Synthesis and Characterization of a New Series of Potential Hemoprotein Analogues: "Arbor" Porphyrins

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The interaction of molecular oxygen with hemoproteins is of primary importance in respiratory and metabolic processes. The development of simple methodologies leading to synthetic analogues for which an increasing number of structural factors is controlled becomes more and more important and has been recently engaged. Indeed, in the two past decades, many different models[1] have been proposed and synthesized by such tedious and expensive methods as high dilution condensation of multiacyl chlorides,[2] reaction of an activated amino acid,[3] or formation of the porphyrin with a prefunctionalized tetra-aldehyde and pyrrole.[4] More recently, a general and convenient method was reported as the "congruent Michael addition":[5] in two steps starting from a readily available porphyrin, a series of aza-compounds was obtained in high yield. Among them, were two new porphyrins, whose Fe^{II} complexes exhibited spectacular dioxygen and carbon monoxide binding.[6] One of these, derived from a triazacyclononane-capped porphyrin, was shown to reduce dioxygen via a $4H^+/4e^-$ process.[7] This was the first model of cytochrome *c* oxidase in which the two coordinating structures (a porphyrin for the iron and a triazacyclononane for the copper) were maintained in a defined geometry and were part of the same molecule, in contrast to more flexible models[8] or others based on the "self-assembling" strategy.[9] Since then, the structure of cytochrome *c* oxidase has been determined[10] and we now know the coordination environment of the so-called copper (B). Herein, we wish to report the synthesis of a new type of ligand developed to study and characterize the postulated intermediate formed during the catalytic reduction of dioxygen to water.

We wished to make a capping structure that would lie above the coordination site of the copper to prevent intermolecular oxidation and that would allow the required tetrahedral coordination in the reduced stage. To this end, we explored the reaction of TREN (tris(2-aminoethylamine), a member of the general class of molecules called atranes[11]) with a porphyrin bearing four electrophilic groups able to react either by a nucleophilic substitution or a Michael addition (Scheme 1). Depending on the reaction conditions, the TREN cap can be fastened by three or four points of attachment at a desired length from the porphyrin core. For instance, TAPP (isomer αααα of *meso*-(tetra-*o*-aminophenyl)porphyrin) can be derivatized by reaction with acryloyl chloride[5] or chloroacetyl chloride[12] to give the porphyrins **1** and **2** which can then be capped by a TREN molecule to obtain the final compounds **3**, **4** or **5**. We studied the effect of complexation with Ag^+ on the stereochemical course of these reactions. In THF, the reaction of 1 equiv of TREN with 1 equiv of *meso*-(tetra-*o*-chloroacetamidophenyl)porphyrin (**2**) gave exclusively the adduct with tetralinked geometry, corresponding to **4**, whereas use of excess Ag^+, to complex with TREN and form a template,[13] gave exclusively the trilinked derivative corresponding to **3** (Table 1). It is worth noting that when the reaction with the silver cation is heated for 48 h only a trace of porphyrin (**4**) is detected. When the reaction without the silver cation is stopped after 14 h, a mixture of **3** and **4** is observed. In contrast, reaction of TREN with the Michael acceptor **1** gave tetralinked adducts corresponding to **5** even when excess Ag^+ was present. This is probably because all four linkers in **1** are one carbon longer than the linkers in **2**, allowing them to reach the TREN amine groups, even when these are chelated around the silver cation.

Tri- and tetralinked structures (**3** and **4**/**5**) are readily distinguishable by NMR. In the trilinked structures the porphyrin C*H* protons appear as four doublets ($J = 4.7$ Hz), reflecting the C_{2v} geometry. (In addition, mass

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Scheme 1. General Synthetic Route to "Arbor" Porphyrins. i) CH_2=CHCOCl or $ClCH_2COCl$; ii) $N(CH_2$-CH_2-$NH_2)_3$; a: M = 2 H; b: M = Zn

