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Phenyl Substituted Porphyrins. Part 5. Acylation of Aminophenylporphyrins

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Dedicated to Corresponding member of Russian Academy of Sciences Prof. Oscar I. Koifman on the occasion of his 70th Birthday

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Conditions of acylation of aminotetraphenylporphyrins in the presence of carbodiimides were studied. Optimal reaction conditions were determined and a number of tetraphenylporphyrin amides of various structure were synthesized.

Keywords: Porphyrins, acylation, aminotetraphenylporphyrins, carbodiimides, tetraphenylporphyrin amides.

Фенилзамещенные порфирины. 5. Ацилирование аминофенилпорфиринов

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Посвящается Член-корреспонденту РАН Оскару Иосифовичу Койфману по случаю его 70-летнего юбилея

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Изучены условия ацилирования аминофенилпорфиринов карбоновыми кислотами в присутствии карбодиимидов. Найдены оптимальные условия проведения реакции и синтезирован ряд амидов фенилпорфиринов различной структуры.

Ключевые слова: Порфирины, ацилирование, аминотетрафенилпорфирины, карбодиимиды, амиды тетрафенилпорфиринов.

Introduction

Porphyrins bearing reactive hydroxy and amino substituted phenyl rings in *meso*-positions present a considerable interest for synthetic organic chemistry. Modification of their structure can afford porphyrins with various substituents that can interact with metal atoms in the inner reaction site of the macrocycle. Introduction of long-chain substituents allows to immobilize porphyrins on different carriers and favors the formation of supramolecular nanostructures. Acylation is one of the common methods employed for modification of active substituents.

We have earlier reviewed acylation of hydroxyphenylporphyrins.[1] The current paper focuses on the amino group as the porphyrin modification site. The amide bond, formed as a result of acylation, is stronger and more rigid

compared to the ester bond, which renders the modified porphyrins less prone to hydrolysis.

Many protocols of aminophenylporphyrin acylation can be found in literature. The common acylation agents include various carboxylic acid derivatives: chloroanhydrides,[2-13] anhydrides,[14-19] and carboxylic acids themselves as well.[20-26] In the latter case the common solvents are methylene chloride,[24,26] THF[22,23,25] and chloroform.[20,21] The reaction temperature varies from 0 ºC to ambient temperature.[20-26] It should be noted that when carboxylic acids are employed for acylation, activating agents must be added: *N,N'*-dicyclohexylcarbodiimide,[20,21,24-26] 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDAC)[22,23] or mixtures of 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) with *N*-methylmorpholine.[22] As a catalyst, *N,N*-dimethylaminopyridine (DMAP) is generally used.[21-23,25]

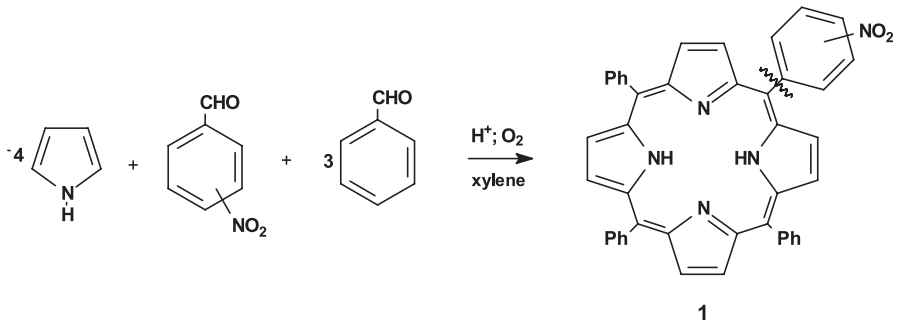
The current paper covers our research on optimal acylation conditions affording maximal yield of acylamidophenylporphyrins.

Results and Discussion

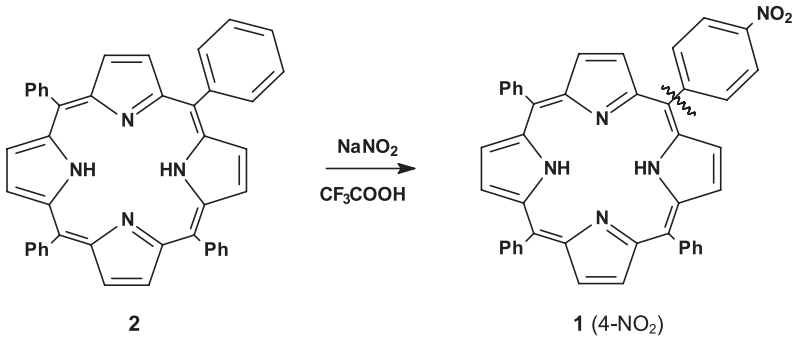
Comparatively available *meso*-aminophenyltriphenylporphyrins **5** and *meso*-aminophenyl-*β*-octaalkylporphyrins **6** (which are closer by structure to natural porphyrins) were used as model compounds.

The synthesis of aminophenylporphyrins **5**, **6** was performed as a two-step procedure. First, nitrophenylporphyrins **1, 4** were obtained (Schemes 1-3); their following reduction by tin(II) chloride in the presence of hydrochloric acid, similarly to the known procedures,[27,28] gave the target products **5**, **6** (Scheme 4).

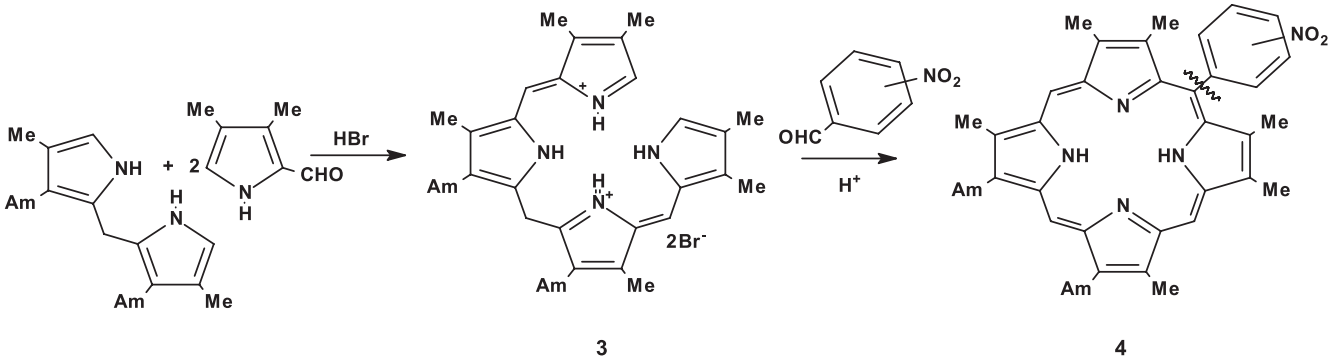
The starting *meso*-nitrophenyltriphenylporphyrins **1** were synthesized by a "mixed aldehyde" condensation of nitrobenzaldehyde isomers and benzaldehyde with pyrrol in a mixture of xylene-chloroacetic acid, similarly to[1], however, as nitroporhyrins possess low polarity, the crude porphyrin mixtures were reduced to aminophenylporphyrins without isolation followed by chromatographic separation from the



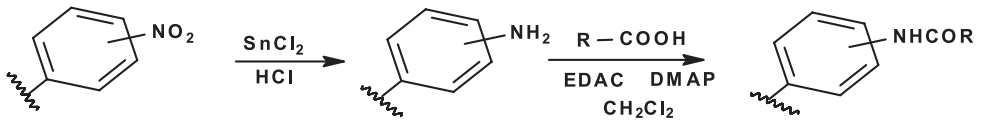
Scheme 1.



Scheme 2.



Scheme 3.



1,4 **5,6** **7,8**

R = $(CH_2)_{10}Br$, $CH_2C_6H_5$, $(CF_2)_7CHF_2$, C_6H_5, 4-$C_6H_4O(CH_2)_{11}CH_3$, 4-$C_6H_4NO_2$, CH_2NHCOO^tBu, $CH[CH_2CH(CH_3)_2]NHCOO^tBu$, $CH[CH(CH_3)CH_2CH_3]NHCOO^tBu$, $CH(CH_2C_6H_5)NHCOO^tBu$.

