A method of introducing fluorinated substituents in porphyrin structure by nucleophilic substitution of fluorine inmeso-tetrakis(pentafluorophenyl)porphyrin and pentafluorobenzaldehyde with polyfluoroaliphatic alcohols

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Abstract: *Various methods for obtaining meso-tetrakis(pentafluorophenyl)porphyrins, additionally modified with polyfluoroalkoxy substituents are considered. One of the variants for macrocycle assembling includes synthesis and condensation of polyfluoroalkylbenzaldehydes obtained by substitution of para- and ortho-fluorines in the starting pentafluorobenzaldehyde by polyfluoroaliphatic alcohols. Direct substitution of fluorines in meso-tetrakis(pentafluorophenyl)porphyrin by polyfluoroaliphatic alcohols was carried out as an alternative.*
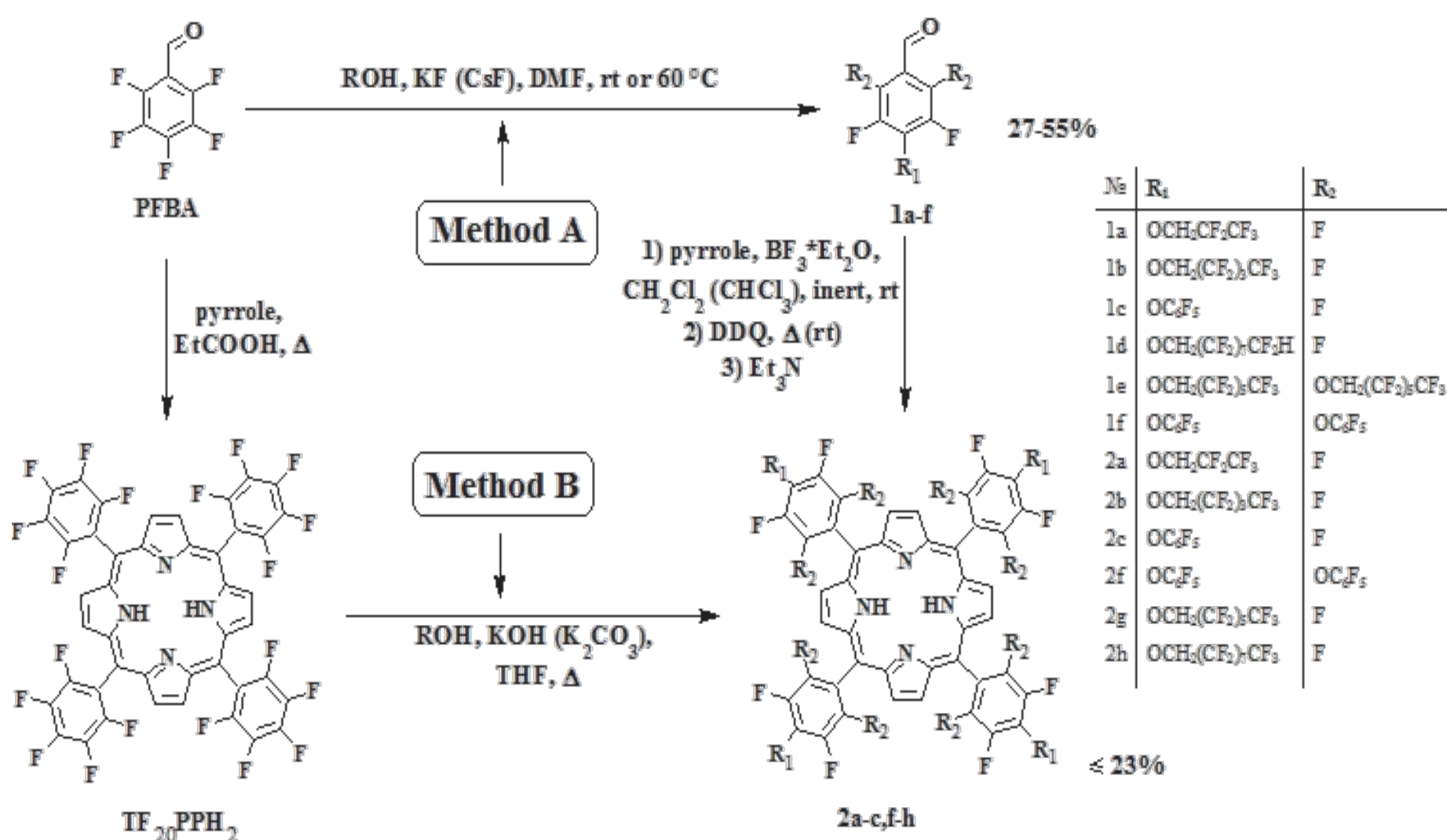
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Porphyrin compounds play the key role in a number of chemical and biochemical processes. The possibility of introducing substituents of various nature in a porphyrin cycle essentially extends the range of their potential applications in various fields of chemical technology as catalysts, components of photoactive materials and pharmaceuticals. Recently the considerable attention has been paid to the studies of fluorinated porphyrins in connection with the development FBS (Fluorous Biphasic System) technology [1,2], the works directed to design of photoelectroactive materials having hydrophobic characteristics [3,4] and expanding the range of effective photosensitizers potentially applicable in photodynamic

