

Demetalation of Copper Undecaarylcorroles: Molecular Structures of a Free-Base Undecaarylisocorrole and a Gold Undecaarylcorrole

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Abstract. Copper undecaarylcorroles were found to undergo acid-induced demetalation with unusual ease under both reductive and nonreductive conditions. The resulting free-base undecaarylcorroles were found to be rather reactive, readily photooxygenating to yield 5/10-hydroxyisocorroles and biliverdines. The use of nonreductive conditions led to fairly good yields of undecaarylisocorroles, a new class of sterically hindered ligands, of which one proved amenable to single-crystal X-ray structural analysis. In one case, interaction of an undecaarylisocorrole with gold(III) acetate resulted in aromatization of the macrocycle and a gold undecaarylcorrole. The Au complex exhibited Au-N distances of 1.941(3)-1.965(3) Å, and no significant nonbonded interactions involving the gold. The significant solubility of this complex in organic solvents, compared with the relative insolubility of gold β -octabromo-*meso*-triarylcorroles, appears to be related to the lack of aurophilic and metallophilic interactions.

Introduction. Metalloporphyrins,^{1,2} particularly copper porphyrins, are typically much more readily functionalized and elaborated in a controlled manner than free-base porphyrins. Subsequent demetalation then has the potential to yield novel, substituted free-base porphyrin ligands. Unfortunately, the demetalation of metalloporphyrins is generally more difficult than that of common metalloporphyrins, requiring both strong acid and an excess of a reductant such as a Fe(II) or Sn(II) salt.^{3,4,5,6,7} A notable success of this ‘reductive demetalation’ approach has been the synthesis of free-base β -octabromoporphyrins^{5,4,7,8} and their subsequent use as ligands.^{9,10} Here we report that copper undecaporphyrins^{11,12,13} demetalate with unusual ease, in a matter of minutes, on exposure to acid, under both reductive and nonreductive conditions.

In what initially appeared to be a setback, free-base undecaporphyrins were found to be rather reactive, readily reacting with ambient oxygen to generate 5-hydroxy- and 10-hydroxy-undecaporphyrins as well as open-chain dioxo compounds. As shown in Figure 1, porphyrins are fascinating ligands in their own right: they are porphyrin-like by virtue of their diprotic or dianionic character and porphyrin-like in affording a spatially constricted cavity for metal coordination.^{14,15,16,17,18} They are thus promising platforms for unusual transition metal spin states. In a pertinent study, Bröring and coworkers have reported that thiaporphyrins, which are structurally similar to porphyrins, give rise to intermediate-spin iron(III) complexes.¹⁹ A second remarkable feature of porphyrins is their strong absorption in the near-infrared,^[17] which is of great relevance to photodynamic therapy.²⁰ Reported herein are optimized syntheses for a family of sterically hindered undecaporphyrin ligands, including the first, single-crystal X-ray structure of a free-base undecaporphyrin.

Furthermore, we have attempted to determine whether undecaporphyrin ligands can be rearomatized on metal complexation, yielding novel undecaporphyrin complexes. This is an important question because, as of today, only copper and cobalt undecaporphyrins have been reported.¹¹⁻¹³ New metalloundecaporphyrins are of considerable interest as shape-selective catalysts and other functional materials. As shown in Figure 2, we found that at least one free-base undecaporphyrin could be smoothly converted to the corresponding gold undecaporphyrin. The same gold complex could also be obtained from a gold β -octabromo-*meso*-triarylporphyrin via a tedious, week-long Suzuki coupling procedure. Remetalation and aromatization of porphyrins to porphyrins, when feasible, thus promises to be a useful transformation.

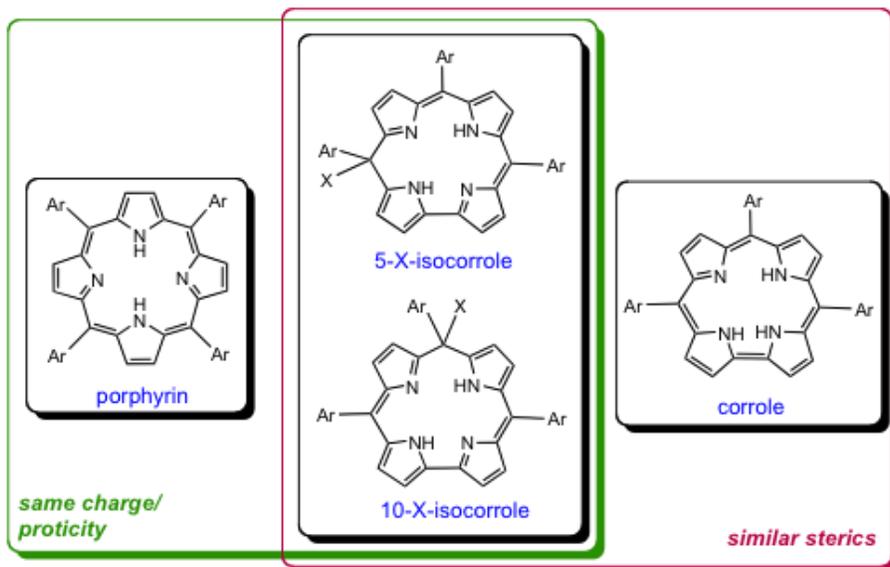


Figure 1. Steric and electronic relationships between porphyrin, corrole, and isocorrole ligands. Whereas porphyrin and isocorroles share the same proticity (both coordinate as dianionic ligands), isocorroles and corroles share similar, constricted coordination cavities.

