

## Synthesis of Porphyrins from $\alpha$ -Unsubstituted Dipyrromethanes

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*Dedicated to Academician of Russian Academy of Sciences O. G. Sinyashin  
on the occasion of his 60<sup>th</sup> birthday*

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*The conditions for the porphyrin synthesis by condensation of  $\alpha$ -unsubstituted dipyrromethanes and ortho-formic ester in the presence of organic acids are investigated. The optimal reaction conditions are found, and a series of  $\beta$ - and meso-substituted porphyrins is synthesized. The methods of the  $\alpha$ -unsubstituted dipyrromethanes synthesis from pyrroles obtained by Knorr method are designed. The synthesized compounds were characterized by spectral methods.*

**Keywords:** Synthesis, dipyrromethanes, porphyrins.

## Синтез порфиринов из $\alpha$ -незамещенных дипирроллилметанов

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*Посвящается Академику РАН О.Г. Синяшину по случаю его 60-летнего юбилея*

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*Изучены условия синтеза порфиринов конденсацией  $\alpha$ -незамещенных дипирроллилметанов с ортомуравьиным эфиром в присутствии органических кислот. Найденны оптимальные условия проведения реакции, и синтезирован ряд  $\beta$ - и мезо-замещенных порфиринов. Разработаны методы синтеза  $\alpha$ -незамещенных дипирроллилметанов из пирролов, полученных по методу Кнорра. Синтезированные соединения охарактеризованы спектральными методами.*

**Ключевые слова:** Синтез, дипирроллилметаны, порфирины.

Tetrapyrrolic macroheterocycles have found widespread application as new functional materials with useful properties. In particular, synthetic porphyrins and their metal complexes are widely used as model compounds for studies of biochemical processes, catalysts and medicinal drugs.<sup>[1]</sup> Easily available meso-tetraarylporphyrins **1** and more related to natural  $\beta$ -octaalkylporphyrins **2** are the most common in practice. Some of them, like 5,10,15,20-tetraphenylporphyrin **1** (Ar=Ph) and 2,3,7,8,12,13,17,18-octaethylporphyrin **2** (Alk=Et) have symmetrically arranged substituents and are sufficiently soluble in organic solvents, unlike a more simple

2,3,7,8,12,13,17,18-octamethylporphyrin **2** (Alk=Me) which is almost not soluble in the majority of organic solvents.

Of interest is a simple method of synthesis of  $\beta$ -substituted alkylporphyrins with the general structure of **6** by condensation of  $\alpha$ -carboxydipyrromethanes **3** (X=COOH) with triethyl-ortho-formate in the presence of an acid (Scheme 1).<sup>[2-7]</sup>

This reaction is assumed to proceed via decarboxylation of the original dipyrromethane **3** with the subsequent formylation to give an  $\alpha$ -formyl derivative **4** which undergoes cyclocondensation unto porphodimethene **5** with the



further oxidation into porphyrin **6**. To achieve this transformation, trichloroacetic or trifluoroacetic acid is used as the catalyst,<sup>[2-7]</sup> the acid and *ortho*-formate are used in significant excess with respect to dipyrromethane and the reaction is carried out in chloroform or methylene chloride in air at reflux.

Finding the optimal conditions for this reaction was the goal of the present study.

An improved method was developed for the synthesis of  $\alpha$ -unsubstituted dipyrromethanes **3** and **11** (Scheme 2) from relatively easily available pyrroles **7**.<sup>[8]</sup> For the synthesis of symmetrically *meso*-unsubstituted dipyrromethanes **11** radical bromination of pyrrolic  $\alpha$ -methyl group in compounds **7** was performed to afford  $\alpha$ -bromomethylpyrroles **8**, in which under the reaction conditions bromine undergoes nucleophilic substitution with the formation of acetoxymethylpyrroles **9** that without preliminary purification undergo self-condensation to 5,5'-diethoxycarbonyldipyrromethanes **10**. Decarboxylation of the latter by potassium hydroxide in refluxing ethylene glycol leads to the target compounds **11**.

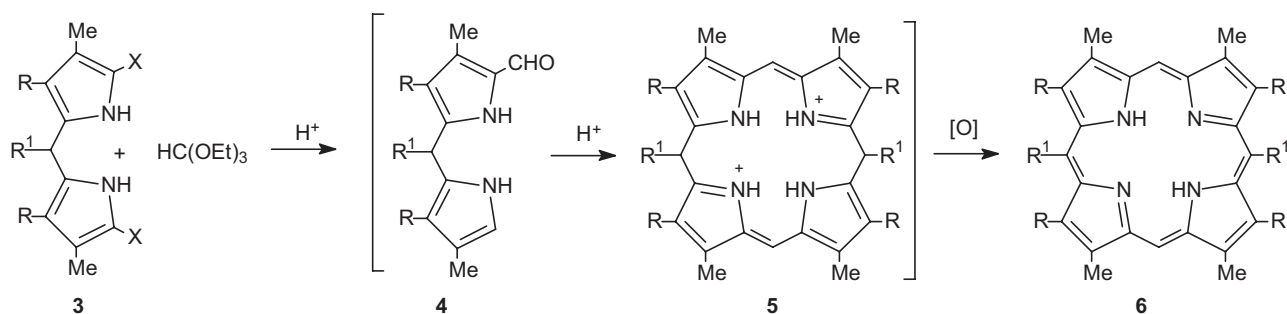
*meso*-Substituted dipyrromethanes **3** are also synthesized from pyrroles **7** by radical chlorination with sulfuryl chloride in ether with the formation of  $\alpha$ -trichloromethylpyrroles **12** followed by their hydrolysis into  $\alpha$ -carboxypyrroles **13**, decarboxylation of the latter to  $\alpha$ -unsubstituted pyrroles **15** (upon heating or by reduction of the intermediate  $\alpha$ -iodopyrroles **14**). By the condensation of **15** with aldehydes *meso*-substituted 5,5'-diethoxycarbonyldipyrromethanes **16** were obtained and decarboxylated to afford **3**.

As a model reaction we chose the synthesis of 2,8,12,18-tetramethyl-3,7,13,17-tetra-*n*-amylporphyrin, which is well-soluble in most common solvents and can be easily isolated from the reaction mixture by column chromatography.

