Metalloporphyrinoids

DOI: 10.1002/ange.200502208

Synthesis and Characterization of a Cyclic Bis-silver(I) Assembly of Four 2-Aza-21-carbaporphyrinatosilver(III) Subunits**

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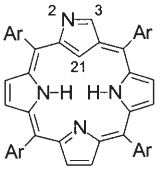
Porphyrins and metalloporphyrins constitute a class of building blocks for the construction of multicomponent 2D and 3D molecular arrays that are being considered as possible biomimetic models, catalysts, or materials for the transport of charge, molecules, and ions. Covalent[1] as well as coordination linkages[2] have been exploited in the design of a variety of discrete porphyrin assemblies. Recently, special attention has been given to systems built up of directly linked porphyrins with strongly interacting aromatic subunits,[3] which represent some of the most promising candidates for potential applications.

Porphyrin analogues[4] exhibit many distinct features that can be exploited in the construction of novel molecular and supramolecular systems. Among them, the N-confused porphyrin **1**[5] is particularly attractive owing to its unique structure, which allows multimodal coordination of the confused pyrrole to metal ions,[6] and its reactivity. The exposed position of the external nitrogen atom (N2) makes this fragment of molecule susceptible to interactions with metal ions.[7]



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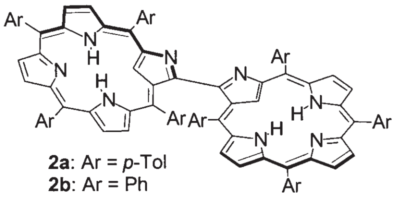
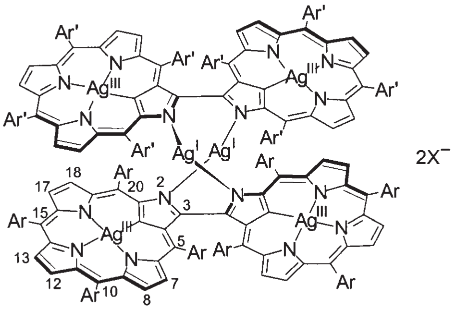
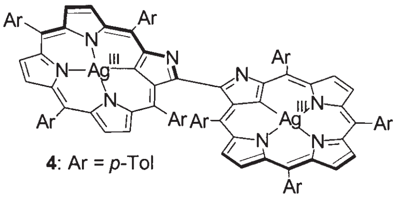


2a: Ar = *p*-Tol
2b: Ar = Ph



3a: Ar = Ar' = *p*-Tol, $X^- = BF_4^-$, $CF_3SO_3^-$
3b: Ar = Ar' = Ph, $X^- = BF_4^-$
3c: Ar = Ph, Ar' = *p*-Tol, $X^- = BF_4^-$



4: Ar = *p*-Tol

Recently, we reported the synthesis of the dimeric N-confused porphyrin **2** (Ar = phenyl, *p*-tolyl (*p*-Tol)),[8] which is a unique isomer that preserves the basic skeleton of a directly β–β-linked bis(porphyrin).[9] The cyclic assemblies **3**, whose synthesis and characterization are presented herein, exemplify a new type of carbaporphyrinoid array that consists of both covalent and coordinating links between the subunits. Owing to the steric factors imposed by *meso*-aryl substituents, the bipyrrolic fragment adopts a cisoid conformation in **2** but deviates strongly from planarity. Such an arrangement determines the coordination mode of this fragment, which, unlike the planar bipyrrole system present in corroles,[10] is preorganized to coordinate two metal ions rather than to form a chelate ring.

Reaction of bis(carbaporphyrinoid) **2** with AgX ($X = BF_4^-$ or $CF_3SO_3^-$) was carried out at room temperature in THF for 30 minutes. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2, and washed with water to remove the excess of silver(I) ions and the acid liberated upon insertion of the metal. The composition and molecular structure of **3** was established on the basis of ESI-MS, NMR

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[**] This work was supported by the Polish Ministry of Scientific Research and Information Technology (Grant 3 T09A 16228).

