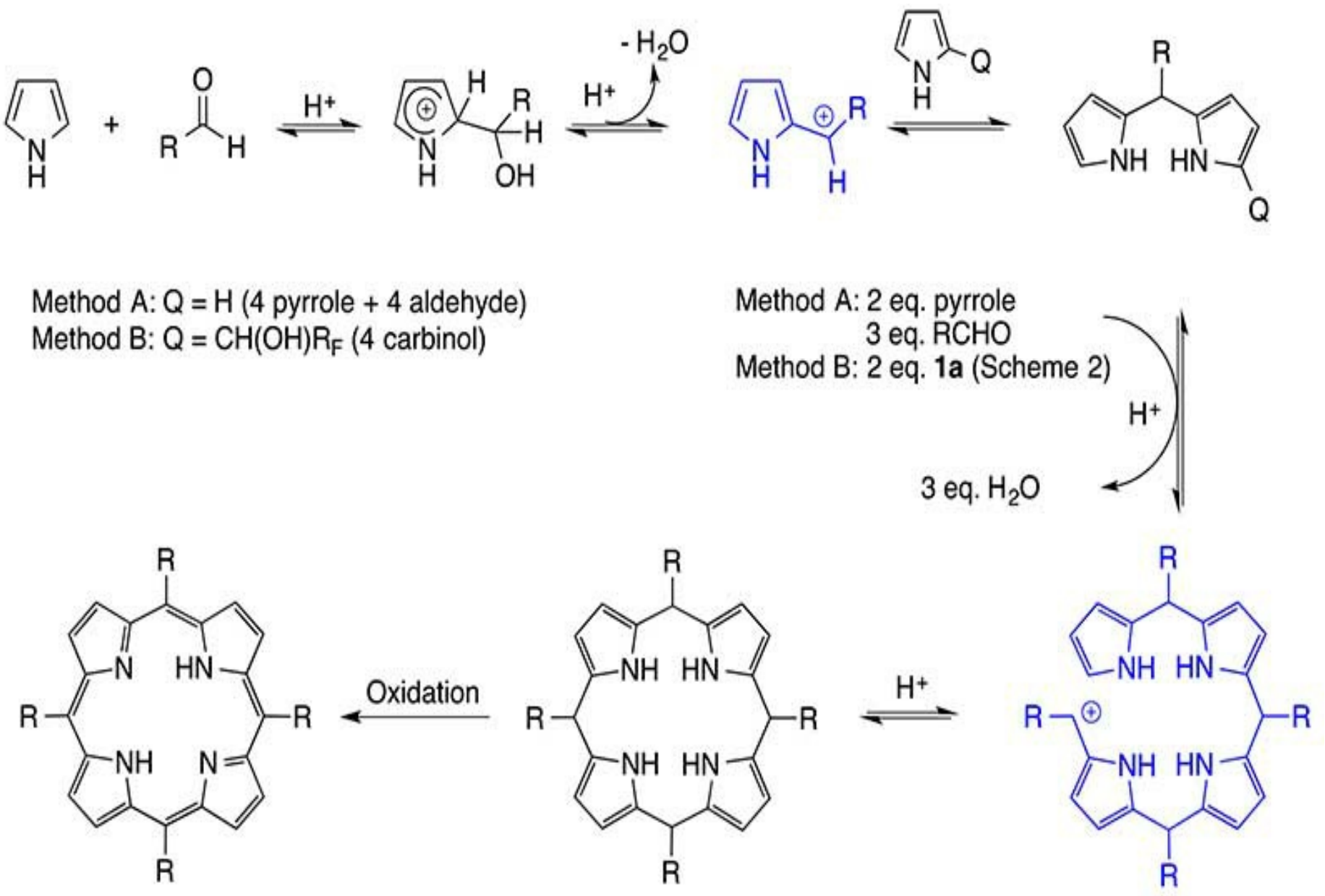


Scheme 3. *Serendipitious synthesis of meso-tetrakis-(perfluoroheptyl)-porphyrin.*

The reason for the formation of **2a** was the azeotropic water removal, which affected beneficially the α-alkylation of pyrryl-carbinols at C5 by the carbocations formed during condensation. This is in complete analogy to the observations of Therien, who disclosed effective synthesis of $(C_3F_7)_4PorH_2$ [11a], along with that of shorter $(CF_3)_4PorH_2$ or longer *F*-chain $(C_7F_{15})_4PorH_2$ homologues *via* carbinol cyclization [11b].

