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Synthesis of 5,10,15,20-tetrakis(2-amino-5-methoxyphenyl)-porphyrin: a versatile building block for porphyrin face selection

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Abstract—A new bis-faced substituted porphyrin has been prepared. The four hydroxyl groups on one side as well as the four amino functions on the other one allow at will, a different functionalization of each face of the macrocycle. The usefulness of this synthon is illustrated.

In Nature most hemoproteins take advantage of their two different distal and proximal sides either to incorporate an exogenous molecule (gas binding, substrate recognition) or to deliver an axial ligand (histidine, cysteine, tyrosine) to the metal inside the porphyrin.[1] To mimic such properties, the chemist has been, for a long time, tackling the recurrent problem of discrimination of the two porphyrin faces in order to obtain different functions on each.[2] Some years ago, in the particular case of a tetra-*o*-aminophenyl porphyrin, a successful example of such a face selection was published with a porphyrin bearing a protected amino group on one side of the porphyrin, and three reactive amino functions on the other.[3] But in order to increase the possibilities, the synthesis of a new class of porphyrin delivering two different functionalities with four identical functional groups on each face is of great interest. For instance, an octa-aminophenyl porphyrin possessing four reactive groups on each porphyrinic side had been reported in 1996 but no selectivity between the eight amino functions was possible.[4] The analogous compounds with either alkoxy,[5] oxycarbonyl,[6] or bromomethyl substituents[7] are also known. To the best of our knowledge, this problem has been clearly circumvented only with particular substituents. Actually, in the report of Rose and co-workers,[8] the chlorine atom in position 5 of the *meso* aromatic ring did not allow any further chemistry and in the work of Nishino et al.,[9] the long dodecane chain was included before the formation of the porphyrin itself. Thus, we report herein the synthesis, atropisomerism and functionalization of a new versatile porphyrin, namely the 5,10,15,20-tetrakis(2-amino-5-methoxyphenyl)porphyrin (TAMPP) as an alternative.

According to Scheme 1, the benzaldehyde derivative **1**, bearing a nitro and methoxy group in positions 2 and 5, respectively, was prepared according to a well-established procedure,[10] starting from 5-hydroxy-2-nitrobenzaldehyde, which was synthesized on a multi-gram scale as previously published.[11] The usual Lindsey's method[12] with a pyrrole concentration of 10^{-2} mol L^{-1} gave the tetraphenylporphyrin derivative **2** with four nitro and four methoxy groups in moderate yield (20%).[†] At this stage, several washings of the crude solid with methanol had to be carried out to remove polymers. In contrast to tetra-*o*-nitrophenyl porphyrin,

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[†] To a degassed solution of 2-nitro-5-methoxybenzaldehyde **1** (3.62 g, 20 mmol) and pyrrole (1.4 cm^3, 20 mmol) in 2 L of CH_2Cl_2, $BF_3{\cdot}OEt_2$ (0.528 mL, 2 mmol) was added. The mixture was stirred 24 h and then 2,3-dichloro-5,6-dicyanobenzoquinone (3.4 g, 15 mmol) was added. After 2 h, triethylamine (1.4 mL, 10 mmol) was added and the mixture was evaporated. The solid was washed with methanol then with toluene, which partially dissolved the porphyrin material to give 0.8 g of an atropisomeric mixture of **2**. After evaporation of toluene, the solid was chromatographed over silica gel eluting with CH_2Cl_2. Then the fast-eluting red bands were collected and evaporated to yield 0.1 g of an atropisomeric mixture of **2**. Finally, the fractions were combined to afford 0.9 g of **2** (0.98 mmol, 20%).