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spectroscopy, and single-crystal X-ray analyses. Owing to the dicationic character of the complex, the dominant peak in the mass spectrum corresponds to the dication ($m/z = 1657$, 100%) with a characteristic half-unit isotopic pattern. The fragmentation peak at $m/z = 1549.5$ (47%) reflects liberation of the dimeric fragment **4**.

The solid-state structure of **3a**-$(OTf)_2$ ($OTf = CF_3SO_3^-$) presents an assembly of four 2-aza-21-carbaporphyrinatosilver(III) subunits,[11] which are organized on the perimeter of a ten-membered ring that contains two silver(I) ions (Figure 1). The assembly of the axially chiral[8] dimeric subunits **4** on the bis-silver(I) template may lead to the formation of diastereomers. However, only *S*,*S* and *R*,*R* enantiomers are observed in the crystal structure (see Supporting Information). Although both monovalent silver centers are two-coordinate, the N-Ag-N fragments are far from linear, being bent outwards with an angle of 147.0(3)°. This is likely due to the geometric constraints imposed on the ring by the structure of the bipyrrolic moiety. The relatively short distance between the bridging silver atoms Ag3–Ag3* (3.107(2) Å) suggests that an "argentophilic" interaction[12] stabilizes the assembly. Such interactions have been shown to influence the outcome of several supramolecular assemblies, and their importance has been crystallographically investigated.[13] The distances within the macrocyclic core (Ag1-C21: 1.974(9); Ag1-N22: 2.030(9); Ag1-N23: 2.052(7); Ag1-N24: 2.027(8) Å) are slightly shorter than those observed in monomeric neutral silver(III) complexes of **1**,[11] an O-confused porphyrin derivative,[14] or the so-called "true" carbaporphyrin.[15] The distances between the external nitrogen atoms and the bridging silver ions (Ag3-N2: 2.175(8); Ag3-N26: 2.169(8)) are typical for the monovalent silver complexes.[13g]