therapy of cancer [5]. It was reported that solubility in perfluorocarbon media and hydrophobicity of porphyrins are provided by introducing not less than four perfluoroalkyl substituents having 3 to 8 carbons [1,2] whereas the presence of trifluoromethyl substituents markedly affect the redox properties [6].

Currently, the main methods for preparing fluorinated porphyrins are catalytic alkylation with perfluoroalkyliodides, or introducing fluorine-containing moieties by nucleophilic substitutions [7]. For the reason of extending sphere of fluorinated porphyrins applications, a search for new methods for their synthesis still remains topical. Our approach for solving this problem consists in either use of polyfluoroaliphatic alcohols in substitutions of fluorines in pentafluorobenzaldehyde under the action of base followed by condensation of the prepared compounds to give a macrocycle (Method A), or the similar substitution of the activated fluorines in aromatic rings of *meso*-tetrakis(pentafluorophenyl) porphyrin (Method B).

Aldehyde-pyrrole condensation of polyfluoroalkoxy substituted benzaldehyde (Method A)

Scheme:

PFBA → (ROH, KF (CsF), DMF, rt or 60 °C) → 1a-f, 27-55%

Method A

1) pyrrole, BF₃*Et₂O, CH₂Cl₂ (CHCl₃), inert, rt
2) DDQ, Δ (rt)
3) Et₃N

pyrrole, EtCOOH, Δ → TF₂₀PPH₂

Method B: ROH, KOH (K₂CO₃), THF, Δ → 2a-c,f-h, ≤ 23%

№	R₁	R₂
1a	OCH₂CF₂CF₃	F
1b	OCH₂(CF₂)₃CF₃	F
1c	OC₆F₅	F
1d	OCH₂(CF₂)ₙCF₂H	F
1e	OCH₂(CF₂)₃CF₃	OCH₂(CF₂)₃CF₃
1f	OC₆F₅	OC₆F₅
2a	OCH₂CF₂CF₃	F
2b	OCH₂(CF₂)₃CF₃	F
2c	OC₆F₅	F
2f	OC₆F₅	OC₆F₅
2g	OCH₂(CF₂)₃CF₃	F
2h	OCH₂(CF₂)ₙCF₃	F

The substitution of the activated fluorine in *para*-position of pentafluorobenzaldehyde **(PFBA)** was earlier demonstrated by the example of a number of phenols [8], wherein such specific bases as potassium and cesium fluorides were used for formation of corresponding phenolates. We took this procedure as a base one for introducing polyfluorinated alcohol residues with relatively high acidity (pKa ~12-13) into PFBA molecule. Actually it was shown that interaction of **PFBA** with equimolar amounts of various polyfluoroaromatic alcohols or pentafluorophenol led to formation polyfluoroalkoxy- and phenoxy-benzaldehyde **(1a-d)**. The reactions were carried out in dimethylformamide at room temperature up to complete conversion of the starting aldehyde (according to TLC data). It should be noted that in the case of three-fold excess of the corresponding alcohols, we didn't observe substitution the *ortho*-fluorines in **PFBA** irrespective of the reaction time. At the same time the possibility of formation of the corresponding 2,4,6-substituted benzaldehyde **(1e,f)** in good yields was demonstrated in the case of increasing the reaction temperature to 60°C.

Aldehyde-pyrrole condensation of the prepared polyfluorophenoxy- and alkoxy-

benzaldehydes **(1a-c)** was carried out using Lindsey method [9] recommended for the synthesis of porphyrins from aldehydes having bulk substituents. The reactions were carried in dichloromethane at room temperature in the presence of boron trifluoride diethyl etherate and using DDQ as an oxidizing agent. The corresponding symmetrical porphyrins **(2a-c)** were synthesized and characterized by NMR and mass spectroscopy. The yields were good for the compounds of this class.

