Asymmetrically substituted tetra(*meso*-aryl)porphyrins bearing peripheral 2,6-diisobornylphenol and 2,6-di-*tert*-butylphenol moieties

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Asymmetrically substituted tetra(*meso*-aryl)porphyrins bearing peripheral diisobornylphenol and di-*tert*-butylphenol moieties were synthesized by a mixed aldehyde condensation.

Key words: mixed aldehyde condensation, tetra(*meso*-aryl)porphyrins, 2,6-diisobornyl-4-methylphenol, 2,6-di-*tert*-butylphenol, hybrid antioxidants.

It is known that antioxidant activity of synthetic phenolic compounds often exceeds those of natural antioxidants.[1] It has been found that phenolic compounds reduce the rate of lipid and protein peroxidation and are promising candidates for treatment of free radical-induced diseases.[1—3] They show antihypoxic, hemorheological, and other important biological activities.[4—16] Significant antioxidant activity (AOA) of 2,6-di-*tert*-butyl-4-methylphenol and 2,6-diisobornyl-4-methylphenol is attributable to the presence in their structures of the bulky substituents positioned *ortho* with respect to the hydroxy group.[17] Lipophilic porphyrin free bases and their metal complexes are capable of incorporating into the lipid bilayer of the cell membranes[18] and inactivating the free radicals.[19] These properties form the basis for the use of porphyrin scaffolds in treatment of the diseases mediated by oxidative stress and make the studies in this field very relevant.[20] Introduction of the fragments of the molecules having their own AOA into the porphyrin periphery noticeably affects the antioxidant activity of these conjugates. Thus, it has been found earlier[19,21—23] that symmetrically substituted tetra(*meso*-aryl)porphyrins bearing peripheral diisobornylphenol and di-*tert*-butylphenol moieties possess antioxidant and antiradical activities. Moreover, porphyrin macrocycle is able to modify the overall biological activity of the molecule not only by changing the reactivity of the phenolic moiety but also by changing the body distribution of the antioxidant.[20]

It is interesting to vary the number of terpenephenolic substituents appended to the porphyrin framework because it gives possibility to examine the impact of these fragments into overall AOA of the compound. Consequently, the synthesis of asymmetrically substituted porphyrins bearing different number of terpenephenolic substituents is actual. In the present work, we studied a mixed aldehyde condensation of either 4-hydroxy-3,5-di(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)benzaldehyde (**1**) or 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (**2**) with benzaldehyde (**3**) (4-methoxybenzaldehyde (**8**)) and pyrrole to synthesize asymmetrically substituted tetra(*meso*-aryl)porphyrins bearing one diisobornylphenol or di-*tert*-butylphenol group (Scheme 1 and 2).

Results and Discussion

It is known[18] that a mixed aldehyde condensation of pyrrole and two different aldehydes gives, in principal, a set of six porphyrins. By using the excess of one of aldehyde, the significant simplification of the reaction mixture is possible. In this case, two porphyrins are predominantly formed, *i.e.*, a symmetrically substituted porphyrin derived from the excess aldehyde and an asymmetrically substituted porphyrin bearing one substituent derived from the limiting aldehyde. In most cases, the separation of the mixture of formed porphyrins could be accomplished. Thus, mixed aldehyde condensation is an expedient approach to achieve our goals.

Condensation of pyrrole, aldehyde **1**, and four-fold excess of benzaldehyde **3** (with respect to aldehyde **1**) affords a mixture of porphyrins **4**—**7** (Scheme 1). Unfortunately, we failed to separate this mixture due to close polarity of the formed porphyrins.

Thin layer chromatography indicates that the reaction produces a mixture of four porphyrins. The composition of the mixture was examined by electrospray ionization mass spectrometry, ^{1}H NMR spectroscopy, and UV spectroscopy. Mass spectrum of the obtained mixture shows the peaks of the protonated molecular ions of porphyrins **4**—**7**. The UV spectrum contains the Soret band and the bands characteristic of the tetra-*meso*-substituted porphyrin chromophore. ^{1}H NMR spectrum exhibits signals characteristic of the porphyrin framework at