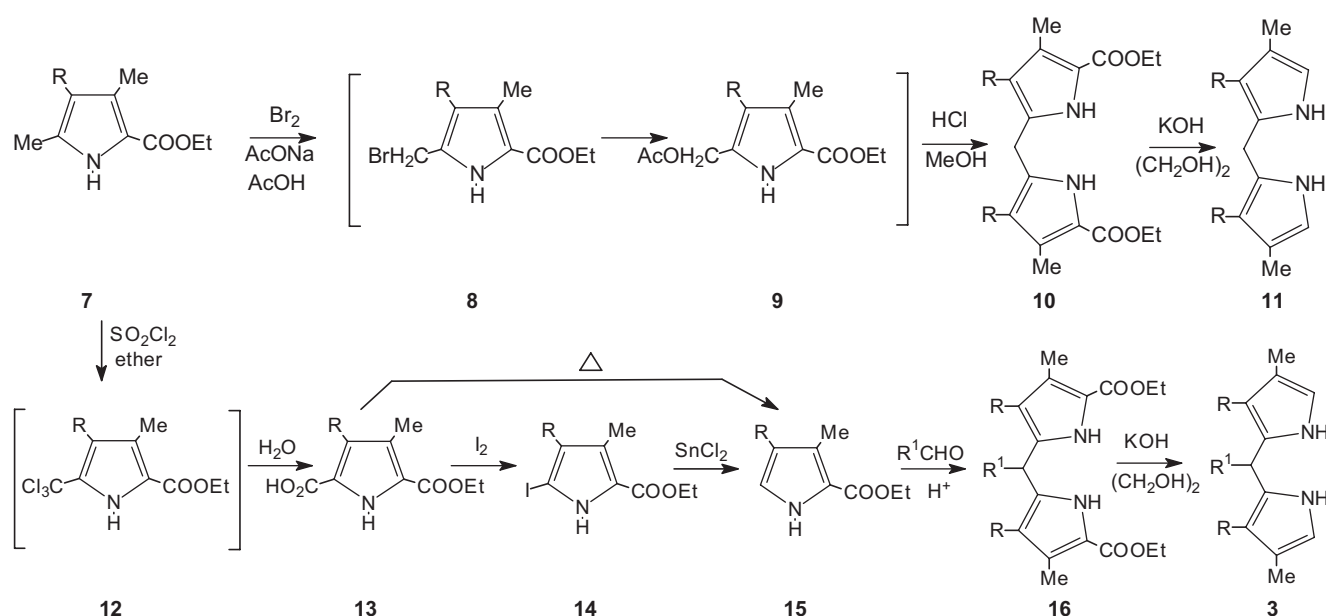
We have found it was more beneficial to use  $\alpha$ -unsubstituted dipyrromethane **11** for the synthesis, not its

$\alpha$ -carboxyl derivative, because of the yield in this case was significantly increased (Table 1) (exp. 1, 2). The concentration of dipyrromethane affects the porphyrin yield weakly (exp. 3, 6). Using other non-polar solvents instead of chloroform slightly lowers the yield (exp. 7-9), with the lowest one being in the case of methylene chloride (exp. 9) which is possibly caused by its low boiling point. A two-fold increase of the concentration of *ortho*-formate and trifluoroacetic acid with respect to dipyrromethane (from 3-fold excess to 6-fold) leads to a decrease of the porphyrin yield by 10 %, while reduction of their content to 1.5-fold excess gives a boost of the yield by 30 % (exp. 2-4). The oxidant used in the reaction does not influence the yield much (exp. 10-12), however it is lower than for *p*-chloranil (exp. 6) and a two-fold reduction the oxidant amount results in a two-fold reduction of the yield (exp. 13). It is interesting that using atmospheric oxygen as the oxidant leads to an increased yield of the porphyrin (exp. 14). Replacing trifluoroacetic acid with trichloroacetic (exp. 15) leads to a significant drop of the yield. When the reaction time is shortened from 4 to 2 hours the yield is decreased by 14 % (exp. 5).

We used the found optimal reaction conditions to conduct syntheses of a number of porphyrins with substituents of different length at  $\beta$ -positions of the porphyrin core and with substituents in *meso*-positions (Table 2). It was established that the porphyrin with only 4 substituents in  $\beta$ -positions (**6**, R,R<sup>1</sup>=H) is formed with the lowest yield, which is typical even for other porphyrins with unsubstituted  $\beta$ -positions.<sup>[9,10]</sup> The porphyrins which are poorly soluble in the majority of organic solvents (**6**, R=Me, R<sup>1</sup>=H; **6**, R=Et, R<sup>1</sup>=H; **6**, R=Bz, R<sup>1</sup>=H, and **6**, R=Et, R<sup>1</sup>=Ph) are also formed with low yields and need to be purified by re-precipitation with trifluoroacetic acid from the reaction mixture. For porphyrin **6** (R=Am, R<sup>1</sup>=H) as well as for the other porphyrins the yields are much higher when an unsubstituted dipyrromethane is used instead of



Scheme 1.



Scheme 2.

**Table 1.** Examples of the synthesis of 2,8,12,18-tetramethyl-3,7,13,17-tetra-*n*-amylporphyrin **6** (R=Am, R<sup>1</sup>=H) by the condensation of dipyrromethane **11** (R=Am) with ethyl *ortho*-formate in the presence of an acid (CA = chloranil, BQ=benzoquinone).

N	<b>3</b> (mmol)	Solvent (ml)	HC(OEt) <sub>3</sub> (equivalents against <b>3</b> )	CF <sub>3</sub> COOH (equivalents against <b>3</b> )	Oxidant (equivalents against <b>3</b> )	Time (h)	Yield (%)
1	2.0 <sup>a</sup>	100 (CHCl <sub>3</sub> )	6.3	7.1	1.0 (CA)	4	39.4
2	1.91	100 (CHCl <sub>3</sub> )	6.3	7.1	1.0 (CA)	4	68.0
3	1.91	100 (CHCl <sub>3</sub> )	3.1	3.6	1.0 (CA)	4	83.7
4	1.91	100 (CHCl <sub>3</sub> )	1.6	1.8	1.0 (CA)	4	53.1
5	1.91	100 (CHCl <sub>3</sub> )	3.1	3.6	1.0 (CA)	2	69.2
6	1.84	50 (CHCl <sub>3</sub> )	3.3	3.7	1.0 (CA)	4	80.6
7	1.97	50 (C <sub>6</sub> H <sub>6</sub> )	3.1	3.5	1.0 (CA)	4	70.3
8	1.97	50 (CCl <sub>4</sub> )	3.1	3.5	1.0 (CA)	4	67.1
9	1.97	50 (CH <sub>2</sub> Cl <sub>2</sub> )	3.1	3.5	1.0 (CA)	4	58.2
10	1.91	100 (CHCl <sub>3</sub> )	3.1	3.6	1.0 (BQ)	4	75.7
11	1.97	100 (CHCl <sub>3</sub> )	3.1	3.5	1.0 (I <sub>2</sub> )	4	67.1
12	1.97	50 (CHCl <sub>3</sub> )	3.1	3.5	1.0 (DDQ)	4	67.1
13	1.84	100 (CHCl <sub>3</sub> )	3.3	3.7	0.5 (CA)	4	40.3
14	1.65	50 (CHCl <sub>3</sub> )	3.6	4.1	Air	4	87.5
15	1.59	50 (CHCl <sub>3</sub> )	3.8	4.0 (Cl <sub>3</sub> CCO <sub>2</sub> H)	1.0 (CA)	4	54.1

<sup>a</sup> dipyrromethane-5,5'-dicarboxylic acid

its 5,5'-carboxyl derivative. The reason for the relatively low yields of porphyrins obtained from *meso*-substituted dipyrromethanes **3** is not clear, it can be possibly related to stable unreactive conformations of the starting compounds in the reaction media which hinders cyclization.

## Experimental

The electron absorption spectra (EAS) were recorded on a SPEC SSP-715 scanning spectrophotometer in chloroform. The <sup>1</sup>H

NMR spectra were obtained on a Bruker 500 instrument (TMS as the internal standard, 500 MHz, 20 °C) in the shared research center "Upper Volga regional physicochemical research center" of the Krestov Institute of Solution Chemistry of the Russian Academy of Sciences. Thin layer chromatography (TLC) was performed on Silufol plates.

