One-Pot Synthesis of a bis-Pocket Corrole through a 14-fold Bromination Reaction

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A one-pot protocol, effecting 14-fold bromination with elemental bromine, has afforded copper β-octabromo-*meso*-tris(2,6-dibromo-3,5-dimethoxyphenyl)corrole, a new bis-pocket metallocorrole. The Cu complex underwent smooth demetalation under reductive conditions, affording the free corrole ligand, which in turn could be readily complexed to Mn[III] and Au[III]. A single-crystal X-ray structure was obtained for the Mn[III] complex.

bis-Pocket porphyrins and corroles afford sterically protected environments that may potentially stabilize high-valent transition metal-oxo, -imido, and -nitrido intermediates.[1–6] Of the wide variety of such ligands reported, porphyrins and corroles with 2,6-disubstituted *meso*-aryl groups are among the more easily accessible. Even so, the syntheses of such corroles rarely proceed in yields higher than 10%. Thus, condensation of pyrrole and the appropriate 2,6-disubstituted benzaldehyde provides 5,10,15-tris(2′,6′-dichlorophenyl)corrole[7] in 9% yield and *meso*-trimesitylcorrole[8] and 5,10,15-tris(2′,4′,6′-triphenylphenyl)corrole[5] each in 7% yield. Recently, a dipyrromethane–aldehyde condensation led to 5,10,15-tris(2′,6′-dibromophenyl)-corrole in 11% yield.[9] Bhyrappa and co-workers reported an elegant, if serendipitous, solution to the problem of low yields involving the direct bromination of copper 5,10,15,20-tetrakis(3′,5′-dimethoxyphenyl)porphyrin with elemental bromine, which resulted in the hexadecabromo bis-pocket complex copper 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(2′,6′-dibromo-3′,5′-dimethoxyphenyl)porphyrin in nearly 80% yield.[10] Reported herein is an analogous protocol for the smooth 14-fold bromination of copper 5,10,15-tris(3′,5′-dimethoxyphenyl)corrole, Cu[T*m,m*′MeOPC] (**1**), affording the copper 2,3,7,8,12,13,17,18-octabromo-5,10,15-tris(2′,6′-dibromo-3′,5′-dimethoxyphenyl)corrole, Cu[Br$_{14}$T*m,m*′MeOPC] (**1-Br$_{14}$**,

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Figure 1) in 55% yield. As discussed below, bis-pocket complex **1-Br$_{14}$** proved to be a valuable starting material for the syntheses for other bis-pocket metallocorrole complexes.
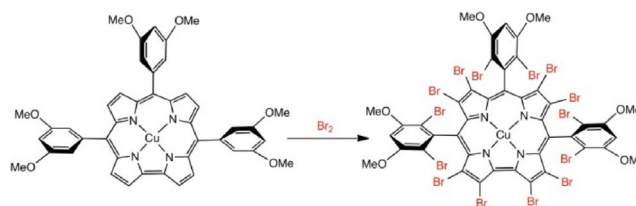

Figure 1. Synthesis of **1-Br$_{14}$**.

Exposure of readily accessible Cu[T*m,m*′MeOPC] (**1**) to an excess of elemental bromine in chloroform yielded the bis-pocket complex Cu[Br$_{14}$T*m,m*′MeOPC] (**1-Br$_{14}$**) in yields of over 55% and quantities of >100 mg per batch, with clear indications that the synthesis could be scaled up further.[11] The tetradecabromocorrole product was contaminated with trideca- and dodecabrominated impurities (as inferred from mass spectrometric analysis), which fortunately could be readily removed by overnight recrystallization from chloroform/methanol. To our satisfaction, **1-Br$_{14}$** underwent smooth reductive demetalation with anhydrous FeCl$_2$ and concentrated H$_2$SO$_4$, affording the free-base ligand H$_3$[Br$_{14}$T*m,m*′MeOPC] (**2-Br$_{14}$**) in 77% yield.[12,13] To demonstrate its utility as a transition-metal ligand, **2-Br$_{14}$** was used to synthesize its Au[III][14] (**3-Br$_{14}$**) and Mn[III][15,16] (**4-Br$_{14}$**) complexes, which proceeded in good yields. A high-quality single-crystal X-ray structure was obtained for the Mn[III] complex **4-Br$_{14}$·H$_2$O** (Figure 2 and Table 1), providing conclusive proof of composition and structure for the unusual 14-fold brominated complex. An attempt at rhenium insertion, however, led to a mixture of partially debrominated products Re[Br$_n$T*m,m*′MeOPC](O) (*n* < 14), presumably reflecting the inability of the sterically hindered macrocycle to adopt the domed conformation observed for ReO corroles.[17]

