Phenyl Substituted Porphyrins. 6. Acylation of Alcohols with Carboxyphenylporphyrins

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Pyrrolic precursors and benzaldehydes were used to afford meso-carboxyphenylporphyrins bearing one or four carboxyl groups. The reaction conditions for the acylation of alcohols with the obtained carboxyphenylporphyrins in the presence of carbodiimides were studied. Optimal reaction conditions were found and a series of phenylporphyrin esters of various structure was synthesized.

Keywords: Porphyrins, acylation, perfluorinated alcohols, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDAC), 4-dimethylaminopyridine (DMAP).

Introduction

meso-Substituted porphyrins bearing active groups in phenyl substituents present a considerable interest in the aspect of using them as basis for more complex conjugates in order to study the influence of substituents on the properties of the porphyrin core.

Previously we have described the procedures for acylation of hydroxy[1] and aminophenyl[2] porphyrins with carbonic acids and the synthesis of tetraphenylporphyrin fluoroalkyl derivatives.[3] Here we present the study of the specifics of alcohols acylation with carboxyphenyl porphyrins resulting in the formation of esters.

Various methods of acylation of amino[4-11] and hydroxyl compounds[12-15] with carboxyphenylporphyrins have been published. The acylation agents can be either the carboxyphenylporphyrins themselves in the presence of activators,[8-11,13-15] or the corresponding chloroanhydrides.[4-7,12] Acylation is conducted in methylene chloride,[6,9,10,13,14] chloroform,[7,8] THF,[15] DMF,[11] and other solvents with...
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pyridine added,\textsuperscript{[4,5,12]} DCC\textsuperscript{[13,15]} or EDAC\textsuperscript{[9,10,14,15]} in the presence of DMAP are used as the condensing agents.

Results and Discussion

Firstly, we obtained a series of carboxyphenyl porphyrins of various nature, such as tetraphenylporphyrin derivatives bearing one (5, 9) or four carboxyl groups (11), as well as several \( \beta \)-octaalkyl substituted porphyrins (14). Carboxyphenylporphyrins \([5 (X=-), 5 (X=OCH_2), 9]\) were obtained in the course of a “mixed aldehyde condensation”. The presence of the carboxyl group does not allow the separation by chromatography, so the synthesis was conducted using the corresponding esters of carboxybenzaldehydes (2, 6) with the subsequent hydrolysis of the resulting esters \([4 (X=-; R=Me), 8.1 \text{ % yield}; 4 (X=OCH_2; R=Et), 10 \text{ % yield} \text{ and } 8, 9.6 \text{ % yield}] (Schemes 1, 2).

Via the condensation of 3- and 4-carboxybenzaldehydes 10 with pyrrole 1 in a mixture of propionic acid with nitrobenzene, symmetrically substituted 5,10,15,20-tetrakis(3- and 4-carboxyphenyl)porphines (11) were obtained with the yields of 55.6 and 43.0 \%, correspondingly (Scheme 3).

A two-step one-pot procedure analogous to\textsuperscript{[16-18]} was employed to afford carboxyporphyrins 14 by the condensation of biladiene 12 with benzaldehydes 2 \((X=-; R=H \text{ and } X=OCH_2; R=Et)\) in butanol and further hydrolysis of the obtained esters 13 \((X=-; R=Me \text{ and } X=OCH_2; R=Bu)\). The yields were 20.8 \% and 45.6 \%, correspondingly (Scheme 4). It should be noted that in the course of the synthesis of the ester of carboxymethylenoxyphenylporphyrin, interesterification occurs and butyl ester 13 \((X=OCH_2; R=Bu)\) is obtained.

\[ \text{Scheme 1.} \]

\[ \text{Scheme 2.} \]

\[ \text{Scheme 3.} \]
instead of the methyl one. When benzaldehyde 2 is used (X=−; R=H), esterification is insignificant and porphyrin 13 (X=−; R=Bu) is formed with 3.5% yield. However, for chromatographic purification the porphyrin 13 (X=−; R=H) was converted into its methyl ester 13 (X=−; R=Me). The obtained esters were then subjected to hydrolysis with almost quantitative yields of the target carboxyporphyrins 14.