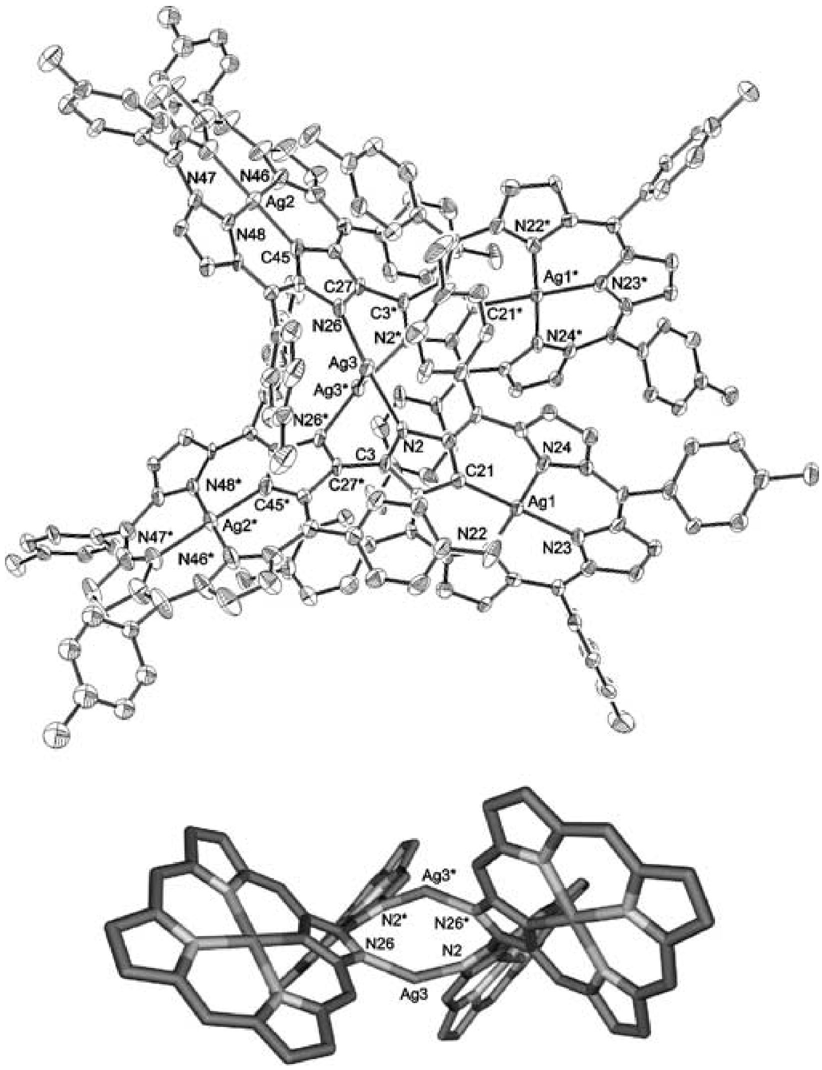

Figure 1. Molecular structure of the assembly **3a**. Top: ORTEP view with thermal ellipsoids scaled at the 30% probability level (hydrogen atoms, triflate anions, and solvent molecules are omitted); bottom: wire-frame representation of the structure with all aryl substituents omitted for clarity.

As a consequence of the crystal-packing forces, the molecule displays only twofold symmetry in the solid state. In contrast, the effective symmetry of the molecule in solution is fourfold, as inferred from the ^1H NMR spectra which reveal only one set of signals (Figure 2a,b). The spectra support the stereoselectivity of the formation of the assembly, as diastereomers are expected to exhibit different ^1H NMR spectra. Owing to the nonplanar character of the system and freezing of rotation of the *meso*-aryl substituents, each proton of the subunit in **3** is represented by a unique signal and can be assigned on the basis of 2D NMR experiments (see Supporting Information). Analysis of the chemical shifts and interprotonic through-space interactions observed in NOESY or ROESY experiments allowed a model to be built that has the same molecular topology as the solid-state structure of **3a** but which displays fourfold symmetry.

A neutral diamagnetic bis-silver(III) complex **4** can be obtained by treating a solution of **3** in chloroform with either an aqueous solution of sodium halogenide or with a solution of tetraalkylammonium bromide in chloroform to remove bridging silver(I) ions.[16] Protonation of **3** with one equivalent of trifluoroacetic acid or the addition of pyridine (500-fold excess) breaks the assembly reversibly. The process can be fully reversed upon addition of water or by evaporation of the solvents. Thus, reconstruction of **3** is possible as long as silver(I) ions are present in the solution.

A slow exchange reaction can be observed upon mixing of the solutions of **3a** and **3b** to result, after 20 h at room temperature, in an equilibrium of starting complexes and a mixed-ligand species **3c** that can be identified by ESI-MS (observed: $m/z = 1602.4$; calcd: $m/z = 1601.7$) and ^1H NMR spectroscopy (Figure 2d). Formation of **3c**, which exhibits twofold symmetry, indicates the lability of the system but also provides additional support for the preservation of the tetrameric structure in solution.

The charge on the external nitrogen atom of the confused pyrroles strongly influences redox properties of the metal ion that is coordinated in the macrocyclic core.[7f,17] Thus, it can be expected that

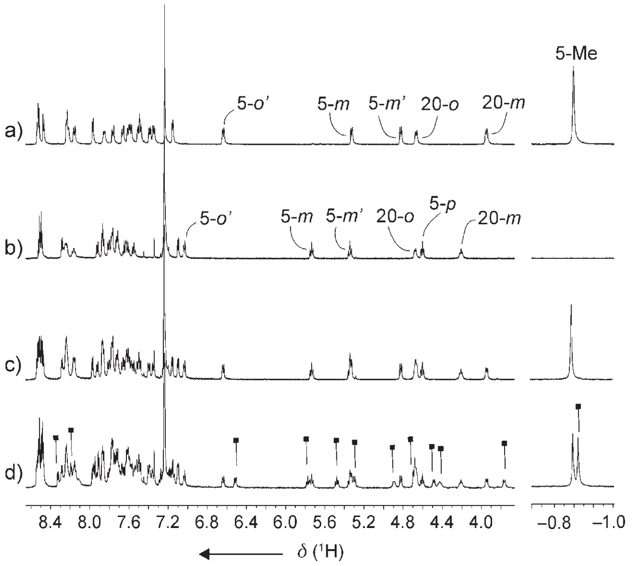

Figure 2. Fragments of the ^{1}H NMR spectra ($CDCl_3$, 298 K) of the assemblies a) **3a**, b) **3b**, c) **3a** + **3b** immediately after mixing, and d) **3a** + **3b** 40 h after mixing (some of the new features, attributed to the mixed-ligand species **3c**, are indicated by ■). Signal assignments of the most upfield-shifted *meso*-aryl protons in **3a** and **3b** are presented in (a) and (b), with numbers indicating *meso* positions.