According to literature data, the presence of even small substituents (for example methyl or methoxy) in positions 2 and 6 of benzaldehydes significantly hinders formation of porphyrins. Condensation of *ortho*-substituted benzaldehydes with pyrrole resulting to porphyrins requires the use of a cocatalyst (ethanol), as had been demonstrated by the example of mesitylaldehyde [10]. Application of this procedure to condensation of aldehyde **(1f)** with pyrrole led to formation of the corresponding porphyrin **(2f)**, but the yield of this product did not exceed 2%. The attempt to carry out the reaction with aldehyde **(1e)** has failed, this can be explained either by the greater steric bulk of the substituents (1,1-H,H-perfluoroheptyloxy- in comparison with pentafluorophenoxy-group) or low solubility of intermediate compounds in chloroform that we observed in both cases.

Substitution of activated fluorines in aromatic rings of *meso*-tetrakis(pentafluorophenyl)porphyrin by polyfluoroalkoxy moieties (Method B) [11].

As we mentioned above, the reaction of *meso*-tetrakis(pentafluorophenyl)porphyrin **(TF$_{20}$PPH$_2$)** with various fluorine-containing N-, S-, and O-nucleophiles under the action of bases [7] can be also used as a method for introducing polyfluoroalkyl substituents in a porphyrin molecule. At the same time any examples with using of long-chain polyfluoroaliphatic alcohols in these reactions were not reported in literature, therefore we based on the procedure proposed for their non-fluorinated analogues [12].

The substitution reactions were carried out by heating **TF$_{20}$PPH$_2$** in tetrahydrofuran with polyfluoroaliphatic alcohols in the presence of potassium hydroxide or potassium carbonate (see Scheme, Method B). The best results were achieved when $HOCH_2C_6F_{13}$ and $HOCH_2C_8F_{17}$ were used, tetrasubstituted porphyrins **(2g,h)** were isolated in 37% and 47% yields, respectively. The formation of mono-, di- and tri-substituted porphyrins as the by-products of this reaction was observed (according to NMR and mass-spectroscopy), these products make it difficult to isolate and purify of the tetrasubstituted porphyrins. The use of substantial excess of the polyfluoroaliphatic alcohol in this reaction (by the example of $HOCH_2(CF_2)_2H$) and increasing the reaction time didn't result in selective formation of tetrasubstituted porphyrin. However in this case we observed that in the reaction mixtures contained the products of substituting fluorines not only in *para*-positions, but also in *ortho*- and *meta*-positions of pentafluorophenyl moieties.

Experimental

NMR spectra ^{1}H and ^{19}F were recorded on a Bruker AMX-400 and AMX-300 spectrometer with frequency 400.13 and 376.50 MHz at 20°C. Chemical shifts of ^{1}H and ^{19}F were determined relatively to proton signal of solvent (CDCl$_3$) and trifluoroacetic acid (TFA) as external standard.

The ESI (1) and APCI (2) mass-spectra were registered on the Finnigan LCQ Advantage tandem dynamic mass-spectrometer. Nitrogen 10/0 (1) or 70/10 (2) served as a sheath and auxiliary gas. Flow rate acetonitrile 50 μl/min (1) or 350 μl/min (2).The temperature of the heated capillary was 150 °C, the electric potential between the needle and the counter electrode was 4.5 kV (1) or 6.0 kV (2). The samples with the concentration of 10^{-4} mol/l in

acetonitrile solution were introduced into the ion source through the Reodyne injector with the 5 µl loop. Mass-spectra (EI-DIP) were recorded on mass-spectrometer Finnigan Polaris Q, ionization energy – 70 eV, procedure of sample injection – DIP.

Monitoring of the reaction course and purity of products were controlled by Merck Kieselgel 60 F254 plates. For column chromatography silica gel (MN Kieselgel 60) and aluminium oxide (neutral, 100-200 µm) were used. Elemental analysis was performed in the laboratory of elemental analysis INEOS RAS.

Reagents and solvents: tetrahydrofuran (THF), triethylamine (Et_3N) and dimethylformamide (DMF) were dried with help of standard procedures. Chloroform and dichloromethane were purified by distillation over $CaCl_2$ and CaH_2 respectively. Pyrrole and boron trifluoride etherat were distilled before using. Potassium and cesium fluorides were annealed and stored in a sealed container. Polyfluorinated alcohols and pentafluorobenzaldehyde were purchased from "P&M Invest". *Meso*-tetrakis(pentafluorophenyl)porphyrine was synthesized from pyrrole and pentafluorobenzaldehyde according to the literature procedure [13].