Scheme 4.

accompanying *meso*-tetraphenylporphyrin **2** (Schemes 1, 4). 5-(4-Nitrophenyl)-10,15,20-triphenylporphyrin (**1**, 4-NO_2) was also obtained by nitration of *meso*-tetraphenylporphyrin **2** (side product of the "mixed aldehyde" condensation) with sodium nitrite in trifluoroacetic acid, similarly to [29,30] (Scheme 2), with subsequent reduction, which afforded significantly increased total yield of aminophenylporphyrin **5** (4-NH_2).

The isomeric 5-nitrophenyl-2,3,7,8,12,18-hexamethyl-13,18-di-*n*-amylporphyrins (**4**) were synthesized via condensation of 4,4'-dimethyl-3,3'-di-*n*-amyldipyrrolylmethane[31] with 2-formyl-3,4-dimethylpyrrole[31] in butanol containing hydrobromic acid with formation of the corresponding biladiene **3** and its further treatment with nitrobenzaldehydes, similarly to[31,32] (Scheme 3).

Acylation of aminophenylporphyrins with EDAC-activated caboxyilic acids in the presence of DMAP was performed in a similar manner to acylation of hydroxyphenylporphyrins[1] (Scheme 4), however the process has its peculiarities. While the formation of esters requires a slight excess of the acid and EDAC (~1.1 eq.) and the reaction time is usually 3 h,[1] the formation of amides requires a double amount of the acid and EDAC (~2.0 eq.) and the reaction time increases considerably (a full day or more). The yield of amides is usually higher than that of esters (for ~15%).

The influence of the nature of acids used for acylation on the reaction time and amide yield was studied. Aliphatic and aromatic carboxylic acids give the same yields but introduction of electron-withdrawing fluorine atoms into the aliphatic chain results in a significant increase of the reaction time and a dramatic decrease of the yield, while using sterically strained α-amino acids results in increased reaction time with the same yield. Moreover, in the two latter cases the amount of the activating agent must be increased.

The position of amino group that is to undergo acylation in the phenyl ring has a strong influence on the yield of the amide products: it decreases from the easily accessible *para*- and *meta*-positions to the hindered *ortho*-position. In the case of **6** (2-NH_2) the reaction does not occur at all. Comparing **5** (4-NH_2) to **6** (4-NH_2), the amide yield is about the same, while **6** (3-NH_2) affords almost twice less amide while the reaction time increases greatly.

Experimental

Electronic absorption spectra were recorded in chloroform on a SPEC SSP-715 scanning spectrophotometer, IR spectral data were obtained on Avatar 360 FT-IR instrument (in KBr pellets), and proton magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker 500 in deuterated chloroform (with TMS as the internal standard). Thin layer chromatography (TLC) was performed on Silufol® plates.

*5-(4'-Aminophenyl)-10,15,20-triphenylporphine (**5** 4-NH_2).* a) To a boiling solution of 14 g (~5%) of chloroacetic acid in 300 ml of xylene isomers mixture a solution of 2.7 g (18 mmol) of 4-nitrobenzaldehyde, 5.4 ml (54 mmol) benzaldehyde and 5.0 ml (72 mmol) of pyrrole in 50 ml of xylene was added dropwise. The reaction mixture was refluxed under argon atmosphere for 0.5 h and then for an additional 1 h in air. The solvent was removed by steam distillation, the residue was filtered, washed with water and dried. The residue was then dissolved in chloroform and subjected to column chromatography on Al_2O_3 (Brockmann grade III) using chloroform as the eluent. The dark-red band was collected, which corresponds to a mixture of porphyrins. Chloroform was evaporated and the remaining mixture was treated with 100 ml of hydrochloric acid containing 10.0 g $SnCl_2{\cdot}2H_2O$ and stirred for 2 h at 65 ºC (water bath). The mixture was then diluted with 150 ml of water, filtered and the precipitate was washed with water, aqueous ammonia, again water and dried at ambient temperature to a constant weight. The precipitate was then dissolved in 50 ml of chloroform and subjected to column chromatography on Al_2O_3 (Brockmann grade III) eluting with chloroform. The dark-red band of the TPP and mono-aminophenylporphyrin was collected. The porphyrins were isolated by a secondary chromatographic separation on Al_2O_3, chloroform as the eluent. The solvent was evaporated and the porphyrins were precipitated with methanol. Yield – 1.7 g (15.0%) (**5** 4-NH_2) and 2.25 g (27.0%) **2**.

b) To a solution of 2.25 g (3.66 mmol) of tetraphenylporphyrin **2** in 40 ml of trifluoroacetic acid 0.5 g (7.25 mmol) of sodium nitrite in 3 ml of water was added. The reaction mixture was stirred for 3 min and poured into 250 ml of water. The precipitate was filtered, washed with water and stirred in 100 ml of hydrochloric acid containing 10.0 g (44.3 mmol, ~4.5-fold excess) of $SnCl_2{\cdot}2H_2O$ for 1 h at 80 ºC, the mixture was then diluted with 100 ml of water, the precipitate was filtered, washed with water, diluted aqueous ammonia and again water, and dried to constant weight. The precipitate was then dissolved in 50 ml of chloroform and subjected to column chromatography on Al_2O_3 (Brockmann grade III) eluting with chloroform. The eluate was evaporated and the porphyrin was precipitated with methanol. Yield – 1.3 g (56.7%) (in terms of **2**). The total yield of the two steps - 3.0 g (26.5%) (in terms of pyrrole). R_f - 0.21 (chloroform). UV-vis λ_{max} (lgε): 648 (3.98); 592 (3.98); 554 (4.18); 517 (4.42); 421 (5.89) IR cm^{-1}: ν_{as}NH 3450; ν_sNH 3330. ^{1}H NMR δ ppm: 8.97 d (2H, J = 3.5 Hz, 3,7-H); 8.84-8.89 m (6H, 2,8,12,13,17,18-H); 8.24 d (6H, ^1J = 6.4 Hz, *o*-H-Ph); 8.02 d (2H, ^2J = 7.8 Hz, 2',6'-H); 7.74-7.83 m (9H, *m,p*-H-Ph); 7.10 d (2H, ^2J = 7.8 Hz, 3',5'-H); 4.05 bs (2H, 4'-NH_2); -2.73 s (2H, NH).

*5-(3'-Aminophenyl)-10,15,20-triphenylporphine (**5** 3-NH_2)* was synthesized analogously to method (a). Yield - 1.8 g (16%) **5** 3-NH_2 and 1.3 g (15.7%) **2**. R_f = 0.32 (chloroform). IR cm^{-1}: ν_{as}NH 3480; ν_sNH 3390. UV-vis λ_{max} (lg ε): 648 (3.73); 590 (3.81); 550 (3.89); 516 (4.28); 419 (5.59). ^{1}H NMR δ ppm: 8.99 d (2H, J = 2.6 Hz, 3,7-H); 8.91 d (2H, J = 2.6 Hz, 2,8-H); 8.89 s (4H, 12,13,17,18-H); 8.27 d (6H, ^1J = 6.6 Hz, *o*-H-Ph); 8.15 d (1H, ^1J = 7.8 Hz, 6'-H); 7.77-7.82 m (9H, *m,p*-H-Ph); 7.58 s (1H, 2'-H); 7.53

t (1H, ^1J = 7.8 Hz, 5'-H); 7.11 d (1H, ^1J = 7.8 Hz, 4'-H); 3.89 bs (2H, NH_2); -2.73 bs (2H, NH).