*2-Chloromethyl-4-methyl-3,5-diethoxycarbonylpyrrole.* Sul-furyl chloride (28.4 ml, 0.35 mol) in acetic acid (60 ml) was added to a stirred suspension of 2,4-dimethyl-3,5-diethoxycarbonylpyrrole (84.0 g, 0.35 mol) in glacial acetic acid (700 ml). The temperature during the addition was maintained at 50-60 °C, then it was raised to 70 °C for 0.5 h. The mixture was slowly cooled, the

**Table 2.** The yield of porphyrins **6** obtained by the condensation of dipyrromethanes **3** or **11** with ethyl *ortho*-formate in the presence of trifluoroacetic acid in chloroform, oxidation with air.

Porphyrin <b>6</b>		Yield (%)
R	R <sup>1</sup>	
H	H	5.2
Me	H	31.9
Et	H	65.5
Pr	H	52.8 (64.5) <sup>a</sup>
Bu	H	68.8
Am	H	87.5 (39.4)
Hex	H	52.5 (25.7)
Hep	H	43.5 (25.7)
Bz	H	31.4
Et	Ph	35.4
Et	4-MeOPh	25.7 (15.5)
Bu	PH	35.2
Bu	4-MeOPh	39.2

<sup>a</sup>the yield for dipyrromethane-5,5'-dicarboxylic acid as the starting material is given in brackets.

pyrrole precipitate filtered, washed with 100 ml of petroleum ether and dried in air at ambient temperature. Yield: 64.6 g (67.4 %). M.p.: 153-154 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{\text{H}}$  ppm: 9.75 (bs, 1H, NH); 4.99 (s, 2H, CH<sub>2</sub>Cl); 4.40 (q, 2H, *J*=7.1 Hz, CH<sub>2</sub>-Et); 4.33 (q, 2H, *J*=7.1 Hz, OCH<sub>2</sub>-Et); 2.59 (s, 3H, CH<sub>3</sub>); 1.41 (q(t+t), 6H, *J*=7.1 Hz, CH<sub>3</sub>-Et).

**3,3',5,5'-Tetraethoxycarbonyl-4,4'-dimethyldipyrromethane (10, R=CO<sub>2</sub>Et).** 2-Chloromethyl-4-methyl-3,5-diethoxycarbonylpyrrole (60.0 g, 0.22 mol) was dissolved with stirring in refluxing acetic acid (80 ml), then water (80 ml) was gradually added, and the mixture was further refluxed for 1.5 hours, slowly cooled, and the precipitate was filtered, washed with water, dried in air at ambient temperature. Yield: 45.3 g (89.0 %). M.p.: 134-136 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{\text{H}}$  ppm: 10.14 (bs, 2H, NH); 4.51 (s, 2H, *ms*-CH<sub>2</sub>); 4.39 (q, 4H, *J*=7.1 Hz, OCH<sub>2</sub>-Et); 4.31 (q, 4H, *J*=7.1 Hz, OCH<sub>2</sub>-Et); 2.53 (s, 6H, CH<sub>3</sub>); 1.44 (t, 6H, *J*=7.1 Hz, CH<sub>3</sub>-Et); 1.37 (t, 6H, *J*=7.1 Hz, CH<sub>3</sub>-Et).

**5,5'-Diethoxycarbonyl-3,3'-di-*n*-amyl-4,4'-dimethyldipyrrolylmethane (10, R=Am).** A suspension of 2,4-dimethyl-3-*n*-amyl-5-carboethoxypyrrole (100.0 g, 0.42 mol) and anhydrous sodium acetate (69.0 g, 0.84 mole) in acetic acid (500 ml) was stirred with cooling in a cold water bath. Bromine (21.6 ml, 0.42 mol) was gradually introduced. The suspension was stirred for 0.5 hours and poured into 3 liters of cold water, the precipitate was filtered, washed with water and refluxed for 3 hrs with a mixture of methanol (0.5 l) and concentrated hydrochloric acid (10 ml). After cooling the mixture was left overnight, the precipitate filtered, washed with water and dried. Yield: 54.5 g (56.5 %). M.p.: 125-126 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{\text{H}}$  ppm: 9.08 (bs, 2H, NH); 4.26 (q, 4H, *J*=7.2 Hz, OCH<sub>2</sub>-Et); 3.88 (s, 2H, *ms*-CH<sub>2</sub>); 2.39 (t, 4H, *J*=7.3 Hz, CH<sub>2</sub>-Am); 2.28 (s, 6H, CH<sub>3</sub>); 1.40 (qv, 4H, *J*=7.3 Hz, CH<sub>2</sub>-Am); 1.32 (t, 6H, *J*=7.2 Hz, CH<sub>3</sub>-Et); 1.31 (m, 8H, CH<sub>2</sub>-Am); 0.90 (t, 6H, *J*=7.3 Hz, CH<sub>3</sub>-Am).

In a similar way the following compounds were obtained:

**5,5'-Diethoxycarbonyl-3,3',4,4'-tetramethyldipyrrolylmethane (10, R=Me).** Yield: 52.5 %. M.p.: 195-197 °C (197 °C – lit.). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{\text{H}}$  ppm: 9.03 (bs, 2H, NH); 4.25 (q, 4H, *J*=7.1 Hz, OCH<sub>2</sub>-Et); 3.84 (s, 2H, *ms*-CH<sub>2</sub>); 2.24 (s, 6H, 4,4'-CH<sub>3</sub>); 1.95 (s, 6H, 3,3'-CH<sub>3</sub>); 1.30 (t, 6H, *J*=7.1 Hz, CH<sub>3</sub>-Et).

**5,5'-Diethoxycarbonyl-3,3'-diethyl-4,4'-dimethyldipyrrolylmethane (10, R=Et).** Yield: 57.6 %. M.p.: 130-131 °C. (130 °C –

lit.). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{\text{H}}$  ppm: 9.77 (bs, 2H, NH); 4.27 (q, 4H, *J*=7.1 Hz, OCH<sub>2</sub>-Et); 3.94 (s, 2H, *ms*-CH<sub>2</sub>); 2.47 (q, 4H, *J*=7.6 Hz, CH<sub>2</sub>-3,3'-Et); 2.31 (s, 6H, 4,4'-CH<sub>3</sub>); 1.31 (t, 6H, *J*=7.1 Hz, CH<sub>3</sub>-Et); 1.07 (t, 6H, *J*=7.6 Hz, CH<sub>3</sub>-3,3'-Et). <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta_{\text{H}}$  ppm: 9.83 (bs, 2H, NH); 4.03 (q, 4H, *J*=7.2 Hz, OCH<sub>2</sub>-Et); 3.73 (s, 2H, *ms*-CH<sub>2</sub>); 2.30 (q, 4H, *J*=7.5 Hz, CH<sub>2</sub>-3,3'-Et); 2.17 (s, 6H, 4,4'-CH<sub>3</sub>); 1.23 (t, 6H, *J*=7.2 Hz, CH<sub>3</sub>-Et); 1.00 (t, 6H, *J*=7.5 Hz, CH<sub>3</sub>-3,3'-Et).