4-(1,1-H,H-perfluoropropyl-1-oxy)-2,3,5,6-tetrafluorobenzaldehyde (1a)

To a solution of 1,1-H,H-perfluoropropan-1-ol (3.37 g, 23 mmol) in DMF (40 ml) pentafluorobenzaldehyde (2.65 g, 20 mmol) and KF (2.65 g, 50 mmol) were added. Reaction mixture was stirred at room temperature for 5 h (reaction course was controlled by TLC). Then diethyl ether (70 ml) was added, and mixture was washed with saturated aqueous solution of NH_4Cl (2 x 40 ml) and water (2 x 40 ml). Organic layer was separated and dried over $CaCl_2$. After removing of solvent partially crystallizing yellow viscous liquid was obtained. Product was purified by flash-chromatography (aluminium oxide, hexane-chloroform = 1:1) to afford 2.77 g of light yellow liquid (yield 38%). ^1H NMR ($CDCl_3$, δ, ppm): 4.78 (t, 2H, J=12.08 Hz, OCH_2), 10.20 (s, 1H, CHO). ^{19}F NMR ($CDCl_3$, δ, ppm): -78.85 (s, 2F, C_{Ar}-F^{orto}), -68.04 (s, 2F, C_{Ar}-F^{meta}), -47.35 (s, 2F, CF_2), -6.34 (s, 3F, CF_3). Anal. calcd for $C_{10}H_3F_9O_2$ (%): C, 36.83; H, 0.93; F: 52.43. Found (%): C, 36.48; H: 1.02; F, 52.12.

4-(1,1-H,H-perfluoropentyl-1-oxy)-2,3,5,6-tetrafluorobenzaldehyde (1b)

To a solution of 1,1-H,H-perfluoropentan-1-ol (4.21 g, 17 mmol) in DMF (40 ml) pentafluorobenzaldehyde (3.00 g, 15 mmol) and KF (2.05 g, 30 mmol) were added. Reaction mixture was stirred at room temperature for 5 h (reaction course was controlled by TLC). Then diethyl ether (70 ml) was added, and mixture was washed with saturated aqueous solution of NH_4Cl (2 x 40 ml) and water (2 x 40 ml). Organic layer was separated and dried over $CaCl_2$. After removing of solvent partially crystallizing yellow viscous liquid was obtained. Product was purified by flash-chromatography (aluminium oxide, hexane-chloroform = 1:1) to afford 1.97 g of light yellow liquid (yield 27%). ^1H NMR ($CDCl_3$, δ, ppm): 4.82 (t, 2H, J = 2.72 Hz, OCH_2), 10.23 (s, 1H, CHO). ^{19}F ЯМР ($CDCl_3$, δ, ppm): -78.63 (d, 2F, J = 11.00 Hz, C_{Ar}-F^{orto}), -67.79 (dd, 2F, J_1 = 11.00 Hz, J_2 = 8.25 Hz, C_{Ar}-F^{meta}), -49.03 (s, 2F, CF_2), -46.78 (s, 2F, CF_2), -43.57 (s, 2F, CF_2), -3.73 (s, 3F, CF_3). MS (EI-DIP), m/z: 477.1 $[M+H]^+$, 459.1 $[C_4F_9CFCHOC_6F_4CHF]^+$, 193.2 $[M-C_5F_{11}CH_2]^+$, 151.2 $[CF_3CFHCF_2]^+$.

4-(1,1,9-H,H,H-perfluorononyl-1-oxy)-2,3,5,6-tetrafluorobenzaldehyde (1d)

To a solution of 1,1,9-H,H,H-perfluorononan-1-ol (8.64 g, 20 mmol) in DMF (20 ml) pentafluorobenzaldehyde (3.92 g, 20 mmol) and KF (2.32 g, 40 mmol) were added. Reaction mixture was stirred at room temperature for 10 h (reaction course was controlled by TLC). Then diethyl ether (70 ml) was added, and mixture was washed with saturated

aqueous solution of NH$_4$Cl (2 x 40 ml) and water (2 x 40 ml). Organic layer was separated and dried over CaCl$_2$. After removing of solvent partially crystallizing yellow viscous liquid was obtained. Product was purified by flash-chromatography (silica gel, ethyl acetate) to afford 6.72 g of light yellow solid (yield 55%). ^{1}H NMR (CDCl$_3$, δ, ppm): 4.82 (t, 2H, J_1 = 12.72 Hz, J_2 = 12.47 Hz, OC$\underline{H}_2$), 6.08 (tt, 1H, J_1 = 51.84 Hz, J_2 = 5.14 Hz, CF$_2\underline{H}$), 10.27 (s, 1H, C$\underline{H}$O). ^{19}F NMR (CDCl$_3$, δ, ppm): -78.03 (dd, 2F, J_1 = 11.97 Hz, J_2 = 8.98 Hz, C$_{Ar}$-F^{orto}), -67.10 (dd, 2F, J = 8.98 Hz, C$_{Ar}$-F^{meta}), -59.34 (s, 2F, C$\underline{F}_2$), -51.63 (s, 2F, C$\underline{F}_2$), -45.64 (s, 2F, C$\underline{F}_2$), -45.44 (s, 2F, C$\underline{F}_2$), -44.29 (s, 6F, C$\underline{F}_2$C$\underline{F}_2$C$\underline{F}_2$), -42.92 (s, 2F, C$\underline{F}_2$). MS (EI-DIP), m/z: 608.3 [M]$^+$, 193.2 [M-HCF$_2$C$_7$F$_{14}$CH$_2$]$^+$.