*5-(2'-Aminophenyl)-10,15,20-triphenylporphine (**5** 2-NH_2)* was synthesized analogously to method (a). Yield – 0.8 g (7%) **5** 2-NH_2 and 1.8 g (21.7%) **2**. R_f - 0.36 (chloroform). IR cm^{-1}: ν_{as}NH 3390; ν_sNH 3300. UV-vis λ_{max} (lg ε): 648 (3.70); 591 (3.77); 551 (3.89); 516 (4.28); 420 (5.70). ^{1}H NMR δ ppm: 8.93 d (2H, J = 4.4 Hz, 3,7-H); 8.84-8.91 m (6H, *β*-H); 8.24 d (6H, ^1J = 6.8 Hz, *o*-H-Ph); 7.91 d (1H, ^2J = 7.6 Hz, 6'-H); 7.75-7.84 m (9H, *m,p*-H-Ph); 7.63 t (1H, ^2J = 7.6 Hz, 4'-H); 7.20 t (1H, ^2J = 7.6 Hz, 5'-H); (1H, ^2J = 7.6 Hz, 3'-H); -2.71 bs (2H, NH).

*5-(4'-Nitrophenyl)-2,3,7,8,12,18-hexamethyl-13,17-di-n-amylporphine (**4**, 4-NO_2)*. To a stirred solution of 1.3 g (4.13 mmol) of 4,4'-dimethyl-3,3'-di-*n*-amyldipyrrolylmethane and 1.02 g (8.27 mmol) of 2-formyl-3,4-dimethylpyrrol in 100 ml of butanol at ambient temperature 2.0 ml (16.6 mmol) of concentrated hydrobromic acid was added (biladiene **3 was** precipitated). After 1 h 1.5 g (9.92 mmol, ~2.5-fold excess) of 4-nitrobenzaldehyde was added. The mixture was refluxed for 4 h, then 0.9 g (8.3 mmol) of *p*-benzoquinone was added and the stirring was continued for 10 min. Butanol was removed by steam distillation, the residue was filtered, washed with water and dried to constant weight. The precipitate was dissolved in 50 ml of methylene chloride and subjected to column chromatography on Al_2O_3 (Brockmann grade II) with methylene chloride as the eluent. The eluate was evaporated and the porphyrin precipitated with methanol. Yield – 0.96 g (35.4%). R_f - 0.51 (benzene). IR cm^{-1}: $\nu_s NO_2$ 1344; $\nu_{as}NO_2$ 1521. UV-vis λ_{max} (lg ε): 624 (3.63); 572 (3.91); 538 (3.95); 504 (4.22); 402 (5.25). ^{1}H NMR δ ppm: 10.19 s (2H, 10.20-H); 9.98 s (1H, 15-H); 8.59 d (2H, J = 8.2 Hz, 2',6'-H-Ar); 8.23 d (2H, J = 8.2 Hz, 3',5'-H-Ar); 4.04 t (4H, ^1J = 7.5 Hz, CH_2-Am); 3.65 s (6H, 12.18-CH_3); 3.54 s (6H, 2,8-CH_3); 2.41 s (6H, 3,7-CH_3); 2.32 qv (4H, ^1J = 7.5 Hz, CH_2-Am); 1.75 qv (4H, ^1J = 7.5 Hz, CH_2-Am); 1.57 sc (4H, ^1J = 7.5 Hz, CH_2-Am); 0.99 t (6H, ^1J = 7.5 Hz, CH_3-Am); -3.19 bs, -3.32 bs (2×1H, NH).

*5-(3'-Nitrophenyl)-2,3,7,8,12,18-hexamethyl-13,17-diamylporphine (**4**, 3-NO_2)* was obtained in a similar manner. Yield – 0.7 g (25.8%). R_f - 0.54 (benzene). IR cm^{-1}: $\nu_s NO_2$ 1346; $\nu_{as}NO_2$ 1531. UV-vis λ_{max} (lg ε): 625 (3.66); 572 (3.91); 539 (3.97); 505 (4.21); 403 (5.24). ^{1}H NMR δ ppm: 10.18 s (2H, 10,20-H); 9.99 s (1H, 15-H); 9.00 s (1H, 2'-H-Ar); 8.70 d (1H, J = 7.8 Hz, 6'-H-Ar); 8.35 d (1H, J = 7.8 Hz, 4'-H-Ar); 7.88 t (1H, J = 7.8 Hz, 5'-H-Ar); 4.04 t (4H, ^1J = 7.5 Hz, CH_2-Am); 3.65 s (6H, 12,18-CH_3); 3.54 s (6H, 2.8-CH_3); 2.41 s (6H, 3.7-CH_3); 2.32 qv (4H, ^1J = 7.5 Hz, CH_2-Am); 1.75 qv (4H, ^1J = 7.5 Hz, CH_2-Am); 1.56 sc (4H, ^1J = 7.5 Hz, CH_2-Am); 0.99 t (6H, ^1J = 7.5 Hz, CH_3-Am); -3.17 bs, -3.31 bs (2×1H, NH).

*5-(2'-Nitrophenyl)-2,3,7,8,12,18-hexamethyl-13,17-diamylporphine (**4**, 2-NO_2)* was obtained in a similar manner. Yield – 0.3 g (11.1%). R_f - 0.32 (benzene). IR cm^{-1}: $\nu_s NO_2$ 1401; $\nu_{as}NO_2$ 1525. UV-vis λ_{max} (lg ε): 625 (3.60); 573 (3.86); 536 (3.92); 504 (4.18); 402 (5.23). ^{1}H NMR δ ppm: 10.16 s (2H, 10,20-H); 9.96 s (1H, 15-H); 9.41 d (1H, J = 7.7 Hz, 6'-H-Ar); 8.06 d (1H, J = 7.7 Hz, 3'-H-Ar); 7.97 t (1H, J = 7.7 Hz, 4'-H-Ar); 7.92 t (1H, J = 7.7 Hz, 5'-H-Ar); 4.03 t (4H, ^1J = 7.6 Hz, CH_2-Am); 3.63 s (6H, 12,18-CH_3); 3.54 s (6H, 2,8-CH_3); 2.46 s (6H, 3,7-CH_3); 2.31 qv (4H, ^1J = 7.6 Hz, CH_2-Am); 1.74 qv (4H, ^1J = 7.6 Hz, CH_2-Am); 1.55 sc (4H, ^1J = 7.6 Hz, CH_2-Am); 0.98 t (6H, ^1J = 7.6 Hz, CH_3-Am); -3.11 bs, -3.27 bs (2×1H, NH).

*5-(4'-Aminophenyl)-2,3,7,8,12,18-hexamethyl-13,17-di-n-amylpoprhine (**6**, 4-NH_2)*. A stirred mixture of 1.0 g (1.52 mmol) of 5-(4'-nitrophenyl)-2,3,7,8,12,18-hexamethyl-13,17-di-*n*-amylporphine, 2.5 g (11.1 mmol) of $SnCl_2{\cdot}2H_2O$, 4 ml (~44.8 mmol) of concentrated hydrochloric acid in 100 ml of methanol was refluxed for 1 h. Then a solution of 5.0 g (89.1 mmol) KOH in 50 ml of water was introduced. After cooling of the mixture the porphyrin precipitate was filtered, washed with water and dried. The porphyrin was dissolved in 50 ml of methylene chloride and chomatographically purified on silica (L 100/250), methylene chloride-methanol (10:1) used as the eluent. The eluate was evaporated and the porphyrin was precipitated with methanol. Yield – 0.9 g (94.6%). R_f - 0.75 (benzene-methanol 10:1). UV-vis λ_{max} (lg ε): 624 (3.53); 571 (3.89); 537 (3.89); 504 (4.22); 405 (5.32). ^{1}H NMR δ ppm: 10.16 s (2H, 10,20-H); 9.95 s (1H, 15-H); 7.79 d (2H, J = 8.1 Hz, 2',6'-H); 7.09 d (2H, J = 8.1 Hz, 3',5'-H); 4.05 t (4H, ^1J = 7.6 Hz, CH_2-Am); 3.65 s (6H, 12,18-CH_3); 3.56 s (6H, 2,8-CH_3); 2.60 s (6H, 3,7-CH_3); 2.32 qv (4H, ^1J = 7.6 Hz, CH_2-Am); 1.75 qv (4H, ^1J = 7.6 Hz, CH_2-Am); 1.57 sc (4H, ^1J = 7.6 Hz, CH_2-Am); 0.99 t (6H, ^1J = 7.6 Hz, CH_3-Am); -3.20 bs (1H, NH); -3.27 bs (1H, NH).

