Asymmetrically protected porphyrin *meso*-tetraphenols and their application in the synthesis of pentaporphyrin dendrimers.

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Dedicated to Professor Georges Hoornaert on his 65th birthday

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Abstract

The readily available tetrakis(4-hydroxyphenyl)porphyrin core **1** was silylated to the trisprotected **2a** and the tetraprotected **3a**. These two molecules were used, respectively as monomers and core reagents in a synthesis of pentaporphyrin dendrimers **7a-c** with benzyl ether branches or hexadecyl groups as the peripheral groups.

Keywords: Dendrimers, porphyrins, protection

Introduction

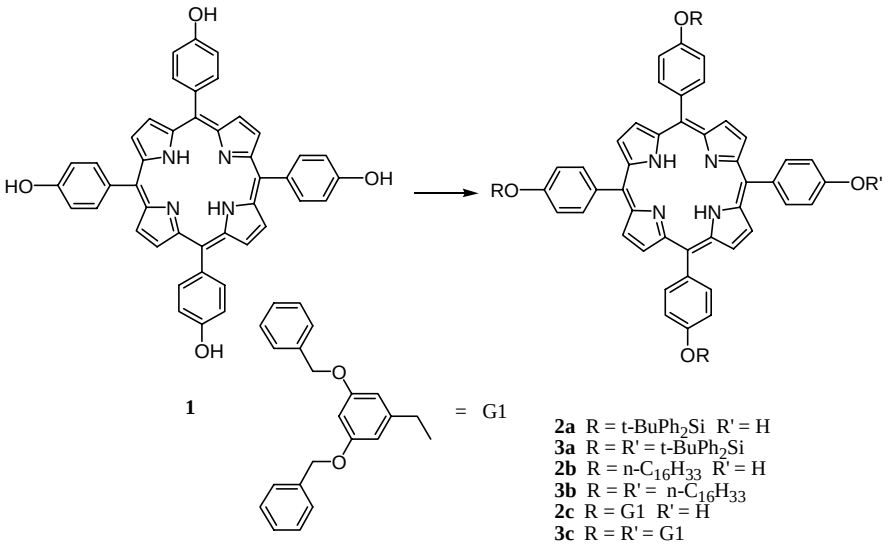
Numerous research groups have used porphyrins or metalloporphyrins as central building blocks (cores) in dendrimers. [1-11] The first example was described by Inoue and Aida. [1] It has been suggested that dendritic porphyrins could act as model sytems for natural electron transfer hemoproteins such as cytochrome c or hemoglobin. [2,3] Because of their large size and the possibility of host-guest interactions, the porphyrins represent attractive cores for the design of dendritic sensors and catalysts. Introduction of bulky dendrons at the peripheral positions of a metalloporphyrin results in steric protection and could provide regio- and stereoselective catalysis. [4]

In earlier work, we described benzyl ether dendrimers derived from the readily available tetrakis(4-hydroxyphenyl)porphyrin core **1**. [11] We wanted to devise a synthesis of dendrimers having porphyrins at several levels of the macromolecule. [12] Therefore, it was necessary to desymmetrize **1**. We previously have used the *t*-butyldiphenylsilyl (TBDPS) group previously [13,14] as a protecting group for the 3,5-dihydroxybenzyl alcohol monomer in the accelerated synthesis of benzyl ether [15] dendrons previously described by Fréchet. An additional

advantage of the bulky silyl group is its solubilizing ability, which adresses the main problem associated with working with **1**.