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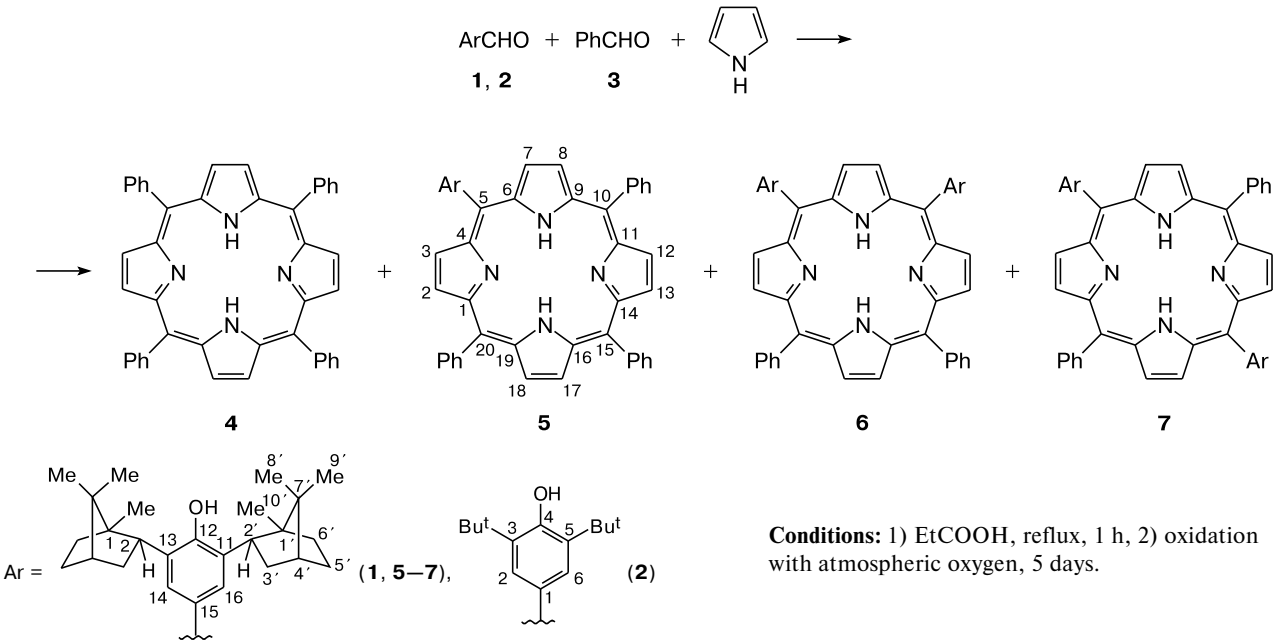
Scheme 1



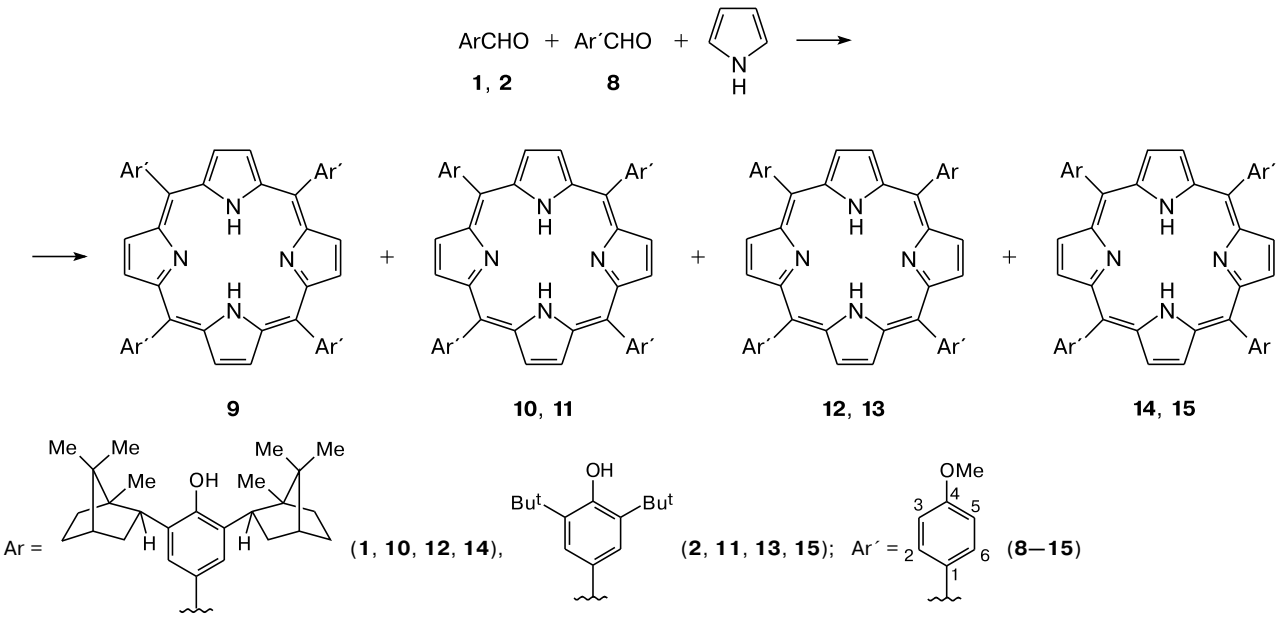
the δ 8.64—9.07 range and at δ −2.71 (signals of the H(β) proton of the pyrrole rings and the NH groups, respectively). Condensation of aldehyde **2**, benzaldehyde **3**, and pyrrole carried out under similar conditions gives predominantly tetra(*meso*-phenyl)porphyrin **4** along with the non-porphyrin products (see Scheme 1).