*5-(3'-Aminophenyl)-2,3,7,8,12,18-hexamethyl-13,17-di-n-amylporphine (**6**, 3-NH_2)* was obtained in a similar manner. Yield – 0.63 g (94.1%). R_f - 0.78 (benzene-methanol 10:1). UV-vis λ_{max} (lg ε): 623 (3.58); 571 (3.92); 537 (3.94); 503 (4.25); 404 (5.32). ^{1}H NMR δ ppm: 10.17 s (2H, 10,20-H); 9.96 s (1H, 15-H); 7.53 t (1H, J = 7.5 Hz, 5'-H); 7.50 d (1H, J = 7.5 Hz, 6'-H); 7.36 s (1H, 2'-H); 7.14 d (1H, J = 7.5 Hz, 4'-H); 4.05 t (4H, ^1J = 7.5 Hz, CH_2-Am); 3.89 bs (2H, NH_2); 3.65 s (6H, 12,18-CH_3); 3.56 s (6H, 2.8-CH_3); 2.64 s (6H, 3,7-CH_3); 2.32 qv (4H, ^1J = 7.5 Hz, CH_2-Am); 1.75 qv (4H, ^1J = 7.5 Hz, CH_2-Am); 1.57 sc (4H, ^1J = 7.5 Hz, CH_2-Am); 0.99 t (6H, ^1J = 7.5 Hz, CH_3-Am); -3.22 bs (1H, NH); -3.30 bs (1H, NH).

*5-(2'-Aminophenyl)-2,3,7,8,12,18-hexamethyl-13,17-di-n-amylporphine (**6**, 2-NH_2)*. A stirred mixture of 0.3 g (0.45 mmol) of 5-(2'-nitrophenyl)-2,3,7,8,12,18-hexamethyl-13,17-di-*n*-amylporphine, 2.0 g (8.8 mmol) of $SnCl_2{\cdot}2H_2O$, 1.5 ml (~16.7 mmol) of concentrated hydrochloric acid in 50 ml of methanol was refluxed for 3 h. Then a solution of 2.0 g (35.7 mmol) of KOH in 50 ml of water was introduced. After cooling of the mixture the porphyrin precipitate was filtered, washed with water and dried. The porphyrin was dissolved in 50 ml of methylene chloride and chomatographically purified on silica (L 100/250), methylene chloride-methanol (10:1) used as the eluent. The eluate was evaporated and the porphyrin was precipitated with methanol. Yield – 0.27 g (95.9%). R_f - 0.17 (benzene); 0.85 (benzene-methanol 10:1). UV-vis λ_{max} (lg ε): 623 (3.57); 571 (3.87); 537 (3.92); 503 (4.20); 404 (5.29). ^{1}H NMR δ ppm: 10.18 s (2H, 10,20-H); 9.99 s (1H, 15-H); 7.64 d (1H, J = 7.7 Hz, 6'-H); 7.62 t (1H, J = 7.7 Hz, 4'-H); 7.20 t (1H, J = 7.7 Hz, 5'-H); 7.13 d (1H, J = 7.7 Hz, 3'-H); 4.06 t (4H, ^1J = 7.6 Hz, CH_2-Am); 3.66 s (6H, 12,18-CH_3); 3.58 s (6H, 2.8-CH_3); 2.70 s (6H, 3,7-CH_3); 2.32 qv (4H, ^1J = 7.6 Hz, CH_2-Am); 1.75 qv (4H, ^1J = 7.6 Hz, CH_2-Am); 1.55 m (4H, CH_2-Am); 0.98 t (6H, ^1J = 7.6 Hz, CH_3-Am); -3.16 bs (1H, NH); -3.32 bs (1H, NH).

*5-[4'-(10"-Bromodecylcarbonylamido)phenyl]-10,15,20-triphenylporphine (**7**, 4-NHCOR, R = $(CH_2)_{10}$Br)*. A mixture of 50 mg (0.080 mmol) of **5** (4-NH_2), 46 mg (0.173 mmol) of 11-bromouncanoic acid, 12 mg (0.095 mmol) of DMAP and 33 mg (0.170 mmol) of EDAC in 15 ml of anhydrous methylene chloride was magnetically stirred for 1.5 with cooling in an ice bath and then at ambient temperature until the completion of the reaction according to TLC (1 day). The resulting solution was subjected to column chromatography on silica (L 100/250), methylene chloride as the eluent. The eluate was evaporated and the porphyrin was precipitated with methanol. Yield – 60 mg (86.0%). R_f = 0.1 (benzene); 0.33 (benzene-methanol 20:1). IR cm^{-1}: νCONH 1596. UV-vis λ_{max} (lg ε): 646 (3.88); 591 (3.95); 552 (4.08); 516 (4.34); 419 (5.71). ^{1}H NMR δ ppm: 8.84-8.92 m (8H, *β*-H); 8.23 d (6H, J = 6.6 Hz, *o*-H-Ph); 8.19 d (2H, ^1J = 7.9 Hz, 2',6'-H); 7.94 d (2H, ^1J = 7.9 Hz, 3',5'-H); 7.87 bs (1H, 4'-NHCO); 7.75-7.82 m (9H, *m,p*-H-Ph); 3.46 t (2H, ^2J = 6.7 Hz, CH_2CO), 2.56 t (2H, ^3J = 7.3 Hz, CH_2Br); 1.86-1.95 m (4H, CH_2); 1.55-1.61 m (12H, CH_2); -2.77 s (2H, NH).

*5-[4'-(Phenylacylamido)phenyl]-10,15,20-triphenyolporphine (**7**, 4-NHCOR, R = $CH_2C_6H_5$)*. The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}$Br) using 24 mg (0.174 mmol) of phenylacetic acid. Yield 45.4 mg (76.4%). R_f - 0.07 (benzene). IR cm^{-1}: νNHCO 1652. UV-vis λ_{max} (lg ε): 646 (3.78); 591 (3.87); 554 (4.01); 516 (4.31); 420 (5.70). ^{1}H NMR δ ppm:

8.85-8.90 m (8H, *β*-H); 8.23-8.27 m (6H, *o*-H-Ph); 8.16 d (2H, *J* = 8.1 Hz, 2',6'-H); 7.84 d (2H, *J* = 8.1 Hz, 3',5'-H); 7.81 s (1H, NHCO); 7.75-7.82 m (3H, *m,p*-H-Ph'); 7.42-7.47 m (2H, o-H-Ph'); 3.93 s (2H, CH_2); -2.75 bs (2H, NH).

5-[4'-(8"-H-Perfluorooctylcarbonylamido)phenyl]-10,15,20-triphenylporphine (7, 4-NHCOR, R = $(CF_2)_7CHF_2$). The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}Br$), using 237 mg (0.540 mmol) of 9'-*H*-perfluorononaoic acid, 21 mg (0.174 mmol) of DMAP and 104 mg (0.547 mmol) of EDAC. The reaction time was 6 days. Yield – 24.4 mg (29.1%). R_f - 0.60 (benzene). IR cm^{-1}: νCONH 1627. UV-vis λ_{max} (lg ε): 646 (3.78); 591 (3.88); 551 (4.01); 516 (4.31); 419 (5.70). ^{1}H NMR δ ppm: 8.84-8.91 m (8H, *β*-H); 8.31 d (2H, *J* = 8.3 Hz, 2',6'-H); 8.20 bs (1H, NHCO); 8.24 d (6H, ^1J = 6.8 Hz, *o*-H-Ph); 8.01 d (2H, *J* = 8.3 Hz, 3',5'-H); 7.76-7.84 m (9H, *m,p*-H-Ph); 6.12 tt (1H, ^2J = 51.9 Hz, ^3J = 5.0 Hz, CHF_2); -2.75 s (2H, NH).