coordination of the Ag^I cation to the external nitrogen atom destabilizes the trivalent silver center in each subunit to allow the reduction of the metal. Such a reduction process has not been observed to date for any of the carbaporphyrinoid silver(III) complexes. In cyclic voltammograms of **3a** and **3b** (CH_2Cl_2 solutions; tetrabutylammonium perchlorate as the supporting electrolyte; glassy carbon as a working electrode; all data are referenced to ferrocene/ferrocenium internal standard), a pair of two-electron couples ($E_{1/2} = -1100$ mV, $\Delta E_{ac} = 40$ mV, $E_{1/2} = -1230$ mV, $\Delta E_{ac} = 46$ mV for **3a**; $E_{1/2} = -1055$ mV, $\Delta E_{ac} = 40$ mV, $E_{1/2} = -1175$ mV, $\Delta E_{ac} = 46$ mV for **3b**) is attributable to a stepwise reduction of silver(III) centers in the strongly interacting covalently linked subunits.[8,18] Each reduction step takes place at the same potential in two nondirectly connected, and thus non-interacting subunits, which is accounted for by the two-electron character of the processes. Two overlapping couples observed for **3a** around −1425 mV and those better-resolved for **3b** ($E_{1/2} = -1330$ mV, $\Delta E_{ac} = 36$ mV, $E_{1/2} = -1440$ mV, $\Delta E_{ac} = 30$ mV) reflect reductions of the ligand. For **4** only ligand reductions represented by two couples at −1470 and −1600 mV are observed.

In conclusion, we have shown the very facile diastereoselective formation of a molecular assembly that consists of four carbaporphyrinoids and which is effectively formed despite steric overcrowding imposed by the substituents in the vicinity of the donor sites. It seems that access to the bridging silver–silver fragment is hindered which may stabilize the cyclic structure. Experiments are underway to explore the application of this novel coordination mode of the nonplanar bipyrrolic moiety in the construction of larger redox-active assemblies that consist of covalently linked N-confused porphyrin derivatives.

Experimental Section

3a-$(BF_4)_2$: 3,3'-Bis(5,10,15,20-tetrakis(*p*-tolyl)-2-aza-21-carbaporphyrin) (**2a**; 20 mg, 0.015 mmol) was dissolved in THF (20 mL) and stirred with silver tetrafluoroborate (10 mg, 0.115 mmol) for 0.5 h. The solvent was then removed by evaporation, and the solid residue was dissolved in dichloromethane (10 mL). The solution was shaken with three portions of water (10 mL each). After separation of the organic phase, the solution was filtered and then the solvent was removed. The solid residue was dissolved in dichloromethane, and the solution was left to crystallize slowly after the addition of hexane to yield the olive-colored product **3a**-$(BF_4)_2$ (26 mg, 94%). A similar procedure using AgOTf instead of $AgBF_4$ or **2b** instead of **2a** yielded **3a**-$(OTf)_2$ or **3b**-$(BF_4)_2$, respectively. Spectral data recorded in the solution state were independent of the counteranion present in the complex. See Supporting Information for NMR spectroscopic data for **3a** and **3b**.

3a-$(BF_4)_2$: UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 258 (5.23), 313 (5.00), 378 (5.08), 451 (sh), 472 (5.51), 533 (4.80), 596 (4.67), 636 (sh), 686 nm (4.52); ESI-MS: *m/z* calcd for $C_{192}H_{136}N_{16}Ag_6$: 1657.7 ($[M]^{2+}$); found: 1657.4; elemental analysis: calcd (%) for $C_{192}H_{136}N_{16}Ag_6B_2F_8\cdot 2(CH_2Cl_2)$: C 63.70, H 3.86, N 6.13; found: C 63.40, H 3.56, N 6.12.