Electrochemical (Figure 3) and UV/Vis (Figure 4) measurements (see Table 2 for select data) showed that 14-fold bromination has a substantial impact on the electronic character Cu[T*m,m*′MeOPC] (**1**) and Au[T*m,m*′MeOPC] (**3**).The most significant effect is an upshift of approximately 500 mV of both the oxidation and reduction potentials of the two metallocorroles. These upshifts are significantly higher than the 300–350 mV effect of β-octabromination on the oxidation and reduction potentials of Cu triarylcorroles,[12] but similar to those observed for other corrole derivatives.[18] Interestingly, 14-fold bromination of **1** engenders a significantly smaller redshift (ca. 15 nm)
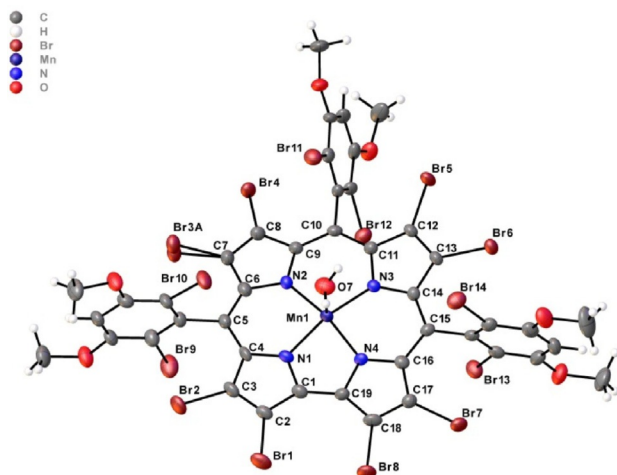
Figure 2. X-ray structure of **4-Br$_{14}$**·H$_2$O. Selected distances (Å): Mn(1)-N(1) 1.918(4), Mn(1)-N(2) 1.936(4), Mn(1)-N(3) 1.931(4), Mn(1)-N(4) 1.918(4), and Mn(1)-O(7) 2.182(4).

Table 1. Selected X-ray data for **4-Br$_{14}$**·H$_2$O.	
Parameter	Value
Chemical formula	C$_{53.80}$H$_{33.80}$Br$_{14}$O$_{7.06}$N$_4$Mn
Formula mass	2022.82
Crystal system	trigonal
Space group	R-3
λ [Å]	0.7749
a [Å]	42.0826(16)
c [Å]	23.8267(11)
Z	18
V [Å^3]	36543(3)
Temperature [K]	100(2)
Density [g cm^{-3}]	1.655
Measured reflections	153835
Unique reflections	13947
Parameters	717
Restraints	1
R_{int}	0.0804
θ range [°]	2.111–27.231
R_1, wR_2 all data	0.0367, 0.0889
S (GooF) all data	1.068
Max/min res. Dens. [e/Å^3]	1.295/−0.851