5-[4'-(Benzoylamido)phenyl]-10,15,20-triphenylporphine (7, 4-NHCOR, R = C_6H_5). The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}Br$), using 21 mg (0.174 mmol) of benzoic acid. Yield 45.1 mg (77.6%). R_f - 0.09 (benzene). IR cm^{-1}: νNHCO 1653. UV-vis λ_{max} (lg ε): 648 (3.84); 592 (3.90); 554 (4.09); 517 (4.34); 420 (5.69). ^{1}H NMR δ ppm: 8.82-9.01 m (8H, *β*-H); 8.21-8.31 m (6H, *o*-H-Ph); 8.19 s (1H, NHCO); 8.02 d (2H, *J* = 7.7 Hz, 2',6'-H); 8.05-8.11 m (2H, *o*-H-Ph'); 7.74-7.85 m (9H, *m,p*-H-Ph); 7.56-7.70 m (3H, *m,p*-H-Ph'); 7.08 d (2H, *J* = 7.7 Hz, 3',5'-H); -2.74 bs (2H, NH).

5-[4'-(Dodecyloxyphenylcarbonylamido)phenyl]-10,15,20-triphenylporphine (7, 4-NHCOR, R = 4-$C_6H_4O(CH_2)_{11}CH_3$). The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}Br$), using 53 mg (0.174 mmol) of 4-dodecyloxybenzoic acid, 18 mg (0.144 mol) of DMAP and 96 mg (0.502 mmol) of EDAC. The reaction time was 6 days. Yield – 62.1 mg (85.2%). R_f - 0.21 (benzene). IR cm^{-1}: νNHCO 1606. UV-vis λ_{max} (lg ε): 647 (3.91); 591 (3.96); 554 (4.10); 517 (4.35); 420 (5.71). ^{1}H NMR δ ppm: 8.85-9.00 m (8H, *β*-H); 8.21-8.32 m (8H, 2',6'-H+*o*-H-Ph); 8.13 s (1H, NHCO); 8.06 d (2H, *J* = 7.9 Hz, 3',5'-H); 8.02 d (2H, ^1J = 8.3 Hz, 2",6"-H); 7.75-7.85 m (9H, *m,p*-H-Ph); 7.07 d (2H, ^1J = 8.3 Hz, 3",5"-H); 4.07 t (2H, ^2J = 6.9 Hz, OCH_2); 1.86 qv (2H, ^2J = 6.9 Hz, CH_2); 1.52 qv (2H, ^2J = 6.9 Hz, CH_2); 1.46-1.26 m (16H, CH_2); 0.94 t (3H, ^2J = 6.9 Hz, CH_3); -2.72 bs (2H, NH).

5-[4'-(Nitrophenylcarbonylamido)phenyl]-10,15,20-triphenylpoprhine (7, 4-NHCOR, R = 4-$C_6H_4NO_2$). The compound was obtained similar to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}Br$), using 29 mg (0.175 mmol) of 4-nitrobenzoic acid, 15 mg (0.122 mmol) of DMAP and 81 mg (0.422 mmol) of EDAC. The reaction time was 4 days. Yield – 40.1 mg (64.6%). R_f - 0.83 (benzene-methanol 10:1). IR cm^{-1}: νNHCO 1639; $\nu_s NO_2$ 1347; $\nu_{as} NO_2$ 1523. UV-vis λ_{max} (lg ε): 646 (3.84); 591 (3.92); 552 (4.07); 516 (4.33); 420 (5.68). ^{1}H NMR δ ppm: 8.85-8.97 m (8H, *β*-H); 8.33 d (2H, *J* = 8.1 Hz, 2',6'-H); 8.21-8.30 m (8H, 3",5"-H+*o*-H-Ph); 8.09 d (2H, ^1J = 8.2 Hz, 2",6"-H); 8.00 d (2H, *J* = 8.1 Hz, 3',5'-H); 7.75-7.86 m (9H, *m,p*-H-Ph); -2.73 bs (2H, NH).

5-[4'-(N-tert-Butyloxycarbonylglycylamido)phenyl]-10,15,20-triphenylporphyrin (7, 4-NHCOR, R = CH_2NHCOO^tBu). The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}Br$), using 30 mg (0.172 mmol) of *N-tert*-butoxycarbonylglycine, 11 mg (0.086 mmol) of DMAP and 33 mg (0.170 mmol) of EDAC. Yield – 54.2 mg (85.7%). R_f - 0.18 (benzene-methanol 10:1). IR cm^{-1}: νCONH 1694. UV-vis λ_{max} (lg ε): 646 (3.77); 590 (3.87); 551 (4.03); 516 (4.31); 419 (5.70). ^{1}H NMR δ ppm: 8.83-8.93 m (8H, *β*-H); 8.56 bs (1H, NHCO); 8.19-8.27 m (2+6H, 2',6'-H+*o*-H-Ph); 7.94 d (2H, *J* = 7.8 Hz, 3',5'-H-Ar); 7.73-7.83 m (9H, *m,p*-H-Ph); 5.38 bs (1H, NHCO); 4.12 d (2H, ^1J = 5.5 Hz, CH_2-Gly); 1.60 s (9H, ^{t}Bu); -2.75 bs (2H, NH).

5-[4'-(N-tert-Butyloxycarbonyl-L-leucylamido)phenyl]-10,15,20-triphenylporphyrin (7, 4-NHCOR, R = $CH[CH_2CH(CH_3)_2]NHCOO^tBu$). The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}Br$), using 40 mg (0.171 mmol) of *N-tert*-butyloxycarbonyl-*L*-leucine, 10 mg (0.085 mmol) of DMAP and 130 mg (0.684 mmol) of EDAC. The reaction time was 3 days. Yield – 50 mg (74.7%). R_f - 0.79 (benzene-methanol 10:1). IR cm^{-1}: νCONH 1640. UV-vis λ_{max} (lg ε): 648 (3.87); 591 (3.88); 552 (4.04); 517 (4.30); 420 (5.68). ^{1}H NMR δ ppm: 8.80-8.93 m (8H, *β*-H); 8.74 bs (1H, NH); 8.23 d (2H, *J* = 7.3 Hz, 2',6'-H-Ar); 8.20 d (6H, ^1J = 7.8 Hz, *o*-H-Ph); 7.98 d (2H, *J* = 7.3 Hz, 3',5'-H-Ar); 7.66-7.82 m (9H, *m,p*-H-Ph); 5.07 bs (1H, NH); 4.45 bs (1H, CH-Leu); 1.96-2.04 m, 1.86-1.96 m (2×1H, CH_2-Leu); 1.59 s (9H, H-^{t}Bu); 1.11 t (6H, ^2J = 6.6 Hz, CH_3-Leu); -2.75 bs (2H, NH).

5-[4'-(N-tert-Butyloxycarbonyl-D-leucylamido)phenyl]-10,15,20-triphenylporphyrin (7, 4-NHCOR, R = $CH(CH_2CH(CH_3)_2)NHCOO^tBu$). The compound was obtained similar to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}Br$), using 40 mg (0.171 mmol) of *N-tert*-butyloxycarbonyl-*D*-leucine, 11 mg (0.09 mmol) of DMAP and 131 mg (0.686 mmol) of EDAC. The reaction time was 3 days. Yield – 47 mg (69.9%). R_f - 0.79 (benzene-methanol 10:1). IR cm^{-1}: νCONH 1634. UV-vis λ_{max} (lg ε): 647 (3.86); 592 (3.89); 554 (4.03); 516 (4.31); 420 (5.69). ^{1}H NMR δ ppm: 8.80-8.93 m (8H, *β*-H); 8.77 bs (1H, NH); 8.23 d (2H, *J* = 7.4 Hz, 2',6'-H-Ar); 8.15-8.23 m (6H, *o*-H-Ph); 7.98 d (2H, *J* = 7.4 Hz, 3',5'-H-Ar); 7.68-7.83 m (9H, *m,p*-H-Ph); 5.09 bs (1H, NH); 4.46 bs (1H, CH-Leu); 1.96-2.04 m, 1.87-1.96 m (2×1H, CH_2-Leu); 1.59 s (9H, H-^{t}Bu); 1.11 t (6H, ^2J = 6.5 Hz, CH_3-Leu); -2.75 bs (2H, NH).