Results and Discussion

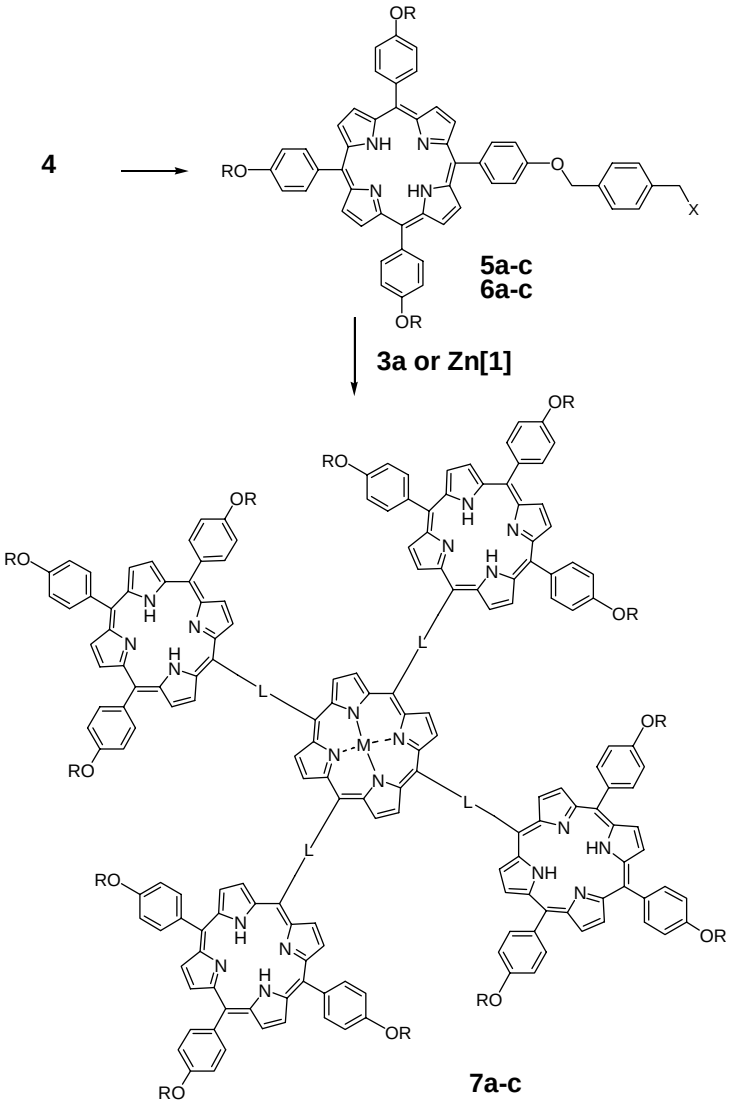
The tetraphenol **1** is readily available in 95 % yield from the corresponding tetramethoxy derivative by demethylation with pyridinium hydrochloride. Then, reaction of **1** with 4.4 equivalents of TBDPS-Cl and nine equivalents of imidazole gave a mixture of products from which the trisprotected **2a** and the tetraprotected **3a** could be isolated by flash chromatography, respectively in 34 and 38 % yield. As expected, **2a** and **3a** had excellent solubilities in most organic solvents. In comparison, alkylation of **1** with 1-bromohexadecane was very sluggish and gave, after painstaking chromatography, the trisalkylated and tetraalkylated porphyrins **2b** and **3b** in 10 and 12 % yield, respectively. The use of the G1 benzylic bromide to desymmetrize **1** afforded only 24 % of the desired **2c**, together with 60 % of the tetrasubstituted **3c**. The products **2b-c** and **3b-c** were much less soluble in organic solvents than their silylated analogs **2a** and **3a**.

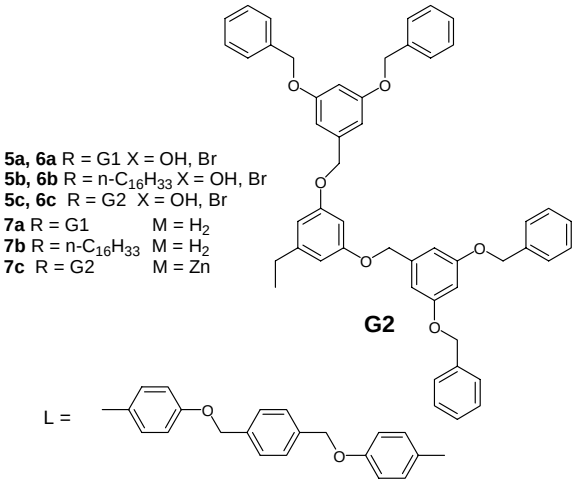


Mitsunobu reaction of **2a** with an excess of 1,4-benzenedimethanol gave a good yield (85 %) of the porphyrin **4**, having a single benzyl alcohol function. Reaction of **4** with the benzylic G1-Br, using deprotection/realkylation conditions described earlier [13,14], gave the corresponding dendron **5a** in 95 % yield. Bromination using soft conditions (CBr_4/PPh_3) gave the bromide **6a** in 83 % yield. In preliminary work, **6a** was obtained in 70 % yield from **2c** and 1,4-bis(bromomethyl)benzene. The pentaporphyrin **7a** was then prepared in 48 % yield by combining the tetraprotected porphyrin core **3a** with the bromide **6a** under deprotection/realkylation conditions.