**5,5'-Diethoxycarbonyl-3,3'-di-*n*-propyl-4,4'-dimethyldipyrromethane (10, R=Pr).** Yield: 51.4 %. M.p.: 136-138 °C (116 °C – lit.). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{\text{H}}$  ppm: 9.43 (bs, 2H, NH); 4.25 (q, 4H, *J*=7.1 Hz, OCH<sub>2</sub>-Et); 3.90 (s, 2H, *ms*-CH<sub>2</sub>); 2.38 (t, 4H, *J*=7.4 Hz, CH<sub>2</sub>-Pr); 2.28 (s, 6H, 4,4'-CH<sub>3</sub>); 1.46 (sc, 4H, *J*=7.4 Hz, CH<sub>2</sub>-Pr); 1.30 (t, 6H, *J*=7.1 Hz, CH<sub>3</sub>-Et); 0.94 (t, 6H, *J*=7.4 Hz, CH<sub>3</sub>-Pr).

**5,5'-Diethoxycarbonyl-3,3'-di-*n*-butyl-4,4'-dimethyldipyrromethane (10, R=Bu).** Yield: 56.0 %. M.p.: 118-121 °C (125 °C – lit.). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{\text{H}}$  ppm: 9.25 (bs, 2H, NH); 4.16 (q, 4H, *J*=7.1 Hz, OCH<sub>2</sub>-Et); 3.80 (s, 2H, *ms*-CH<sub>2</sub>); 2.31 (t, 4H, *J*=7.2 Hz, CH<sub>2</sub>-Bu); 2.19 (s, 6H, 4,4'-CH<sub>3</sub>); 1.21 (m, 8H, CH<sub>2</sub>-Bu); 1.21 (t, 6H, *J*=7.1 Hz, CH<sub>3</sub>-Et); 0.84 (t, 6H, *J*=7.2 Hz, CH<sub>3</sub>-Bu). <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta_{\text{H}}$  ppm: 10.09 (bs, 2H, NH); 4.15 (q, 4H, *J*=7.1 Hz, OCH<sub>2</sub>-Et); 3.84 (s, 2H, *ms*-H); 2.34 (t, 4H, *J*=7.0 Hz, CH<sub>2</sub>-Bu); 2.18 (s, 6H, CH<sub>3</sub>); 1.29-1.37 (m, 8H, CH<sub>2</sub>-Bu); 1.26 (t, 6H, *J*=7.1 Hz, CH<sub>3</sub>-Et); 0.91 (t, 6H, *J*=7.0 Hz, CH<sub>3</sub>-Bu).

**5,5'-Diethoxycarbonyl-3,3'-di-*n*-hexyl-4,4'-dimethyldipyrromethane (10, R=Hex).** Yield: 62.1 %. M.p.: 134-136 °C (136 °C – lit.). <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta_{\text{H}}$  ppm: 9.91 (bs, 2H, NH); 4.16 (q, 4H, *J*=7.1 Hz, OCH<sub>2</sub>-Et); 3.86 (s, 2H, *ms*-H); 2.33 (t, 4H, *J*=6.9 Hz, CH<sub>2</sub>-Hc); 2.18 (s, 6H, CH<sub>3</sub>); 1.24-1.36 (m, t 6+16H, *J*=7.1 Hz, CH<sub>3</sub>-Et + CH<sub>2</sub>-Hc); 0.88 (t, 6H, *J*=6.9 Hz, CH<sub>3</sub>-Hc).

**5,5'-Diethoxycarbonyl-3,3'-di-*n*-heptyl-4,4'-dimethyldipyrromethane (10, R=Hep).** Yield: 58.6 %. M.p.: 130-133 °C. <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta_{\text{H}}$  ppm: 9.81 (bs, 2H, NH); 4.17 (q, 4H, *J*=7.1 Hz, OCH<sub>2</sub>-Et); 3.83 (s, 2H, *ms*-H); 2.34 (t, 4H, *J*=7.2 Hz, CH<sub>2</sub>-Hp); 2.18 (s, 6H, CH<sub>3</sub>); 1.20-1.38 (m, t 6+20H, *J*=7.1 Hz, CH<sub>3</sub>-Et + CH<sub>2</sub>-Hp); 0.88 (t, 6H, *J*=7.2 Hz, CH<sub>3</sub>-Hp).

**5,5'-Diethoxycarbonyl-3,3'-dibenzyl-4,4'-dimethyldipyrromethane (10, R=Bz).** Yield: 46.8 %. M.p.: 121-122 °C (120 °C – lit.). <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta_{\text{H}}$  ppm: 10.05 (bs, 2H, NH); 7.28-6.82 (m, 10H, H-Ph); 4.03 (q, 4H, *J*=7.1 Hz, OCH<sub>2</sub>-Et); 3.70 (s, 2H, *ms*-CH<sub>2</sub>); 3.48 (s, 4H, CH<sub>2</sub>Ph); 1.20 (t, 6H, *J*=7.1 Hz, CH<sub>3</sub>-Et).

**2-Carboxy-3-ethyl-4-methyl-5-ethoxycarbonylpyrrole (13, R=Et).** 2-Ethoxycarbonyl-3,5-dimethyl-4-ethylpyrrole (50.0 g, 0.26 mol) was dissolved with stirring and cooling in 500 ml of ether, and sulfuric chloride (68.5 ml, 0.85 mol) was gradually added. The mixture was kept overnight at ambient temperature, then ether was distilled off and a mixture of acetone (100 ml) and water (100 ml) was added to the residue. The mixture was refluxed for 20 min, and a solution of sodium acetate trihydrate (150 g, 1.1 mol) in water (200 ml) was added with subsequent reflux for 2 hrs. Acetone was distilled off and after cooling the precipitate was filtered and washed with water. The precipitate was then treated with ethanol (100 ml) and 500 ml of aqueous solution of sodium carbonate decahydrate (70.0 g, 0.24 mol) was added with stirring. The mixture was then extracted with ether the aqueous solution acidified with diluted (1:5 v/v) hydrochloric acid, the sediment was filtered off, washed with water and dried in air at 70 °C. The yield was 41.2 g (62.6 %). M.p.: 208-210 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{\text{H}}$  ppm: 9.51 (bs, 1H, NH); 4.39 (q, 2H, *J*=7.1 Hz, OCH<sub>2</sub>-Et); 2.82 (q, 2H, *J*=7.5 Hz, CH<sub>2</sub>-Et); 2.32 (s, 3H, 4-CH<sub>3</sub>); 1.41 (t, 3H, *J*=7.1 Hz, CH<sub>3</sub>-OEt); 1.15 (t, 3H, *J*=7.5 Hz, CH<sub>3</sub>-Et).