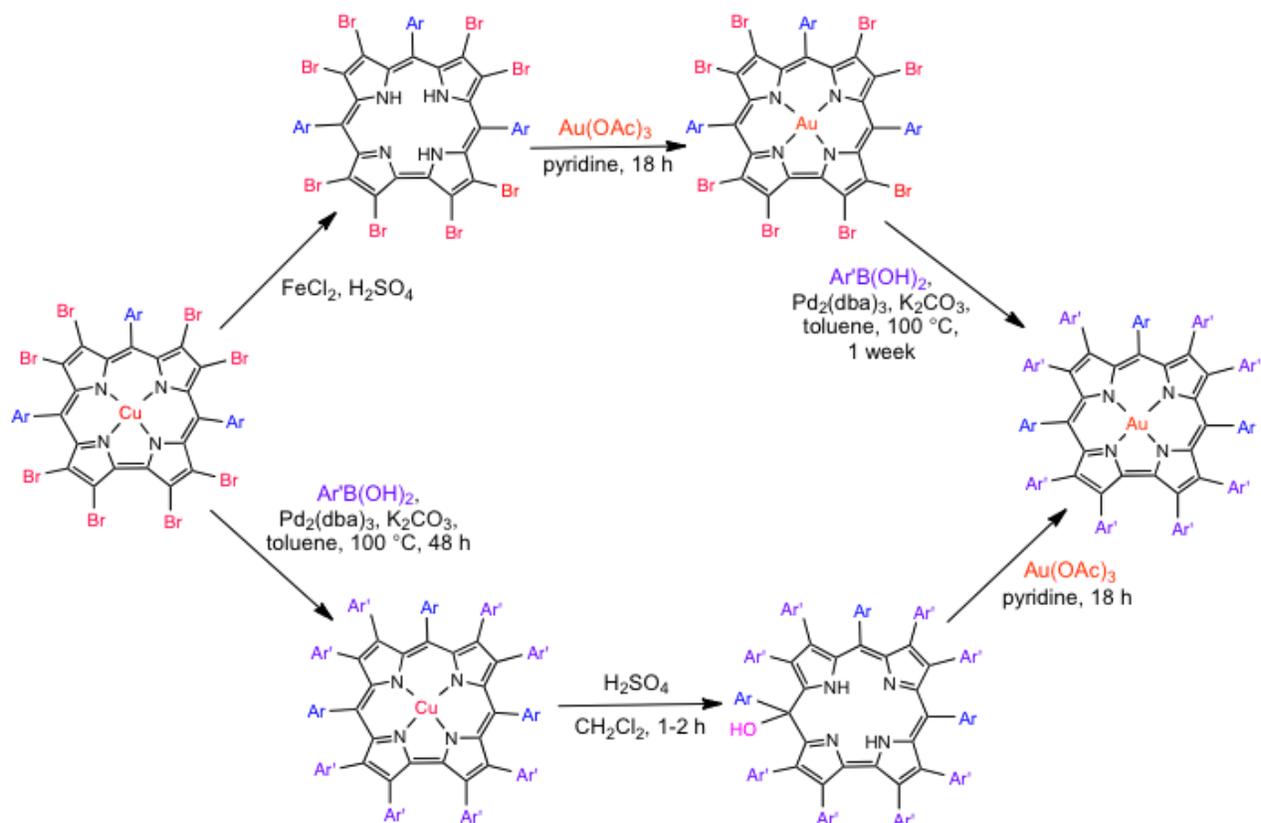


Figure 2. Two alternative synthetic routes to a gold undecaarylcorrole.

Results and Discussion

(a) **Demetallation of copper undecaarylcorroles and isocorrole formation.** Four different copper undecaarylcorroles were demetallated in this study, copper β -octakis(*p*-X-phenyl)-*meso*-tris(*p*-methylphenyl)corrole, where X = H, F, and CF₃, and copper β -octakis(*p*-trifluoromethylphenyl)-*meso*-triphenylcorrole (Figure 3). For brevity, we will refer to these complexes as Cu[X₈Me₃]. We will also refer to the corresponding free-base corroles as H₃[X₈Me₃] and the isocorroles as H₂[X₈Me₃(5-OH)]. Reductive demetallation of Cu[X₈Me₃] with concentrated sulfuric acid and ~10 equiv of anhydrous FeCl₂ led to ~70% yields of the free-base corroles, H₃[X₈Me₃], in a matter of minutes, but in the presence of air and light, free-base undecaarylcorroles quickly decomposed to open-chain dioxotetrapyrroles such as biliverdines and small quantities of the isocorroles, H₂[X₈Me₃(5/10-OH)]. Eliminating reductive conditions (i.e., FeCl₂) proved to be an effective way of improving the yield of isocorroles, the key targets of this study, as did the presence of an organic solvent such as dichloromethane. The final optimized conditions, involving demetallation in dichloromethane and concentrated sulfuric acid, led to 50-65% yields of highly stable, free-base isocorroles, with negligible quantities of corroles.