Acylation of alcohols with carboxyphenylporphyrins was carried out by a previously developed procedure,[1,2] with porphyrins being the acylating agents.

The specifics of acylation of n-perfluoro-1,1,9-H-nonyl alcohol with 5-(4-carboxyphenyl)-2,3,7,8,12,18-hexamethyl-13,17-di-n-amylporphyrin 14 (X=−), resulting in the formation of porphyrin 16 (Scheme 5) (Table 1) was studied. The reaction conditions appeared to be the same for

Table 1. Dependency of the yield of porphyrin 16 on the amount of n-perfluoro-1,1,9-H-nonyl alcohol, EDAC and DMAP.

<table>
<thead>
<tr>
<th>Alcohol (eq)</th>
<th>EDAC (eq)</th>
<th>DMAP (eq)</th>
<th>Yield, %</th>
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<tbody>
<tr>
<td>1.1</td>
<td>2</td>
<td>0.6</td>
<td>50.8</td>
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<tr>
<td>1.1</td>
<td>1.5</td>
<td>0.6</td>
<td>52.5</td>
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<tr>
<td>1.5</td>
<td>1.5</td>
<td>0.6</td>
<td>54.6</td>
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<tr>
<td>1.5</td>
<td>2</td>
<td>0.6</td>
<td>66.1</td>
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<tr>
<td>1.5</td>
<td>1.1</td>
<td>0.6</td>
<td>33.5</td>
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<tr>
<td>2</td>
<td>2</td>
<td>0.6</td>
<td>64.4</td>
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<tr>
<td>1.5</td>
<td>1.5</td>
<td>1</td>
<td>47.2</td>
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<tr>
<td>1.5</td>
<td>2</td>
<td>1</td>
<td>57.5</td>
</tr>
<tr>
<td>1.5</td>
<td>2.5</td>
<td>0.6</td>
<td>65.7</td>
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</table>

Scheme 4.
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the acylation of aminophenylporphyrins with carbonic acids.[2] Acylation of cholesterol with porphyrin 14 (X=OCH$_3$) afforded a conjugate 18 (12 % yield).

This method was also used to convert 5 (X=O-) and 9 into porphyrins 17, bearing polyfluorinated substituents (Scheme 6). The yields were 63 and 45 %, correspondingly.

Porphyrins that may exhibit the properties of liquid crystals were synthesized. In three steps we obtained a porphyrin-cholesterol conjugate 19, which has a discotic and cholesteric residues linked by a long decamethylene spacer (Scheme 7). Alkylation of oxyphenylporphyrin 20 with methyl ester of 11-bromoundecanoic acid gives the ester 21 (84 % yield), which after alkaline hydrolysis affords carboxyporphyrin 22 (67 % yield) and the reaction with cholesterol results in the target conjugate 19. The yield was 32 %, while using the corresponding chloroanhydride afforded only 13 % yield.

In a similar way, the reaction of 22 with aminophenylporphyrin 23 was used to obtain a dimeric porphyrin 24 with 35 % yield (Scheme 8).

While the symmetric compound 5,10,15,20-tetrakis-(4-hexadecyloxyphenyl)porphine exhibits a monotropic liquid crystal phase that vitrifies preserving the meso-phase texture, polarization microscopy studies of the mesomorphic properties of unsymmetrical analogs showed that compound 20 is not mesomorphic.[3]

In order to study the discotic liquid crystal properties of porphyrins we synthesized symmetric porphyrins
bearing ester groups with long-chain substituents of different nature (aliphatic and perfluorinated residues) 25, by the acylation of the corresponding alcohols with meso-tetracarboxyphenylporphyrins 11 (Scheme 9) (Table 2).