5-[4'-(*N-tert-Butyloxycarbonyl-L-isoleucylamido)phenyl]-10,15,20-triphenylporphine (7, 4-NHCOR, R = $CH[CH(CH_3)CH_2CH_3]NHCOO^tBu$).* The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}Br$), using 40 mg (0.171 mmol) of *N-tert*-butyloxycarbonyl-*L*-isoleucine, 11 mg (0.09 mmol) of DMAP and 99 mg (0.517 mmol) of EDAC. The reaction time was 3 days. Yield – 48 mg (71.8%). R_f - 0.58 (benzene-methanol 10:1). IR cm^{-1}: νCONH 1640. UV-vis λ_{max} (lg ε): 648 (3.85); 592 (3.87); 552 (4.04); 517 (4.31); 420 (5.70). ^{1}H NMR δ ppm: 8.80-8.92 m (8H, *β*-H); 8.44 bs (1H, NH); 8.24 d (2H, *J* = 7.4 Hz, 2',6'-H-Ar); 8.15-8.23 m (6H, *o*-H-Ph); 7.98 d (2H, *J* = 7.4 Hz, 3',5'-H-Ar); 7.68-7.82 m (9H, *m,p*-H-Ph); 5.26 bs (1H, NH); 4.28 t (1H, ^1J = 7.5 Hz, CH-Ile); 1.77 bs (1H, CH-Ile); 1.58 s (9H, ^{t}Bu); 1.30-1.41 m (2H, CH_2-Ile); 1.20 d (3H, ^2J = 6.7 Hz, CH_3-Ile); 1.08 t (3H, ^3J = 7.4 Hz, CH_3); -2.75 bs (2H, NH).

5-[4'-(N-tert-Butyloxycarbonyl-L-phenylalanylamido)phenyl]-10,15,20-triphenylporphine (7, 4-NHCOR, R = $CH(CH_2C_6H_5)NHCOO^tBu$). The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}Br$), using 46 mg (0.173 mmol) of *N-tert*-butyloxycarbonyl-*L*-phenylalanine, 11 mg (0.09 mmol) of DMAP and 97 mg (0.508 mmol) of EDAC. The reaction time was 3 days. Yield – 57 mg (82.5%). R_f - 0.63 (benzene-methanol 10:1). IR cm^{-1}: νCONH 1640. UV-vis λ_{max} (lg ε): 648 (3.82); 591 (3.84); 554 (3.99); 517 (4.27); 420 (5.66). ^{1}H NMR δ ppm: 8.83-8.92 m (8H, *β*-H); 8.20-8.27 m (6H, *o*-H-Ph); 8.18 d (2H, *J* = 8.3 Hz, 2',6'-H-Ar); 8.12 bs (1H, NH); 7.81 d (2H, *J* = 8.3 Hz, 3',5'-H-Ar); 7.72-7.80 m (9H, *m,p*-H-Ph); 7.35-7.48 m (5H, Ph-Phe); 5.28 bs (1H, NH); 4.68 bs (1H, CH-Phe); 3.33 d (2H, ^1J = 6.0 Hz, CH_2-Phe); 1.55 s (9H, ^{t}Bu) -2.72 bs (2H, NH).

5-[3'-(10"-Bromodecylcarbonylamido)phenyl]-10,15,20-triphenylporphine (7, 3-NHCOR, R = $(CH_2)_{10}Br$). The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}Br$), using **5** (3-NH_2). Yield – 54.6 mg (78,5%). R_f = 0.19 (benzene). IR cm^{-1}: νCONH 1638. UV-vis λ_{max} (lg ε): 648 (3.85); 591 (3.89); 551 (4.00); 516 (4.32); 419 (5.69). ^{1}H NMR δ ppm: 8.91 s (8H, *β*-H); 8.27 d (6H, *J* = 5.9 Hz, *o*-H-Ph); 8.21 s (1H, 2'-H); 8.15 d (1H, ^1J = 7.1 Hz, 6'-H); 8.00 d (1H, ^1J = 7.1 Hz, 4'-H); 7.75-7.85 m (9H, *m,p*-H); 7.65-7.75 m (1H, 5'-H); 7.41 s (1H, NHCO); 3.39 t (2H, ^2J = 6.9 Hz, CH_2CO); 2.27-2.36 m (2H, CH_2Br); 1.83 qv (2H, ^2J = 6.9 Hz, CH_2); 1.68-1.76 m (2H, CH_2); 1.38-1.44 m (2H, CH_2); 1.26-1.32 m (10H, CH_2); -2.72 bs (2H, NH).

5-[3'-(8"-H-Perfluorooctylcarbonylamido)phenyl]-10,15,20-triphenylporphine (7, 3-NHCOR, R = $(CF_2)_7CHF_2$). The compound was obtained similarly to porphyrin **7** (4-NHCOR, R =

$(CH_2)_{10}Br$), using **5** (3-NH_2) and 157 mg (0.352 mmol) of 9'-*H*-perfluorononaoic acid, 23 mg (0.187 mmol) of DMAP and 50 mg (0.430 mmol) of EDAC. The reaction time was 6 days. Yield – 36.8 mg (44.0%). R_f = 0.69 (benzene). IR cm^{-1}: νCONH, 1630. UV-vis λ_{max} (lg ε): 648 (3.89); 591 (3.92); 550 (4.03); 516 (4.33); 419 (5.69). ^{1}H NMR δ ppm: 8.83-8.96 m (8H, *β*-H); 8.33 s (1H, 2'-H); 8.25 d (6H, *J* = 6.8 Hz, *o*-H-Ph); 8.19 bs (1H, NHCO); 8.15 d (1H, J^1 = 7.6 Hz, 6'-H); 7.75-7.89 m (13H, *m,p*-H-Ph, 5'-H); 7.58 d (1H, J^1 = 7.6 Hz, 4'-H); 6.07 tt (1H, J^2 = 5.0 Hz, J^3 = 51.9 Hz, CHF_2); -2.77 s (2H, NH).

5-[3'-(4''-Dodecyloxyphenylcarbonylamido)phenyl]-10,15,20-triphenylporphine (7, 3-NHCOR, R = 4-$C_6H_4O(CH_2)_{11}CH_3$). The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}Br$), using **5** (3-NH_2) and 54 mg (0.175 mmol) of 4-dodecyloxybenzoic acid, 6 mg (0.05 mmol) of DMAP and 50 mg (0.261 mmol) of EDAC. The reaction time was 6 days. Yield – 10 mg (13.5%). R_f = 0.28 (benzene). IR cm^{-1}: νCONH 1633. UV-vis λ_{max} (lg ε): 648 (3.85); 590 (3.89); 551 (4.00); 516 (4.32); 419 (5.70). ^{1}H NMR δ ppm: 8.84-8.98 m (8H, *β*-H); 8.30 bs (1H, NHCO); 8.25 d (6H, *J* = 6.0 Hz, *o*-H-Ph); 8.12 d (1H, ^1J = 7.3 Hz, 6'-H); 8.03 s (1H, 2'-H); 7.88 d (2H, ^2J = 8.7 Hz, 2'',6''-H); 7.74-7.83 m (1+9H, 5'-H+*m,p*-H-Ph); 7.58 d (1H, ^1J = 7.3 Hz, 4'-H); 6.94 d (2H, ^2J = 8.7 Hz, 3'',5''-H); 3.98 t (2H, ^3J = 7.0 Hz, OCH_2); 1.79 qv (2H, ^3J = 7.0 Hz, CH_2); 1.46 qv (2H, ^3J = 7.0 Hz, CH_2); 1.24-1.39 m (16H, CH_2), 0.90 t (3H, ^3J = 7.0 Hz, CH_3); -2.75 bs (2H, NH).