4-(pentafluorophenyloxy)-2,3,5,6-tetrafluorobenzaldehyde (1c)

To a solution of pentafluorophenol (1.84 g, 10 mmol) in DMF (10 ml) pentafluorobenzaldehyde (1.96 g, 10 mmol) and CsF (2.84 g, 20 mmol) were added. Reaction mixture was stirred at room temperature for 2 h. Reaction mixture was poured into water and product was extracted by ethyl acetate. Organic layer was separated and dried over CaCl$_2$. After removing of solvent partially crystallizing yellow viscous liquid was obtained. Product was crystallized from diethyl ether to afford 1.81 g of light yellow solid (yield 50%). ^{1}H NMR (CDCl$_3$, δ, ppm): 10.28 (s, 1H, C$\underline{H}$O). ^{19}F NMR (CDCl$_3$, δ, ppm): -83.26 (t, 2F, J = 20.53 Hz, C$_6\underline{F}_5$O (meta-F)), -80.13 (t, 1F, J = 21.80 Hz, C$_6\underline{F}_5$O (para-F)), -78.12 (d, 2F, J = 10.90 Hz, C$_6\underline{F}_4$CHO (meta-F)), -77.89 (d, 2F, J = 19.62 Hz, C$_6\underline{F}_5$O (orto-F)), -66.52 (dd, 2F, J_1 = 10.90 Hz, J_2 = 8.72 Hz, C$_6\underline{F}_4$CHO (orto-F)). Anal. calcd. for C$_{13}$HF$_9$O$_2$ (%): C, 43.36; H, 0.28. Found (%): C, 43.25; H, 0.28.

2,4,6-tri(1,1-H,H-perfluoroheptyl-1-oxy)-3,5-difluorobenzaldehyde (1e)

To a solution of 1,1-H,H-perfluoroheptan-1-ol (11.55 g, 33 mmol) in DMF (15 ml) pentafluorobenzaldehyde (1.96 g, 10 mmol) and KF (3.83 g, 66 mmol) were added. Reaction mixture was stirred at 60°C for 124 h (reaction course was controlled by TLC) and cooled down to room temperature. Then diethyl ether (50 ml) was added, and mixture was washed with saturated aqueous solution of NH$_4$Cl (2 x 30 ml) and water (2 x 20 ml). Organic layer was separated and dried over CaCl$_2$. After removing of solvent partially crystallizing yellow viscous liquid was obtained. Product was crystallized from dichloromethane to afford give 5.01 g of light-yellow solid (yield 42%). ^{1}H NMR (CDCl$_3$, δ, ppm): 10.32 (s, 1H, C$\underline{H}$O). ^{19}F NMR (CDCl$_3$, δ, ppm): -69.64 (s, 2F, C$_{Ar}$-F^{meta}); -48.62 (s, 6F, C$\underline{F}_2$); -45.65 (s, 6F, CF$_2$); -45.26 (s, 6F, C$\underline{F}_2$); -44.56 (s, 6F, C$\underline{F}_2$); -43.07 (s, 6F, C$\underline{F}_2$); -3.29 (m, 9F, C$\underline{F}_3$).

2,4,6-tri(pentafluorophenyloxy)-3,5-difluorobenzaldehyde (1f)

To a solution of pentafluorphenol (6.07 g, 33 mmol) in DMF (15 ml) pentafluorobenzaldehyde (1.96 g, 10 mmol) and KF (3.83 g, 66 mmol) were added. Reaction mixture was stirred at 60°C for 60 h (reaction course was controlled by TLC) and cooled down to rt. Then diethyl ether (50 ml) was added, and mixture was washed with saturated aqueous solution of NH$_4$Cl (2 x 30 ml) and water (2 x 20 ml). Organic layer was separated and dried over CaCl$_2$. After removing of solvent partially crystallizing yellow viscous liquid was obtained. Product was crystallized from dichloromethane to afford give 1.88 g of light yellow solid (yield 27%). ^{1}H NMR (CDCl$_3$, δ, ppm): 10.48 (s, 1H, C$\underline{H}$O). ^{19}F NMR (CDCl$_3$, δ, ppm): -83.06 (t, 4F, J_1 = 21.36 Hz, J_2 = 18.31 Hz, orto-OC$_6\underline{F}_5$(para-F)); -79.64 (t, 1F, J_1 = 21.36 Hz, J_2 = 24.41 Hz, para-OC$_6\underline{F}_5$(para-F)); -78.56 (d, 4F, J_1 = 18.31 Hz, orto-OC$_6\underline{F}_5$(orto-F)); -77.70 (d, 2F, J_1 = 18.31 Hz, para-OC$_6\underline{F}_5$(orto-F)); -69.53 (s, 2F,