The same reaction sequence, starting from **4** and using 1-bromohexadecane instead of G1-Br, gave 90 % of the dendron **5b**, 65 % of bromide **6b** (90 % from **2b** and 1,4-bis(bromomethyl)-

benzene) and 18 % of the pentaporphyrin **7b**. Starting from **4** and the Fréchet G2-Br, **5c** (70 %), **6c** (80 %) were obtained. The final pentaporphyrin **7c** was prepared from **6c** and Zn[**1**](not **3a**) in 40 % yield. Only a very small amount of Zn[**1**] was necessary, so there were no solubility problems in this case. Thus, this modular approach allows the preparation of oligoporphyrins metallated at a chosen level within the dendrimer structure.





The pentaporphyrins **7a-c** were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy (for **7a** and **7b**), MALDI-TOF mass spectrometry and GPC (for **7a** and **7c**). The latter technique gave an M_n (respectively 7513 and 11305) that was very close to the theoretically expected one (7496 and 12588), proving that these dendrimers still have a very open structure. Also, the dendrimers **7a** and **7c** are essentially monodisperse (PD = 1.04). All dendrimers **7a-c** gave only the theoretically expected MALDI TOF MS peak for MH^+.

Conclusions

The tetrakis(4-hydroxyphenyl)porphyrin **1** can be desymmetrized to the trisilylated **2a** and the latter compound can be used as a soluble building block for the synthesis of pentaporphyrin systems **7a-c**, possessing Fréchet dendrons (first and second generation) or hexadecyl groups as the terminal groups.

Experimental Section

General Procedures. ^{1}H NMR or ^{13}C NMR spectra were measured with a 400 MHz Bruker apparatus. Mass spectra were obtained on a Micromass Quatro II in ESI (infusion 50 μl MeOH/CH_2Cl_2-NH_4OAc (0.1 M in MeOH) with a Harvard pump, model 11) or in APCI (250 μl MeOH/CH_2Cl_2 using a Hewlett Packard HP 1100 binary pump and infusion of 20-30 μl MeOH/CH_2Cl_2 -NH_4OAc (0.1 M in MeOH) with a Harvard pump model 11). The higher molecular mass compounds were measured with a MALDI-TOF apparatus, using a tetrahydrofuran solution of indoleacrylic acid (0.4 M) as the matrix. GPC (Waters apparatus) used polystyrene standards and absorbance detection.

5,10,15,20-Tetrakis(4-hydroxyphenyl)porphyrin (1). A mixture of pyridine (64 ml) and hydrochloric acid (72 ml) was evaporated during 1h until an inner temperature of at least 170°C was reached. Then the tetrakis(4-methoxyphenyl)porphyrin (10 g) was added. The mixture was heated at reflux while stirring for a further 3 h. After cooling, water (200 ml) was added and the resulting precipitate was filtered and washed with a saturated sodium acetate solution. The resulting solid was redissolved in a mixture of acetone (150 ml) and triethylamine (5ml). Then, 600 ml of hexane was added. The resulting precipitate (95 % yield) was isolated and consists of **1**, of sufficient purity for further synthesis.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 4H, OH), 8.88 (s, 8H, β-pyrrole), 8.01 (d, *J* = 7.6 Hz, 8H, 2,6-phenyl-H), 7.22 (d, *J* = 7.6 Hz, 8H, 3,5-phenyl-H), -2.83 (s, 2H, NH) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 135.5, 131.9, 131.3, 120.0, 113.9.