of the Soret maximum than β-octabromination does for Cu tri-arylcorroles (ca. 27 nm).[12] Unfortunately, our attempts to relate these observations to the molecular structures of **1-Br$_{14}$** and **3-Br$_{14}$** were thwarted by our inability to grow X-ray quality crystals of either compound. A few speculative, explanatory remarks, however, may still be entertained. Copper corroles are inherently saddled as a result of a specific Cu(d$_{x^2-y^2}$)–corrole(π) orbital interaction.[19–21] Octabromination considerably enhances the saddling.[19b, 21] The 27 nm Soret redshift resulting from octabromination of Cu triarylcorroles is thought to reflect both the direct electronic effect of the bromine atoms and the enhanced saddling.[19b, 21] The six *ortho* bromine atoms in **1-Br$_{14}$** presumably result in somewhat diminished saddling relative to regular Cu β-octabromo-*meso*-triarylcorroles, which would explain the reduced Soret redshift of **1-Br$_{14}$** relative to **1**. Whether
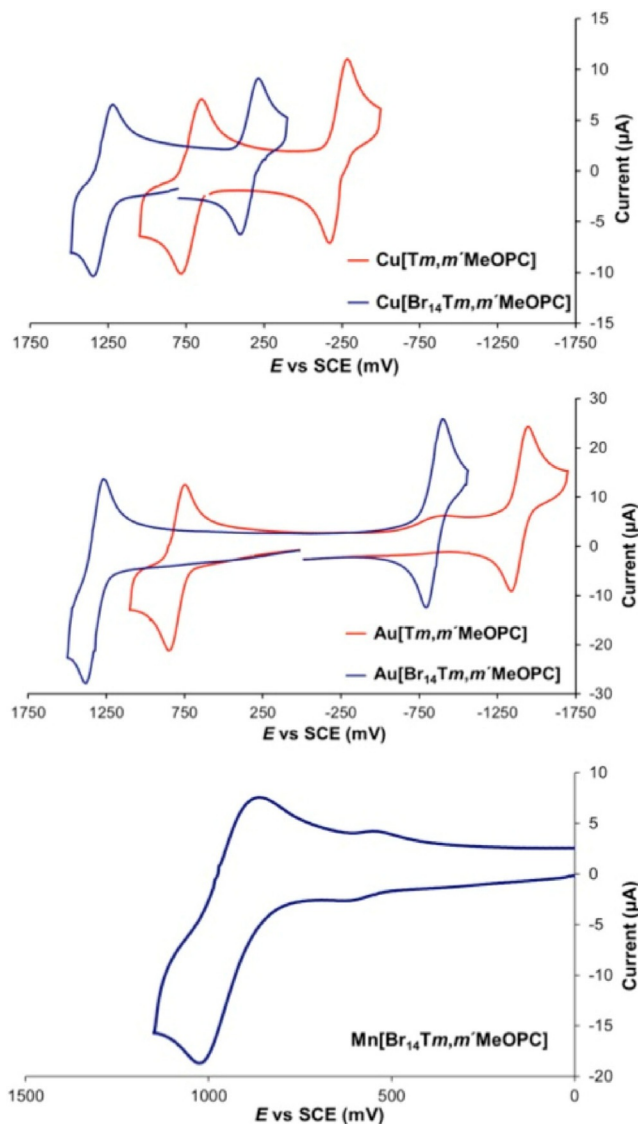

Figure 3. Cyclic voltammograms in CH$_2$Cl$_2$ (V vs. SCE).

4-Br$_{14}$ and other transition-metal derivatives of the new bis-pocket corrole exhibit improved catalytic properties has not been examined herein and remains a key question for the future.[22]

Experimental Section

Materials

All reagents and solvents were obtained from Sigma Aldrich and used as purchased, unless otherwise noted. Dimethylformamide was dried and stored over 4 Å molecular sieves under argon. The metal salts Au(OAc)$_3$, Cu(OAc)$_2$·4H$_2$O, and Mn(OAc)$_2$·4H$_2$O were obtained from Merck. Pyrrole was passed over a short column of basic alumina (Merck, 1 cm width, ca. 5 cm height) to remove brownish impurities and stored at −20° C. Silica gel 60 (0.04–0.063 mm particle size; 230–400 mesh, Merck) was used for flash chromatography. Silica gel 60 preparative thin-layer chromato-
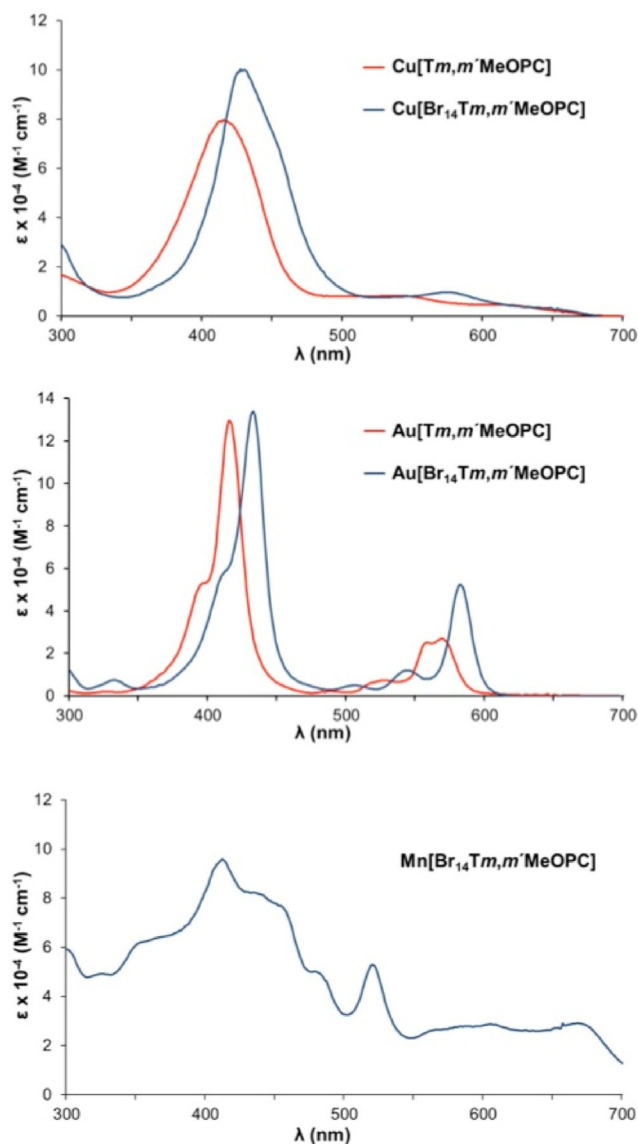
Figure 4. UV/Vis spectra in CH_2Cl_2.