The probability of successful mixed aldehyde condensation increases by using aldehydes of similar reactivity, for instance, 4-methoxybenzaldehyde **8**, in the reaction with pyrrole. Moreover, introduction of the polar group into phenyl substituents located at the periphery of the porphyrin core greatly simplifies the separation of the product mixture. To synthesize porphyrins bearing one phenol substituent by the mixed aldehyde condensation, we used an excess of aldehyde **8** with the respect to aldehydes **1** and **2**. To minimize the formation of non-porphyrin material, the total molar amount of aldehydes used in the reaction was equal to molar amount of pyrrole (Scheme 2).

Condensation of pyrrole with a 4 : 1 mixture of 4-methoxybenzaldehyde **8** and aldehyde **1** produces a mixture of porphyrins **9**, **10**, **12**, and **14** (see Scheme 2). We succeeded in isolation of pure porphyrins **9**, **10**, and **12** by chromatographic separation of this mixture on a column filled with Al_2O_3 and SiO_2 (see Experimental). Porphyrin **14** was not isolated in pure state due to close polarity of products **12** and **14** and low yield of **14**. Similar reaction of pyrrole and a mixture of aldehydes **8** and **2** gives a mixture of porphyrins **9**, **11**, **13**, and **15** (see Scheme 2). Note that porphyrin **15** was not isolated pure from this mixture.

Structures of newly synthesized porphyrins **10—13** were established by IR and UV spectroscopy, NMR spectroscopy, and mass spectrometry. Electrospray ionization mass spectra of compounds **10—13** reveal the cluster peaks with m/z one mass unit ($[MH]^+$) and two mass units ($[M + 2\ H]^+$) larger than the molecular ion peak. UV spectra of the synthesized porphyrins show the Soret band and the bands characteristic of the tetra-*meso*-substituted porphyrin core. IR spectra of porphyrins **10—13** bearing 2,6-diisobornylphenol and 2,6-di-*tert*-butylphenol fragments exhibit stretching vibrations of the N—H bonds of the porphyrin framework and the O—H bonds of the hydroxy groups of the phenol moieties. ^{1}H NMR spectra of compounds **10—13** contain the signals of the porphyrin core (the H(β) pyrrole protons and the intracyclic NH protons) and the signals of diisobornylphenol (compounds **10** and **12**) and *tert*-butylphenol (compounds **11** and **13**) fragments. The integral intensity ratios of the signals of the protons of the porphyrin and phenol fragments indicate the presence of one phenol substituent in compounds **10** and **11** and two phenol moieties in compounds **12** and **13**. In ^{13}C NMR spectra, the carbon atoms of the diisobornyl (compounds **10** and **12**) and *tert*-butyl substituents (compounds **11** and **13**) resonate at δ_C 10—51 and δ_C 30—40, respectively. The positions of these signals ensure the retained structure of these fragments. The characteristic feature of the ^{13}C NMR spectra is the presence of the widened signals at δ_C 129—132. According to HSQC and HMBC experiments, these signals belongs to the C(α) and C(β) atoms of the pyrrole and pyrrolidene rings. Both ^{1}H—^{13}C HSQC

Scheme 2



Conditions: 1) EtCOOH, reflux, 1 h, 2) oxidation with atmospheric oxygen, 5 days.

and $^{1}H—^{13}C$ HMBC NMR spectra of the synthesized compounds show the cross-peaks between the H(β) of the pyrrole and pyrrolidene rings and the carbon atom at δ_C 129—132.