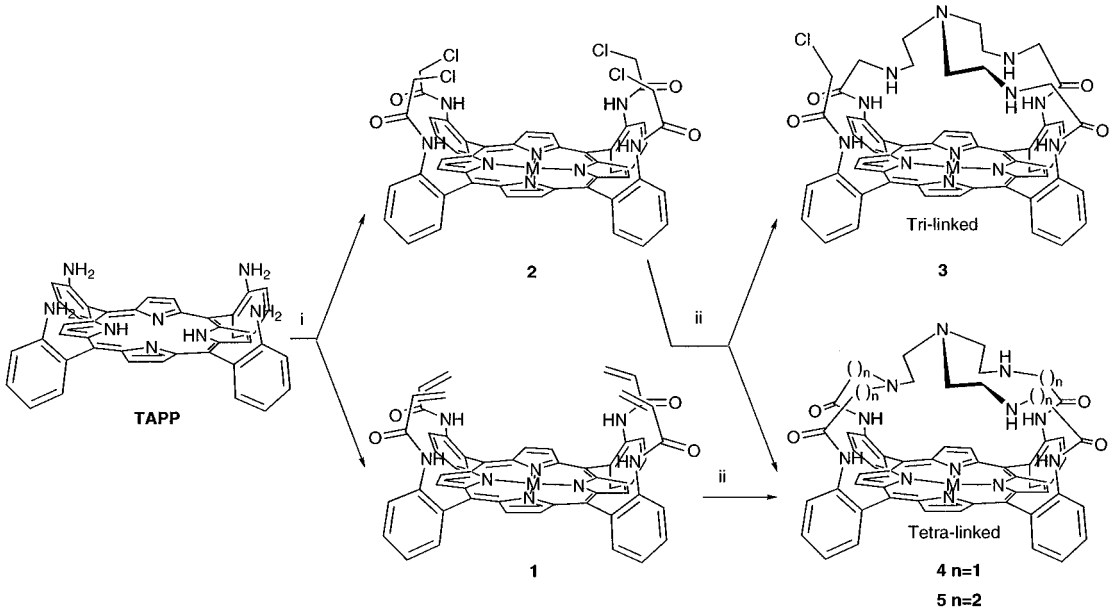

Table 1. Template Effect on the Product Geometry

		without Ag^+	with Ag^+
Michael picket (**1**)	2H	**5a**	**5a**
	Zn	**5b**	**5b**
chloroacetamido picket (**2**)	2H	**4a**	**3a**
	Zn	**4b**	**3b**

spectrometry reveals the remaining unlinked picket.) In the tetralinked compounds (**4**/**5**) the porphyrin C*H* protons show as two singlets and two doublets (J = 4.7 Hz).[14] Moreover, consistent with the assigned structure, the stability of these tetralinked compounds in refluxing toluene for 12 h represents a additional proof as it is known that a free picket is able to isomerize under these conditions.[7b,12]

In conclusion, we have developed methods for synthesizing two potentially useful families of TREN-capped porphyrins containing sterically hindered coordination cavities. We call them arbor porphyrins.

Experimental Section

General Methods.

All solvents (ACS for analysis) were purchased from Carlo Erba. THF was distilled from potassium, whereas methanol was distilled from magnesium turns. CH_2Cl_2 was used as received.

The starting materials were generally used as received (Acros, Aldrich) without any further purification except for tris(2-aminoethylamine), which was distilled under argon just before use.

All reactions were performed under an argon atmosphere and monitored by TLC (silica, CH_2Cl_2/MeOH). Porphyrins **1**[5] and **2**[13] were prepared according to the literature.

Column flash chromatography was performed on silica gel (Merck TLC-Kieselgel 60H, 15 μm). Generally, the eluent consisted of increasing amounts of methanol in dichloromethane.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX 500 spectrometer and referenced to the residual proton solvents. Mass spectra were performed at the University of Rennes I (CRMPO). UV−vis and IR spectra were recorded on a Varian Cary 1 and a Bruker IFS 66 spectrometer, respectively. Elemental analyses were obtained on an EA 1108 Fisons Instruments.