5-[3'-(N-tert-Butyloxycarbonyl-L-leucylamido)phenyl]-10,15,20-triphenylporphine (7, 3-NHCOR, R = $CH(CH_2CH(CH_3)_2)NHCOO^tBu$). The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}Br$), using **5** (3-NH_2) and 59 mg (0.256 mmol) of *N-tert*-butyloxycarbonyl-*L*-leucine, 6 mg (0.050 mmol) of DMAP and 49 mg (0.257 mmol) of EDAC. The reaction time was 7 days. Yield – 40.8 mg (61.2%). R_f = 0.09 (benzene). IR cm^{-1}: νCONH 1676. UV-vis λ_{max} (lg ε): 647 (3.83); 590 (3.88); 551 (3.99); 516 (4.31); 419 (5.69). ^{1}H NMR δ ppm: 8.84-8.96 m (8H, *β*-H); 8.81 bs (1H, NHCO); 8.36 s (1H, 2'-H); 8.20-8.28 m (6H, *o*-H-Ph); 8.12 d (1H, *J* = 7.3 Hz, 6'-H); 7.98 d (1H, *J* = 7.3 Hz, 4'-H); 7.72-7.83 m (9H, *m,p*-H-Ph); 7.69 t (1H, *J* = 7.3 Hz, 5'-H); 5.07 bs (1H, NHCOO); 4.42 bs (1H, CH-Leu); 1.83-1.90 m, 1.74-1.83 m (2×1H, CH_2-Leu); 1.42 s (9H, ^{t}Bu); 0.98 t (6H, ^1J = 6.2 Hz, CH_3-Leu); -2.74 bs (2H, NH).

5-[2'-(10''-Bromodecylcarbonylamido)phenyl]-10,15,20-triphenylporphine (7, 2-NHCOR, R = $(CH_2)_{10}Br$). The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}Br$), using **5** (2-NH_2) under reflux for 4 days. Yield – 15 mg (16.7%). R_f = 0.2 (benzene). IR cm^{-1}: νCONH 1633. UV-vis λ_{max} (lg ε): 650 (3.88); 590 (3.84); 549 (3.93); 516 (4.25); 419 (5.56). ^{1}H NMR δ ppm: 8.86-8.94 m (6H, *β*-H); 8.80 d (2H, *J* = 4.6 Hz, *β*-H); 8.25 d (1H, J^1 = 7.2 Hz, 6'-H); 8.23 d (6H, J^2 = 7.5 Hz, *o*-H-Ph); 8.06 d (1H, J^1 = 7.2 Hz, 3'-H); 7.76-7.87 m (10H, 5'-H, *m,p*-H-Ph); 7.52 t (1H, 4'-H); 6.80 s (1H, NHCO); 3.39 t (2H, J^3 = 7.2 Hz, CH_2Br); 1.55 qv (2H, J^3 = 7.2 Hz, CH_2); 1.34 t (2H, J^3 = 7.2 Hz, $COCH_2$); 1.12 qv (2H, J^3 = 7.2 Hz, CH_2); 0.86 qv (2H, J^3 = 7.2 Hz, CH_2); 0.78 qv (2H, J^3 = 7.2 Hz, CH_2); 0.73 qv (2H, J^3 = 7.2 Hz, CH_2); 0.61 qv (2H, J^3 = 7.2 Hz, CH_2); 0.46-0.55 m (4H, CH_2); -2.72 bs (2H, NH).

5-(2'-Phenylacetamidophenyl)-10,15,20-triphenylporphine (7, 2-NHCOR, R = $CH_2C_6H_5$). The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}Br$), using **5** (2-NH_2) and 24 mg (0.176 mmol) of phenylacetic acid, 12 mg (0.098 mmol) of DMAP and 64 mg (0.334 mmol) of EDAC under 2 day reflux. Yield – 11.6 mg (19.5%). R_f = 0.17 (benzene). IR cm^{-1}: νCONH 1632. UV-vis λ_{max} (lg ε): 651 (4.02); 592 (3.90); 548 (4.00); 516 (4.33); 419 (5.64). ^{1}H NMR δ ppm: 8.93 s (4H, 12,13,17,18-H); 8.79 d (2H, *J* = 4.8 Hz, 2,8-H); 8.77 d (1H, ^1J = 7.5 Hz, 6'-H); 8.57 d (2H, *J* = 4.8 Hz, 3,7-H); 8.20-8.34 m (6H, *o*-H-Ph); 7.98 d (1H, ^1J = 7.5 Hz, 3'-H); 7.74-7.90 m (10H, 4'-H+*m,p*-H-Ph); 7.48 t (1H, ^1J = 7.5 Hz, 5'-H); 6.69 s (1H, NHCO); 5.32 d (2H, ^2J = 7.6 Hz, *o*-H-Ph'); 4.03 t (2H, ^2J = 7.6 Hz, *m*-H-Ph'); 3.32 t (1H, ^2J = 7.6 Hz, *p*-H-Ph'); 2.68 s (2H, CH_2); -2.85 bs (2H, NH).

*5-[4'-(10''-Bromodecylcarbonylamido)phenyl]-2,3,7,8,12,18-hexamethyl-13,17-diamylporphine (**8**, 4-NHCOR, R = $(CH_2)_{10}Br$).* The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}Br$), using 50 mg (0.08 mmol) **6** (4-NH_2). Yield – 59 mg (84.0%). R_f = 0.2 (benzene); 0.89 (benzene-methanol 10:1). IR cm^{-1}: νNHCO 1627. UV-vis λ_{max} (lg ε): 624 (3.58); 571 (3.92); 537 (3.93); 503 (4.24); 404 (5.36). ^{1}H NMR δ ppm: 10.15 s (2H, 10,20-H); 9.96 s (1H, 15-H); 7.99 d (2H, *J* = 8.2 Hz, 2',6'-H); 7.94 d (2H, *J* = 8.2 Hz, 3',5'-H); 7.51 s (1H, NHCO); 4.05 t (4H, J^1 = 7.5 Hz, CH_2-Am); 3.65 s (6H, 12,18-CH_3); 3.54 s (6H, 2,8-CH_3); 3.47 t (2H, CH_2CO); 2.55 t (2H, CH_2Br); 2.51 s (6H, 3,7-CH_3); 2.32 qv (4H, J^1 = 7.5 Hz, CH_2-Am); 1.87-1.95 m (4H, CH_2); 1.75 qv (4H, J^1 = 7.5 Hz, CH_2-Am); 1.52-1.61 m (8H, CH_2, CH_2-Am); 1.36-1.43 m (8H, CH_2); 0.99 t (6H, J^1 = 7.5 Hz, CH_3-Am); -3.30 bs (2H, NH).

*5-[4'-(8''-H-Perfluorooctylcarbonyloxy)phenyl]-2,3,7,8,12,18-hexamethyl-13,17-di-n-amylporphine (**8**, 4-NHCOR, R = $(CF_2)_7CHF_2$).* The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}Br$), using 50 mg (0.08 mmol) of **6** (4-NH_2) and 238 mg (0.541 mmol) of 9'-*H*-perfluorononaoic acid, 23 mg (0.185 mmol) of DMAP and 134 mg (0.698 mmol) of EDAC. The reaction time was 7 days. Yield – 14.9 mg (17.9%). R_f = 0.36 (benzene). IR cm^{-1}: νNHCO 1627. UV-vis λ_{max} (lg ε): 624 (3.64); 572 (3.92); 538 (3.95); 504 (4.23); 405 (5.32). ^{1}H NMR δ ppm: 10.17 s (2H, 10,20-H); 9.97 s (1H, 15-H); 8.34 bs (1H, NHCO); 8.08 d (2H, *J* = 7.7 Hz, 2',6'-H); 7.98 d (2H, *J* = 7.7 Hz, 3',5'-H); 6.14 tt (1H, J^1 = 4.9 Hz, J^2 = 51.9 Hz); 4.05 t (4H, J^3 = 7.5 Hz, CH_2-Am); 3.65 s (6H, 12,18-CH_3); 3.54 s (6H, 2,8-CH_3); 2.49 s (6H, 3,7-CH_3); 2.32 qv (4H, J^3 = 7.5 Hz, CH_2-Am); 1.75 qv (4H, J^3 = 7.5 Hz, CH_2-Am); 1.51-1.62 m (4H, CH_2-Am); 0.99 t (6H, J^3 = 7.5 Hz, CH_3-Am); -3.26 bs (2H, NH).