In summary, the present work describes the mixed aldehyde condensation of pyrrole with a mixture of either 4-hydroxy-3,5-di(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)benzaldehyde (**1**) or 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (**2**) and benzaldehyde **3** (4-methoxybenzaldehyde **8**) to synthesize asymmetrically substituted tetra(*meso*-aryl)porphyrins bearing one peripheral phenol substituent. A series of asymmetrically substituted porphyrins bearing the peripheral diisobornylphenol and di-*tert*-butylphenol moieties was synthesized. The reaction conditions were optimized to synthesize tetra(*meso*-aryl)porphyrins bearing one diisobornylphenol or di-*tert*-butylphenol substituent.

Experimental

IR spectra were recorded with a Shimadzu IR Prestige 21 K Fourier transform infrared spectrophotometer in KBr pellets. UV spectra were obtained with a Shimadzu UV-1700 spectrophotometer using the 10-mm quarts cells against chloroform in the reference cell. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance II instrument (working frequencies of 300 and 75 MHz, respectively) in $CDCl_3$. In some cases, the signals were attributed by using 2D NMR experiments (HSQC and HMBC). Electrospray ionization (ESI) mass spectrometry was performed with a Thermo Finnigan LCQ Fleet instrument. The course of the reaction was monitored by TLC on the Sorbfil precoated plates. The column chromatography was carried out with alumina 40/200 μm (pure grade) and silica gel 70/230μ (Alfa Aesar). Physicochemical studies of the synthesized compounds were carried out on the equipment of the Center for Collective Use "Chemistry" of the Institute of Chemistry of the Komi Scientific Center of the Ural Branch of the Russian Academy of Sciences.

Synthesis of 4-hydroxy-3,5-di(1,7,7-trimethylbicyclo[2.2.1]-hept-*exo*-2-yl)benzaldehyde (**1**) and its spectral properties have been described earlier.[24]

3,5-Di-*tert*-butyl-4-hydroxybenzaldehyde (**2**) was synthesized following the known procedure.[25]

Mixed aldehyde condensation of pyrrole, aldehyde 1, and benzaldehyde (3). A solution of 4-hydroxy-3,5-di(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)benzaldehyde **1** (0.29 g, 0.74 mmol), benzaldehyde **3** (0.30 mL, 2.94 mmol), and pyrrole (0.25 mL, 3.68 mmol) in propionic acid (15 mL) was added to the refluxing propionic acid (20 mL). The mixture was refluxed for 1 h, cooled down, and kept in air at room temperature for 5 days. The reaction mixture was diluted with chloroform, washed with water until neutral to remove excess propionic acid and other water soluble impurities. The organic layer was dried with anhydrous Na_2SO_4 and concentrated *in vacuo*. According to TLC and mass spectrometry, the residue (0.03 g) is a mixture of porphyrins **4**—**7**. The residue was washed with hexane to obtain violet fine crystalline powder. UV ($CHCl_3$), λ_{max}/nm (*I* (%)): 650 (2), 595 (1), 555.0 (2), 518 (4), 422.5 (100). MS (ESI), found: *m/z* 615.5 $[MH]^+$. $C_{44}H_{31}N_4$. Calculated: 615.3 (porphyrin **4**). Found: *m/z* 903.7 $[MH]^+$. $C_{64}H_{63}N_4O$. Calculated: 903.5 (porphyrin **5**). Found: *m/z* 1191.7 $[MH]^+$. $C_{84}H_{95}N_4O_2$. Calculated: 1191.8 (porphyrins **6** and **7**).