The low yields of porphyrins 25 are caused, to our suggestion, by the complete insolubility if the starting carboxyphenylporphyrins in methylene chloride that hinders the formation of the intermediate O-acylureas. This assumption is confirmed by increased (by ~6 %) yields when preliminary ultrasonic treatment of the starting compounds is performed. Moreover, the presence of four carboxyl groups leads to the formation of porphyrinic mixtures in which only the tetrsubstituted porphyrins are chromatographically mobile.[1]

Furthermore we conducted the synthesis of tetracarboxyporphyrin esters 25 by nucleophilic substitution of halogen in alkyl halides in DMF in the presence of potash, however the yields in this case are also low and the reaction proceeds slowly (Scheme 9).

All the obtained porphyrins were analyzed using a complex of spectral studies (UV-vis, IR and 1H NMR spectroscopy) and their purity and identity were confirmed by TLC.

![Scheme 8.](image)

![Scheme 9.](image)

<table>
<thead>
<tr>
<th>Table 2. Yields of the symmetrically substituted esters 25.</th>
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<tr>
<td><strong>R = -(CH$_2$)$_n$CH$_3$</strong></td>
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<tr>
<td><strong>Position of the substituent</strong></td>
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<td><strong>n</strong></td>
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**Phenyl Substituted Porphyrins**

**Experimental**

The electronic absorption spectra (EAS) were recorded on a SPEC SPP-715 scanning spectrometer in chloroform, the IR spectra were taken on an Avatar 360 FT-IR in KBr pellets, the H NMR spectra were recorded on a Bruker 500 MHz instrument in deuterated chloroform (TMS as the internal standard) in the joint research center “The Upper-Volga Regional Center of Physico-Chemical Studies” of the G.A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences. The TLC was performed on Silufol plates. The solvents used were dried and purified by standard procedures.[9]

4-Ethoxy carbonylmethylenoxybenzaldehyde (2, X=OCH₂, R=E). 5.0 g (40.9 mmol) of 4-oxo benzaldehyde, 9.0 mL (85.1 mmol) of ethyl ester of chloroacetic acid, 3.0 g (21.7 mmol) of potassium carbonate in DMF (75 mL) were refluxed with stirring for 1 h. The mixture was then cooled, poured into 200 mL of water and extracted with ether. The etheral solution was washed with water and dried with sodium sulfate. Ether was evaporated off and the residue was distilled under the vacuum of a water jet pump, the fraction boiling at ~185 °C was collected. Yield: 7.3 g (86 %). 1H NMR (CCl₄) δ ppm: 9.57 s (1H, CHO); 7.57 d (2H, J=8.0 Hz, 2.6-H); 6.72 d (2H, J=8.0 Hz, 3.5-H); 4.45 s (2H, OCH₂CO); 4.00 q (2H, J=7.1 Hz, OCH₂-Et).

5-Ethoxycarbonylmethylenoxybenzaldehyde (2). X=OCH₂, R=Me. To a stirred suspension of 4-carboxy benzaldehyde (12.0 g, 0.08 mol) and potassium carbonate (35.0 g, 0.25 mol) in 250 mL of acetic anhydride (5.5 mL, 0.088 mol) was added. The mixture was refluxed with stirring for 4 h, the residue was filtered off, washed with acetic acid and the acetone was then evaporated. The residue was recrystallized from methanol. Yield: 11.6 g (88 %), m.p. 60–62 °C. 1H NMR (CCl₄) δ ppm: 9.35 s (1H, CHO); 7.72 d (2H, J=8.1 Hz, 3.5-H); 7.57 d (2H, J=8.1 Hz, 2.6-H); 4.30 s (3H, OCH₃).

**5-Hexacyclohexylenebenzaldehyde** (7). A mixture of 20.0 g (0.164 mol) of 4-oxo benzaldehyde, 50 mL (0.164 mol) of cetyl bromide, 25.0 g (0.181 mol) of potassium carbonate and 200 mL of n-butanol was refluxed with stirring for 3 h. The mixture was then cooled, the precipitate was filtered, washed with water and air-dried at ambient temperature. Yield: 43.9 g (77 %), m.p. 60–62 °C. 1H NMR (CCl₄) δ ppm: 9.89 s (1H, CHO); 7.83 d (2H, J=8.5 Hz, 2.6-H); 7.01 d (2H, J=8.5 Hz, 3.5-H); 4.05 q (2H, J=7.0 Hz, OCH₃); 1.83 qv (2H, J=7.0 Hz, CH₂); 1.44-1.52 m (2H, CH₂); 1.23-1.41 m (24H, CH₃); 0.90 t (6H, J=7.0 Hz, CH₃).