*5-[4'-(N-tert-Butyloxycarbonylglycylamido)phenyl]-2,3,7,8,12,18-hexamethyl-13,17-diamylporphine (**8**, 4-NHCOR, R = CH_2NHCOO^tBu).* The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}Br$), using 50 mg (0.08 mmol) of **6** (4-NH_2) and 31 mg (0.176 mmol) of *N-tert*-butyloxycarbonylglycine, 11 mg (0.09 mmol) of DMAP and 48 mg (0.253 mmol) of EDAC. The reaction time was 6 days. Yield – 31 mg (50.0%). R_f = 0.54 (benzene-methanol 10:1). IR cm^{-1}: νNHCO 1688. UV-vis λ_{max} (lg ε): 624 (3.68); 571 (3.95); 537 (3.96); 503 (4.25); 404 (5.35). ^{1}H NMR δ ppm: 10.15 s (2H, 10,20-H); 9.96 s (1H, 15-H); 8.51 bs (1H, NHCO); 8.01 d (2H, *J* = 8.1 Hz, 2',6'-H); 7.95 d (2H, *J* = 8.1 Hz, 3',5'-H); 5.39 bs (1H, NHCOO); 4.15 d (2H, J^1 = 5.7 Hz, CH_2-Glu); 4.05 t (4H, J^2 = 7.5 Hz, CH_2-Am); 3.64 s (6H, 12,18-CH_3); 3.52 s (6H, 2,8-CH_3); 2.51 s (6H, 3,7-CH_3); 2.32 qv (4H, J^2 = 7.5 Hz, CH_2-Am); 1.76 qv (4H, J^2 = 7.5 Hz, CH_2-Am); 1.61 s (9H, ^{t}Bu); 1.56 sc (4H, J^2 = 7.5 Hz, CH_2-Am); 0.99 t (6H, J^2 = 7.5 Hz, CH_3-Am); -3.28 bs (2H, NH).

*5-[4'-(N-tert-Butyloxycarbonyl-L-isoleucylamido)phenyl]-2,3,7,8,12,18-hexamethyl-13,17-diamylporphine (**8**, 4-NHCOR, R = $CH[CH(CH_3)CH_2CH_3]NHCOO^tBu$).* The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}Br$), using 50 mg (0.08 mmol) of **6** (4-NH_2) and 41 mg (0.176 mmol) of *N-tert*-butyloxycarbonyl-*L*-isoleucine, 11 mg (0.09 mmol) of DMAP and 64 mg (0.336 mmol) of EDAC. The reaction time was 10 days. Yield – 48 mg (72.0%). R_f = 0.93 (benzene-methanol 10:1). IR cm^{-1}: νNHCO 1683. UV-vis λ_{max} (lg ε): 624 (3.64); 571 (3.92); 537 (3.95); 503 (4.23); 405 (5.31). ^{1}H NMR δ ppm: 10.14 s (2H, 10,20-H); 9.97 s (1H, 15-H); 8.46 bs (1H, NHCOCH); 8.01 d (2H, *J* = 8.0 Hz, 2',6'-H); 7.96 d (2H, *J* = 8.0 Hz, 3',5'-H); 5.30 bs (1H, NHCOO); 4.32 bt (1H, CH-Ile); 4.06 t (4H, ^1J = 7.5 Hz, CH_2-Am); 3.64 s (6H, 12,18-CH_3); 3.46 s (6H, 2,8-CH_3); 2.51 s (6H, 3,7-CH_3); 2.20-2.28 m (1H, CH-Ile); 2.33 qv (4H, ^1J = 7.5 Hz, CH_2-Am); 1.76 qv (4H, ^1J = 7.5 Hz, CH_2-Am); 1.60 s, 1.58 sc (13H, ^1J = 7.5 Hz, CH_2-Am); 1.32-1.42 m (2H, CH_2-Ile); 1.22 d (3H, ^2J = 5.7 Hz, CH_3-Ile); 1.10 t (3H, ^3J = 7.0 Hz, CH_3-Ile); 1.00 t (6H, ^1J = 7.5 Hz, CH_3-Am); -3.25 bs (2H, NH).

*5-[4'-(N-tert-Butyloxycarbonyl-L-phenylalanylamido)phenyl]-2,3,7,8,12,18-hexamethyl-13,17-diamylporphine (**8**, 4-NHCOR,*

R = CH(CH$_2$C$_6$H$_5$)NHCOO^{t}Bu). The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}$Br), using 50 mg (0.08 mmol) of **6** (4-NH$_2$) and 46 mg (0.174 mmol) of *N-tert*-butyloxycarbonyl-*L*-phenylalanine, 11 mg (0.09 mmol) of DMAP and 48 mg (0.251 mmol) of EDAC. The reaction time was 7 days. Yield – 54 mg (77.0%). R_f = 0.83 (benzene-methanol 10:1); 0.08 (benzene). IR cm^{-1}: νNHCO 1690. UV-vis λ_{max} (lg ε): 624 (3.74); 571 (3.99); 537 (4.00); 503 (4.28); 404 (5.38). ^{1}H NMR δ ppm: 10.16 s (2H, 10,20-H); 9.97 s (1H, 15-H); 8.10 bs (1H, NHCO); 7.98 d (2H, *J* = 8.1 Hz, 2',6'-H); 7.80 d (2H, *J* = 8.1 Hz, 3',5'-H); 7.36-7.49 m (5H, H-Ph); 4.68 s (1H, CH); 4.06 t (4H, J^1 = 7.6 Hz, CH$_2$-Am); 3.65 s (6H, 12,18-CH$_3$); 3.53 s (6H, 2,8-CH$_3$); 3.31-3.39 m (2H, CH$_2$-Phe); 2.50 s (6H, 3,7-CH$_3$); 2.33 qv (4H, J^1 = 7.6 Hz, CH$_2$-Am); 1.76 qv (4H, J^1 = 7.6 Hz, CH$_2$-Am); 1.58 sc (4H, J^1 = 7.6 Hz, CH$_2$-Am); 1 55 s (9H, ^{t}Bu); 0.99 t (6H, J^1 = 7.6 Hz, CH$_3$-Am); -3.26 bs (2H, NH).

*5-[3'-(10''-Bromodecylcarbonylamido)phenyl]-2,3,7,8,12,18-hexamethyl-13,17-diaminoporphine (**8**, 3-NHCOR, R = (CH$_2$)$_{10}$Br).* The compound was obtained similarly to porphyrin **7** (4-NHCOR, R = $(CH_2)_{10}$Br), using 50 mg (0.08 mmol) of **6** (3-NH$_2$). The reaction time was 5 days. Yield – 38 mg (54.0%). R_f = 0.07 (benzene); 0.96 (benzene-methanol 10:1). IR cm^{-1}: νNHCO 1628. UV-vis λ_{max} (lg ε): 624 (3.30); 571 (3.76); 537 (3.81); 503 (4.14); 404 (5.26). ^{1}H NMR δ ppm: 10.14 s (2H, 10,20-H); 9.93 s (1H, 15-H); 8.16 d (1H, *J* = 7.4 Hz, 6'-H); 7.98 s (1H, 2'-H); 7.78 d (1H, *J* = 7.4 Hz, 4'-H); 7.67 t (1H, *J* = 7.4 Hz, 5'-H); 7.39 s (1H, NHCO); 4.03 t (4H, J^1 = 7.5 Hz, CH$_2$-Am); 3 63 s (6H, 12,18-CH$_3$); 3.53 s (6H, 2,8-CH$_3$); 3.38 t (2H, J^2 = 7.0 Hz, CH$_2$CO); 2.52 s (6H, 3,7-CH$_3$); 2.31 qv (6H, J^1 = 7.5 Hz, CH$_2$-Am); 1.82 qv (2H, J^2 = 7.0 Hz, CH$_2$); 1.67-1.79 m (6H, CH$_2$-Am, CH$_2$Br); 1.39 m (2H, CH$_2$); 1.22-1.42 m (14H, CH$_2$); 0.99 t (6H, J^1 = 7.5 Hz, CH$_3$-Am); -3.41 bs (2H, NH).

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