Zn[1] : A solution of **1** (0.50g, 0.73 mmol) in methanol (20 ml) was treated with zinc acetate (1.35g, 7.40 mmol). The mixture was stirred for 2h at room temperature, poured in ethyl acetate (50 ml) and washed with water (3x 50 ml). After drying on magnesium sulfate, the solvent was removed *in vacuo* and the residue chromatographed over silica with a ethyl acetate / hexane 3:2 mixture. This gave Zn [**1**](0.49g, 90 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 4H, OH), 8.80 (s, 8H, β-pyrrole), 7.94 (d, *J* = 8.3 Hz, 8H, 2,6-phenyl-H), 7.16 (d, *J* = 8.3 Hz, 8H, 3,5-phenyl-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 149.6, 135.2, 133.4, 131.3, 120.2, 113.5; UV/Vis (λ_{max}, nm, dichloromethane) 424.0, 557.1, 598.2; ESI MS 742 (MH^+).

Silylation of 1. Porphyrin 1 (2.00 g, 2.90 mmol), chloro-t-butyldiphenylsilane (3.57 g, 13 mmol) and imidazole (1.77 g, 26 mmol) were dissolved in dimethylformamide (30 ml) and stirred at ambient temperature under inert atmosphere for 12 h. The solvent was removed *in vacuo* and the residue chromatographed over silica with a dichloromethane/hexane 1:1 mixture. This gave 3a (1.81g, 38 %) as a first fraction. Further elution gave 2a (1.38g, 34 %).

5-(4-Hydroxyphenyl)-10,15,20-tris(4-t-butyldiphenylsilyloxyphenyl)porphyrin (2a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 4H, β-pyrrole), 8.79 (d, *J* = 4.8 Hz, 2H, β-pyrrole), 8.73 (d, *J* = 4.8 Hz, 2H, β-pyrrole), 8.01 (d, *J* = 8.4 Hz, 2H), 7.93 (m, 12H), 7.86 (d, *J* = 9.0 Hz, 6H), 7.53-7.46 (m, 18H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 9.0 Hz, 6H), 1.22 (s, 27 H, t-Bu), -2.90 (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 155.3, 135.8, 135.7, 135.3, 135.1, 134.9, 133.1, 130.1, 127.9, 119.8, 119.4, 118.2, 113.6, 26.7, 19.7; UV/Vis (λ_{max}, nm, dichloromethane) 421.1, 518.3, 555.0, 593.4, 649.9; ESI MS 1395 (MH^+).

5,10,15,20-Tetrakis(4-t-butyldiphenylsilyloxyphenyl)porphyrin (3a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 8H, β-pyrrole), 7.93 (m, 16H), 7.86 (d, *J* = 8.4 Hz, 8H), 7.51 (m, 24H), 7.12 (d, *J* = 8.4 Hz, 8H), 1.20 (s, 36H, t-Bu), -2.90 (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 135.8, 135.3, 135.1, 133.1, 130.1, 127.9, 119.7, 118.2, 26.7, 19.7; UV/Vis (λ_{max}, nm, dichloromethane) 421.4, 518.7, 555.4, 593.9, 649.6; ESI MS 1633 (MH^+).

Hexadecylation of 1. Porphyrin **1** (1g, 1.47 mmol), 1-bromohexadecane (1.49 g, 4.87 mmol) and potassium carbonate (0.67g, 4.85 mmol) were added to 30 ml of dimethylformamide. The mixture was heated at reflux under argon for 48 h. After cooling, 50 ml of dichloromethane was

added and the organic layer was washed with water (3x50ml), and dried on magnesium sulfate. The solvent was removed *in vacuo* and the residue chromatographed over silica with a dichloromethane / hexane 1:1 mixture. This gave the known [16] **3b** (0.21g, 12 %) as a first fraction. Further elution gave **2b** (0.24g, 10 %).

5-(4-Hydroxyphenyl)-10,15,20-tris(4-n-hexadecyloxyphenyl)porphyrin (2b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 4H, β-pyrrole), 8.82 (d, *J* = 4.8 Hz, 2H, β-pyrrole), 8.80 (d, *J* = 4.8 Hz, 2H, β-pyrrole), 8.07 (d, *J* = 8.1 Hz, 6H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 6H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.17 (t, *J* = 6.4 Hz, 6H), 1.94 (m, 6H), 1.59 (m, 6H), 1.27 (m, 72 H), 0.88 (t, *J* = 7.0 Hz, 9H), -2.70 (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 155.2, 135.6, 135.5, 135.4, 130.9, 119.9, 113.5, 112.7, 68.3, 31.9, 29.7, 29.5, 29.4, 26.9, 26.5, 22.7, 14.1; UV/Vis (λ_{max}, nm, dichloromethane) 421.7, 517.9, 555.8, 594.4, 649.9; ESI MS 1351 (MH^+).