In a similar way the following compounds were obtained:

**2-Carboxy-3-*n*-butyl-4-methyl-5-ethoxycarbonylpyrrole (13, R=Bu).** Yield: 71.0 %. M.p.: 178-181 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{\text{H}}$  ppm: 9.49 (bs, 1H, NH); 4.39 (q, 2H, *J*=7.1 Hz, OCH<sub>2</sub>-Et); 2.78 (t, 2H, *J*=7.5 Hz, CH<sub>2</sub>-Bu); 2.31 (s, 3H, 4-CH<sub>3</sub>); 1.51 (qv, 2H, *J*=7.5 Hz, CH<sub>2</sub>-Bu); 1.41 (t+1.40sc, 5H, *J*=7.1 Hz, *J*=7.5 Hz, CH<sub>3</sub>-OEt+CH<sub>2</sub>-Bu); 0.95 (t, 3H, *J*=7.5 Hz, CH<sub>3</sub>-Bu).

**2-Iodo-3-ethyl-4-methyl-5-ethoxycarbonylpyrrole (14, R=Et).**

Potassium bicarbonate (12.0 g, 0.12 mol) in water (100 ml) was added to a solution of 2-carboxy-3-ethyl-4-methyl-5-ethoxycarbonylpyrrole (9.0 g, 0.04 mol) in methanol (100 ml). The mixture was heated to 60 °C, after which a mixture of iodine (10.5 g, 0.04 mmol) and potassium iodide (17.2 g, 0.1 mol) in water (100 ml) was gradually added. The mixture was additionally stirred for 15 min, cooled, the precipitate was filtered, washed with water and dried in open air at ambient temperature to constant weight. The yield was 10.6 g (86 %). M.p.: 113-116 °C. <sup>1</sup>H NMR (CCl<sub>4</sub>) δ<sub>H</sub> ppm: 9.14 (bs, 1H, NH); 4.37 (q, 2H, J=7.1 Hz, OCH<sub>2</sub>-Et); 2.28 (t, 2H, <sup>1</sup>J=7.5 Hz, CH<sub>2</sub>-Et); 2.30 (s, 3H, CH<sub>3</sub>); 1.27 (7H, J=7.1 Hz, CH<sub>3</sub>-OEt); 1.05 (t, 3H, <sup>1</sup>J=7.5 Hz, CH<sub>3</sub>-Et).

**2-Iodo-3-n-butyl-4-methyl-5-ethoxycarbonylpyrrole (14, R=Bu)**

was obtained in a similar way. Yield: 77.5 %. M.p.: 102-106 °C. <sup>1</sup>H NMR (CCl<sub>4</sub>) δ<sub>H</sub> ppm: 9.34 (bs, 1H, NH); 4.32 (q, 2H, J=7.1 Hz, OCH<sub>2</sub>-Et); 2.33 (t, 2H, <sup>1</sup>J=7.2 Hz, CH<sub>2</sub>-Bu); 2.26 (s, 3H, CH<sub>3</sub>); 1.31-1.44 (m,t, 7H, J=7.1 Hz, CH<sub>3</sub>-Et+CH<sub>2</sub>-Bu); 0.95 (t, 3H, <sup>1</sup>J=7.2 Hz, CH<sub>3</sub>-Bu).

**3-Ethyl-4-methyl-5-ethoxycarbonylpyrrole (15, R=Et).**

a) 2-Iodo-3-ethyl-4-methyl-5-ethoxycarbonylpyrrole (15.0 g), tin(II) chloride dihydrate (12.5 g), potassium iodide (0.7 g) and concentrated sulfuric acid (20.0 ml) in ethanol (150 ml) were refluxed for 2 hrs. The mixture was then poured into an equal volume of water and extracted with ether. The ether was evaporated and the residue distilled under reduced pressure. The yield was 4.3 g (48.6 %). b) 2-Carboxy-3-ethyl-4-methyl-5-ethoxycarbonylpyrrole (8.0 g, 33.8 mmol) was heated on an oil bath at 250 °C until no more carbon dioxide was evolved (~2 hrs), then the residue was distilled *in vacuo* of a waterjet pump. The yield was 2.9 g (47.4 %). M.p.: 25 °C. <sup>1</sup>H NMR (CCl<sub>4</sub>) δ<sub>H</sub> ppm: 10.03 (bs, 1H, NH); 6.99 (d, 1H, J=2.9 Hz, 5-H); 4.70 (q, 2H, <sup>1</sup>J=7.2 Hz, OCH<sub>2</sub>-Et); 2.80 (q, 2H, <sup>2</sup>J=7.6 Hz, 4-CH<sub>2</sub>-Et); 2.64 (s, 3H, 3-CH<sub>3</sub>); 1.77 (t, 3H, <sup>1</sup>J=7.2 Hz, CH<sub>3</sub>-OEt); 1.56 (t, 3H, <sup>2</sup>J=7.6 Hz, 4-CH<sub>2</sub>-Et).

**3-n-Butyl-4-methyl-5-ethoxycarbonylpyrrole (15, R=Bu)**

was obtained similarly. Yield: 50.3 % (yellowish oily liquid). <sup>1</sup>H NMR (CCl<sub>4</sub>) δ<sub>H</sub> ppm: 10.14 (bs, 1H, NH); 6.95 (d, 1H, J=2.6 Hz, 5-H); 4.65 (q, 2H, <sup>1</sup>J=7.1 Hz, OCH<sub>2</sub>-Et); 2.75 (t, 2H, <sup>2</sup>J=7.6 Hz, 4-CH<sub>2</sub>-Bu); 2.62 (s, 3H, 3-CH<sub>3</sub>); 1.25-1.48 (m,t, 7H, <sup>1</sup>J=7.1 Hz, CH<sub>3</sub>-Et+CH<sub>2</sub>-Bu); 0.90 (t, 3H, <sup>1</sup>J=7.2 Hz, CH<sub>3</sub>-Bu).

**5,5'-Diethoxycarbonyl-*ms*-phenyl-3,3'-diethyl-4,4'-dimethyldipyrrromethane (16, R=Et, R'=Ph).** The solution of 3-ethyl-4-methyl-5-ethoxycarbonylpyrrole (6.3 g, 34.8 mmol), benzaldehyde (1.8 ml, 17.8 mmol) and conc. hydrochloric acid (5.0 ml) in methanol (50 ml) was refluxed for 1 h, then cooled, the precipitate was filtered, washed with methanol and dried. The yield was 5.8 g (74.1 %). M.p.: 116-118 °C. <sup>1</sup>H NMR (CCl<sub>4</sub>) δ<sub>H</sub> ppm: 9.71 (bs, 2H, NH); 6.79 (d, 2H, J=8.6 Hz, 2,6-H-Ar); 6.58 (d, 2H, J=8.6 Hz, 3,5-H-Ar); 5.40 (s, 1H, *ms*-H); 3.95-4.10 (m), 3.81-3.94 (m, 2x2H, OCH<sub>2</sub>-Et); 2.38 (q, 4H, <sup>1</sup>J=7.5 Hz, CH<sub>2</sub>-Et); 2.20 (s, 6H, 4,4'-CH<sub>3</sub>); 1.16 (t, 6H, <sup>2</sup>J=7.1 Hz, CH<sub>3</sub>-OEt); 0.90 (t, 6H, <sup>1</sup>J=7.5 Hz, CH<sub>3</sub>-Et).