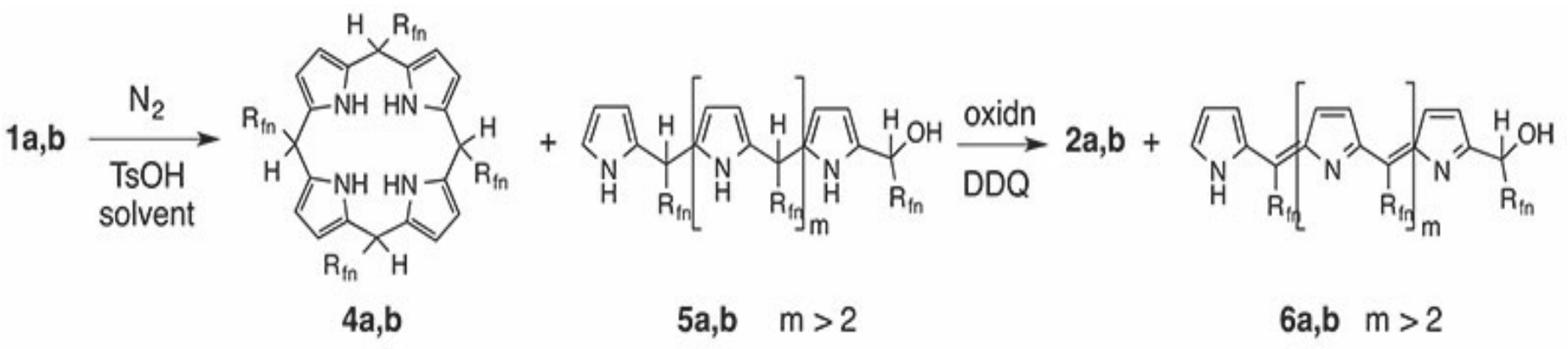
There was known earlier that azeotropic removal of water increases the yields of octaethyl-porphyrin prepared by condensation of 3,4-diethylpyrrole and formaldehyde [18], or that of a series of *meso*-tetraaryl-porphyrins obtained by acid catalysed condensation of pyrrole and aromatic aldehydes [19].

These observations are in accordance with the proposed mechanisms of the ”4×pyrryl-carbinol” [11] and of the ”4 pyrrole + 4 aldehyde” [14] cyclization methods, where α-pyrryl-cations and porphyrinogen are common intermediates. In both cases under anaerobic condition this sequence is reversible and the tetrameric species may undergo cyclization to afford porphyrinogen which should be quenched at their maximal concentration by DDQ. Otherwise, under inert and reversible reaction conditions a significant increase of oligomeric side products is possible. However, their formation is not shown here (Scheme 4).



Scheme 4. *Mechanism of the porphyrin formation according to Lindsey. (Common intermediates of the Lindsey[14] and Therien [11] methods are shown in blue color.)*

As a consequence of the formation mechanism optimal yields could be achieved if the reaction conditions are optimized for porphyrinogen formation, then this intermediate is quenched with an appropriate oxidazing agent, such as DDQ [20]. This oxidation converts the oligopyrromethane (**5a,b**) side products into dark coloured oligopyrromethenes (**6a,b**) (Scheme 5).