Dendronisation (G1) of 1. A mixture of porphyrin **1** (1g, 1.47 mmol), G1-Br (1.86g, 4.87 mmol), potassium carbonate (1.34g, 9.69 mmol) and 18-crown-6 (40 mg, 0.15 mmol) in dimethylformamide (30 ml) was heated while stirring in argon at 80°C for 48h. After removal of the solvent *in vacuo*, the residue was dissolved in dichloromethane (50 ml) and washed with water (3x50 ml). The organic layer was dried on magnesium sulfate. The solvent was removed *in vacuo* and the residue chromatographed over silica with a dichloromethane / hexane 9:1 mixture. This gave the known [11] **3c** (1.67g, 60 %) as a first fraction. Further elution gave **2c** (0.56g, 24 %).

5-(4-Hydroxyphenyl)-10,15,20-tris(4-(3,5-bis(benzyloxy)benzyloxy)phenyl)porphyrin (2c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 8H, β-pyrrole), 8.09 (d, *J* = 8.5 Hz, 6H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 12 H), 7.38 (m, 12H), 7.32 (d, *J* = 8.5 Hz, 6H), 7.30 (m, 6H), 7.16 (d, *J* = 8.5 Hz, 6H), 6.79 (d, *J* = 2.0 Hz, 6H), 6.66 (t, *J* = 2.0 Hz, 3H), 5.26 (s, 6H), 5.13 (s, 12H), -2.70 (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 158.6,155.2, 139.5, 136.9, 135.7(2), 135.0, 134.9, 128.6, 128.0, 127.6, 119.7, 113.7, 113.2, 113.0, 106.7, 101.8, 70.3, 67.1; UV/Vis (λ_{max}, nm, dichloromethane) 421.6, 518.7, 555.3, 593.2, 650.3; ESI MS 1589 (MH^+).

5,10,15-Tris(4-t-butyldiphenylsilyloxyphenyl)-20-(4-(4-(hydroxymethyl)benzyloxy)-phenyl)porphyrin (4). Porphyrin 2a (0.50g, 0.36mmol), 1,4-benzenedimethanol (0.49g, 3.59 mmol), diethyl azodicarboxylate (90 mg, 0.54 mmol) and triphenylphosphine (0.14 g , 0.54 mmol) were dissolved in dry tetrahydrofuran (5ml). The mixture was stirred for 3h at ambient temperature, evaporated *in vacuo* and redissolved in dichloromethane (15 ml). After washing with water (3x20ml) the organic layer was dried over magnesium sulfate. The solvent was removed *in vacuo* and the residue chromatographed over silica with a dichloromethane / hexane 3:1 mixture. This afforded the porphyrin 4 (0.47g, 85 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.7 Hz, 2H, β-pyrrole), 8.73 (d, *J* = 4.7 Hz, 2H, β-pyrrole), 8.72 (s, 4H, β-pyrrole), 8.08 (d, *J* = 8.6 Hz, 2H), 7.93 (m, 12 H), 7.87 (d, *J* = 8.4 Hz, 6H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.55-7.45 (m, 18H), 7.49 (d, *J* = 5.1 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 6H), 5.34 (s, 2H), 4.77 (d, *J* = 5.6 Hz, 2H), 1.49 (t, *J* = 5.6 Hz, 1H), 1.28 (s, 27H), -2.90 (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 155.6, 140.9, 136.6, 135.8, 135.6, 135.3, 135.1, 135.0, 133.1, 131.0, 128.0, 127.9, 127.3, 119.8, 119.5, 118.2, 113.1,

70.1, 65.2, 26.8, 19.7; UV/Vis (λ_{max}, nm, dichloromethane) 422.4, 518.4, 555.5, 593.5, 649.5; ESI MS 1516 (MH^+).