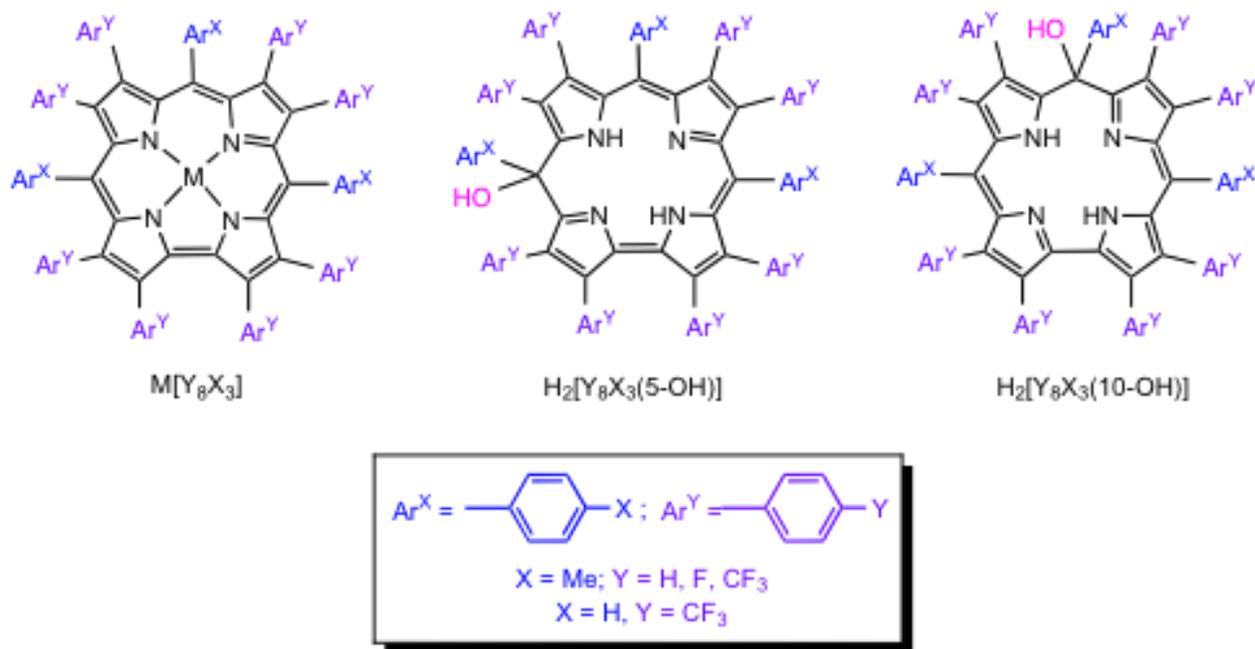


Figure 3. Corrole and Isocorrole derivatives investigated in this study.

Each demetallation led to both 5- and 10-OH isocorroles, with the former dominating. Although not separable by column chromatography, the two regioisomers could be separated by preparative thin-layer chromatography. Except for one case, H₂[(CF₃)₈Me₃(10-OH)], however, the pure 10-regioisomer was not obtained in large enough quantities for full characterization. Examples of preferential formation of one or the other regioisomer occur in the literature.^{21,22,23} Thus, a convenient isocorrole synthesis, involving DDQ oxidation of *meso*-triarylcorroles in methanol, was found to lead preferentially to 5-OMe isocorroles.¹⁸ On the other hand, nonreductive demetallation of Cu[Br₈H₃] (i.e., copper β -octabromo-*meso*-triphenylcorrole) with H₂SO₄/CHCl₃ led to preferential formation of the 10-OH isocorrole, H₂[Br₈H₃(10-OH)].³ A combination of electronic and steric factors is presumably responsible for the preponderance of one isomer over the other.

Literature reports suggest that the oxygen in 5/10-OH isocorroles arises from O₂ rather than water, although the latter has not been strictly ruled out.^{22,23} To determine the source of oxygen in the isocorroles obtained in this study, we carried out isotope labeling experiments with H₂¹⁸O and ¹⁸O₂. The freshly purified, vacuum-dried corrole H₃[(CF₃)₈Me₃], upon stirring in anhydrous dichloromethane and H₂¹⁸O under argon, showed no evidence of ¹⁸O incorporation with electrospray ionization (ESI) mass spectrometry (MS). In contrast, bubbling ¹⁶O₂ into a solution of pure H₃[(CF₃)₈Me₃] in anhydrous dichloromethane revealed the incorporation of both one and two oxygen atoms via ESI-MS. Flushing the ESI mass spectrometer with ¹⁸O₂ also resulted in the incorporation of both one and two ¹⁸O atoms into H₃[(CF₃)₈Me₃], confirming the strong affinity of free-base undecaarylcorroles for dioxygen. A plausible pathway for the oxidative decomposition of free-base corroles, based on both literature precedence^{22,23,24,25} and our own experiments, is depicted in Figure 4.

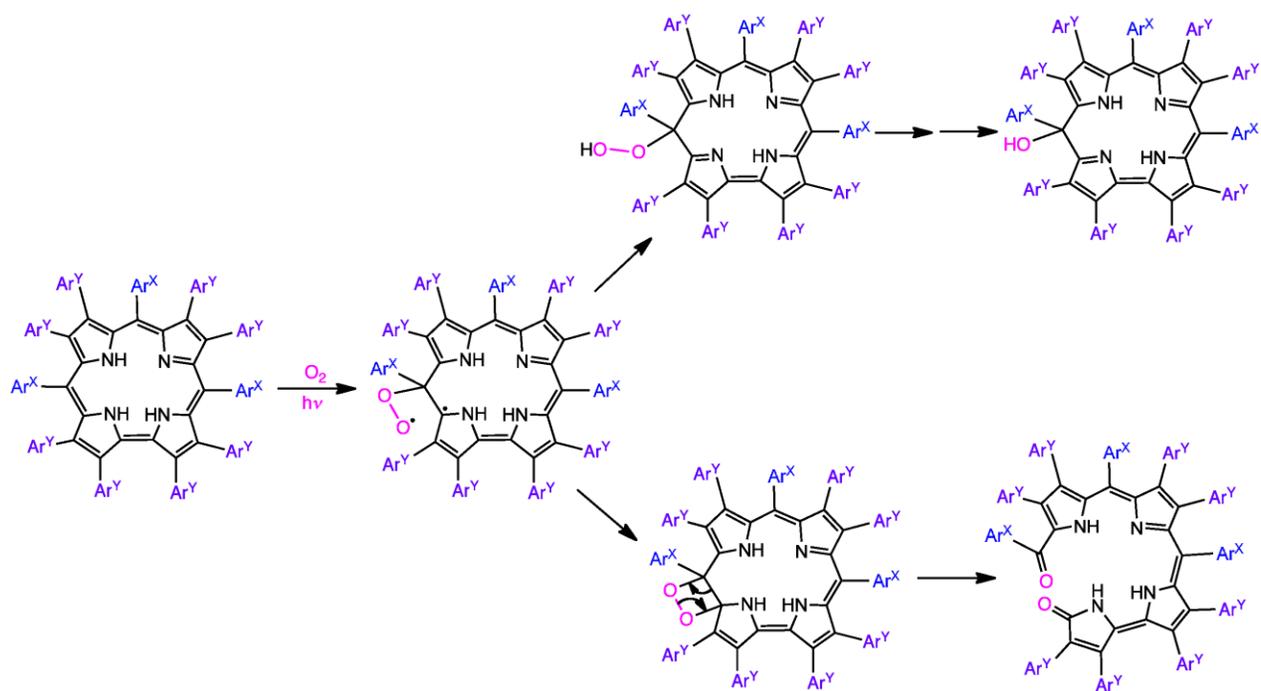


Figure 4. Proposed pathway for photooxygenation of a free-base undecaarylcorrole.