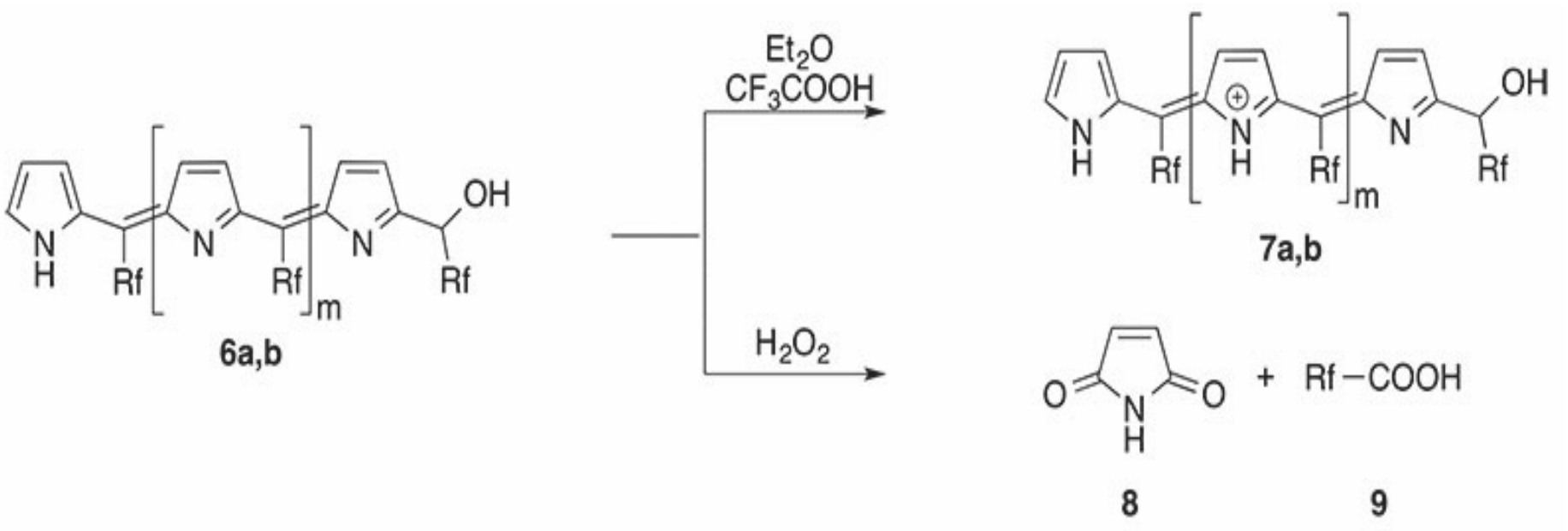
Scheme 5. *Two step synthesis of meso-(perfluoroalkyl)-porphyrins**.***
*Carbinols:**1**; Porphyrinogens:**4**; Oligopyrromethanes:**5**; Porphyrins:**2**; Oligopyrromethenes:**6***

UV-Vis Spectroscopy of meso-Tetrakis(Perfluoroalkyl)Porphyrins.

The intensity of the Soret-band increases if a few drops of CF_3CO_2H is added to the $CF_2ClCFCl_2$ = R-113/or ether solution of such fluorous samples. This is in line with the formation of double protonated porphyrin molecules, which are exposing $[(R_{fn})_4PorH_4]^{2+}$ type