**5-(4-Ethoxycarbonylmethoxyphenyl)-10,15,20-triphenyloporphyrin (4, X=OCH₂, R=E).** To a solution of 410 mg (2.5 mmol) of 4-methoxy carbonylmethylenoxybenzaldehyde, 0.7 mL (10 mmol) of pyrrole and 0.9 mL (9.8 mmol) of benzaldehyde in 1000 mL of methylene chloride 1.0 g of tin powder was added, the mixture was refluxed with stirring for 1 h. The mixture was then concentrated, the precipitate was filtered, washed with water, butanol was removed by steam distillation, the residue was filtered, washed with water and air-dried at 70 °C. The mixture was dissolved in methylene chloride and subjected to chromatography on silica gel eluting with methylene chloride. The eluate was evaporated and the porphyrin was precipitated with methanol. Yield: 100 mg (3.5 %), (X=OCH₂, R=Me). The insoluble precipitate was precipitated for several days at ambient temperature in a mixture of sulfuric acid (4 mL) and methanol (150 mL). Half of the methanol was removed, the precipitate was diluted with water and neutralized with aqueous ammonia, the precipitate was filtered, washed with water and air-dried at 70 °C. It was then dissolved in methylene chloride and chromatographed on silica gel eluting with methylene chloride. The eluate was evaporated and the porphyrin was precipitated with methanol. Yield: 0.6 g (20.8 %), (X=OCH₂, R=Me). EAS λmax (lgε): 624 (3.83); 571 (3.88); 538 (3.91); 504 (4.18); 405 (4.36). 1H NMR δ ppm: 10.18 s (2H, 10.20-H); 9.97 s (1H, 11-H); 8.46 d (2H, J=7.8 Hz, 2.6-H-Ar); 8.21 d (2H, J=7.8 Hz, 3.5-H-Ar); 4.53 t (8H, J=6.9 Hz, OCH₂-Bu); 4.04 t (4H, J=7.5 Hz, CH₂-Am); 3.62 s (6H, 12.18-CH₃); 3.51 s (6H, 2.8-CH₂); 2.48 s (6H, 3.7-CH₃); 2.32 qv (4H, J=7.5 Hz, CH₂-Am); 1.94 qv (2H, J=6.9 Hz, CH₂-Bu); 1.75 qv (4H, J=7.5 Hz, CH₂-Am); 1.52-1.46 m (6H, CH₂-Bu+CH₂-Am); 1.17 t (3H, J=6.9 Hz, CH₃-Bu); 0.99 (6H, J=7.5 Hz, CH₂-Am); -3.36 bs (2H, NH). 13C (X=OCH₂, R=Me): δ ppm: 62.4 (3.83); 57.1 (3.88); 538 (3.91); 504 (4.21); 405 (5.25). 13NMR δ ppm: 10.18 s (2H, 10.20-H); 9.97 s (1H, 11-H); 8.46 d (2H, J=7.8 Hz, 2.6-H-Ar); 8.21 d (2H, J=7.8 Hz, 3.5-H-Ar); 4.53 t (8H, J=6.9 Hz, OCH₂-Bu); 4.04 t (4H, J=7.5 Hz, CH₂-Am); 3.62 s (6H, 12.18-CH₃); 3.51 s (6H, 2.8-CH₂); 2.48 s (6H, 3.7-CH₃); 2.32 qv (4H, J=7.5 Hz, CH₂-Am); 1.94 qv (2H, J=6.9 Hz, CH₂-Bu); 1.75 qv (4H, J=7.5 Hz, CH₂-Am); 1.52-1.46 m (6H, CH₂-Bu+CH₂-Am); 1.17 t (3H, J=6.9 Hz, CH₃-Bu); 0.99 (6H, J=7.5 Hz, CH₂-Am); -3.36 bs (2H, NH).
diacylpyromethane and 0.52 g (4.26 mmol) of 2-formyl-3,4-dimethylpyrrole in 50 mL of n-butanol at ambient temperature, concentrated hydrobromic acid (1.0 mL, 8.3 mmol) was added with stirring. The mixture was stirred for 1 h, then 3.0 mL (~6-fold excess) of 4-ethoxy carbonylmethyleneoxybenzaldehyde was added for 4 h. After cooling, 2 mL of conc. aqueous ammonia was introduced. The mixture was filtered off with water and dried. Yield of the potassium salt: 3.2 g.