Synthesis and Characterization. Tetralinked C1 TREN Capped Free Base Porphyrin (4a). Yield: 33%. In a 100 mL round-bottom flask equipped with a stir bar, a reflux condenser, and a nitrogen inlet were heated **2a** (0.120 mmol, 120 mg) and THF (40 mL) at 55 °C. Then, 1,8-diazabicyclo[5.4.0]-undecene-7 (DBU) (0.576 mmol, 80 mg) was added. Finally, TREN (0.120 mmol, 18 μL) was allowed to react and the mixture heated for 48 h. The solvent was then removed under vacuum and the remaining material taken in CH_2Cl_2. The organic layer was washed twice with aqueous 5% NaOH, rotary concentrated, and directly loaded on a 15 μm silica gel column (3 × 20 cm). The first eluted product was the unreacted porphyrin, whereas the major product, eluted with 5% MeOH/CH_2Cl_2, corresponded to the desired compound. Evaporation of the solvents yielded a crystalline purple product. ^{1}H NMR ($CDCl_3$, 500 MHz, 50 °C) δ: 9.05 (d, J = 5.0 Hz, 2 H); 8.92 (d, J = 5.0 Hz, 2 H); 8.81 (s, 2 H); 8.74 (broad m, 4 H); 8.72 (s, 2 H); 8.61 (d + s, J = 7.0 Hz, 4 H); 8.11 (d, J = 7.0 Hz, 2 H); 7.92 (t, J = 7.0 Hz, 2 H); 7.89 (d, J = 7.5 Hz, 2 H); 7.76 (t, J = 7.5 Hz, 2 H); 7.55 (d + s, J = 8.0 Hz, 4 H); 2.89 (d, J = 15.0 Hz, 2 H); 2.69 (d, J = 17.0 Hz, 2 H); 2.51 (d, J = 17.0 Hz, 2 H); 2.35 (d, J = 16.0 Hz, 2 H); 1.70 (broad m, 2 H); 0.96 (broad m, 2 H); 0.60 (broad m, 2 H); 0.01 (broad m, 2 H); −0.52 (broad m, 2 H); −1.79 (broad m, 2 H); −2.34 (s, 2 H); −2.90 (broad m, 2 H). UV−vis (CH_2Cl_2) λ nm ($10^{-3}\epsilon$, dm^3 mol^{-1} cm^{-1}): 424 (161.4); 517 (9.5); 552 (3.8); 591 (3.7); 648 (2.2). MS m/z; 980.4343 [M − H]$^+$ for $C_{58}H_{53}N_{12}O_4$ (LSIMS). Anal. Calcd. for $C_{58}H_{52}N_{12}O_4$·CH_2Cl_2: C, 66.47; H, 5.11; N, 15.77. Found: C, 66.62; H, 5.15; N, 15.44.

Tetralinked C1 TREN Capped Zn Porphyrin (4b). Yield: 27%. The previous procedure was used with **2b**. ^{1}H NMR (d_5-pyridine, 500 MHz, 50 °C) δ: 9.29 (d, J = 8.5 Hz, 2 H); 9.26 (s, 2 H); 9.12 (d, J = 8.5 Hz, 2 H); 9.10 (s, 2 H); 9.04 (s, 2 H); 8.96 (d, J = 4.5 Hz, 2 H); 8.93 (d, J = 4.5 Hz, 2 H); 8.65 (d, J = 7.5 Hz, 2 H); 8.26 (d, J = 7.5 Hz, 2 H); 7.90 (t, J = 8.0 Hz, 2 H); 7.88 (t, J = 8.0 Hz, 2 H); 7.68 (t, J = 7.5 Hz, 2 H); 7.57 (s, 2 H); 7.54 (t, J = 7.5 Hz, 2 H); 3.00 (d, J = 15.0 Hz, 2 H); 2.73 (d, J = 15.0 Hz, 2 H); 2.49 (d, J = 15.0 Hz, 2 H); 2.48 (t, J = 15.0 Hz, 2 H); 1.00 (broad m, 2 H); 0.80 (s, 2 H); 0.70 (broad t, 2 H); 0.04 (broad m, 2 H); −0.08 (broad m, 2 H); −1.55 (broad m, 2 H); −3.15 (broad m, 2 H). ^{13}C NMR (d_5-pyridine, 125.8 MHz, 50 °C) δ: 170.0; 167.0; 135.0; 134.0; 133.0; 132.8; 132.0; 129.0; 123.0; 122.5; 122.2; 120.0; 62.0; 52.0; 51.0; 45.0; 42.0. UV−vis (CH_2Cl_2) λ nm ($10^{-3}\epsilon$, dm^3 mol^{-1} cm^{-1}): 430 (353.4); 559 (15.3); 598 (5.4). MS m/z: 1043.343 [M − H]$^+$ for $C_{58}H_{51}N_{12}O_4Zn$ (LSIMS). Anal. Calcd. for $C_{58}H_{50}N_{12}O_4Zn$·H_2O: C, 65.57; H, 4.93; N, 15.82. Found: C, 65.64; H, 4.91; N, 15.69.