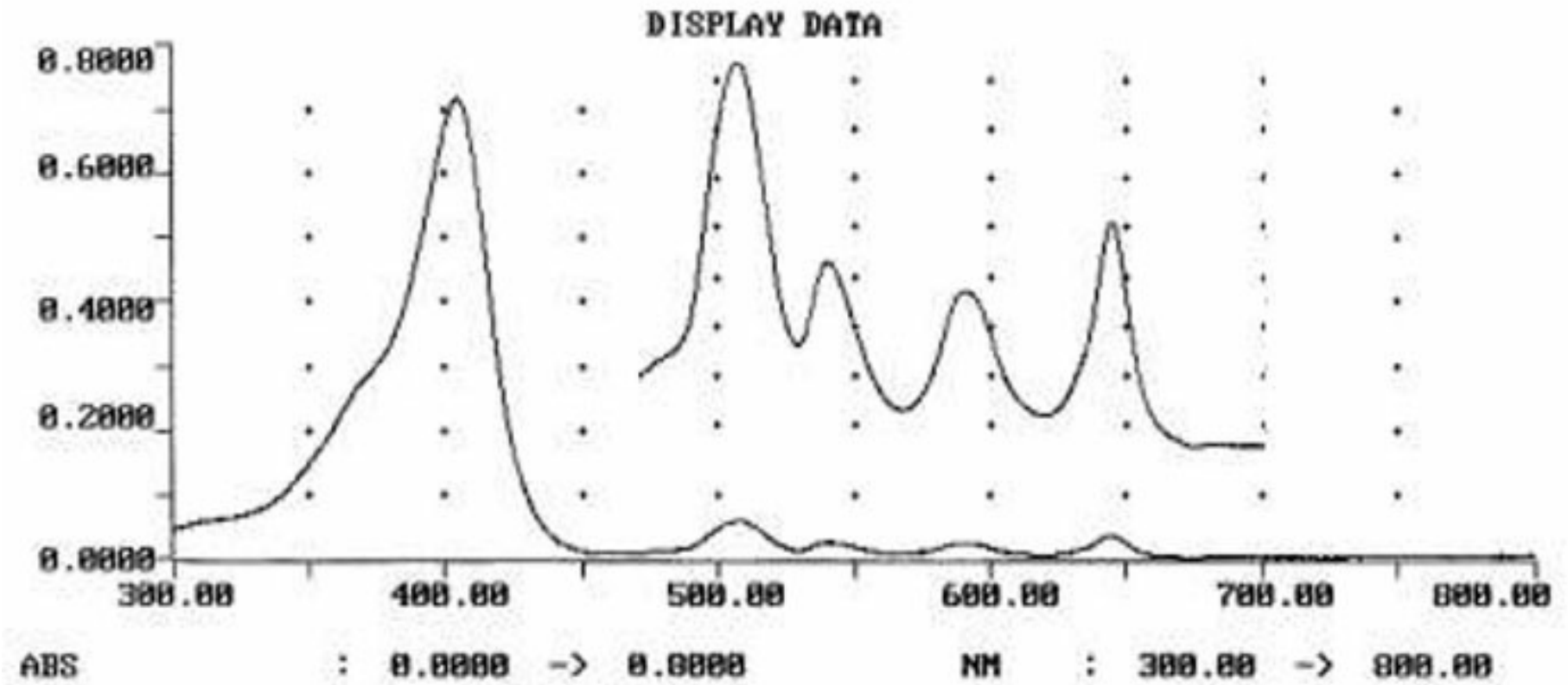
dications. However, this acid-base equilibrium can be reversed by adding a few drops of CH_3OH, a stronger base than the porhyrins studied.

We have shown that oligopyrromethenes **6** are more basic than the respective porphyrines **2**, thus allowing the formation of polycation type species (**7**) and they are oxidized much faster with hydrogen peroxide in CF_3CO_2H than the parent porhyrins (**2**) to afford more polar product such as maleimid (**8**) and the corresponding perfluoroalkane carboxylic acid (**9**) (Scheme 6).



Scheme 6. *Acid-base reaction (protonation) and oxidation characteristics of oligopyrromethenes**6a,b**.*

These characteristic properties allow the easy separation of target *fluorous* porphyrins **2a,b** from polycation type species **7a,b** by precipitation with methanol or from more polar products formed by the oxidation of oligopyrromethenes. *At one hand*, the addition of excess methanol to a concentrated ethereal/CF_3CO_2H solution of a crude mixture of porphyrins and oligopyrrolenes will deprotonate only the porphyrin content and induce their precipitation as waxy solid materials, while the protonated side products remain in solution (UWP-1).*On the other hand*, following atwo phase oxidative treatment of the crude porhyrin and oligopyrrolene mixtures with aq-H_2O_2/HCO_2H, a simple alkaline extraction of filtration through basic Al_2O_3 may result in the formation of pure solutions of the target fluorous porphyrines (UWP-2).