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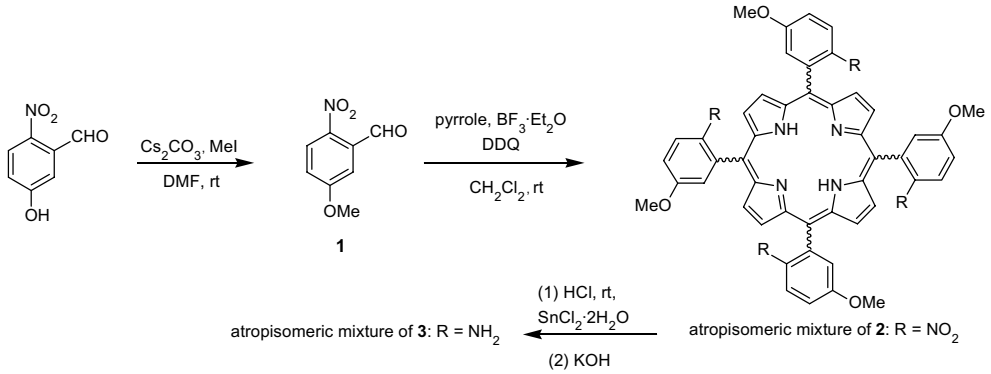


Scheme 1. Synthesis of **3**.

which crystallizes out in boiling acetic acid,[13] all the atropisomers of **2** apart from the αααββ one are soluble in methylene chloride and could therefore be isolated by elution with CH_2Cl_2 on silica gel chromatography, although the atropisomeric mixture of **2** can be used without further purification.

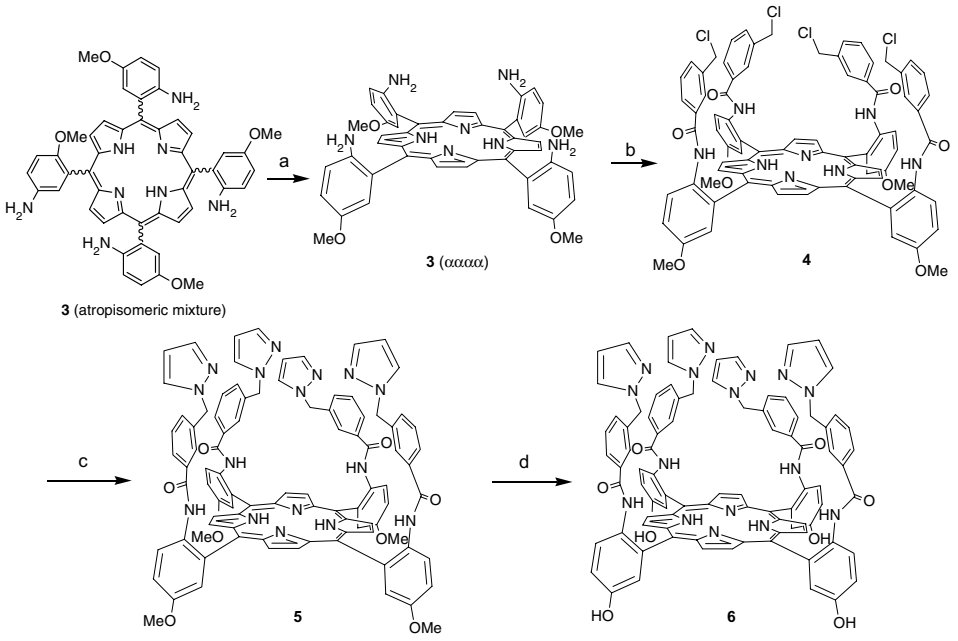
Accordingly, the four nitro groups of **2** were reduced by $SnCl_2{\cdot}2H_2O$ in HCl at room temperature for 3 days. After neutralization and silica gel chromatography, TAMPP **3** was eluted with CH_2Cl_2 as a mixture of the four atropisomers with a global yield of 59%.[‡] The effective ratio of αβαβ:ααββ:αααβ:αααα (13:24:56:7) is slightly different from the statistical abundance (12.5:25:50:12.5) effectively observed for the tetra-*o*-aminophenyl porphyrin.

The advantage of our approach is twofold. Firstly, all the atropisomers can be obtained at this stage, with both amino and methoxy substituents. Indeed, it is worth noting that atropisomer αααα was not isolated by thermal isomerization when the methoxy was replaced by a $OC_{12}H_{25}$ chain.[14] Secondly, the methyl group protecting the phenol is known to be removable without the elevated temperatures, which would induce atropisomerization.[15] Thus, the desired atropisomer is selected with a masked phenol, then the amino group can be functionalized and the protective methoxy group removed. Additionally, displacement of the natural abundance of the αααα atropisomer as described by Lindsey[16] for tetrakis-*o*-aminophenyl porphyrin (TAPP) is also efficient for this new porphyrin. This method, when applied to the mixture of atropisomers dissolved in toluene, leads to the αααα isomer in 57% yield. As mentioned earlier, the goal of the synthesis is the preparation of supramolecular systems in which the two different faces of the macrocycle can be modified selectively.