Table 2. Soret, $Q \lambda_{max}$ [nm], and $E_{1/2}$ values [V] for selected complexes.

Complex	Soret	Q	$E_{1/2ox}$	$E_{1/2red}$	ΔE
Cu[Tm,m'MeOPC]	415	539	0.775	−0.180	0.955
Au[Tm,m'MeOPC]	418	530, 561	0.800	−1.400	2.200
Cu[Br$_{14}$Tm,m'MeOPC]	430	575	1.285	0.340	0.945
Au[Br$_{14}$Tm,m'MeOPC]	436	509, 548, 585	1.325	−0.850	2.175
Mn[Br$_{14}$Tm,m'MeOPC]	412, 435	520, 589, 605, 630, 668	0.940	–	–

graphic plates (20 cm × 20 cm, 0.5 mm thick, Merck) were used for the final purification of the new complexes.

Instrumentation

UV/Vis spectra were recorded on an HP 8453 spectrophotometer in CH_2Cl_2. Cyclic voltammetry was performed with an EG&G model 263A potentiostat having a three-electrode system, including a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). Tetra(*n*-butyl)ammonium perchlorate, recrystallized twice from absolute ethanol and dried in a desiccator for at least 2 weeks, was used as the supporting electrolyte. The reference electrode was separated from the bulk solution by a fritted-glass bridge filled with a solvent/supporting electrolyte mixture. The anhydrous dichloromethane solutions were purged with argon for at least 5 min prior to measurements and an argon blanket was maintained over the solutions all through the measurements. All potentials were referenced to the SCE and a scan rate of 100 mV s^{-1} was used. ^{1}H NMR spectra (400 MHz) were recorded in CDCl$_3$ (referenced to 7.26) at 298 K on a Varian Inova spectrometer. High-resolution electrospray-ionization (HR-ESI) mass spectra were recorded from methanolic solution on an LTQ Orbitrap XL spectrometer. Elemental analyses were obtained from Atlantic Microlabs, Inc. In general, the Br$_{14}$ derivatives failed to yield satisfactory elemental analyses; whether the high degrees of bromination lead to interference in the analyses remains uncertain at this point. Proof of composition and purity of these compounds, thus, came from fully assigned ^{1}H NMR spectra, HR-ESI spectra, thin-layer chromatography, and, in one case (4-Br$_{14}$), also from single-crystal X-ray structure analysis.