Scheme 7. *UV-Vis of pure **2a**(in R-113): Soret at 404.4, Q_1-Q_4(insert) at 506.4, 541.3, 588.9, 644.6 nm. Near to baseline absorbance at 300 nm indicates that oligomeric side products were successfully removed.*

Oxidation properties of mezo-perfluoroalkyl-porhyrins and F-oligopyrrolenes

Fainting experiments with aq-H_2O_2/CF_3CO_2H during UV-Vis measurements showed an initial sharpening of the Soret-band, but on the long run resulted in the complete oxidative degradation of all the porphyrins studied. These experiments clearly indicated that even highly 'electronpoor' fluorous porphyrins and their metal complexes does not survive oxidative conditions where formation of peroxide intermediates is possible. Such oxidations were performed at 20°C usually in a two liquid-liquid phase system, consisting of 30% aq-H_2O_2/CF_3CO_2H – R-113 solvent pair. Later the ozone depleting R-113 solvent was replaced with benzotrifluoride (BTF) or CH_2Cl_2 depending on solubility pattern of crude *F*-porphyrins. To slow down the oxidation of the porphyrin content of the crude samples that allow preparative scale separations CF_3CO_2H was changed to HCO_2H. With the expense of sacrifying only a small part of porphyrins, all side products were converted to more polar compounds – using aq-H_2O_2-HCO_2H/BTF, toluene or CH_2Cl_2 systems – which are easily adsorbed on basic alumina or could partly be removed by aq-NaOH-extraction.

Method_A**:**

*We used acid catalyzed carbinol cyclization at high dilution (2.5-5 × 10^{-3} M) in benzene with simultanous water removal via azeotropic solvent distillation as reported by Therien et al., followed with DDQ quenching of the porphyrinogen, but using liquid-liquid two phase oxidation and crystallization for improved product isolation. We obtained porphyrin **2a** [230 mg (7.1%)] in pure state with mp = 248-249°C. In our hands only the crude yields of **2a** were as high as the reported 34%.*

Method_B**:**

*Lantane(III)-chloride assisted carbinol cyclization method at high dilution in toluene(2.2 × 10^{-3} M) was executed by silica supported sulfuric acid assisted condensation and simultanous water removal via azeotropic solvent distillation, which is followed with DDQ quenching of the porphyrinogen intermediate, but using liquid-liquid two phase oxidation and crystallization for improved product isolation.We obtained porphyrin **2a** [900 mg (18.8%)] in pure state with*

*mp = 248-249°C. The success of this novel procedure may be related to coordination complex formation between oxophilic La^{3+} cations and the precursor carbinols (template-effect). Without $LaCl_3$ no detectable porhyrin formation was observed, but complete decomposition of the carbinol when H_2SO_4*SiO_2 was introduced.*

Method_C**:**

Clay supported acid [21] catalyzed carbinol cyclization at high dilution in toluene with simultanous water removal via azeotropic solvent distillation, followed with DDQ quenching of the porphyrinogen intermediate, but using liquid-liquid two phase oxidation and crystallization for improved product isolation. Samples of *pure$(C_7F_{15})_4porH_2$ and $(CF_3)_4porH_2$ with sharp meting points are easily obtained at the gram scale in 15 or 25% yields, respectively.*

Experimental

Pyrryl-carbinols were prepared by $NaBH_4$ reduction of the precursor ketones as shown below and they stored at 0°C until used. Solvents and reagents were purchased from Sigma-Aldrich and Molar. ^{1}H-, ^{13}C- and ^{19}F-NMR spectra were recorded on Bruker Avance 250 instrument using a 5 mm inverse ^{1}H/^{13}C/^{31}P/^{19}F probe head at room temperature. Chemical shifts (δ) are given in parts per million (ppm) units relatively to the internal standard TMS (δ=0.00 for ^{1}H, δ=0.00 for ^{13}C) and to $CFCl_3$ as external standard (δ=0.00 for ^{19}F). Melting points were determined on a Boetius micro-melting point apparatus and are uncorrected. The reactions were monitored by TLC (SiO_2 and Al_2O_3 plates), UV-Vis spectra (Carry) and gas chromatography (Hewlett-Packard 5890 Series II, PONA [crosslinked methylsilicone gum] 50 m x 0.2 mm x 0.5 µm column, H_2 carrier gas, FID detection; Program: 120 °C, 5 min, 10 °C/min, 250 °C, 5 min; Inj.: 250 °C, Det.: 280 °C).