A mixture of 50 mg (0.073 mmol) of 5-(4-carboxybenzaldehyde)-10,15,20-triphenylporphine (II) in 10 mL of water was refluxed for 24 h. The formed precipitate was filtered, washed with methanol and dried. 290 mg (0.37 mmol) of the obtained potassium salt of 5-(4-carboxybenzamidinophenytoxy) porphine was treated with a solution of 1 mL of 35% hydrochloric acid in 5 mL of water, then water (20 mL) was introduced. The mixture was stirred with the organic solution until the color changed from green to red. The solution was dried with sodium sulfate, chloroform was evaporated and the residue was air-dried.

Yield: 80 mg (81.8%). EAS λ max nm (lgε): 646 (3.67); 581 (3.64); 555 (3.87); 518 (4.09). Rf = 0.67 (benzene:methanol = 20:1).

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A mixture of 50 mg (0.116 mmol) of n-perfluoro-1,1,9-H-nonyl alcohol, 6 mg (0.049 mmol) of DMAP and 30 mg (0.156 mmol) of EDAC was dissolved in 15 mL of methylene chloride and stirred at 0 °C for 1 h, then at ambient temperature until the reaction was complete according to TLC (5 days). The reaction mixture was purified by chromatography on silica gel (L 100/250), using methylene chloride as the eluent. The eluate was evaporated and the porphyrin was precipitated with methanol.

The eluate was evaporated and the porphyrin was precipitated with methanol.

Yield: 43.0%. EAS (2% KOH in water) λ max (lgε): 639 (3.66); 581 (3.78); 554 (3.85); 518 (4.09); 414 (5.49).
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was purified by chromatography on silica gel (L 100/250), us-

completion of the reaction (4 days, TLC). The reaction mixture

was filtered, washed with methanol and dried. Yield: 30.5 mg

HC=O (6H, 3.7-CH

2

potassium carbonate in 50 mL of DMF was refluxed for 5 h, then

and dried. Yield: 0.48 g (83.7 %). R

obtained porphyrin was dissolved in chloroform and purified on

washed with water and dried at ambient temperature in air. The

temperature for a day. The porphyrin was purified on Al

another 30 minutes. The mixture was maintained at ambient

45 mg (0.368 mmol) of DMAP and 45 mg (0.218 mmol) of DCC

of 50.0 mg of (0.073 mmol) 5-(4-carboxymethyleneoxyphenyl-

was evaporated and the porphyrin was precipitated with methanol.

Brockmann grade), eluting with methylene chloride. The eluate

with water until the color changed from green to red, methylene

with water for 1 h. The mixture was cooled, the precipitate was filtered,

washed with propanol and stirred for another 30 minutes. The mixture was maintained at ambient

temperature for a day. The porphyrin was purified on Al₂O₃ (II

Brockmann grade), eluting with methylene chloride. The eluate was evaporated and the porphyrin was precipitated with methanol.

The precipitate was filtered, washed with methanol and dried. Yield: 30.5 mg (44.7 %). Rₖ = 0.83 (benzene).