An illustration of this methodology is depicted in Scheme 2. After purification of the desired atropisomer (αααα in our case) of TAMPP **3**, the amino functions of the latter were acylated using 3-(chloromethyl)benzoyl chloride to afford porphyrin **4** in 85% yield.[§] This particular bifunctional linker was chosen according to previous papers in which it has been clearly established that the residues attached via this linker were either delivered close to the metal center of the porphyrin

[‡] **α,β,α,β-3:** ^{1}H NMR (500 MHz, $CDCl_3$, 283 K) δ −2.73 (2H, s, *N*-pyrrole), 3.31 (8H, s, NH_2), 3.91 (12H, s, OCH_3), 7.08 (4H, d, $J = 8.85$ Hz, 3-Ph), 7.25 (4H, dd, $J_1 = 8.85$ Hz, $J_2 = 2.83$ Hz, 4-Ph), 7.54 (4H, d, $J = 2.83$ Hz, 6-Ph), 8.97 (8H, s, β-pyr); **α,α,β,β-3**: ^{1}H NMR (500 MHz, $CDCl_3$, 273 K) δ −2.77 (2H, s, *N*-pyrrole), 3.34 (8H, s, NH_2), 3.90 (12H, s, OCH_3), 7.10 (4H, d, $J = 9.15$ Hz, 3-Ph), 7.25 (4H, dd, $J_1 = 9.15$ Hz, $J_2 = 3.05$ Hz, 4-Ph), 7.48 (4H, d, $J = 3.05$ Hz, 6-Ph), 8.96 (8H, s, β-pyr); **α,α,α,β-3**: ^{1}H NMR (500 MHz, $CDCl_3$, 273 K) δ 2.79 (2H, s, *N*-pyrrole), 3.32 (8H, s, NH_2), 3.86 (3H, s, OCH_3), 3.87 (3H, s, OCH_3), 3.88 (6H, s, OCH_3), 7.08 (4H, m, 3-Ph), 7.23 (4H, m, 4-Ph), 7.47 (4H, m, 6-Ph), 8.93 (8H, s, β-pyr); **α,α,α,α-3**: ^{1}H NMR (500 MHz, $CDCl_3$, 273 K) δ 2.77 (2H, s, *N*-pyrrole), 3.27 (8H, s, NH_2), 3.88 (12H, s, OCH_3), 7.07 (4H, d, $J = 8.78$ Hz, 3-Ph), 7.23 (4H, dd, $J_1 = 8.78$ Hz, $J_2 = 2.70$ Hz, 4-Ph), 7.50 (4H, d, $J = 2.70$ Hz, 6-Ph), 8.94 (8H, s, β-pyr); HR-MS (ESI-MS) $m/z = 795.3400$ $[M+H]^+$ $C_{48}H_{43}N_8O_4$ requires 795.3407; UV–vis (CH_2Cl_2) λ nm ($10^{-3}\varepsilon$, $M^{-1}\,cm^{-1}$) 414 (351.4), 515 (26.0), 551 (6.7), 589 (7.6), 646 (2.5).