Mixed aldehyde condensation of pyrrole, aldehyde 2, and benzaldehyde (3). A solution of 3,5-di-*tert*-butyl-4-hydroxy-

benzaldehyde **2** (0.20 g, 0.85 mmol), benzaldehyde **3** (0.35 mL, 3.44 mmol), and pyrrole (0.30 mL, 4.29 mmol) in propionic acid (10 mL) was added to the refluxing propionic acid (7 mL). The mixture was refluxed for 1 h, cooled down, and kept in air at room temperature for 5 days. The reaction mixture was diluted with chloroform, washed with water until neutral to remove excess propionic acid and other water soluble impurities. The organic layer was dried with anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was washed with ethanol and separated by column chromatography. The chromatographic column was packed by the wet-loading method with Al_2O_3 (bottom layer) and SiO_2 (upper layer) using CCl_4 as a solvent. The products were eluted in a gradient mode with tetrachloromethane—acetone, 100 : 1→20 : 1. Compound **4** was isolated in the yield of 0.062 g (3%). Violet fine crystalline powder. Spectral properties of the obtained product are in agreement with those published earlier.[18]

Mixed aldehyde condensation of pyrrole, aldehyde 1, and 4-methoxybenzaldehyde (8). A solution of 4-hydroxy-3,5-di(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)benzaldehyde **1** (0.29 g, 0.74 mmol), 4-methoxybenzaldehyde **8** (0.36 mL, 2.96 mmol), and pyrrole (0.26 mL, 3.75 mmol) in propionic acid (15 mL) was added to the refluxing propionic acid (20 mL). The mixture was refluxed for 1 h, cooled down, and kept in air at room temperature for 5 days. The mixture was diluted with chloroform and washed with water until neutral to remove excess propionic acid and other water soluble impurities. The organic layer was dried with anhydrous Na_2SO_4 and concentrated *in vacuo*. According to TLC and mass spectrometry, the residue is a mixture of porphyrins **9**, **10**, **12**, and **14**. The residue was washed with hexane and separated by column chromatography as described above using the column loaded with Al_2O_3 and SiO_2 (successive elution with hexane and chloroform). Purification gives 0.013 g (2%) of the target product **10**, 0.027 g (12%) of porphyrin **9**, 0.006 g (0.65%) of porphyrin **12**, and 0.005 g of the mixture of **12** and **14**.

Tetrakis(*meso*-methoxyphenyl)porphyrin (9). R_f 0.13 (Sorbfil, tetrachloromethane—acetone, 80 : 1). Spectral properties of the obtained product are in agreement with those published earlier.[26]

5-[3,5-Di(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)-4-hydroxyphenyl)]-10,15,20-tris(4-methoxyphenyl)porphyrin (10). Violet fine crystalline powder. R_f 0.36 (Sorbfil, tetrachloromethane—acetone, 80 : 1). ^{1}H NMR ($CDCl_3$), δ: −2.69 (br.s, 2 H, NH); 0.89 (s, 6 H, C(10,10′)H_3); 0.96 (s, 6 H, C(9,9′)H_3); 1.15 (s, 6 H, C(8,8′)H_3); 1.41—2.04 (m, 12 H, H(3,3′,4,4′), C(5,5′)H_2, C(6,6′)H_2); 2.29—2.43 (m, 2 H, H(3,3′)); 3.39 (br.t, 2 H, H(2,2′), J = 8.2 Hz); 4.13 (s, 9 H, C(10,15,20) ArOC$\underline{H}_3$); 5.24 (s, 1 H, OH); 7.32 (d, 6 H, C(10,15,20) ArH(3,5), J = 8.2 Hz); 8.06 (s, 2 H, C(5) ArH(14,16)); 8.16 (d, 6 H, C(10,15,20) ArH(2,6), J = 8.2 Hz); 8.84 (d, 2 H, H(3,7), J = 4.6 Hz); 8.86 (d, 2 H, H(2,8), J = 4.6 Hz); 8.89 (br.s, 6 H, H(12,13,17,18)). ^{13}C NMR ($CDCl_3$), δ: 12.93 (C(10,10′)); 20.37 (C(9,9′)); 21.48 (C(8,8′)); 27.65 (C(5,5′)); 34.24 (C(3,3′)); 40.26 (C(6,6′)); 45.49 (C(4,4′)); 46.39 (C(2,2′)); 48.26 (C(7,7′)); 50.25 (C(1,1′)); 55.59 (C(10,15,20) ArO$\underline{C}H_3$); 112.19 (C(10,15,20) ArC(3,5)); 119.52 and 119.60 (C(*meso*)); 121.33 (C(5) ArC(12)); 126.72 ((C5) ArC(11,13)); 130.26—131.75 (C(α,β)); 132.45 (C(5) ArC(14,16)); 134.78 (C(10,15,20) ArC(4)); 135.54 (C(10,15,20) ArC(2,6)); 153.86 (C(5) ArC(15)); 159.34 (C(10,15,20) ArC(1)). UV ($CHCl_3$), λ_{max}/nm (I (%)): 651 (1), 595 (1), 557 (3), 520 (4), 424 (100). MS (ESI), m/z 993.6 $[MH]^+$. IR (KBr), ν/cm^{-1}: 3599 (OH); 3316 (NH); 2835 (CH_3); 2949, 1607 (C=C); 1510, 1462, 1348, 1248, 1177, 1036, 972, 800, 735.