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Tetralinked C2 TREN Capped Free Base Porphyrin (5a). Yield: 43%. Under argon, a 100 mL two-neck round-bottom flask was charged with the Michael acceptor **1a** (0.45 mmol, 400 mg) and MeOH (40 mL), and the mixture was heated at 55 ° C for 45 min. TREN (0.45 mmol, 72 μL) was then directly added with a Hamilton syringe and heating continued for 48 h. The mixture was cooled, concentrated, and directly poured onto a 15 μm silica gel column (5 × 20 cm). The desired product was eluted with 4% MeOH/CH_2Cl_2. After evaporation to dryness, 234 mg of a purple powder was collected. ^{1}H NMR (d_5-pyridine, 500 MHz, 50 °C) δ: 11.42 (s, 2 H); 9.17 (s, 2 H); 9.08 (d, J = 4.5 Hz, 2 H); 9.06 (broad m, 2 H); 9.02 (d, J = 5.0 Hz, 2 H); 8.96 (s, 2 H); 8.81 (broad m, 4 H); 8.09 (d, J = 6.5 Hz, 2 H); 7.87 (t, J = 7.5 Hz, 2 H); 7.83 (t, J = 7.5 Hz, 2 H); 7.77 (d, J = 7.5 Hz, 2 H); 7.55 (t, J = 7.0 Hz, 2 H); 7.46 (t, J = 7.0 Hz, 2 H); 2.35−2.12 (broad m, 10 H); 2.09−1.99 (broad m, 4 H); 1.86−1.80 (broad m, 2 H); 1.09 (broad m, 2 H); 0.84 (broad m, 2 H); 0.70 (broad m, 2 H); 0.47 (broad m, 2 H); 0.01 (broad m, 2 H); −0.13 (broad m, 2 H); −1.57 (broad m, 2 H); −2.29 (s, 2 H). ^{13}C NMR (d_5-pyridine, 125.8 MHz, 50 °C) δ: 139.0; 137.0; 135.0; 131.4; 131.2; 126.0; 125.0; 124.5; 81.0; 56.0; 50.5; 45.0; 44.8; 43.5; 36.5; 35.5; 34.2; 27.0; 26.8. UV−vis (CH_2Cl_2) λ nm ($10^{-3}\epsilon$, dm^3 mol^{-1} cm^{-1}): 421 (180.4); 515 (9.0); 5.48 (3.1); 588 (3.4); 644 (1.8). MS m/z: = 1037.4929 $[M - H]^+$ for $C_{62}H_{61}N_{12}O_4$ (LSIMS). Anal. Calcd. for $C_{62}H_{60}N_{12}O_4 \cdot 2H_2O$: C, 69.38; H, 6.01; N, 15.66. Found: C, 68.81; H, 5.54; N, 15.79.

Tetralinked C2 TREN Capped Zn Porphyrin (5b). Yield: 64%. The previous procedure was used with **2b**. ^{1}H NMR (d_5-pyridine, 500 MHz, 50 °C) δ: 11.66 (s, 2 H); 9.17 (d, J = 8.0 Hz, 2 H); 9.11 (d, J = 5.0 Hz, 2 H); 9.03 (s, 2 H); 9.02 (d, J = 4.5 Hz, 2 H); 8.92 (s, 2 H); 8.88 (d, J = 8.0 Hz, 2 H); 8.56 (s, 2 H); 8.08 (d, J = 8.0 Hz, 2 H); 7.96 (t, J = 8.0 Hz, 2 H); 7.91 (t, J = 8.0 Hz, 2 H); 7.63 (t, J = 7.0 Hz, 2 H); 7.57 (d, J = 7.0 Hz, 2 H); 7.49 (t, J = 8.0 Hz, 2 H); 2.26−2.10 (broad m, 12 H); 1.87 (broad m, 4 H); 1.02 (broad m, 2 H); 0.90 (broad m, 2 H); 0.69 (broad m, 2 H); 0.43 (broad m, 2 H); −0.14 (broad m, 2 H); −0.32 (broad m, 2 H); −1.72 (broad m, 2 H). UV−vis (CH_2Cl_2) λ nm ($10^{-3}\epsilon$, dm^3 mol^{-1} cm^{-1}): 428 (352.5); 559 (16.6); 599 (5.6). MS m/z: 1099.4051 $[M - H]^+$ for $C_{62}H_{59}N_{12}O_4Zn$ (LSIMS). Anal. Calcd. for $C_{62}H_{58}N_{12}O_4Zn \cdot 3MeOH$: C, 65.24; H, 5.90; N, 14.05. Found: C, 65.80; H, 5.68; N, 13.56.