$C_6\underline{F}_2CHO$ (*meta*-F)). MS (EI-DIP), m/z: 520.0 [M-C_6F_5]$^+$, 167.2 [C_6F_5]$^+$.

meso-tetrakis(4-(2,2,3,3,3-pentafluoropropyl-1-oxy)-2,3,5,6-tetrafluorophenyl)porphyrine (2a)

A solution of **1a** (1.2 g, 3.7 mmol) and pyrrole (0.25 g, 3.7 mmol) in dry dichloromethane (400 ml) was bubbled with argon for 30 min, BF_3 x Et_2O (0.14 ml, 1.1 mmol) was added dropwise, and reaction mixture was stirred at room temperature for 21 h. Then DDQ (0.92 g, 4.07 mmol) was added, and reaction mixture was refluxed for 2 h. After addition of Et_3N (0.2 ml) solvent was removed, residue was washed with cold methanol to uncolored solution. Product was purified in 2 steps: 1) flash-chromatography (silica gel, dicloromethane), 2) column chromatography (silica gel, hexane-chloroform = 1:1) to afford 0.32 g of violet powder (yield 23%). ^{1}H NMR (CDCl$_3$, δ, ppm): -2.89 (s, 2H, N$\underline{H}$); 5.02 (t, 8H, J = 12.08 Hz), 8.96 (s, 8H, Pyr-$\underline{H}$). ^{19}F NMR (CDCl$_3$, δ, ppm): -78,55 (m, 8F, C_{Ar}-F^{orto}); -59.44 (m, 8F, C_{Ar}-F^{meta}); -46.55 (s, 8F, C$\underline{F}_2$); -5,52 (s, 12F, C$\underline{F}_3$).MS (APCI), m/z: 1495.8 [M+H]$^+$.

meso-tetrakis(4-(1,1-H,H-perfluoropentyl-1-oxy)-2,3,5,6-tetrafluorophenyl)porphyrine (2b)

A solution of **1b** (1.97 g, 4.43 mmol) and pyrrole (0.29 g, 4.43 mmol) in dry dichloromethane (500 ml) was bubbled with argon for 30 min, BF_3 x Et_2O (0.17 ml, 1.33 mmol) was added dropwise, and reaction mixture was stirred at room temperature for 21 h. Then DDQ (1.11 g, 4.87 mmol) was added, and reaction mixture was refluxed for 2 h. After addition of Et_3N (0.24 ml) the solvent was removed, residue was washed with cold methanol to uncolored solution. Product was purified in 2 steps: 1) flash-chromatography (silica gel, dichloromethane), 2) column chromatography (silica gel, hexane-chloroform = 1:1) to afford 0.23 g of violet powder (yield 21%). ^{1}H NMR (CDCl$_3$, δ, ppm): -2.89 (s, 2H, N$\underline{H}$); 5.07 (t, 8H, J = 12.87 Hz), 8.94 (s, 8H, Pyr-$\underline{H}$). ^{19}F NMR (CDCl$_3$, δ, ppm): -78.51 (m, 8F, C_{Ar}-F^{orto}); -59.44 (m, 8F, C_{Ar}-F^{meta}); -48.45 (s, 8F, C$\underline{F}_2$), -46.20 (s, 8F, C$\underline{F}_2$); -42.93 (s, 8F, C$\underline{F}_2$), -3.04 (s, 12F, C$\underline{F}_3$). MS (APCI), m/z: 1895.4 [M+H]$^+$.

meso-tetrakis(4-(pentafluorophenyloxy)-2,3,5,6-tetrafluorophenyl)porphyrine (2c)

A solution of **1c** (0.72 g, 2 mmol) and pyrrole (0.18 g, 2,7 mmol) in dry dichloromethane (200 ml) was bubbled with argon for 30 min, BF_3 x Et_2O (0.1 ml, 0.8 mmol) was added dropwise, and reaction mixture was stirred at room temperature for 20 h. Then DDQ (0,61 g, 2,7 mmol) was added, and reaction mixture was refluxed for 2 h. After removing of the solvent product was purified by column chromatography (aluminium oxide, petroleum ether – chloroform = 6:1), washed with cold methanol to uncolored solution to afford 150 mg of violet powder (yield 18%). ^{1}H NMR (CDCl$_3$, δ, ppm): -2.88 (s, 2H, N$\underline{H}$); 8.96 (s, 8H, Pyr-$\underline{H}$). ^{19}F NMR (CDCl$_3$, δ, ppm): -83.37 (t, 8F, J = 20.65 Hz, $C_6\underline{F}_5$O (*meta*-F)); -80.95 (t, 4F, J_1 = 22.95 Hz, J_2 = 20.65 Hz, $C_6\underline{F}_5$O (*para*-F)); -78.66 (d, 8F, J = 18.36 Hz, $C_6\underline{F}_4$-porph (*meta*-F)); -78.07 (d, 8F, J = 18.36 Hz, $C_6\underline{F}_5$O (*orto*-F)); -58.80 (d, 8F, J = 13.77 Hz, $C_6\underline{F}_4$-porph (*orto*-F)). Anal. calcd. for $C_{68}H_{10}F_{36}N_4O_4$ (%): C, 50.08; H, 0.62; N, 3.44; F, 41.94. Found (%): C, 50.11; H, 0.49; N, 3.34; F, 41.65.