Synthesis of Free-Base 5,10,15-tris(3′,5′-Dimethoxyphenyl)-corrole

In a slight modification of a literature protocol,[8] 3,5-dimethoxy-benzaldehyde (5 mmol, 831 mg) and pyrrole (10 mmol, 697 μL) were dissolved in 200 mL MeOH, followed by slow addition of water (200 mL) and of 37% HCl (4.25 mL) under vigorous stirring. The reaction mixture was stirred overnight at room temperature, extracted with CHCl$_3$, washed twice with distilled water, once with saturated aqueous NaHCO$_3$, dried over Na$_2$SO$_4$, and filtered. The filtrate was diluted to 300 mL, followed by addition of *p*-chloranil (1.23 g), and refluxed for 1 h. The reaction mixture was then washed three times with NaHCO$_3$ (aq), dried over Na$_2$SO$_4$, and filtered; the filtrate was rotary-evaporated to dryness. The residue was dissolved in a minimal amount of 1:1 *n*-hexane/CH$_2$Cl$_2$ and chromatographed on silica gel with the same solvent mixture to flush out fast-eluting impurities and subsequently with 1:2 and 1:3 *n*-hexane/CH$_2$Cl$_2$ to elute the bluish-green free-base corrole, which partially overlapped with and was followed by a reddish brown impurity. All fluorescent fractions were combined and evaporated to dryness. Treatment of the residue with cold, 3:1 *n*-hexane/CH$_2$Cl$_2$, sonication, and filtering afforded the desired corrole as a bluish solid. Yield: 206 mg (17%). Analytical data were consistent with literature data.[23]

Synthesis of Copper 5,10,15-tris(3′,5′-Dimethoxyphenyl)-corrole (1)

The procedure used was adapted from the literature.[11] Free-base 5,10,15-*meso*-tris-(3,5-dimethoxyphenyl)corrole (40 mg) and Cu-(OAc)$_2$·4H$_2$O (40 mg) was added to a 100 mL round-bottom flask equipped with a stirrer bar, dissolved in 25 mL of pyridine and stirred for 30 min at room temperature. The solvent was then removed through rotary evaporation and the resulting residue dissolved in a minimum volume of 1:2 *n*-hexane/CH$_2$Cl$_2$. Flash chromatography (silica gel, *n*-hexane/CH$_2$Cl$_2$, 1:1, then 2:3) yielded the target compound as a brownish red fraction. Yield: 37 mg (85%). UV/Vis (CH$_2$Cl$_2$): λ_{max} [ε × 10^{-4} (M^{-1} cm^{-1})] (nm); 415 (8.0), 539 (0.8). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.88 (d, *J*=4.2 Hz, 2H, β-pyrrolic), 7.69 (d, *J*=4.2 Hz, 2H, β-pyrrolic), 7.42 (d, *J*=4.4 Hz, 2H, β-pyr-

rolic), 7.31 (d, $J = 4.5$ Hz, 2H, β-pyrrolic), 6.92 (d, $J = 2.3$ Hz, 4H, 5,15-o), 6.82 (d, $J = 2.3$ Hz, 2H, 10-o), 6.67 (m, 3H, 5,10,15-p), 3.86 (s, 12H, 5,15-methoxy), 3.84 (s, 6H, 10-methoxy). MS (HR-ESI) m/z 766.1856 (M$^+$), calcd 766.1847. Anal calcd for $CuC_{43}H_{35}N_4O_6$ (%): C 67.31, H 4.60, N 7.30. Found (%): C 67.24, H 4.73, N 7.33.

Synthesis of Gold 5,10,15-tris(3′,5′-Dimethoxyphenyl)corrole

A procedure was adapted from the literature[14c] as follows: free-base 5,10,15-meso-tris-(3,5-dimethoxyphenyl)corrole (40 mg, 0.057 mmol) and Au(OAc)$_3$ (70 mg, 0.188 mmol, 3.3 equiv) were added to a 10 mL glass-vial equipped with a stirrer bar, dissolved in 5 mL of pyridine, and stirred for 22 h at room temperature. After rotary evaporation of the solvent, the resulting solids were dissolved in a minimum volume of CH_2Cl_2. Flash chromatography (silica gel, 1:1 n-hexane/CH_2Cl_2 gradually changing to pure CH_2Cl_2) afforded the title compound as the first red fraction. Yield: 8 mg (15%). UV/Vis (CH_2Cl_2): λ_{max} [$\varepsilon \times 10^{-4}$ (M^{-1} cm^{-1})] (nm); 418 (12.8), 530 (0.6), 561 (2.4), 572 (2.6). 1H NMR (400 MHz, Chloroform-d) δ 9.22 (d, $J = 4.3$ Hz, 2H, β-pyrrolic), 9.14 (d, $J = 4.8$ Hz, 2H, β-pyrrolic), 8.97 (d, $J = 4.4$ Hz, 2H, β-pyrrolic), 8.90 (d, $J = 4.9$ Hz, 2H, β-pyrrolic), 7.48 (d, $J = 2.4$ Hz, 4H, 5,15-o), 7.38 (d, $J = 2.4$ Hz, 2H, 10-o), 6.91–6.86 (m, 3H, 5,10,15-p), 4.00 (s, 12H, 5,15-methoxy), 3.97 (s, 6H, 10-methoxy). MS (HR-ESI) m/z 900.2213 (M$^+$), calcd 900.2217; Anal calcd for $AuC_{43}H_{35}N_4O_6$ (%): C 57.34, H 3.92, N 6.22. Found (%): C 57.81, H 4.28, N 5.74.