In a similar way the following compounds were obtained:

**5,5'-Diethoxycarbonyl-*ms*-(4-methoxyphenyl)-3,3'-diethyl-4,4'-dimethyldipyrrromethane (16, R=Et, R'=4-MeOPh).** Yield: 87.3 %. M.p.: 126-128 °C. <sup>1</sup>H NMR (CCl<sub>4</sub>) δ<sub>H</sub> ppm: 9.68 (bs, 2H, NH); 7.05-7.15 (m, 3H, 3,4,5-H-Ph); 7.02 (d, 2H, J=7.5 Hz, 2,6-H-Ph); 5.44 (s, 1H, *ms*-H); 3.64 (s, 3H, OCH<sub>3</sub>); 3.92-4.01 m, 3.83-3.92 (m, 2x2H, OCH<sub>2</sub>-Et); 2.36 (q, 4H, <sup>1</sup>J=7.4 Hz, CH<sub>2</sub>-Et); 2.16 (s, 6H, 4,4'-CH<sub>3</sub>); 1.14 (t, 6H, <sup>2</sup>J=7.1 Hz, CH<sub>3</sub>-OEt); 0.93 (t, 6H, <sup>1</sup>J=7.4 Hz, CH<sub>3</sub>-Et).

**5,5'-Diethoxycarbonyl-*ms*-phenyl-3,3'-di-n-butyl-4,4'-dimethyldipyrrromethane (16, R=Bu, R'=Ph).** Yield: 46.7 %. <sup>1</sup>H NMR (CCl<sub>4</sub>) δ<sub>H</sub> ppm: 9.55 (bs, 2H, NH); 7.10-7.19 (m, 3H, 3,4,5-H-Ph); 6.98 (d, 2H, J=7.3 Hz, 2,6-H-Ph); 5.51 (s, 1H, *ms*-H); 3.93-4.08 (m, 4H, OCH<sub>2</sub>-Et); 2.32 (q, 4H, <sup>1</sup>J=7.4 Hz, CH<sub>2</sub>-Bu); 2.19 (s, 6H, 4,4'-CH<sub>3</sub>); 1.24-1.33 (m, 8H, CH<sub>2</sub>-Bu); 1.20 (t, 6H, <sup>2</sup>J=7.2 Hz, CH<sub>3</sub>-OEt); 0.86 (t, 6H, <sup>1</sup>J=7.4 Hz, CH<sub>3</sub>-Bu).

**5,5'-Diethoxycarbonyl-*ms*-(4-methoxyphenyl)-3,3'-di-n-butyl-4,4'-dimethyldipyrrromethane (16, R=Bu, R'=4-MeOPh).**

Yield: 62 %. <sup>1</sup>H NMR (CCl<sub>4</sub>) δ<sub>H</sub> ppm: 9.65 (bs, 2H, NH); 6.82 (d, 2H, J=8.6 Hz, 2,6-H-Ar); 6.56 (d, 2H, J=8.6 Hz, 3,5-H-Ar); 5.53 (s, 1H, *ms*-H); 3.54 (s, 3H, OCH<sub>3</sub>); 3.98-4.10 (m, 4H, OCH<sub>2</sub>-Et); 2.30 (q, 4H, <sup>1</sup>J=7.5 Hz, CH<sub>2</sub>-Bu); 2.17 (s, 6H, 4,4'-CH<sub>3</sub>); 1.20-1.31 (m, 8H, CH<sub>2</sub>-Bu); 1.20 (t, 6H, <sup>2</sup>J=7.1 Hz, CH<sub>3</sub>-OEt); 0.87 (t, 6H, <sup>1</sup>J=7.5 Hz, CH<sub>3</sub>-Bu).

*A general procedure for the synthesis of 5,5'-unsubstituted dipyrrromethanes [3 (X=H), 11].* A solution of 5,5'-diethoxycarbonyldipyrrromethane (1.0 g) and potassium hydroxide (1.0 g, 17.8 mmol) was refluxed in 15 ml of ethylene glycol. The mixture was cooled, poured into water and the precipitate filtered or extracted with methylene chloride, washed with water and dried in air at ambient temperature or with sodium sulfate and the solvent was distilled off under vacuum and the product was used without further purification.

*A general procedure for the synthesis of 5,5'-dicarboxydipyrrromethanes (3, X=COOH).* A mixture of 5,5'-dicarboxydipyrrromethane (1.0 g), potassium hydroxide (2.0 g, 35.6 mmol), water (5 ml), and methanol (20 ml) was refluxed for 4 hours. The methanol was distilled off and the residue treated with 200 ml of water, filtered and acidified with dilute (1:5 v/v) hydrochloric acid to pH ~ 5. The precipitate was filtered, washed with water and dried in air at ambient temperature.

**2,8,12,18-Tetra-n-amylyl-3,7,13,17-tetramethylporphyrin (6, R=Am, R'=H).** A solution 4,4'-dimethyl-3,3'-di-n-amyldipyrrromethane (0.52 g, 1.65 mmol), ethyl orthoformate (1.0 ml, 6.01 mmol) and trifluoroacetic acid (0.5 ml, 6.8 mmol) in of chloroform (50 ml) was refluxed for 4 hrs (starting from the second hour a weak stream of air was bubbled through). The mixture was cooled and evaporated at ambient temperature. The residue was dissolved in methylene chloride and chromatographed on aluminum oxide (Brockman grade II) using methylene chloride as the eluent. The first red zone of the porphyrin was collected, the solvent was evaporated and the product precipitated with methanol. The porphyrin was filtered, washed with methanol and dried at 70 °C in air. The yield was 0.47 g (87.5 %). Rf: 0.40 (benzene-hexane, 1:1). UV-Vis (CHCl<sub>3</sub>) λ nm (lge): 620 (3.80); 566 (3.89); 533 (4.05); 498 (4.17); 399 (5.25). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ<sub>H</sub> ppm: 10.11s, 10.10s (2 x 2H, *ms*-H); 4.09 (t, 8H, J=7.2 Hz, CH<sub>2</sub>-Am); 3.66 (s, 12H, 3,7,13,17-CH<sub>3</sub>); 2.33 (qv, 8H, J=7.2 Hz, CH<sub>2</sub>-Am); 1.74 (qv, 8H, J=7.2 Hz, CH<sub>2</sub>-Am); 1.55 (sc, 8H, J=7.2 Hz, CH<sub>2</sub>-Am); 0.98 (t, 12H, J=7.2 Hz, CH<sub>3</sub>-Am); -3.75 (bs, 2H, NH). Mass spectrum (MALDI TOF) *m/z*: 646.217 [M]<sup>+</sup>, calculated: 647.008.

In a similar way the following compounds were obtained:

**2,8,12,18-Tetra-n-propyl-3,7,13,17-tetramethylporphyrin (6, R=Pr, R'=H).** Yield: 52.8 %. Rf: 0.45 (benzene-hexane, 1:1). UV-Vis (CHCl<sub>3</sub>) λ nm (lge): 621 (3.74); 568 (3.86); 535 (4.03); 499 (4.15); 400 (5.25). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ<sub>H</sub> ppm: 10.13s, 10.10 (s, 2 x 2H, *ms*-H); 4.09 (t, 8H, J=7.1 Hz, CH<sub>2</sub>-Pr); 3.67 (s, 12H, 3,7,13,17-CH<sub>3</sub>); 2.35 (sc, 8H, J=7.1 Hz, CH<sub>2</sub>-Pr); 1.30 (t, 12H, J=7.1 Hz, CH<sub>3</sub>-Pr); -3.73 (bs, 2H, NH). Mass spectrum (MALDI TOF) *m/z*: 534.185 [M]<sup>+</sup>, calculated: 534.792.