[§] A 100 mL three-neck round-bottom flask equipped with a stir bar was charged with **α,α,α,α-3** (100 mg, 0.13 mmol), dry THF (30 mL), and Et_3N (0.3 mL, 2.08 mmol). After cooling in an ice bath, 3-(chloromethyl)benzoyl chloride (0.143 mL, 1.04 mmol) dissolved in 5 mL of dry THF was added dropwise. The reaction mixture was stirred for 10 h at room temperature. The solvent was finally removed under vacuum. The resulting powder was dissolved in CH_2Cl_2 and directly loaded onto a silica gel chromatography column. The expected compound eluted with 0.3% MeOH/CH_2Cl_2, was obtained in 85% yield (150 mg); ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ −2.55 (2H, s, *N*-pyrrole), 3.25 (8H, s, $CH_{2\,benz}$), 4.00 (12H, s, OCH_3), 6.02 (4H, t, $J = 7.90$ Hz, H_{aro}), 6.41 (4H, d, $J = 7.40$ Hz, H_{aro}), 6.47 (4H, d, $J = 7.90$ Hz, H_{aro}), 6.50 (4H, s), 7.48 (4H, dd, $J_1 = 9.20$ Hz, $J_2 = 2.60$ Hz, H_{aro}), 7.55 (4H, s, N*H*), 7.58 (4H, d, $J = 2.6$ Hz, H_{aro}), 8.69 (4H, d, $J = 9.2$ Hz, H_{aro}), 8.94 (8H, s, β-pyr); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): 44.3, 55.7, 115.0, 121.0, 123.1, 125.6, 126.1, 128.1, 130.5, 131.8; HR-MS (ESI-MS) $m/z = 1425.3351$ $[M+Na]^+$ $C_{80}H_{62}N_8O_8Cl_4Na$ requires 1425.3342; UV–vis (CH_2Cl_2) λ nm ($10^{-3}\varepsilon$, $M^{-1}\,cm^{-1}$) 423 (351.2), 516 (24.4), 549 (4.1), 589 (5.3), 645 (1.5).



Scheme 2. Reagents and conditions: (a) SiO_2, toluene, 80 °C, 57%; (b) 3-(chloromethyl)benzoyl chloride, NEt_3, THF, 0 °C to rt, 85%; (c) i. NaH, pyrazole, THF, rt; ii. **4** in THF, 55 °C, 28%; (d) CH_2Cl_2, 0–40 °C, BBr_3, 78%.

itself[17] or oriented inside the pocket formed by the pickets.[18] Pyrazole was then allowed to react on the 'U-Shaped' acceptor **4** according to a method reported by Lam et al.[19] to afford porphyrin **5** with a yield of 28%.[¶] This moderate yield, lower than that obtained by Naruta and Sasaki[20] for a porphyrin bearing only three pyrazolyl pickets, can be attributed to the steric hindrance induced by the four bulky pickets. The deprotection of the phenol groups was achieved by reaction with boron tribromide in CH_2Cl_2 to afford porphyrin **6** in 78% yield.[‖] The phenol functions could eventually be converted into ether or ester groups by a conventional method.

This particular 2,5 substitution pattern with the hydroxy groups in the *meta* positions can be considered an advantage as the influence of the latter is expected to be negligible on the geometry of the superstructure on the other face of the porphyrin. This property was probed by a comparison of the chemical shifts of different protons. For example, the protons of the pyrazolyl unit in **6** lead to the following signals 7.24 (d), 6.64 (d), and 5.95 (t) instead of 7.05 (d), 6.53 (d), and 5.80 (t) in the analogous compound without the hydroxyl group, prepared from TAPP.[21] This clearly means that the

[¶] A 50 mL three-neck round-bottom flask equipped with a stirrer bar was charged with pyrazole (50 mg, 0.74 mmol) in 10 mL of THF then NaH (20 mg, 0.82 mmol) was added. After 30 min, the mixture was added to porphyrin **4** (130 mg, 0.093 mmol) dissolved in 20 mL of THF. The resulting mixture was stirred at 55 °C for 24 h. THF was finally removed under vacuum. The resulting powder was dissolved in $CHCl_3$ and directly loaded onto a silica gel chromatography column. The expected compound eluted with 2% MeOH/$CHCl_3$, was obtained in 28 % yield (40 mg); ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ −2.32 (2H, s, *N*-pyrrole), 2.44 (8H, s, $CH_{2\,benz}$), 4.04 (12H, s, OCH_3), 5.14 (4H, s, H_{aro}), 5.88 (4H, d, $J = 7.70$ Hz, H_{aro}), 5.95 (4H, t, $J = 1.93$ Hz, H_{pyr}), 6.11 (4H, t, $J = 7.70$ Hz, H_{aro}), 6.64 (4H, d, $J = 1.90$ Hz, H_{pyr}), 6.81 (4H, d, $J = 7.64$ Hz, H_{aro}), 7.24 (4H, d, $J = 1.43$ Hz, H_{pyr}), 7.46 (4H, dd, $J_1 = 2.86$ Hz, $J_2 = 8.90$ Hz, H_{aro}), 7.75 (4H, d, $J = 2.86$ Hz, H_{aro}), 8.08 (4H, d, $J = 8.90$ Hz, H_{aro}), 8.19 (4H, s, NH), 8.76 (8H, s, β-pyr); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 52.8, 56.1, 105.6, 115.2, 121.1, 124.5, 126.1, 127.5, 128.0, 129.1, 129.5, 131.4, 139.2, 156.5, 166.4; HR-MS (ESI-MS) $m/z = 1553.5787$ $[M+Na]^+$ $C_{92}H_{74}N_{16}O_8Na$ requires 1553.5773; UV–vis (CH_2Cl_2) λ nm ($10^{-3}\varepsilon$, $M^{-1}\,cm^{-1}$) 428 (370.3), 521 (33.8), 556 (6.9), 595 (6.7), 653 (3.1).