5,10-Bis[3,5-di(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)-4-hydroxyphenyl)]-15,20-bis(4-methoxyphenyl)porphyrin (12). Violet fine crystalline powder. R_f 0.59 (Sorbfil, tetrachloromethane—acetone, 80 : 1). ^{1}H NMR ($CDCl_3$), δ: −2.69 (br.s, 2 H, NH); 0.90 (s, 12 H, C(10,10′)H_3); 0.96 (s, 12 H, C(9,9′)H_3); 1.15 (s, 12 H, C(8,8′)H_3); 1.41—2.04 (m, 24 H, H(3,3′,4,4′), C(5,5′)H_2, C(6,6′)H_2); 2.30—2.44 (m, 4 H, H(3,3′)); 3.39 (br.t, 4 H, H(2,2′), J = 8.2 Hz); 4.14 (s, 6 H, C(15,20) ArOC$\underline{H}_3$); 5.24 (s, 2 H, OH); 7.33 (s, 4 H, C(15,20) ArH(3,5)); 8.06 (s, 4 H, C(5,10) ArH(14,16)); 8.16 (d, 4 H, C(15,20) ArH(2,6), J = 8.2 Hz); 8.79—8.88 (m, 4 H, H(2,3,12,13)); 8.89 (br.s, 4 H, H(7,8,17,18)). ^{13}C NMR ($CDCl_3$), δ: 12.93 (C(10,10′)); 20.37 (C(9,9′)); 21.47 (C(8,8′)); 27.67 (C(5,5′)); 34.21 (C(3,3′)); 40.25 (C(6,6′)); 45.51 (C(4,4′)); 46.39 (C(2,2′)); 48.27 (C(7,7′)); 50.25 (C(1,1′)); 55.59 (C(15,20) ArO$\underline{C}H_3$); 112.17 (C(15,20) ArC(3,5)); 119.38 and 120.11 (C(*meso*)); 121.35 (C(5,10) ArC(12)); 126.72 (C(5,10) ArC(11,13)); 130.88—132.49 (C(α,β)); 132.49 (C(5,10) ArC(14,16)); 134.93 (C(15,20) ArC(4)); 135.55 (C(15,20) ArC(2,6)); 153.82 (C(5,10) ArC(15)); 159.35 (C(15,20) ArC(1)). UV ($CHCl_3$), λ_{max}/nm (I (%)): 650 (5), 595 (5), 557 (7), 519 (9), 425 (100). MS (ESI), m/z 1252.6 $[M + 2H]^+$. IR (KBr), ν/cm^{-1}: 3595 (OH); 3318 (NH); 2874 (CH_3); 2953, 1605 (C=C); 1510, 1460, 1350, 1248, 1175, 1036, 974, 802, 737.

Mixed aldehyde condensation of pyrrole, aldehyde 2, and 4-methoxybenzaldehyde (8). A solution of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde **2** (0.20 g, 0.85 mmol), 4-methoxybenzaldehyde **8** (0.41 mL, 3.37 mmol), and pyrrole (0.29 mL, 4.22 mmol) in propionic acid (10 mL) was added to the refluxing propionic acid (7 mL). The mixture was refluxed for 1 h, cooled down, and kept in air for 5 days. The reaction mixture was diluted with chloroform and washed with water until neutral. The organic layer was dried with anhydrous Na_2SO_4 and concentrated *in vacuo*. According to TLC and mass spectrometry, the residue is a mixture of porphyrins **9**, **11**, **13**, and **15**. The residue was washed with hexane and separated by column chromatography as described above using the column loaded with Al_2O_3 and SiO_2 (elution with tetrachloromethane—acetone). Purification gives 0.014 g (2%) of the target product **11**, 0.02 g (8%) of porphyrin **9**, 0.006 g (0.76%) of porphyrin **13**, and 0.005 g of the mixture of **13** and **15**.