**2,8,12,18-Tetra-n-butyl-3,7,13,17-tetramethylporphyrin (6, R=Bu, R'=H).** Yield: 68.8 %. R<sub>f</sub>: 0.36 (benzene:hexane, 1:1). UV-Vis (CHCl<sub>3</sub>) λ nm (lge): 620 (3.80); 567 (3.89); 534 (4.05); 499 (4.17); 399 (5.25). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ<sub>H</sub> ppm: 10.11s, 10.10 (s, 2x2H, *ms*-H); 4.10 (t, 8H, J=7.4 Hz, CH<sub>2</sub>-Bu); 3.66 (s, 12H, 3,7,13,17-CH<sub>3</sub>); 2.31 (qv, 8H, J=7.4 Hz, CH<sub>2</sub>-Bu); 1.79 (sc, 8H, J=7.4 Hz, CH<sub>2</sub>-Bu); 1.15 (t, 12H, J=7.4 Hz, CH<sub>3</sub>-Bu); -3.74 (bs, 2H, NH). Mass spectrum (MALDI TOF) *m/z*: 590.294 [M]<sup>+</sup>, calculated: 590.900.

**2,8,12,18-Tetra-n-hexyl-3,7,13,17-tetramethylporphyrin (6, R=Hex, R'=H).** Yield: 52.5 %. R<sub>f</sub>: 0.65 (benzene:hexane, 1:1). UV-Vis (CHCl<sub>3</sub>) λ nm (lge): 620 (3.70); 566 (3.85); 534 (4.01); 500 (4.11); 400 (5.27). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ<sub>H</sub> ppm: 10.11s, 10.10 (s, 2 x 2H, *ms*-H); 4.09 (t, 8H, J=7.4 Hz, CH<sub>2</sub>-Hex); 3.65 (s, 12H, 3,7,13,17-CH<sub>3</sub>); 2.33 (qv, 8H, J=7.4 Hz, CH<sub>2</sub>-Hex); 1.78 (qv, 8H, J=7.4 Hz, CH<sub>2</sub>-Hex); 1.53 (qv, 8H, J=7.4 Hz, CH<sub>2</sub>-Hex); 1.40 (sc, 8H, J=7.4 Hz, CH<sub>3</sub>-Hex); 0.94 (t, 12H, J=7.4 Hz, CH<sub>3</sub>-Hex); -3.74

(bs, 2H, NH). Mass spectrum (MALDI TOF)  $m/z$ : 702.180 [M]<sup>+</sup>, calculated: 703.116.

*2,8,12,18-Tetra-n-heptyl-3,7,13,17-tetramethylporphyrin* (**6**,  $R=Hep$ ,  $R'=H$ ). Yield: 43.5 %.  $R_f$ : 0.61 (benzene:hexane, 1:1). UV-Vis (CHCl<sub>3</sub>)  $\lambda$  nm (lg $\epsilon$ ): 620 (3.80); 567 (3.89); 533 (4.04); 498 (4.16); 399 (5.19). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_H$  ppm: 10.11s, 10.10 (s, 2  $\times$  2H, *ms*-H); 4.09 (t, 8H,  $J=7.1$  Hz, CH<sub>2</sub>-Hep); 3.66 (s, 12H, 3,7,13,17-CH<sub>3</sub>); 2.32 (qv, 8H,  $J=7.1$  Hz, CH<sub>2</sub>-Hp); 1.76 (qv, 8H,  $J=7.1$  Hz, CH<sub>2</sub>-Hp); 1.50-1.62 (m, 8H, CH<sub>2</sub>-Hp); 1.31-1.38 (m, 16H, CH<sub>2</sub>-Hp) 0.89 (t, 12H,  $J=7.1$  Hz, CH<sub>3</sub>-Hp); -3.73 (bs, 2H, NH). Mass spectrum (MALDI TOF)  $m/z$ : 759.180 [M]<sup>+</sup>, calculated: 759.224.

*5,15-Diphenyl-3,7,13,17-tetraethyl-2,8,12,18-tetramethylporphyrin* (**6**,  $R=Et$ ,  $R'=Ph$ ). Yield: 35.4 %.  $R_f$ : 0.12 (benzene:hexane, 1:1). UV-Vis (CHCl<sub>3</sub>)  $\lambda$  nm (lg $\epsilon$ ): 627 (3.45); 576 (3.92); 543 (3.82); 509 (4.26); 410 (5.32). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_H$  ppm: 10.28 (s, 2H, 10.20-H); 8.21 (d, 4H,  $J=7.4$  Hz, 2.6-H-Ph); 7.83 (t, 2H,  $J=7.4$  Hz, 4-H-Ph); 7.70 (t, 4H,  $J=7.4$  Hz, 3.5-H-Ph); 3.58 (s, 12H, 2,8,12,18-CH<sub>3</sub>); 2.81 (q, 8H,  $J=7.5$  Hz, CH<sub>2</sub>-Et); 1.21 (t, 12H,  $J=7.5$  Hz, 2,8,12,18-CH<sub>3</sub>-Et); -2.15 (bs, 2H, NH). Mass spectrum (MALDI TOF)  $m/z$ : 702.180 [M]<sup>+</sup>, calculated: 703.116.

*5,15-Diphenyl-3,7,13,17-tetra-n-butyl-2,8,12,18-tetramethylporphyrin* (**6**,  $R=Bu$ ,  $R'=Ph$ ). Yield: 35.2 %.  $R_f$ : 0.79 (benzene); 0.40 (benzene:hexane, 1:1). UV-Vis (CHCl<sub>3</sub>)  $\lambda$  nm (lg $\epsilon$ ): 625 (3.53); 577 (3.96); 544 (3.87); 510 (4.29); 411 (5.33). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_H$  ppm: 10.28s (2H, 10.20-H); 8.21 (d, 4H,  $J=7.4$  Hz, 2.6-H-Ph); 7.85 (t, 2H,  $J=7.4$  Hz, 4-H-Ph); 7.71 (t, 4H,  $J=7.4$  Hz, 3.5-H-Ph); 3.58 (s, 12H, 2,8,12,18-CH<sub>3</sub>); 2.71-2.78 (m, 8H, CH<sub>2</sub>-Bu); 1.54-1.64 (m, 8H, CH<sub>2</sub>-Bu); 1.25 (sc, 8H,  $J=7.3$  Hz, CH<sub>2</sub>-Bu); 0.94 (t, 12H,  $J=7.3$  Hz, CH<sub>3</sub>-Bu); -2.12 bs. Mass spectrum (MALDI TOF)  $m/z$ : 743.357 [M]<sup>+</sup>, calculated: 743.096.