A single-crystal X-ray structure could be obtained for the free-base undecaarylcorrole $\text{H}_2[(\text{CF}_3)_8\text{Me}_3(5\text{-OH})]$ (Figure 5, Table 1). Despite the considerable steric crowding, the macrocyclic skeleton of $\text{H}_2[(\text{CF}_3)_8\text{Me}_3(5\text{-OH})]$ was found to be essentially planar, as for other free-base isocorroles, but in sharp contrast to free-base corroles, which are generally strongly buckled as a result of steric repulsion among the three inner hydrogens.²⁶ The two central hydrogens could be unambiguously located for $\text{H}_2[(\text{CF}_3)_8\text{Me}_3(5\text{-OH})]$.

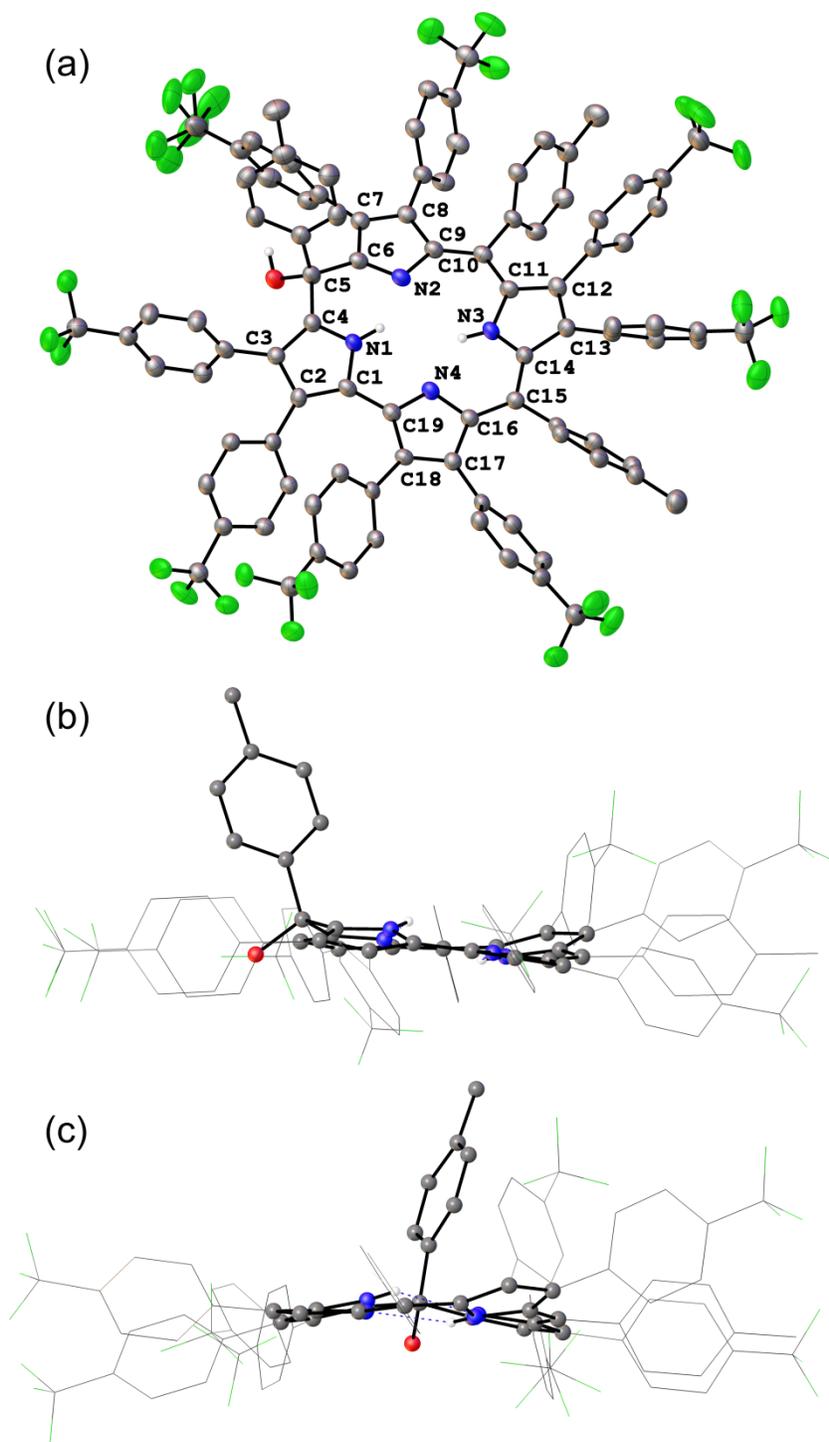


Figure 5. X-ray structure of free-base undecaarylisocorrole $H_2[(CF_3)_8Me_3(5-OH)]$: (a) top view and (b, c) side views.

Table 1. Crystallographic data for H₂[(CF₃)₈Me₃(5-OH)].