Synthesis of Copper β-Octabromo-5,10,15-tris(2′,6′-Dibromo-3′,5′-dimethoxyphenyl)corrole (1-Br$_{14}$)

A procedure was adapted from the literature as follows:[11] Copper corrole 1 (85 mg, 0.11 mmol) was dissolved in CHCl$_3$ (30 mL) in a round-bottom flask equipped with a magnetic stirrer bar. To the stirred reaction mixture at room temperature, was added bromine (296 μL, 52.5 equivalents) dissolved in CHCl$_3$ (12 mL) with a dropping funnel over a period of 30 min. After an additional 1 h of stirring, pyridine (561 μL, 63 equivalents) dissolved in CHCl$_3$ (12 mL) was added with a dropping funnel over a period of 15 min. The reaction mixture was stirred at room temperature overnight, shaken with 20 mL of 20% w/v aqueous sodium metabisulfite, dried over MgSO$_4$ and filtered. The filtrate was evaporated to dryness and the residue was flash-chromatographed (silica, n-hexane/CH_2Cl_2, 1:1, then 2:3, then 1:2), affording 1-Br$_{14}$ as the first yellowish brown fraction; the product at this stage was contaminated with small amounts of various tridecabromo and 2′,4′-brominated impurities. Two subsequent overnight recrystallizations from 1:3 CHCl$_3$/MeOH then afforded the pure complex. Pure 1-Br$_{14}$ could also be obtained with only one recrystallization followed by preparatory TLC (silica gel, 1:6 n-hexane/CH_2Cl_2, $R_f = 0.55$). Yield: 113 mg, (55%). UV/Vis (CH_2Cl_2) λ_{max} [$\varepsilon \times 10^{-4}$ (M^{-1} cm^{-1})] (nm): 430 (10.0), 575 (1.0). 1H NMR (400 MHz, CDCl$_3$) δ 6.71(s, 2H, 5,15-p), 6.69 (s, 1H, 10-p), 3.98 (s, 12H, 5,15-methoxy), 3.95 (s, 6H, 10-methoxy). MS (HR-ESI) m/z 1870.9168 (M$^+$), calcd 1870.9184.

Synthesis of Free-Base β-Octabromo-5,10,15-tris(2′,6′-Dibromo-3′,5′-dimethoxyphenyl)corrole (2-Br$_{14}$)

A literature[12a] procedure was adapted as follows: Powdered 1-Br$_{14}$ (45 mg, 24 μmol) and anhydrous FeCl$_2$ beads (608 mg, 4.8 mmol, 200 equiv) were added to a 25-mL round-bottom flask and carefully layered with 3 mL of sulfuric acid (95.0–97.0%). The suspension was sonicated at for 3 h at room temperature and then carefully

quenched with distilled water (10 mL). The mixture was transferred dropwise to a separating funnel containing CHCl$_3$ (25 mL) and saturated NaHCO$_3$ (aq) (50 mL). Upon separation, the organic phase was shaken repeatedly with NaHCO$_3$ (aq), once with distilled H$_2$O (50 mL), dried over anhydrous MgSO$_4$, and filtered and the filtrate rotary-evaporated to dryness. The green residue was dissolved in 1:1 n-hexane/CH_2Cl_2 (aided by sonication) and flash-chromatographed (silica gel, n-hexane/CH_2Cl_2, 1:1, then 1:2-1:4). A few milligrams of unreacted, brown copper corrole eluted first and could be recovered, followed by 2-Br$_{14}$ as a dark green band. Yield: 33.5 mg (77%). UV/Vis (CH_2Cl_2) λ_{max} [$\varepsilon \times 10^{-4}$ (M^{-1} cm^{-1})] (nm): 446 (8.4), 589 (1.8), 630 (1.4), 681 (1.3). 1H NMR (400 MHz, chloroform-d) δ 6.95 (s, 3H, 5,10,15-p), 4.12 (s, 12H, 5,15-methoxy), 4.11 (s, 6H, 10-methoxy). MS (HR-ESI) m/z 1810.0030 (M-H$^+$), calcd 1810.0066.