*5,15-Bis(4-methoxyphenyl)-3,7,13,17-tetra-n-butyl-2,8,12,18-tetramethylporphyrin* (**6**,  $R=Bu$ ,  $R'=4-MeOPh$ ). Yield: 39.2 %.  $R_f$ : 0.45 (benzene). UV-Vis (CHCl<sub>3</sub>)  $\lambda$  nm (lg $\epsilon$ ): 628 (3.32); 578 (3.92); 544 (3.79); 511 (4.29); 412 (5.41). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_H$  ppm: 10.24 (s, 2H, 10.20-H); 8.06 (d, 4H,  $J=8.5$  Hz, 2.6-H-Ar); 3.24 (d, 4H,  $J=8.5$  Hz, 3.5-H-Ar); 4.12 (s, 6H, CH<sub>3</sub>O); 3.57 (s, 12H, 2,8,12,18-CH<sub>3</sub>); 2.81 (t, 8H,  $J=8.4$  Hz, CH<sub>2</sub>-Bu); 1.54-1.63 (m, 8H, CH<sub>2</sub>-Bu); 1.28 (sc, 8H,  $J=7.4$  Hz, CH<sub>2</sub>-Bu); 0.93 (t, 12H,  $J=7.4$  Hz, CH<sub>3</sub>-Bu); -2.14 (bs, 2H, NH). Mass spectrum (MALDI TOF)  $m/z$ : 803.354 [M]<sup>+</sup>, calculated: 803.148.

*3,7,13,17-Tetramethylporphyrin* (**6**,  $R,R'=H$ ). A solution of 4,4'-dimethyldipyrromethane (0.55 g, 3.16 mmol), ethyl *ortho*-formate (1.0 ml, 6.01 mmol) and trifluoroacetic acid (0.5 ml, 6.7 mmol) in chloroform (50 ml) of was refluxed for 4 hrs (from the second the hour a weak stream of air was passed through the mixture). After cooling, diethylamine (1.0 ml, 9.6 mmol) was added to neutralize the acid and the precipitate was filtered and washed with methylene chloride. The precipitate was then dissolved in methylene chloride with addition of trifluoroacetic acid, the solution was filtered and reprecipitation with diethylamine was performed. The precipitate was filtered sediment and washed with methylene chloride. Yield: 30 mg (5.2 %). UV-Vis (CHCl<sub>3</sub>)  $\lambda$  nm (lg $\epsilon$ ): 618 (3.56); 565 (3.78); 527 (3.86); 495 (4.12); 398 (5.27). UV-Vis (CHCl<sub>3</sub>-TFA)  $\lambda$  nm (lg $\epsilon$ ): 547 (4.12); 403 (5.52). <sup>1</sup>H NMR (CDCl<sub>3</sub>-TFA)  $\delta_H$  ppm: 10.88 (s, 2H, 5.15-H); 10.85 (s, 2H, 10.20-H); 9.55 (s, 4H, 2,8,12,18-H); -4.09 (bs, 4H, NH). Mass spectrum (MALDI TOF)  $m/z$ : 366.087 [M]<sup>+</sup>, calculated: 366.468.

In a similar way the following compounds were obtained:

*2,3,7,8,12,13,17,18-Octamethylporphyrin* (**6**,  $R=Me$ ,  $R'=H$ ). Yield: 31.9 %. UV-Vis (CHCl<sub>3</sub>)  $\lambda$  nm (lg $\epsilon$ ): 620 (7.72); 567 (3.82); 532 (3.99); 497 (4.13); 396 (5.19). UV-Vis (CHCl<sub>3</sub>-TFA)  $\lambda$  nm (lg $\epsilon$ ): 590 (3.90); 548 (4.23); 401 (5.60). <sup>1</sup>H NMR (CDCl<sub>3</sub>-TFA)  $\delta_H$  ppm: 10.77 (s, 4H, *ms*-H); 3.70 (s, 24H, CH<sub>3</sub>); -4.46 (bs, 4H, NH). Mass spectrum (MALDI TOF)  $m/z$ : 422.129 [M]<sup>+</sup>, calculated: 422.576.

*2,8,12,18-Tetraethyl-3,7,13,17-tetramethylporphyrin* (**6**,  $R=Et$ ,  $R'=H$ ). Yield: 65.5 %.  $R_f$  (Silufol): 0.22 (benzene:hexane, 1:1). UV-Vis (CHCl<sub>3</sub>)  $\lambda$  nm (lg $\epsilon$ ): 620 (3.83); 566 (3.91); 532 (4.06); 499 (4.18); 398 (5.21). <sup>1</sup>H NMR (CDCl<sub>3</sub>-TFA)  $\delta_H$  ppm: 10.71s, 10.70 (s, 2 $\times$ 2H, *ms*-H); 4.18 (q, 8H,  $J=7.1$  Hz, CH<sub>2</sub>-Et); 3.70 (s, 12H, CH<sub>3</sub>); 1.79 (t, 12H,  $J=7.1$  Hz, CH<sub>3</sub>-Et); -4.01 (bs, 4H, NH). Mass spectrum (MALDI TOF)  $m/z$ : 478.158 [M]<sup>+</sup>, calculated: 478.684.

*2,8,12,18-Tetrabenzyl-3,7,13,17-tetramethylporphyrin* (**6**,  $R=Bz$ ,  $R'=H$ ). Yield: 31.4 %. UV-Vis (CHCl<sub>3</sub>)  $\lambda$  nm (lg $\epsilon$ ): 623 (3.79); 570 (3.90); 534 (4.05); 500 (4.20); 403 (5.29). <sup>1</sup>H NMR (CDCl<sub>3</sub>-TFA)  $\delta_H$  ppm: 10.71s, 10.50 (s, 2 $\times$ 2H, *ms*-CH); 7.21-7.32 (20H, H-Ph); 5.30 (s, 8H, CH<sub>2</sub>Ph); 3.65 (s, 12H, CH<sub>3</sub>); -3.69 (bs, 4H, NH). Mass spectrum (MALDI TOF)  $m/z$ : 743.087 [M]<sup>+</sup>, calculated: 743.096.

*5,15-Bis(4-methoxyphenyl)-3,7,13,17-tetraethyl-2,8,12,18-tetramethylporphyrin* (**6**,  $R=Et$ ,  $R'=4-MeOPh$ ). Yield: 25.7 %.  $R_f$ : 0.21 (benzene). UV-Vis (CHCl<sub>3</sub>)  $\lambda$  nm (lg $\epsilon$ ): 625 (3.47); 577 (3.93); 544 (3.80); 510 (4.26); 411 (5.34). <sup>1</sup>H NMR (CDCl<sub>3</sub>-TFA)  $\delta_H$  ppm: 10.07 (s, 2H, 5.10-H); 8.31 (d, 4H,  $J=8.4$  Hz, 2.6-H-Ar); 7.41 (d, 4H,  $J=8.4$  Hz, 3.5-H-Ar); 4.16 (s, 6H, OCH<sub>3</sub>); 3.15 (s, 12H, 2,8,12,18-CH<sub>3</sub>); 2.59-2.71 (m, 8H, CH<sub>2</sub>-Et); 0.55 (t, 12H,  $J=7.5$  Hz, CH<sub>3</sub>-Et); -1.80 (bs, 4H, NH). Mass spectrum (MALDI TOF)  $m/z$ : 690.260 [M]<sup>+</sup>, calculated: 692.948.

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