Sample	H ₂ [(CF ₃) ₈ Me ₃ (5-OH)]	Au[(CF ₃) ₈ H ₃]
Chemical formula	C ₉₆ H ₅₆ F ₂₄ N ₄	C ₉₅ H ₅₁ F ₂₄ N ₄ Cl ₄ Au
Formula mass	1737.44	2043.16
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> 1	<i>P</i> -1
λ (Å)	0.7749	0.7749
<i>a</i> (Å)	12.783(3)	15.4998(6)
<i>b</i> (Å)	18.085(4)	16.8410(6)
<i>c</i> (Å)	18.600(4)	16.9639(6)
α (deg.)	102.363(3)	106.229(2)
β (deg.)	108.203(3)	91.961(2)
γ (deg.)	96.468(3)	106.901(2)
<i>Z</i>	2	2
<i>V</i> (Å ³)	3914.7(15)	4035.8(3)
Temperature (K)	100(2)	100(2)
Density (g/cm ³)	1.474	1.681
Measured reflections	40303	78866
Unique reflections	15237	29236
Parameters	1169	1256
Restraints	66	646
<i>R</i> _{int}	0.0670	0.0524
θ range (deg.)	2.587 – 28.553	2.165 – 36.007
<i>R</i> ₁ , <i>wR</i> ₂ all data	0.0683, 0.2226	0.0459, 0.1140
<i>S</i> (GooF) all data	1.024	1.030
Max/min res. Dens. (e/Å ³)	0.410/-0.349	2.151/-1.956

(b) Synthesis and molecular structure of a gold undecaarylcorrole. Given the oxidative instability of free-base undecaarylcorroles, we were intrigued by the question whether metal insertion into a free-base undecaarylisocorrole might proceed with concomitant aromatization, thereby providing a pathway to novel metalloundecaarylcorroles. Although a full exploration of this question, involving different isocorroles and metal ions, has not yet been carried out, we were gratified to discover that interaction of free-base H₃[(CF₃)₈H₃(5-OH)] and gold(III) acetate in pyridine leads to the fully aromatized undecaarylcorrole complex Au[(CF₃)₈H₃] in yields of ~40%.^{27,28} We are currently examining the generality of this process and will report on our findings in due course.

Unlike many gold β -octabromocorrole complexes, which tend to be quite insoluble, presumably because of intermolecular metallophilic Au...Br interactions,²⁷ Au[(CF₃)₈H₃] was

found to be moderately soluble. X-ray quality crystals were obtained and single-crystal structure determination revealed a planar Au-corrole, Au-N distances of 1.941(3)-1.965(3) Å, and no significant nonbonded interactions involving the gold (Figure 6).²⁹ The planarity of the gold corrole may be contrasted with the strong nonplanarity of copper corroles, which is believed to be due to ligand noninnocence. Silver corroles exhibit more variable behavior in this regard. Thus, whereas simple silver *meso*-triarylcporroles are only slightly saddled, a recent X-ray structure has provided an example of a strongly saddled silver β -octabromocorrole.³⁰ The substantial variations in corrole geometry in the silver case has been attributed to variations in noninnocent character among the different ligands. By contrast, corrole ligands in gold corroles are thought to be innocent.

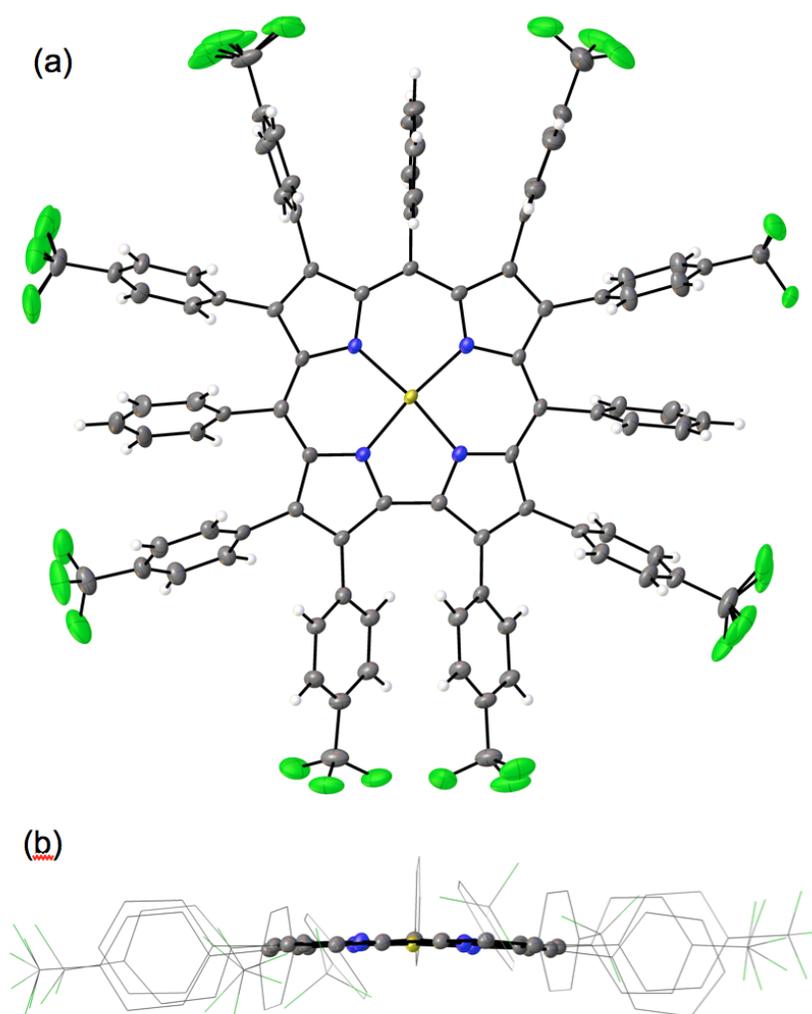


Figure 6. X-ray structure of the gold undecaarylcorrole Au[(CF₃)₈H₃]: (a) top view and (b) side view.

Conclusion

In summary, copper undecaarylcorroles were found to demetallate with unusual ease under standard reductive demetallation conditions. The free-base undecaarylcorroles, however, proved to be light- and oxygen-sensitive, readily oxidizing to biliverdines and 5/10-OH isocorroles. Nonreductive conditions could be devised that led to good yields 65-80% of 5/10-OH undecaarylisocorroles, a new class of sterically hindered and relatively stable macrocyclic ligands. Interaction of one such ligand with gold(III) acetate resulted in rearomatization of the macrocycle and a gold undecaarylcorrole, which proved amenable to single-crystal X-ray diffraction analysis. Unlike the rather insoluble gold β -octabromo-*meso*-triarylcorroles, the gold undecaarylcorrole was found to be moderately soluble in organic solvents. The relatively high solubility appears to be related to the lack of intermolecular aurophilic and metallophilic interactions involving the gold atom.