[‖] To a stirred solution of porphyrin **5** (40 mg, 0.026 mmol) in 10 mL of dry CH_2Cl_2, 20 μL (0.21 mmol) of BBr_3 was added dropwise at 0 °C. The reaction mixture was allowed to stir at reflux for 48 h and then cooled to room temperature. Then ethyl acetate and ice were added. After neutralization with K_2CO_3, the reaction mixture was extracted with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and evaporated in vacuo. The crude product was purified by flash chromatography and the desired compound, eluted with a mixture of 6.4% MeOH/$CHCl_3$, was obtained in 78% yield (30 mg); ^{1}H NMR (500 MHz, DMSO-d_6, 303 K) δ −2.90 (2H, s, *N*-pyrrole), 4.77 (8H, s, $CH_{2\,benz}$), 5.86 (4H, s, H_{pyr}), 6.03 (4H, t, $J = 7.80$ Hz, H_{aro}), 6.24 (4H, d, $J = 7.43$ Hz, H_{aro}), 6.57 (4H, d, $J = 7.47$ Hz, H_{aro}), 7.02 (4H, s, H_{aro}), 7.12 (4H, s, H_{pyr}), 7.14 (4H, s, H_{aro}), 7.24 (4H, d, $J = 8.57$ Hz, H_{aro}), 7.27 (4H, s, H_{pyr}), 7.86 (4H, d, $J = 8.57$ Hz, H_{aro}), 8.88 (8H, s, H_{pyr}), 9.22 (4H, s, O*H*); ^{13}C NMR (125 MHz, DMSO-d_6, 303 K) δ 54.2, 105.6, 116.5, 123.6, 125.5, 126.5, 127.5, 128.1, 129.9, 130.1, 137.7, 139.4, 166.2; HR-MS (ESI-MS) $m/z = 1497.5140$ $[M+Na]^+$ $C_{88}H_{66}N_{16}O_8Na$ requires 1497.5147; UV–vis ($CHCl_3$/10% MeOH) λ nm ($10^{-3}\varepsilon$, $M^{-1}\,cm^{-1}$) 428 (258.3), 521 (16.9), 557 (5.4), 594 (5.2), 653 (2.5).

geometries observed in the case of TAPP derivatives should be retained in compounds synthesized from TAMPP.

As a possible use of this new starting material, we have herein described the preparation of a bis-chelating compound in the αααα geometry where the four hydroxyl groups could be employed, for instance, to incorporate the molecule in a membrane. But another advantage of this synthesis consists in the fact that all the atropisomers can be obtained. Therefore, applications of the ααββ or αβαβ atropisomers in the development of chiral and/or water-soluble molecules can be foreseen.

In conclusion, we report the synthesis of a new bis-functionalized porphyrin, for which a face selection can be performed. We are currently using this methodology for the design of new bi-chelating agents as well as water-soluble dioxygen carriers. Therefore, different supramolecular compounds should be developed in widespread areas such as enzyme mimics,[22] chiral catalysis for oxidation,[23] and cyclopropanation,[24] or molecular recognition.[25]

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