5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-10,15,20-tris(4-methoxyphenyl)porphyrin (11). Violet fine crystalline powder. R_f 0.57 (Sorbfil, tetrachloromethane—acetone, 80 : 1). ^{1}H NMR ($CDCl_3$), δ: −2.67 (br.s, 2 H, NH); 1.68 (s, 18 H, C(5) ArC(C$\underline{H}_3$)$_3$); 4.14 (s, 9 H, C(10,15,20) ArOC$\underline{H}_3$); 5.59 (s, 1 H, OH); 7.33 (d, 6 H, C(10,15,20) ArH(3,5), J = 8.2 Hz); 8.09 (br.s, 2 H, C(5) ArH(2,6)); 8.17 (d, 6 H, C(10,15,20) ArH(2,6), J = 8.2 Hz); 8.90 (br.s, 6 H, H(12,13,17,18)); 8.91 (d, 2 H, H(2,8), J = 4.6 Hz); 8.95 (d, 2 H, H(3,7), J = 4.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 30.69 (C(5) ArC($\underline{C}H_3$)$_3$)); 34.59 (C(5) Ar$\underline{C}$(CH_3)$_3$); 55.61 (C(10,15,20) ArO$\underline{C}H_3$); 112.20 (C(10,15,20) ArC(3,5)); 119.45 and 119.61 (C(*meso*)); 129.66—131.80 (C(α,β)); 132.12 (C(5) ArC(2,6)); 134.05 (C(10,15,20) ArC(4)); 134.83 (C(5) ArC(4)); 135.58 (C(10,15,20) ArC(2,6)); 153.61 (C(5) ArC(1)); 159.40 (C(10,15,20) ArC(1)). UV ($CHCl_3$), λ_{max}/nm (I (%)): 651 (1), 593 (1), 557 (3), 519 (4), 424 (100). MS (ESI), m/z 833.5 $[MH]^+$. IR (KBr), ν/cm^{-1}: 3630 (OH);

3316 (NH); 2835 (CH_3); 2957, 1607 (C=C); 1508, 1468, 1437, 1246, 1177, 1034, 972, 802, 735.

5,10-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-15,20-bis(4-methoxyphenyl)porphyrin (13). Violet fine crystalline powder. R_f 0.70 (Sorbfil, tetrachloromethane—acetone, 80 : 1). ^{1}H NMR ($CDCl_3$), δ: –2.65 (br.s, 2 H, NH); 1.67 (s, 36 H, C(5,10) Ar—C($C\underline{H}_3)_3$); 4.14 (s, 6 H, C(15,20) ArOC$\underline{H}_3$); 5.58 (s, 2 H, OH); 7.33 (d, 4 H, C(15,20) ArH(3,5), J = 8.2 Hz); 8.08 (br.s, 4 H, C(5,10) ArH(2,6)); 8.18 (d, 4 H, C(15,20) ArH(2,6), J = 8.2 Hz); 8.89 (br.s, 2 H, H(17,18)); 8.90 (d, 2 H, H(2,13), J = 4.6); 8.95 (d, 2 H, H(3,12), J = 4.6 Hz); 8.98 (br.s, 2 H, H(7,8)). ^{13}C NMR ($CDCl_3$), δ: 30.69 (C(5,10) ArC($\underline{C}H_3)_3$)); 34.59 (C(5,10) Ar$\underline{C}(CH_3)_3$); 55.61 (C(15,20) ArO$\underline{C}H_3$); 112.18 (C(15,20) ArC(3,5)); 119.33 and 121.44 (C(*meso*)); 129.75—131.70 (C(α,β)); 131.97 (C(5,10) ArC(2,6)); 134.03 (C(15,20) ArC(4)); 134.88 (C(5,10) ArC(4)); 135.55 (C(15,20) ArC(2,6)); 153.57 (C(5,10) ArC(1)); 159.37 (C(15,20) ArC(1)). UV ($CHCl_3$), λ_{max}/nm (I(%)): 651 (2), 595 (2), 558 (3), 520 (4), 425 (100). MS (ESI), m/z 931.6 $[MH]^+$. IR (KBr), ν/cm^{-1}: 3636 (OH); 3318 (NH); 2840 (CH_3); 2957, 1607 (C=C); 1508, 1466, 1435, 1244, 1177, 1034, 974, 802, 735.

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