2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluoro-1-(2’-pyrrolyl)-1-octanone (3a)

To a solution of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoyl chloride (15.15 g, 0.035 mol) in ether (35 mL) was added dropwise the solution of pyrrole (2.41 g, 0.036 mol) in ether (30 mL) under stirring over 30 min period. After the addition the mixture was stirred for an additional 2 h at rt. The reaction mixture was washed with 5% $NaHCO_3$ solution (2 x 50 mL) and water then dried over sodium sulfate. The solvent was removed then the crude product was crystallized from pentane to yield 8.2 g (57 %) pure product. Mp. 48-49 °C.

^{1}H NMR (250 MHz $CDCl_3$) δ (ppm): 6.43 (1H, m), 7.28 (2H, m), 9.98 (1H, s).

2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluoro-1-(2’-pyrrolyl)-1-octanol (1a)

To an ice water cooled and stirred solution of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-(2’-pyrrolyl)-1-octanone (9.27 g, 0.020 mol) in a solvent mixture (130 mL tetrahydrofurane and 60 mL methanol) was carefully added $NaBH_4$ (1.76 g, 0.046 mol) in small portions during 30 min. After stirring for 2 h at rt ether (50 mL) was added and the solution was washed with saturated $NaHCO_3$ (50 mL) then brine. The organic phase was dried over Na_2SO_4. After removal of the solvent the residue was crystallized from toluene (40 mL) to give 7.0 g (75%) pure crystalline product, mp = 93-95 °C.

^{1}H NMR (250 MHz $CDCl_3$) δ (ppm): 2.95 (1H,s), 5.00 (1H, m), 6.23 (1H, m), 6.31 (1H, s), 6.83 (1H, m) 8.59 (1H, s).

2-Trifluoroacetyl-pyrrole (3b)

To an ice cold solution of trifluoroacetic anhydride (46 mL, 0.325 mol) in ether (400 mL) was added dropwise the solution of pyrrole (19.0 g, 0.283 mol) in ether (55 mL) under stirring over 2.5 h period. After the addition the mixture was stirred at 0°C for an additional 4 h. The reaction mixture was washed with water then dried (Na_2SO_4). The solvent was removed then the residue steam distilled. The distillate was cooled to 0 °C and the crystalline solid formed filtered, washed with cold water and dried to yield 32.7 g (71 %) product. Mp. 38-40°C (reported value [17] mp 46-47 °C/ obtained by vacuum sublimation).

^{1}H NMR (250 MHz $CDCl_3$) δ (ppm): 6.43 (1H, t), 7.26 (1H, s), 7.31(1H, s), 10.18 (1H, s)

2,2,2-Trifluoro-1-(2'-pyrrolyl)-1-ethanol (1b)

To an ice water cooled and stirred solution of 2-trifluoroacetyl pyrrole (25 g, 0.153 mol) in methanol (100 mL) was carfully added $NaBH_4$ (12.5 g, 0.33 mol) in small portions during 3 h. After stirring for 1 h saturated $NaHCO_3$ (50 mL) was added and the mixture was extracted with ether (5 x 50 mL) then the combined organic phase was washed with saturated $NaHCO_3$, brine, and then dried over Na_2SO_4. After removal of the solvent the residue was distilled in vacuo to afford 20.3 g (80.4%) colourless oil of bp. 112-120°C/18 mm Hg; which turns to a white solid at room temperature, m.p. = 45-47°C.

^{1}H NMR (250 MHz $CDCl_3$) δ (ppm): 2.95 (1H, s), 5.01 (1H, q), 6.22 (1H, m), 6.31 (1H, s), 6.83 (1H, m), 8.59 (1H,s).

Montmorillonite K10/TsOH*H_2O reagent [Clay/TsOH (4:1 w/w)]

Montmorillonite K10 (50 g) was mixed with a solution of p-toluenesulfonic acid monohydrate (10 g) dissolved in distilled water (150 mL). The mixture was homegenized by evaporating most of the water using Rotavapor, then was further dried in vacuum over P_2O_5 for 3 days. The yield is quantitative (60 g).