EAS λₘₐₓ nm (lgε): 651 (3.53); 593 (3.85); 556 (3.92); 519 (4.16); 423 (5.58). IR cm⁻¹: ν= 1738; νCOO⁻ = 1211. H NMR δ ppm: 8.94 s (8H,

β-H); 8.13 d (8H, 3.5-H-Ar'); 8.10-8.18 m (8H, 2.6-H-Ar'); 7.32 qv (4H, 3.4.5-H-Ph); 6.10 dt (1H, J=7.6 Hz, CH₂); 1.58 t (2H, J=7.6 Hz,

CH₂); 1.45 qy (6H, CH₃); 2.71 bs (2H, NH).

5-(4-O-Cholesterylcarbomethoxyphenyle)napthalone-2,3,7,8,12,18-hexamethyl-17-di-n-amylporphine (18). A solution of 50.0 mg of (0.073 mmol) 5-(4-carboxymethoxyphenyle)napthalone-2,3,7,8,12,18-hexamethyl-17-di-n-amylporphine 14 (X=OCH₃) 45 mg (0.368 mmol) of DMAP and 45 mg (0.218 mmol) of DCC in 15 mL THF was stirred at 0 °C for 1 h, then 275 mg (0.711 mmol) of cholesterol was added and the stirring was maintained for another 30 minutes. The mixture was maintained at ambient temperature for a day. The porphyrin was purified on Al₂O₃ (II Brockmann grade), eluting with methylene chloride. The eluate was evaporated and the porphyrin was precipitated with methanol.

The precipitate was filtered, washed with methanol and dried. Yield: 9.1 mg (11.8 %). Rₖ = 0.82 (benzene:methanol, 20:1). EAS λₘₐₓ nm (lgε): 624 (3.63); 571 (3.95); 537 (3.97); 503 (4.27); 404 (5.36). IR cm⁻¹: ν= 1738; νCOO⁻ = 1211. H NMR δ ppm: 1660; 1710. H NMR (CDCl₃) δ ppm: 10.17 (2H, 10.20, J=9.4 Hz); 9.97 (s, 1H, 15-H); 7.94 (2H, J=7.8 Hz, 2.6-H-Ar); 7.28 d (2H, J=7.8 Hz, 3.5-H-Ar); 5.03 s (2H, OCH₂); 4.06 t (4H, J=7.6 Hz, CH₂-Ar); 3.65 s (6H, 12.18-CH₃); 3.55 s (6H, 2.8-CH₃); 2.50 s (6H, 3.7-CH₂); 2.32 qy (4H, J=7.6 Hz, CH₂-Am); 1.75 qy (4H, J=7.6 Hz, CH₂-Am); 1.58 sc (4H, J=7.6 Hz, CH₂-Am); 0.98 t (6H, J=7.6 Hz, CH₃-Am); -3.23 bs (2H, NH); 1.20-2.15 (a number of cholesterol residue signals).

5-(4-O-Cholesterylcarbomethoxyphenyle)napthalone-2,3,7,8,12,18-hexamethyl-17-di-n-amylporphine 14 (X=OCH₃) was introduced and the mixture was stirred at the same temperature for 30 min. Further stirring at ambient temperature was performed for several days until the reaction was complete. The mixture was purified on silica gel (L 100/250), eluting with methylene chloride. The eluate was evaporated and the porphyrin was precipitated with methanol. The precipitate was filtered, washed with methanol and dried. Yield: 8.2 mg (13.4 %). Method B (from acid). A solution of 50 mg (0.033 mmol) of 22, 14.5 mg (0.019 mmol) of DMAP and 25 mg (0.121 mmol) of EDAC in 25 mL of THF was stirred at 0 °C for 1 h, then 45 mg (0.166 mmol) of cholesterol was introduced and the mixture was stirred at the same temperature for 30 min. Further stirring at ambient temperature was performed for several days until the reaction was complete. The mixture was purified on silica gel (L 100/250), eluting with methylene chloride. The eluate was evaporated and the porphyrin was precipitated with methanol. The precipitate was filtered, washed with methanol and dried. Yield: 20 mg (32.3 %). A similar synthesis in methylene chloride afforded 4.9 mg (7.8 %) of the porphyrin. Rₖ = 0.59 (benzene).