Experimental section

Materials. All reagents and solvents were used as purchased unless stated otherwise. Anhydrous toluene (Sigma-aldrich) was stored over pre-activated 3 Å molecular sieves. Silica gel 150 (35-70 μm particle size, Davisil) was used for flash chromatography and silica gel 60 plates (20 \times 20 cm; 0.5 mm thick, Merck) were used for preparative thin-layer chromatography (PLC). Copper β -octabromo-*meso*-tris(4-methylphenyl)corrole, $\text{Cu}[\text{Br}_8\text{Me}_3]$ and copper β -octabromo-*meso*-triphenylcorrole, $\text{Cu}[\text{Br}_8\text{H}_3]$, served as the starting materials for copper undecaarylcorroles and were synthesized as previously described.³¹ Copper β -octakis(*p*-trifluoromethylphenyl)-*meso*-triphenylcorrole], $\text{Cu}[(\text{CF}_3)_8\text{H}_3]$, was also synthesized according to a literature method.¹¹

Instrumentation. Ultraviolet-visible (UV-vis) spectra were recorded with CH_2Cl_2 as solvent on an HP 8453 spectrophotometer. ^1H NMR spectra were obtained at 298 K on either a Mercury Plus Varian spectrometer (400 MHz) in CDCl_3 (referenced to 7.26 ppm), in CD_2Cl_2 (referenced to 5.30 ppm), and in C_6D_6 (referenced to 7.20 ppm) or a Varian Inova spectrometer (600MHz) equipped with a cryogenically cooled inverse triple-resonance probe in 1,1,2,2-tetrachloroethane- d_2 ($\text{CDCl}_2\text{-CDCl}_2$, referenced to 5.91ppm). ^{19}F NMR spectra (376 MHz) were recorded at 298-333K on a Mercury Plus Varian spectrometer and referenced to 2,2,2-trifluoroethanol- d_3 ($\delta = -77.8$ ppm). Electrospray ionization mass spectra were recorded on an LTQ Orbitrap XL spectrometer.

General Procedure for the Synthesis of Copper Undecaarylcorroles. The syntheses were carried essentially according to the procedure reported by Ghosh and coworkers. Into a 50-mL three-necked round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser were introduced Cu[Br₈Me₃], the arylboronic acid of choice (40 equiv), potassium carbonate (40 equiv), and Pd₂(dba)₃·CHCl₃ (0.1 equiv). After degassing with argon, dry toluene (10 mL) was added. After purging with argon for 10 min, the suspension was stirred at 100–105 °C under argon for 1–2 days. Progress of the reaction was monitored by mass spectrometry. When product formation appeared to have stabilized, the reaction mixture was cooled to room temperature, diluted with 10 mL of CH₂Cl₂, and washed with saturated aqueous NaHCO₃ and then with distilled water. The CH₂Cl₂ phase was dried with anhydrous Na₂SO₄, filtered, and evaporated. The brown residue obtained was chromatographed on a silica gel column with hexane/CH₂Cl₂ as eluent. The product eluted as a dark brown band, which was collected and evaporated to dryness. The residue was purified by preparative thin-layer chromatography (PLC), as detailed below for each corrole.

Synthesis of Copper 2,3,7,8,12,13,17,18-octakis(4-fluorophenyl)-meso-tris(*p*-methylphenyl)corrole, Cu[F₈Me₃]. The reaction employed 0.025 mol (32 mg) of Cu[Br₈TMePC] and was complete after ~2 days (45 h). Both the column chromatography and subsequent PLC were carried out with 3:1 hexane/CH₂Cl₂ as eluent. The pure product Cu[F₈Me₃] (26.6 mg, 76%) eluted as the most intense brown band. UV-vis (CH₂Cl₂): λ_{max}, nm (ε × 10⁻⁴, M⁻¹ cm⁻¹): 448 (3.56), 644 (0.32). ¹H NMR (CDCl₃, 400 MHz, δ in ppm): δ 6.87 (d, *J*=8.0 Hz, 2H, 10-*o*, 4-CH₃Ph), 6.80-6.74 (m, 4H, 2,18-*o*, 4-FPh; 4H, 5,15-*o*, 4-CH₃Ph), 6.57-6.51 (m, 4H, 3,17-*o*, 4-FPh; 4H, 2,18-*m*, 4-FPh), 6.47-6.26 (m, 4H, 8,12-*o*, 4-FPh; 4H, 7,13-*o*, 4-FPh; 4H, 3,17-*m*, 4-FPh; 4H, 5,15-*m*, 4-CH₃Ph; 4H, 7,13-*m*, 4-FPh; 4H, 8,12-*m*, 4-FPh; 2H, 10-*m*, 4-CH₃Ph), 2.02 (s, 6H, 5,15-*p*, 4-CH₃Ph), 1.91 (s, 3H, 10-*p*, 4-CH₃Ph). ¹⁹F NMR (CDCl₃): δ -116.31 to -116.39 (m, 2F), -118.08 to -118.21 (m, 4F), -118.62 to -118.70 (m, 2F). MS (HR-ESI major isotopomer): M⁺ = 1380.34 (expt), 1380.34 (calcd).