H_2SO_4/SiO_2 reagent [10% w/w H_2SO_4/SiO_2]

Sulfuric acid (5.00 g, 96%) was mixed in a flask with SiO_2 (45 g, Merck Kieselgel 40, 35-70 mesh). Some heat was evolved. The flask was stoppered and hand-shaked until a free-flowing reagent obtained. Then heated to 80°C and vacuum applied (16 mmHg) for 5 min. Finally allowed to cool to room temperature and stored in a well stoppered flask. Assay: ~1.0 mmol H_2SO_4/g solid.

***meso*-Tetrakis(perfluoroheptyl)porphin (2a)**

Title compound was prepared by Method A using 5×10^{-3} Mcarbinol in the presence of 2.5×10^{-3} M TsOHcatalyst. Under an N_2 atmosphere 3.40 g (7.31 mmol) C_7F_{15}-(α-pyrryl)-carbinol (**1a**); 1.5 L benzene and 0.72 g (3.78 mmol) TsOH*H_2O were stirred and ½ vol of the solvent was distilled off. DDQ (1.73 g, 7.62 mmol) was added and refluxed 1 h. Filtered and evaporated to dryness. The residue was treated with $CF_2ClCFCl_2$ (700 mL) and HCO_2H (350 mL) and 30% aq-H_2O_2 (35 mL) and refluxed for 5 h. Diluted with water (350 mL), phases were separated and the $CF_2ClCFCl_2$ layer was washed with 0.2 M NaOH (5 × 700 mL). Dried over Na_2SO_4 and the filtrate evaporated. The crude solid was recryst. from $CF_3C_6H_5/CH_3OH$ to afford 230 mg (0.129 mmol, 7.1%) of **2a** with m.p. = 248-249°C.

The spectroscopic data were in agreement with those reported in [11b]. ^{1}H NMR (250 MHz, $CDCl_3$, $CF_2ClCFCl_2$): δ 9.54 (s, 8 H), -2.25 (s 2 H); ^{19}F NMR ($CDCl_3$): δ-80.7, (br, 2 F),

-82.3, (br, 3 F), -115.3, (br, 2 F), -121.7, (br, 2 F), -122.1, (br, 2 F), -122.8, (br, 2 F), -126.7, (br, 2 F); Vis($CF_2ClCFCl_2$) of $(R_{f7})_4PorH_2$: λ_{max} = 404 nm (ε_{max}= 143,760 Soret); $[(R_{f7})_4porH_4]^{2+}$: λ_{max} = 423 nm (*dication formation by CF_3CO_2H resulted in 19 nm red shift*).

meso-Tetrakis(perfluoroheptyl)porphin (2a)

*Title compound was prepared by Method B using 2×10^{-3} M carbinol and 1×10^{-3} M $LaCl_3*7H_2O$ template in toluene.*Under N_2 atmosphere a mixture of **1a** (5.00 g, 10.75 mmol), $LaCl_3*7H_2O$ (2.00 g, 5.39 mmol) and toluene (5 L) was stirred and heated to reflux with the aid of an electric heating mantle and about 1 L toluene was distilled off (~30 min). Faint purple colour was developed. More toluene (1 L) was added along with of 10%H_2SO_4@SiO_2 (2.50 g; = 250 mg H_2SO_4, 2.55 mmol) stirred and refluxed longer and toluene (500 mL) distilled off during the next 30 min to display darkened colour. Then DDQ (2.50 g, 11.0 mmol) was added and the mixture refluxed for 1 h. The mixture was filtered while hot and evaporated (Rotavapor). This solid was washed with CH_3OH (200 mL) and dried to yield 3.10 g of crude product. It was dissolved in $CF_2ClCFCl_2$(500 mL) and strirred with a mixture of HCO_2H (250 mL) and 30% aq-H_2O_2 (25 mL) for 12 h. The separated lower phase was washed with 85% HCO_2H (3×100 mL), then with water (3×200 mL), 1M KOH (3×200 mL) and finally with brine. Dried over Na_2SO_4, filtered and the solvent recovered by atmospheric distillation to afford an enriched solid porphyrin fraction: 1.76 g (~36%) after dried at 80°C/16 mm Hg. Two times recrystallization from a mixture of $CF_3C_6H_5$ (12 mL) and CH_3OH (5 mL) gave 900 mg (18.8 %) of analytically pure $(R_{f7})_4PorH_2$ as dark purple needles; m.p. = 248-249°C. UV-Vis (R-113): Soret 404 nm (ε = 143,760).