3b-$(BF_4)_2$: UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 256 (5.19), 323 (sh), 378 (5.08), 452 (sh), 471 (5.47), 531 (4.75), 594 (4.67), 641 (sh), 691 nm (4.48); ESI-MS: *m/z* calcd for $C_{176}H_{104}N_{16}Ag_6$: 1545.7 ($[M]^{2+}$); found: 1545.2; elemental analysis: calcd (%) for $C_{176}H_{104}N_{16}Ag_6B_2F_8\cdot 2(CH_2Cl_2)$: C 62.27, H 3.17, N 6.53; found: C 62.40, H 3.32, N 6.23.

Crystals of suitable quality for X-ray analysis were obtained by slow diffusion of hexane into a solution of **3a**-$(OTf)_2$ in toluene. Crystal data for **3a**-$(OTf)_2$: $C_{231.5}H_{172}N_{16}Ag_6\cdot 2CF_3SO_3$, $M_W = 4099.19$, $T = 100$ K, $Cu_{K\alpha}$ radiation, monoclinic, space group *C2/c*, $a = 24.208(4)$, $b = 34.279(4)$, $c = 24.175(4)$ Å, $\beta = 103.35(3)$, $V = 19519(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.395$ mg m^{-3}, $\lambda = 1.54178$ Å, $\mu = 5.485$ mm^{-1}, $F(000) = 8356$, Oxford Diffraction Xcalibur PX with KM4CCD Sapphire detector, $3.19 \leq \theta \leq 68.00°$, 15171 collected reflections, 8504 independent reflections with $I > 2\sigma(I)$, 1104 parameters, $R1(F) = 0.0827$, $wR2(F^2) = 0.2102$, $S = 1.064$, largest difference peak and hole 1.861 and −1.06 e Å^{-3}. All non-hydrogen atoms were refined with anisotropic displacement parameters except for those of the disordered solvents, triflate anion, and one *meso*-tolyl ring. Hydrogen atoms were excluded from the geometry of molecules and refined isotropically. The asymmetric unit contains half of the molecule of **3a**, consisting of two subunits linked by a silver ion, one disordered triflate anion, a half molecule of hexane, and one and a half molecules of toluene displaced into six different sites. CCDC 276104 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4: Complex **3a** (10 mg, 3 μmol) was dissolved in CH_2Cl_2 (20 mL), and the solution was stirred vigorously for 0.5 h with a 1 M aqueous solution of NaBr (10 mL) until the originally olive-colored solution turned red-brown. The layers were then separated, and the organic phase was washed with two 10-mL portions of water. After drying over a small amount of anhydrous K_2CO_3 and filtration, the volume of the solution was reduced to 10 mL, and hexane (5 mL) was added which caused precipitation of **4** as a brown powder (6.1 mg, 65%). ^{1}H NMR: see Supporting Information; UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 254 (5.20), 285 (sh), 323 (5.02), 384(sh), 412(sh), 450 (sh), 468 (5.50), 533 (4.88), 621 (sh), 661 nm (4.45); ESI-MS: *m/z* calcd for $C_{96}H_{68}N_8Ag_2$: 1549.4 ($[M{+}1]^+$); found: 1549.5; elemental analysis: calcd (%) for $C_{96}H_{68}N_8Ag_2\cdot CH_2Cl_2\cdot C_6H_{14}$: C 71.90, H 4.89, N 6.51; found: C 71.94, H 4.78, N 6.22.

Received: June 23, 2005
Published online: September 8, 2005

Keywords: nitrogen heterocycles · oligomers · porphyrinoids · silver · supramolecular chemistry

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[16] After isolation from the solution, **4** is sparingly soluble in organic solvents, which may suggest its association leading to the formation of a polymer. Solid **4** is readily converted back into **3a** upon its treatment with a solution of a silver salt in THF or methanol.

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[18] Probably as a result of the labile character of the assembly, an irreversible reduction of "free" silver(I) ion takes place to result in the deposition of metallic silver on the surface of the electrode. The appearance of an oxidation peak at 380 mV follows cathodic scans below −950 mV.