Synthesis of Copper 2,3,7,8,12,13,17,18-Octakis(4-trifluoromethylphenyl)-5,10,15-tris(4-methylphenyl)corrole, Cu[(CF₃)₈Me₃]. The reaction employed 0.020 mol (25 mg) of Cu[Br₈TMePC] and was complete after 24 h. Both the column chromatography and subsequent PLC were carried out with 3:1 hexane/CH₂Cl₂ as eluent. The pure product Cu[(CF₃)₈Me₃] (18.4 mg, 52%) eluted as the most intense brown band. UV-vis (CH₂Cl₂): λ_{max}, nm (ε × 10⁻⁴, M⁻¹ cm⁻¹): 454 (4.34), 642 (0.44), 841 (0.59). ¹H NMR (CDCl₃, 600 MHz, δ in ppm): δ 7.09 (d, *J*=4.0 Hz,

4H, 2,18-*o*, 4-CF₃Ph), 6.97 (d, *J*=4.0 Hz, 4H, 2,18-*m*, 4-CF₃Ph), 6.94 (d, *J*=4.0 Hz, 4H, 3,17-*o*, 4-CF₃Ph), 6.89 (d, *J*=4.0 Hz, 4H, 7,13-*o*, 4-CF₃Ph), 6.85 (d, *J*=4.0 Hz, 4H, 8,12-*o*, 4-CF₃Ph), 6.81 (d, *J*=8.0 Hz, 2H, 10-*o*, 4-CH₃Ph), 6.75 (d, *J*=4.0 Hz, 4H, 3,17-*m*, 4-CF₃Ph), 6.69 (d, *J*=8.0 Hz, 4H, 5,15-*o*, 4-CH₃Ph), 6.62 (d, *J*=8.0 Hz, 8H, 7,8,12,13-*m*, 4-CF₃Ph), 6.25 (d, *J*=4.0 Hz, 4H, 5,15-*m*, 4-CH₃Ph), 6.19 (d, *J*=8.0 Hz, 2H, 10-*m*, 4-CH₃Ph), 1.93 (s, 6H, 5,15-*p*, 4-CH₃Ph), 1.82 (s, 3H, 10-*p*, 4-CH₃Ph). ¹⁹F NMR (CDCl₃): δ -63.07 (s, 6F), -63.17 (s, 6F), -63.29 (s, 6F), -63.46 (s, 6F). MS (HR-ESI major isotopomer): M⁺= 1780.31 (expt), 1780.32 (calcd).

Synthesis of Copper 2,3,7,8,12,13,17,18-octaphenyl-5,10,15-tris(4-methylphenyl)corrole, Cu[H₈Me₃]. The reaction employed 0.021 mol (27 mg) of Cu[Br₈TMePC] and was complete after 48 h. Column chromatography was carried out with hexane/CH₂Cl₂ as eluent, while 3:1 *n*-hexane/CH₂Cl₂ was used for the PLC. The pure product Cu[H₈Me₃] (12.1 mg, 46%) eluted as the most intense brown band. UV-vis (CH₂Cl₂): λ_{max}, nm (ε x 10⁻⁴, M⁻¹ cm⁻¹): 448 (6.17), 544 (0.77), 645 (0.49). ¹H NMR (CD₂Cl₂, 600 MHz, δ in ppm): δ 6.86 (d, *J*=8.4 Hz, 2H, 10-*o*, 4-CH₃Ph), 6.85-6.82 (m, 4H, 2,18-*o*, Ph; 2H, 2,18-*p*, Ph), 6.80-6.76 (m, 4H, 2,18-*m*, Ph), 6.74 (d, *J*=7.8 Hz, 4H, 5,15-*o*, 4-CH₃Ph), 6.72-6.68 (m, 2H, 3,17-*p*, Ph), 6.65-6.63 (m, 4H, 3,17-*o*, Ph; 4H, 3,17-*m*, Ph), 6.62-6.58 (m, 2H, 7,13-*p*, Ph; 4H, 7,13-*m*, Ph), 6.58-6.57 (m, 2H, 8,12-*p*, Ph), 6.57-6.54 (m, 4H, 8,12-*m*, Ph; 4H, 8,12-*o*, Ph), 6.54-6.52 (m, 4H, 7,13-*o*, Ph), 6.19 (d, *J*=7.2 Hz, 4H, 5,15-*m*, 4-CH₃Ph), 6.16 (d, *J*=7.8 Hz, 2H, 10-*m*, 4-CH₃Ph), 1.90 (s, 6H, 5,15-*p*, 4-CH₃Ph), 1.80 (s, 3H, 10-*p*, 4-CH₃Ph). MS (HR-ESI major isotopomer): M⁺= 1237.42 (expt), 1237.42 (calcd).

Undecaarylisocorrole H₂[F₈Me₃(5-OH)]. Into a 50 mL round-bottomed flask was placed 25 mg (0.018 mmol) of Cu[F₈Me₃] and dissolved in 3 mL of CH₂Cl₂. Subsequently, 3 mL of concentrated H₂SO₄ (95-97%, Merck) was added. The mixture was then stirred and sonicated at room temperature. Progress of the reaction was monitored by ESI mass spectrometry. After 2 h, the reaction mixture was carefully poured into 300 mL of distilled H₂O and then extracted with CHCl₃. The organic phase was washed once with distilled water and twice with saturated aqueous NaHCO₃. Upon washing with NaHCO₃, the color of the organic phase changed from brown to green. The organic phase was then dried with anhydrous Na₂SO₄, filtered, and the filtrate rotary-evaporated to dryness. The residue obtained was chromatographed on a silica gel column with CH₂Cl₂/1%-MeOH. The product was further purified by PLC with 2:3 *n*-hexane/CH₂Cl₂; upon completion of the PLC, the pure product H₂[F₈Me₃(5-OH)] (14.4 mg, 60%) was obtained as the most intense green band in the middle of the plate. UV-vis (CH₂Cl₂): λ_{max}, nm (ε x 10⁻⁴, M⁻¹ cm⁻¹