meso-Tetrakis(perfluoroheptyl)porphin (2a)

*Title compound was prepared by Method C using 2×10^{-3} M carbinol and 5×10^{-4} M TsOH*momoK10 in toluene.*
A mixture of toluene (5.0 L) and 1:5 w/w supported TsOH*H_2O/Montmorillonite K10 (600 mg; 0.53 mmol TsOH) and of **1a** (5.00 g, 10.75 mmol) was stirred and heated under a slow stream of N_2 and about 1 L of toluene distilled off during 1 h. Next the mixture is treated with DDQ (3.50 g, 15.4 mmol) and boiled with stirring for 1h longer. The reaction mixture was filtered on filter paper while hot. This toluene filtrate gave dark precipitate at 20°C but significant amount of porphyrin remained in solution. It was evaporated in vacuum (Rotavap) and the residue was leached with CH_3OH (400 mL) to remove any nonfluorous (quinone/hydroquinone) side products. The fluorous precipitates and residues were combined by dissolving them in $CF_2ClCFCl_2$ (500 mL), then the $CF_2ClCFCl_2$ extract of the crude fluorous porphyrin and oligomeric pyrromethenes were stirred with a mixture of HCO_2H (250 mL) and 30% aq-H_2O_2 (25 mL) for 24 h. The two liquid phase system was worked up as follows: the separated $CF_2ClCFCl_2$ layer was washed consecutively with 85% HCO_2H (100 mL), then H_2O (2×100 mL), 1M KOH (3×200 mL) and brine (2×50 mL). The solution was dried (Na_2SO_4), filtered and evaporated to give ~2.5 g enriched product. Repeated (2×) recrystallization of that from a 3:2 $^{v}/_{v}$mixture of $CF_3C_6H_5$ and CH_3OH gave dark purple needles, 1.208 g (0.6778 mmol, 25.2%) of $(R_{f7})_4PorH_2$, with m.p. = 246-248°C.UV-Vis (R-113): Soret 404 nm (ε = 143,760).

meso-Tetrakis(trifluoromethyl)porphin (2b)

Title compound was prepared by Method C using 6×10^{-3} M CF_3-carbinol and 3×10^{-4} M

*TsOH*momoK10 in toluene.*
A mixture of toluene (5.0 L) and 1:5 w/w supported TsOH*H_2O/Montmorillonite K10 (1.60 g; 1.40 mmol TsOH) and of **1b** (5.00 g, 30.3 mmol) was stirred and heated under a slow stream of N_2 and about 1 L of toluene distilled off during 1 h. DDQ (6.0 g, 26.4 mmol) was added to the mixture and boiled for 1h. Then basic (Brockman I) Al_2O_3 (250 g) was added and the mixture filtered while hot and the filtrate was evaporated in vacuum (Rotavap). The residue was dissolved in $CF_2ClCFCl_2$ (500 mL) and then stirred with a solution of 30% H_2O_2 (50 mL) in 98% HCO_2H (500 mL) at RT for 24 h. Liquid phases were separated, then the $CF_2ClCFCl_2$ layer was washed with H_2O (2×100 mL), 1M KOH (3×200 mL) and brine (100 mL). The $CF_2ClCFCl_2$ solution was dried (Na_2SO_4), filtered and evaporated to give ~2 g enriched product. It was recrystallised from $CF_3C_6H_5$-CH_3OH (9:1 v/v), and then 2-propanol (25 mL/100 mg) to yield 670 mg (1.15mM, 15.2%) analytically pure dark blue lustrous crystals; mp = 192-196°C.

The spectroscopic data were in agreement with those reported in [11b]. ^{1}H NMR (250 MHz, $CDCl_3$): δ 9.60 (s, 8H), -2.08 (s, 2H); ^{19}F NMR ($CDCl_3$): δ -38.41 (s, 3F). Vis (CH_2Cl_2): Soret 403 nm (ε = 120,226), 510, 545, 593, 649.

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