General procedure for deprotection/realkylation

5,10,15-Tris(4-(3,5-bis(benzyloxy)-benzyloxy)phenyl)-20-(4-(4-(hydroxymethyl)benzyloxy) phenyl)porphyrin (5a). Porphyrin 4 (180 mg, 0.12 mmol), G1-Br (0.21g, 0.55 mmol), potassium fluoride (58 mg, 1 mmol) and 18-crown-6 (0.26g, 0.98 mmol) were added to acetone (10ml) and heated at reflux for 24h while stirring under an argon atmosphere. After cooling, the mixture was added to dichloromethane (25 ml) and the organic layer was washed with water (3x30ml) and dried over magnesium sulfate. The solvent was removed *in vacuo* and the residue chromatographed over silica with a dichloromethane / diethyl ether 19:1 mixture. This afforded the porphyrin 5a (0.17g, 90 %).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 8H, β-pyrrole), 8.06 (d, *J* = 8.6 Hz, 6H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.45 (m, 12H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.38 (m, 12H), 7.30 (m, 6H), 7.24 (d, *J* = 8.6 Hz, 6H), 6.84 (d, *J* = 2.2 Hz, 6H), 6.65 (t, *J* = 2.2 Hz, 3H), 5.22 (s, 2H), 5.17 (s, 2H), 5.16 (s, 4H), 5.10 (s, 12H), 4.68 (s, 2H), 1.64 (s, 1H), -2.30 (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 158.6, 158.5, 140.8, 139.4, 136.9, 136.4, 135.6, 135.4, 134.9, 131.0, 128.6, 128.0, 127.8, 127.6, 127.2, 119.7, 113.1, 70.2, 70.0; UV/Vis (λ_{max}, nm, dichloromethane) 421.4, 518.5, 555.8, 593.5, 650.1; ESI MS 1708 (MH^+).

5,10,15-Tris(4-n-hexadecyloxyphenyl)-20-(4-(4-(hydroxymethyl)benzyloxy)-phenyl)porphyrin (5b). Porphyrin 5b was prepared analogously in 90 % yield from 4 and 1-bromohexadecane. The reaction was carried out at room temperature in dimethylformamide (24h).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 4H, β-pyrrole), 8.84 (d, *J* = 4.7 Hz, 2H, β-pyrrole), 8.83 (d, *J* = 4.7 Hz, 2H, β-pyrrole), 8.07 (d, *J* = 8.4 Hz, 8H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 6H), 5.22 (s, 2H), 4.70 (s, 2H), 4.18 (t, *J* = 6.4 Hz, 6H), 3.60 (s, 1H), 1.94 (s, 6H), 1.58 (s, 6H), 1.27 (m, 72H), 0.86 (t, *J* = 7.0 Hz, 9H), -2.70 (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 158.6, 140.9, 136.5, 135.6, 135.0, 134.4, 127.9, 127.2, 119.8, 119.5, 113.1, 112.7, 70.1, 68.3, 65.1, 31.9, 29.6, 29.5, 29.4, 26.2, 25.7, 22.7, 14.1; UV/Vis (λ_{max}, nm, dichloromethane) 422.1, 518.9, 556.2, 595.0, 650.8; ESI MS 1473 (MH^+).

5,10,15-Tris(4-(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)phenyl)-20-(4-(4-(hydroxymethyl)benzyloxy)phenyl)porphyrin (5c). Porphyrin 5c was prepared analogously in 70 % yield from 4 and G2-Br.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 8H, β-pyrrole), 8.08 (d, *J* = 8.5 Hz, 8H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.45-7.25 (m, 68 H), 6.85 (d, *J* = 2.3 Hz, 6H), 6.73 (d, *J* = 2.3 Hz, 12H), 6.63 (t, *J* = 2.3 Hz, 3H), 6.58 (t, *J* = 2.3 Hz, 6H), 5.28 (s, 2H), 5.21 (s, 6H), 5.04 (s, 12H), 5.02 (s, 24H), 4.72 (d, *J* = 4.2 Hz, 2H), 1.71 (t, *J* = 4.2 Hz, 1H), -2.75 (s, 2H, NH) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 158.6, 140.8, 139.5, 139.3, 136.7, 135.6, 135.0, 128.5, 127.9, 127.5, 127.3, 119.7, 113.1, 106.7, 106.5, 101.8, 101.6, 70.3, 70.1, 65.1; MALDI TOF 2980.5 (MH^+).