Synthesis of Gold β-Octabromo-5,10,15-tris(2′,6′-Dibromo-3′,5′-dimethoxyphenyl)corrole (3-Br$_{14}$)

In an adaptation of a literature procedure,[14c] free-base 2-Br$_{14}$ (15 mg, 0.00825 mmol) and Au(OAc)$_3$ (13 mg, 0.033 mmol, 4 eqv.) were dissolved in pyridine (6 mL) and stirred overnight at room temperature. The reaction mixture was rotary-evaporated to dryness, dissolved in a minimum volume of CH_2Cl_2, and flash-chromatographed (silica gel, n-hexane/CH_2Cl_2, 1:1, then 1:2 and 1:3). The target compound 3-Br$_{14}$ eluted as a red band (yellowish when dilute). Yield: 15 mg (90%). UV/Vis (CH_2Cl_2) λ_{max} [$\varepsilon \times 10^{-4}$ (M^{-1} cm^{-1})] (nm): 436 (13.4), 509 (0.5), 548 (1.2), 585 (5.2). 1H NMR (400 MHz, chloroform-d) δ 7.04–7.01 (m, 3H, 5, 10, 15-p), 4.15 (s, 12H, 5, 15-methoxy), 4.13 (s, 6H, 10-methoxy); MS (HR-ESI) m/z 2043.9221 (M+K$^+$), calcd 2043.9191.

Synthesis of Manganese β-Octabromo-5,10,15-tris-(2′,6′-Dibromo-3′,5′-dimethoxyphenyl)corrole (4-Br$_{14}$)

In an adaptation of literature procedures,[16] free-base 2-Br$_{14}$ (27 mg, 0.0149 mmol) and Mn(OAc)$_2$·4H$_2$O (36 mg, 0.149 mmol) were added to a 50 mL two-necked round-bottom flask equipped with a condenser and a magnetic stirrer bar and dissolved in 10 mL of anhydrous dimethylformamide. The system was sealed with rubber septa and connected to an oil-bubbler outlet. The reaction mixture was deoxygenated by bubbling argon through the solution under vigorous stirring for 10 min. The mixture was then refluxed for 2 h under argon, cooled to room temperature, and rotary-evaporated to dryness. Flash chromatography (silica gel, n-hexane/EtOAc, 1:1, then 1:2–1:3) of the residue afforded 4-Br$_{14}$ as the first green fraction. X-ray-quality crystals were obtained from slow vapor-diffusion of n-heptane into a benzene solution of the complex. Yield: 18 mg (65%). UV/Vis (CH_2Cl_2) λ_{max} [$\varepsilon \times 10^{-4}$ (M^{-1} cm^{-1})] (nm): 412 (9.6), 435 (8.2), 520 (5.3), 589 (52.8), 605 (2.9), 630 (2.6), 668 (2.9). MS (HR-ESI) m/z 1863.9326 (M+H), calcd 1863.9341.

X-ray Structure Determination

X-ray data for 4-Br$_{14}$·H$_2$O were collected on beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. Samples were mounted on MiTeGen® kapton loops and placed in a 100(2) K nitrogen cold stream provided by an Oxford Cryostream 800 Plus low-temperature apparatus on the goniometer head of a Bruker D8 diffractometer equipped with a PHOTON100 CMOS detector operating in shutterless mode. Diffraction data were collected by using synchrotron radiation monochromated using sili-

con(111) to a wavelength of 0.7749(1) Å. An approximate full-sphere of data was collected by using a combination of phi and omega scans with scan speeds of 1 s per degree for the phi scans, and 1 and 3 s per degree for the omega scans at $2\theta = 0$ and -45, respectively. The structures were solved by intrinsic phasing (SHELXT) and refined by full-matrix least squares on F^2 (SHELXL-2014). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically calculated and refined as riding atoms. Additional crystallographic information has been summarized in Table 1 and the crystal structure reported herein has been deposited to the Cambridge Crystallographic Data Centre.[24]

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

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[24] CCDC 1507046 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.