EAS λₘₐₓ nm (lgε): 650 (3.48); 594 (3.48); 557 (3.70); 519 (3.83); 422 (5.24). IR cm⁻¹: ν= 1743. H NMR δ ppm: 8.89 s (8H, β-H); 8.10-8.18 s (8H, 2.6-CH₃-Ar); 7.26-7.35 m (8H, 3.5-H-Ar); 4.33-4.44 m (8H, OCH₂); 2.43-2.54 m (2H, COCH₂); -2.74 bs (2H, NH); 0.6-2.10 (a series of resonance signals of alkyl chains and cholesterol residue).

Dimeric porphyrin (24). A solution of 50 mg (0.033 mmol) of 5-[4-(carboxymethoxyphenyle)-10,15,20-tris(4-hexadecyloxyporphine)porphine 22, 24 mg (0.116 mmol) of EDAC and 14 mg (0.015 mmol) of DMAP in 20 mL of methylene chloride was cooled in a water bath to 0 °C and then stirred for 1 h followed by the addition of solution of 5-(4-aminophenyl)-10,15,20-triphenylporphine 23 (24.5 mg, 0.039 mmol) in 5 mL of methylene chloride. The mixture was stirred at ambient temperature for 24 h and then refluxed while protected with a calcium chloride tube for 1 day. The dimer was purified by chromatography on silica gel (L 100/250), eluting with methylene chloride. The eluate was evaporated and the dimeric porphyrin was precipitated with
methanol. The precipitate was filtered, washed with methanol and dried. Yield: 24.5 mg (35.1%). \( R = 0.21 \) (benzene). EAS \( \lambda_{\text{max}} \) (lge): 649 (4.23); 592 (4.26); 554 (4.45); 517 (4.65); 420 (6.03). IR cm\(^{-1}\): 1666. \( ^1\)H NMR \( \delta \) ppm: 8.83–8.95 m (16H, \( \beta \)-H); 8.19–8.28 m (6H, 2.6-H-PPh); 8.07–8.17 m (10H, 2.6-H-Ar); 7.71–7.86 m (9H, 3.45-H-PPh); 7.35 bs (1H, NCOO); 7.22–7.34 m (10H, 3.5-H-Ar); 4.19–4.32 m (8H, OCH\(_2\)); 2.53 t (8H, \( J = 7.0 \) Hz, CH\(_2\)O); 1.80–2.06 m (10H, CH\(_2\)); 1.59–1.74 m (10H, CH\(_2\)); 1.24–1.46 m (90H, CH\(_2\)).

5,10,15,20-Tetra(4-propyloxycarbonylphenyl)porphine (25, para-, \( R = -(\text{CH}_2)_3\)). A mixture of 50 mg (0.063 mmol) of 5,10,15,20-tetra(4-carboxyphenyl)porphine 11 (para-, 0.5 mL (6.7 mmol) of propyl alcohol, 33 mg (0.271 mmol) of DMAP and 73 mg (0.381 mmol) of EDAC was dissolved in 15 mL of methylene chloride and refluxed for 12 h, then diluted with 100 mL of water. The precipitate was filtered, washed with water and dried at 70 °C, dissolved in methylene chloride, filtered on a silica gel eluting with methylene chloride, evaporated and precipitated with methanol. The precipitate was filtered, washed with methanol and dried in air at ambient temperature. Yield: 90 mg (21.3%). \( R = 0.88 \) (benzene). EAS \( \lambda_{\text{max}} \) (lge): 646 (3.87); 590 (3.98); 550 (4.10); 516 (4.37); 420 (5.75). IR cm\(^{-1}\): \( \nu_{\text{OCO}} = 1700 \). EAS \( \lambda_{\text{max}} \) (lge): 647 (3.77); 591 (3.93); 551 (4.04); 516 (4.38); 421 (5.73). IR cm\(^{-1}\): \( \nu_{\text{OCO}} = 1718 \). \( ^1\)H NMR \( \delta \) ppm: 8.83 s (8H, \( \beta \)-H); 8.44 d (8H, J = 7.9 Hz, 2.6-H-Ar); 8.31 d (8H, J = 8.0 Hz, 3.5-H-Ar); 4.53 t (8H, J = 6.7 Hz, CH\(_2\)); 1.25 t (12H, J = 6.7 Hz, CH\(_2\)); –2.76 bs (2H, NH).