Trilinked C1 TREN Capped Free Base Porphyrin (3a). Yield: 19.7%. Under argon, TREN (0.2 mmol, 33 μL) and AgI (0.3 mmol, 70 mg) were added to 50 mL of dry degassed THF, and the mixture was heated at 55 °C for 15 min. DBU (1.6 mmol, 240 mg) and **2a** (0.2 mmol, 200 mg) diluted in 10 mL of THF were then directly added with a syringe. The reaction was allowed to proceed for 14 h. The mixture was evaporated to dryness, giving a purple material that was suspended in CH_2Cl_2 and filtered. The filtrate was washed twice with 50 mL of aqueous 5% NaOH, concentrated to 5 mL by rotary evaporation, and poured onto a 15 μm silica gel column (3 × 20 cm) prepared with CH_2Cl_2. Unreacted porphyrin was eluted first (30 mg, 0.03 mmol) followed by **3a** (4% MeOH/CH_2Cl_2) (40 mg, 0.04 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz, 27 °C) δ: 9.79 (s, 1 H); 9.03 (d, J = 8.5 Hz, 1 H); 8.94 (s, 1 H); 8.86 (d, J = 4.5 Hz, 2 H); 8.83 (d, J = 4.5 Hz, 2 H); 8.80 (d, J = 4.5 Hz, 2 H); 8.77 (d, J = 4.5 Hz, 2 H); 8.76 (d, J = 8.5 Hz, 3 H); 8.59 (s, 2 H); 8.25 (d, J = 7.5 Hz, 2 H); 7.87 (broad t + d, 5 H); 7.68 (d, J = 7.0 Hz, 1 H); 7.06 (t, J = 6.5 Hz, 2 H); 7.44 (broad t + d, 2 H); 3.83 (s, 2 H); 2.85 (s, 2 H); 2.77 (d, J = 20.0 Hz, 2 H); 2.43 (d, J = 20.0 Hz, 2 H); 1.28 (s, 1 H); 0.89 (broad m, 4 H); 0.39 (broad m, 1 H); 0.11 (broad m, 6 H); 0.02 (broad m, 2 H); −0.61 (broad m, 2 H); −1.29 (broad m, 2 H); −1.43 (broad m, 2 H); −2.48 (s, 2 H). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 27 °C) δ: 136.0; 134.7; 134.4; 130.4; 124.5; 123.3; 122.9; 121.2; 120.8; 119.9; 53.0; 52.8; 51.8; 47.6; 46.0; 45.5; 44.0. UV−vis (CH_2Cl_2) λ nm ($10^{-3}\epsilon$, dm^3 mol^{-1} cm^{-1}): 422 (151.8); 516 (8.9); 548 (3.0); 588 (3.6); 644 (1.5). MS m/z: 1151.41 [M + m-NBA − H_2O] for $C_{58}H_{54}ClN_{12}O_4 + C_7H_7NO_3 - H_2O$ (LSIMS, m-NBA = matrix = m-nitrobenzylic alcohol). Anal. Calcd for $C_{58}H_{53}ClN_{12}O_4$: C, 68.46; H, 5.25; N, 16.52. Found: C, 68.00; H, 5.26; N, 16.11.

Trilinked C1 TREN Capped Zn Porphyrin (3b). Yield: 28%. The previous procedure was used with **2b**. ^{1}H NMR ($CDCl_3$, 500 MHz, 50 °C) δ: 8.89 (d, J = 7.0 Hz, 1 H); 8.87 (d, J = 5.0 Hz, 2 H); 8.75 (d, J = 5.0 Hz, 2 H); 8.74 (d, J = 5.0 Hz, 2 H); 8.72 (d, J = 5.0 Hz, 2 H); 8.63 (d, J = 8.0 Hz, 1 H); 8.39 (d, J = 8.0 Hz, 2 H); 8.21 (s, 2 H); 8.13 (d, J = 7.5 Hz, 2 H); 7.98 (d, J = 7.5 Hz, 1 H); 7.80 (t, J = 8.0 Hz, 2 H); 7.78 (d J = 8.0 Hz, 2 H); 7.60 (t, J = 8.0 Hz, 2 H); 7.50 (t, J = 8.0 Hz, 2 H); 7.17 (t, J = 7.6 Hz, 2 H); 7.12 (d, J = 8.0 Hz, 1 H); 3.32 (s, 2 H); 2.37 (d, J = 15.0 Hz, 2 H); 2.35 (s, 2 H); 2.07 (d, J = 15.0 Hz), 2 H); 0.74 (broad m, 2 H); 0.11 (broad s, 2 H); −0.10 (broad m, 2 H); −0.30 (broad, 3 H); −0.69 (broad m, 2 H); −1.76 (broad m, 2 H); −2.70 (broad m, 2 H). UV−vis (CH_2Cl_2) λ nm ($10^{-3}\epsilon$, dm^3 mol^{-1} cm^{-1}): 430 (380.3); 564 (18.1); 602 (5.3). MS m/z: 1003.34 [M + 2H − $COCH_2Cl$]$^+$ (loss of the remaining chloroacetamido picket) for $C_{56}H_{51}N_{12}O_4Zn$(LSIMS). Anal. Calcd for $C_{58}H_{51}ClN_{12}O_4Zn \cdot 2H_2O$: C, 62.36; H, 4.96; N, 15.04. Found: C, 62.28; H, 4.80; N, 15.03.

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