meso-tetrakis(2,4,6-tri(pentafluorophenyloxy)-3,5-difluorophenyl)porphyrine (2f)

A solution of **1f** (0.68 g, 1 mmol) and pyrrole (0.06 g, 1 mmol) in dry chloroform (100 ml with addition of ethanol – 0.8 vol. %) was bubbled with argon for 30 min, BF_3 x Et_2O (0.05

ml, 0.4 mmol) was added dropwise, and reaction mixture was stirred at room temperature for 8 h. Then DDQ (0.23 g, 1 mmol) was added, and reaction mixture was stirred for 1.5 h. After addition of Et_3N (0.05 ml) the solvent was removed, residue was washed with cold methanol to uncolored solution. Product was purified in 2 steps: 1) flash-chromatography (silica gel, chloroform), 2) column chromatography (silica gel, hexane-chloroform = 5:1) to afford 10 mg of violet powder (yield over 1%). ^{1}H NMR ($CDCl_3$, δ, ppm): -3.44 (s, 2H, N$\underline{H}$); 9.01 (s, 8H, Pyr-$\underline{H}$). ^{19}F NMR ($CDCl_3$, δ, ppm): -85.65 (t, 16F, J_1 = 18.31 Hz, J_2 = 21.36 Hz, *orto*-$OC_6\underline{F}_5$(*meta*-F)); -84.49 (t, 8F, J_1 = 21.36 Hz, J_2 = 18.31 Hz, *para*-$OC_6\underline{F}_5$(*meta*-F)); -83.27 (t, 8F, J_1 = 18.31 Hz, *orto*-$OC_6\underline{F}_5$(*para*-F)); -81.14 (t, 4F, J = 21.36 Hz, *para*-$OC_6\underline{F}_5$(*para*-F)); -79.80 (d, 16F, J = 18.31 Hz, *orto*-$OC_6\underline{F}_5$(*orto*-F)), -78.55 (d, 8F, J = 21.36 Hz, *para*-$OC_6\underline{F}_5$(*orto*-F)); -71.09 (s, 8F, $C_6\underline{F}_2$-porph (*meta*-F)).

meso-tetrakis(4-(1,1-H,H-perfluoroheptyl-1-oxy)-2,3,5,6-tetrafluorophenyl)porphyrine (2g)

To a solution of *meso*-tetrakis(pentafluorophenyl)porphyrine (0.5 g, 0.51 mmol) and 1,1-H,H-perfluoroheptan-1-ol (2.16 g, 6.2 mmol) in THF (200 ml) KOH (2.86 g, 51 mmol) was added. Reaction mixture was refluxed under argon for 4 h. After removing of the solvent residue was poured into water and extracted by diethyl ether. Organic layer was washed with saturated aqueous solution of $NaHCO_3$ (2 x 40 ml) and dried over $CaCl_2$. After removing of the solvent product was purified by column chromatography (silica gel, chloroform) to afford 0.55 g of violet powder (yield 47%). ^{1}H NMR ($CDCl_3$, δ, ppm): -2.86 (s, 2H, N$\underline{H}$), 5.11 (t, 8H, J_1 = 12.79 Hz, J_2 = 12.56 Hz, OC$\underline{H}_2$), 8.97 (s, 8H, Pyr-$\underline{H}$). ^{19}F NMR ($CDCl_3$, δ, ppm): -78.48 (m, 8F, C_{Ar}-F^{orto}), -59.44 (dd, 8F, J_1 = 13.79 Hz, J_2 = 8.19 Hz, C_{Ar}-F^{meta}), -48.38 (m, 8F, C$\underline{F}_2$), -45.14 (m, 8F, C$\underline{F}_2$), -44.33 (m, 8F, C$\underline{F}_2$), -42.73 (m, 8F, C$\underline{F}_2$), -2.98 (t, 12F, J = 9.05 Hz, C$\underline{F}_3$). Anal. calcd. for $C_{72}H_{18}F_{68}N_4O_4$ (%): C, 35.00; H, 0.43; N, 2.00; F, 56.50. Found (%): C, 37.68; H, 0.79; N, 2.44; F, 56.30.