5,10,15,20-Tetra(4-n-hexadecyloxycarbonylphenyl)porphine (25, para-, \( R = -(\text{CH}_2)_{25}, \text{para-}, \ R = -(\text{CH}_2)_{12}, \text{meta-}, \ R = -(\text{CH}_2)_{11} \)). A mixture of 100 mg (0.126 mmol) of 5,10,15,20-tetra(4-carboxyphenyl)porphine 11 (para-, 0.5 mL (5.5 mmol) of n-propyl-1,1,3-propyl alcohol. The reaction time was 2 days. Yield: 51 mg (64.8%). \( R = 0.72 \) (benzene). EAS \( \lambda_{\text{max}} \) (lge): 647 (3.77); 591 (3.91); 551 (4.04); 516 (4.35); 421 (5.68). IR cm\(^{-1}\): \( \nu_{\text{OCO}} = 1734 \); \( \nu_{\text{OCO}} = 1273 \). \( ^1\)H NMR \( \delta \) ppm: 8.86 s (8H, \( \beta \)-H); 8.51 d (8H, J = 8.2 Hz, 2.6-H-Ar); 8.38 d (8H, J = 8.3 Hz, 3.5-H-Ar); 1.61 tt (4H, J = 5.9 Hz, J = 1.5 Hz, CH\(_2\)); 0.96 s (12H, J = 13.3 Hz, OCH\(_3\)); 2.78 bs (2H, NH).

5,10,15,20-Tetra(4-n-hexyloxycarbonylphenyl)porphine (25, para-, \( R = -(\text{CH}_2)_{12} \)). A mixture of 0.4 g (0.5 mmol) 11 (para-, 1.0 g (7.24 mmol) potash and 2.0 mL (13.60 mmol) hexyl iodide in 20 mL DMF was refluxed for 12 h, then poured into 200 mL of water, the precipitate was filtered, washed with water and dried at 70 °C. The precipitate was dissolved in methylene chloride, filtered, evaporated and chromatographed on silica gel (L 100/250), eluting with methylene chloride. The crude was evaporated and the product was precipitated with methanol. The precipitate was filtered, washed with methanol and dried. Yield: 84 mg (27.2%). Method B. A mixture of 100 mg of 0.126 mmol of 11 (para-, 30 mL of methylene chloride was subjected to ultrasonication for 1 h. Then 250 mg (0.579 mmol) of \( \text{n-perfluoro-1,1,9-H-} \) n-alkyl alcohol, 37 mg (0.301 mmol) of EDAC and 150 mg (0.782 mmol) of DMAP were added to the suspension and stirred at 0 °C for 1.5 h, then at ambient temperature until completion of the reaction (4 days, TLC). The porphyrin was isolated by chromatography on silica gel (L 100/250), eluting with methylene chloride. The eluate was evaporated and the product was precipitated with methanol. The precipitate was filtered, washed with methanol and dried. Yield: 105 mg (33.0%). \( R = 0.80 \) (benzene). EAS \( \lambda_{\text{max}} \) (lge): 648 (3.84); 591 (3.96); 551 (4.08); 516 (4.37); 421 (5.67). IR cm\(^{-1}\): \( \nu_{\text{OCO}} = 1738 \); \( \nu_{\text{OCO}} = 1273 \). \( ^1\)H NMR \( \delta \) ppm: 8.85 s (8H, \( \beta \)-H); 8.50 d (8H, J = 8.0 Hz, 2.6-H-Ar); 8.38 d (8H, J = 8.0 Hz, 3.5-H-Ar); 1.61 tt (4H, J = 5.9 Hz, J = 1.5 Hz, CH\(_2\)); 0.96 s (12H, J = 13.3 Hz, OCH\(_3\)); –2.79 bs (2H, NH).

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References


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