General procedure for bromination

5,10,15-Tris(4-(3,5-bis(benzyloxy)benzyloxy)-phenyl)-20-(4-(4-(bromomethyl)benzyloxy) phenyl)porphyrin (6a). To a solution of porphyrin 5a (0.50g, 0.29 mmol) and CBr_4 (0.292g,

0.88mmol) in dry tetrahydrofuran (5ml) was added triphenylphosphine (0.231g, 0.88mmol) and the mixture was stirred for 1h at ambient temperature and then added to water (20 ml). The mixture was extracted (3x20ml) with dichloromethane and the organic layer was dried over magnesium sulfate. The solvent was removed *in vacuo* and the residue chromatographed over silica with a dichloromethane / hexane 3:1 mixture. This yielded 6a (0.43g, 83 %). Alternatively, 6a was obtained in 70 % yield from 2c and 10 equivalents of 1,4-bis(bromomethyl)benzene using potassium carbonate (2 equivalents), 18-crown-6 (0.5 equivalents), in tetrahydrofuran at reflux for 12h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 8H, β-pyrrole), 8.08 (d, *J* = 8.05 Hz, 8H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.47 (m, 12H), 7.39 (m, 6H), 7.30 (m, 12H), 7.29 (d, *J* = 8.3 Hz, 8H), 6.86 (d, *J* = 2.0 Hz, 6H), 6.66 (t, *J* = 2.0 Hz, 3H), 5.27 (s, 2H), 5.23 (s, 6H), 5.11 (s, 12H), 4.54 (s, 2H), -2.54 (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 158.5, 158.2, 148.0, 139.5, 137.7, 137.4, 135.6, 135.0, 131.0, 129.4, 128.6, 128.0, 127.6, 119.6, 113.1; 106.6, 101.8, 70.2, 69.8, 69.7, 33.2; UV/Vis (λ_{max}, nm, dichloromethane) 422.0, 518.6, 555.7, 593.7, 650.3; ESI MS 1769 (MH^+).

5,10,15-Tris(4-n-hexadecyloxyphenyl)-20-(4-(4-bromomethyl)benzyloxy)phenyl)-porphyrin (6b). Porphyrin 6b was prepared analogously from 5b in 65 % yield. Alternatively, 6b was obtained in 90 % yield from 2b and 10 equivalents of 1,4-bis(bromomethyl)benzene.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 8H, β-pyrrole), 8.83 (d, *J* = 4.6 Hz, 2H, β-pyrrole), 8.81 (d, *J* = 4.6 Hz, 2H, β-pyrrole), 8.08 (d, *J* = 8.0 Hz, 6H), 8.05 (d, *J* = 7.7 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 6H), 5.18 (s, 2H), 4.52 (s, 2H), 4.17 (t, *J* = 6.4 Hz, 6H), 1.94 (m, 6H), 1.59 (m, 6H), 1.27 (m, 72H), 0.88 (t, *J* = 7.0 Hz, 9H), -2.70 (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 158.5, 137.6, 137.4, 135.6, 135.4, 135.1, 130.9, 129.4, 128.0, 119.9, 119.5, 113.0, 112.7, 69.8, 14.1; UV/Vis (λ_{max}, nm, dichloromethane) 421.9, 518.7, 556.1, 593.9, 650.6; ESI MS 1533 (MH^+).

5,10,15-Tris(4-(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)phenyl)-20-(4-(4-(bromomethyl)benzyloxy)phenyl)porphyrin (6c). Porphyrin 6c was prepared analogously from 5c in 80 % yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 8H, β-pyrrole), 8.08 (d, *J* = 8.4 Hz, 8H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.45-7.24 (m, 68 H), 6.85 (d, *J* = 2.0 Hz, 6H), 6.73 (d, *J* = 2.0 Hz, 12H), 6.63 (t, *J* = 2.0 Hz, 3H), 6.58 (t, *J* = 2.0 Hz, 6H), 5.27 (s, 2H), 5.21 (s, 6H), 5.04 (s, 12H), 5.02 (s, 24H), 4.53 (s, 2H), -2.75 (s, 2H, NH) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 158.6, 139.4, 139.3, 137.6, 137.4, 136.7, 135.6, 135.0, 129.4, 128.5, 128.0, 127.5, 119.7, 113.1, 106.7, 106.4, 101.7, 101.6, 70.3, 70.1; MALDI TOF **3043.4** (MH^+).