meso-tetrakis(4-(1,1-H,H-perfluorononyl-1-oxy)-2,3,5,6-tetrafluorophenyl)porphyrine (2h)

To a solution of *meso*-tetrakis(pentafluorophenyl)porphyrine (0.1 g, 0.1 mmol) and 1,1-H,H-perfluorononan-1-ol (1.2 g, 0.54 mmol) in THF (50 ml) K_2CO_3 (1.38 g, 10 mmol) was added. Reaction mixture was refluxed under argon for 12 h (reaction course was controlled by TLC). After removing of the solvent residue was poured into water and extracted by diethyl ether. Organic layer was washed with by saturated aqueous solution of $NaHCO_3$ (2 x 40 ml) and dried over $CaCl_2$. After removing of the solvent product was purified in 2 steps: 1) flash-chromatography (aluminium oxide, hexane – chloroform = 1:1), 2) column chromatography (aluminium oxide, gradient elution hexane - chloroform) to afford 95 mg of violet powder (yield 35%). ^{1}H NMR ($CDCl_3$, δ, ppm): -2.89 (s, 2H, N$\underline{H}$), 5.06 (t, 8H, J = 12.72 Hz, OC$\underline{H}_2$), 8.94 (s, 8H, Pyr-$\underline{H}$),. ^{19}F NMR ($CDCl_3$, δ, ppm): -78.47 (m, 8F, C_{Ar}-F^{orto}), -59.43 (m, 8F, C_{Ar}-F^{meta}), -48.34 (s, 8F, C$\underline{F}_2$), -45.17 (s, 8F, C$\underline{F}_2$), -44.92 (s, 8F, C$\underline{F}_2$), -44.07 (s, 24F, C$\underline{F}_2$C$\underline{F}_2$C$\underline{F}_2$), -42.65 (s, 8F, C$\underline{F}_2$), -3.00 (s, 12F, C$\underline{F}_3$). MS (APCl), m/z: 1834.6 [M+H-2$C_8F_{17}CH_2$]$^+$.

References

1. DiMagno, S. G.; Dussault, P. H.; Schultz, J. A. *J. Am. Chem. Soc.* **1996**, *118*, 5312–

5313.

2. Pozzi, G.; Colombani, I.; Miglioli, M.; Montanari, F.; Quici, S. *Tetrahedron* **1997**, *53*, 6145–6162.

3. Nakahara, H.; Liang, W.; Fukuda, K.; Wang, L.; Wada, T.; Sasabe, H. *J. Colloid Interface Sci.* **1998**, *208*, 14–22.

4. Sun, H.; Smirnov, V. V; DiMagno, S. G. *Inorg. Chem.* **2003**, *42*, 6032–6040.

5. Grancho, J. C. P.; Pereira, M. M.; Miguel, M. D. G.; Gonsalves, A. M. R.; Burrows, H. D. *Photochem. Photobiol.* **2002**, *75*, 249–256.

6. Goll, J. G.; Moore, K. T.; Ghosh, A.; Therien, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 8344–8354.

7. Yi, W. Bin; Ma, J. J.; Jiang, L. Q.; Cai, C.; Zhang, W. *J. Fluor. Chem.* **2014**, *157*, 84–105.

8. Gryko, D.; Wyrostek, D.; Nowak-Król, A.; Abramczyk, K.; Rogacki, M. *Synthesis (Stuttg).* **2008**, *2008*, 4028–4032.

9. Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827–836.

10. Lindsey, J.; Wagner, R. *J. Org. Chem.* **1989**, 828–836.

11. Preliminary results of this study have been published in the abstract book - *X. German-Russian-Ukrainian Symposium on Fluorine Chemistry*, Berlin, November 26-28, **2014**, P.19 (Belyaeva, E.; Sigan, A.; Gervits, L.; Chkanikov N.). Subsequently, it turned that at the same time this approach have been investigated by Golf H. R. A. and co-workers and was published in A. *European J. Org. Chem.* **2015**, *2015*, 1548–1568. Reactions of **TF$_{20}$PPH$_2$** with the number of fluorinated alkochols were considired there.

12. Figueira, A. C. B.; de Oliveira, K. T.; Serra, O. A. *Dye. Pigment.* **2011**, *91*, 383–388.

13. Hyun, M. Y.; Jo, Y. D.; Lee, J. H.; Lee, H. G.; Park, H. M.; Hwang, I. H.; Kim, K. B.; Lee, S. J.; Kim, C. *Chem. - A Eur. J.* **2013**, *19*, 1810.

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