General procedure for synthesis of pentaporphyrins

5, 10, 15, 20-Tetrakis(4-(4-(4-(5,10,15-tris(4-(3,5-bis(benzyloxy)benzyloxy)phenyl)porphyrin-20-yl) fenoxymethyl)-benzyloxy)phenyl)porphyrin (7a). A solution of porphyrin 6a (0.24g, 0.13 mmol), porphyrin 3a (50 mg, 30 μmol), and 18-crown-6 (0.110 g, 0.42 mmol) in acetone (3ml) was treated with potassium fluoride (30 mg, 0.46 mmol). The resulting mixture was heated for 48h at reflux under an argon atmosfere. After cooling, the mixture was added to dichloromethane (25 ml) and the organic layer was washed with water (3x30ml) and dried over magnesium sulfate. The solvent was removed *in vacuo* and the residue chromatographed over silica with a

dichloromethane/hexane 3:1 mixture. The pentaporphyrin was further purified by precipitation from a dichloromethane solution in methanol to afford pure 7a (0.11g, 48%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 8H, β-pyrrole), 8.83 (m, 32H, β-pyrrole), 8.09 (m, 40H), 7.62 (s, 16H), 7.45-7.19 (m, 160H), 6.81(d, *J* = 2.0 Hz, 24H), 6.62 (t, *J* = 2.0 Hz, 12H), 5.25 (s, 8H), 5.21 (s, 8H), 5.14 (s, 8H), 5.12 (s, 16H), 5.08 (s, 16H), 5.06 (s, 32H), -2.70 (s, 10H, NH); UV/Vis (λ_{max}, nm, dichloromethane) 422.6, 518.8, 556.0, 593.8, 650.4; GPC M_n = 7513, PD = 1.04; MALDI TOF 7496 (MH^+).

5, 10, 15, 20-Tetrakis(4-(4-(4-(5,10,15-tris(4-(n-hexadecyloxy)phenyl)-porphyrin-20-yl)-fenoxymethyl)benzyloxy)phenyl)porphyrin (7b). Pentaporphyrin 7b was prepared from 6b and 4 in 18 % yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (m, 40H, β-pyrrole), 8.11 (d, *J* = 8.6 Hz, 40H), 7.60 (d, *J* = 8.1 Hz, 8H), 7.47 (d, *J* = 8.1 Hz, 8H), 7.31 (d, *J* = 8.6 Hz, 8H), 7.25 (d, *J* = 8.6 Hz, 32H), 5.31 (s, 8H), 5.18 (s, 8H), 4.20 (t, J = 6.4 Hz, 24H), 1.96 (m, 24H), 1.27 (m, 144H), 0.88 (t, *J* = 7.0 Hz), -2.60 (s, 10H, NH); ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 158.5, 135.6, 135.1, 134.4, 128.6, 127.9, 113.0, 112.7, 70.1, 68.3, 68.1, 31.9, 29.6, 29.5, 29.4, 26.2, 25.7, 22.7, 14.1; UV/Vis (λ_{max}, nm, dichloromethane) 422.1, 518.6, 555.3, 593.1, 650.4; MALDI TOF 6496 (MH^+).

5, 10, 15, 20-Tetrakis(4-(4-(4-(5,10,15-tris(4-(3,5-(3,5-bis(benzyloxy)benzyloxy)benzyl-oxy)phenyl)porphyrin-20-yl)fenoxymethyl)benzyloxy)phenyl)porphyrin (7c). Pentaporphyrin 7c was prepared from 6c (50 μmol) and Zn[1] (10 μmol) in 40 % yield. The reaction was carried out in dimethylformamide with potassium carbonate base (50 μmol) at 50°C.

The NMR spectra were broadened, GPC M_n = 11305, PD = 1.04; MALDI TOF 12588 (MH^+)

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