¹): 433 (3.37), 683 (0.69). ¹H NMR (C₆D₆, 600 MHz, δ in ppm): δ 8.05 (d, *J* = 8.1 Hz, 2H, 5-*o*, 4-CH₃Ph), 7.01 (d, *J* = 8.3 Hz, 2H, 5-*m*, 4-FPh), 6.81 (d, *J* = 8.1 Hz, 1H, 10-*o*, 4-CH₃Ph), 6.80 (d, *J* = 8.6 Hz, 2H, 3-*o*, 4-FPh), 6.70 (d, *J* = 8.0 Hz, 1H, 7-*o*, 4-FPh), 6.69 (t, *J* = 7.6 Hz, 1H, 7-*m*, 4-FPh), 6.60 (d, *J* = 8.6 Hz, 2H, 2-*o*, 4-FPh), 6.55 (t, *J* = 8.5 Hz, 2H, 3-*m*, 4-FPh), 6.44 (overlapping, 1H, 7-*o*, 4-FPh), 6.42 (o, 12-*o*, 4-FPh), 6.36 (o, 1H, 7-*m*, 4-FPh), 6.33 (o, 1H, 10-*m*, 4-CH₃Ph), 6.29 (o, 1H, 8-*m*, 4-FPh), 6.25 (t, *J* = 8.8 Hz, 2H, 2-*m*, 4-FPh), 6.20 (o, 1H, 8-*o*, 4-FPh), 6.11 (o, 1H, 8-*m*, 4-FPh), 6.07 (d, *J* = 8.4 Hz, 1H, 10-*o*, 4-CH₃Ph), 6.02 (t, *J* = 8.5 Hz, 0.5H, 12-*m*, 4-FPh), 5.65 (d, *J* = 7.8 Hz, 1H, 10-*m*, 4-CH₃Ph), 2.29 (s, 1H, -OH), 2.05 (s, 3H, 5-*p*, 4-CH₃Ph), 1.86 (s, 3H, 15-*p*, 4-CH₃Ph), 1.72 (s, 3H, 10-*p*, 4-CH₃Ph). ¹⁹F NMR (CDCl₃): δ -115.96 to -116.08 (m, 1F), -116.25 to -116.36 (m, 1F), -116.45 to -116.59 (m, 1F), -117.38 to -117.49 (m, 1F), -117.79 to -117.88 (m, 1F), -117.95 to -118.09 (m, 2F), -118.25 to -118.35 (m, 1F). MS (HR-ESI major isotopomer): M⁺ = 1337.44 (expt), 1337.44 (calcd).

Undecaarylisocorroles H₂[(CF₃)₈Me₃(5-OH)] and H₂[(CF₃)₈Me₃(10-OH)]. Into a 50 mL round-bottomed flask, 20 mg (0.0112 mmol) of Cu[(CF₃)₈Me₃] was added and dissolved in 4 mL of CH₂Cl₂. Subsequently, 2 mL of concentrated H₂SO₄ (95-97%, Merck) was added. The mixture was stirred and sonicated at room temperature. The progress of the reaction was monitored by ESI mass spectrometry. After 4 hours the reaction was quenched by pouring the mixture into 300 mL distilled H₂O and then extracted with CHCl₃. The brown organic phase was washed once with distilled water and once with saturated aqueous NaHCO₃. Upon washing with NaHCO₃ the color of organic phase changed from brown to green. The organic phase was dried with anhydrous Na₂SO₄, filtered and evaporated under vacuum. The residue obtained was chromatographed on a silica gel column with 2:1 *n*-hexane/CH₂Cl₂. The product was further purified by PLC with 2:1 *n*-hexane/CH₂Cl₂. The most intense green band in the middle of the plate was pure H₂[(CF₃)₈Me₃(5-OH)] (11 mg, 57%) and the most intense light-green band below that was H₂[(CF₃)₈Me₃(10-OH)] (3.7 mg, 19%). X-ray quality crystals of H₂[(CF₃)₈Me₃(5-OH)] were grown by slow diffusion of *n*-heptane into the benzene solution. Analytical data for the two isomers are as follows.

Undecaarylisocorrole H₂[(CF₃)₈Me₃(5-OH)]. UV-vis (CH₂Cl₂): λ_{max}, nm (ε × 10⁻⁴, M⁻¹ cm⁻¹): 435 (4.19), 683 (0.92). ¹H NMR (C₆D₆, 600 MHz, δ in ppm): δ 7.95 (d, *J* = 8.0 Hz, 2H, 5-*o*, 4-CH₃Ph), 7.22 (d, *J* = 8.0 Hz, 1H, 7-*m*, 4-CF₃Ph), 7.05 (d, *J* = 8.0 Hz, 2H, 3-*m*, 4-CF₃Ph), 7.03 (d, *J* = 8.1 Hz, 2H, 5-*m*, 4-CH₃Ph), 6.87 (d, *J* = 7.9 Hz, 2H, 3-*o*, 4-CF₃Ph), 6.75 (d, *J* = 8.4 Hz, 1H, 7-*m*, 4-CF₃Ph), 6.72 (d, *J* = 8.0 Hz, 1H, 7-*o*, 4-CF₃Ph), 6.68 (o, 1H, 10-*o*, 4-CH₃Ph), 6.61 (d,

$J = 8.6$ Hz, 1H, 8-*m*, 4-CF₃Ph), 6.61 (o, 2H, 12-*m*, 4-CF₃Ph), 6.61 (o, 1H, 15-*m*, 4-CH₃Ph), 6.6 (o, 2H, 2-*m*, 4-CF₃Ph), 6.6 (o, 2H, 2-*o*, 4-CF₃Ph), 6.57 (o, 1H, 15-*m*, 4-CH₃Ph), 6.53 (d, $J = 8.2$ Hz, 1H, 8-*m*, 4-CF₃Ph), 6.44 (d, $J = 8.4$ Hz, 1H, 7-*o*, 4-CF₃Ph), 6.37 (broad, 1H, 15-*o*, 4-CH₃Ph), 6.35 (d, $J = 8.6$ Hz, 1H, 8-*o*, 4-CF₃Ph), 6.26 (b, 1H, 15-*o*, 4-CH₃Ph), 6.17 (d, $J = 7.9$ Hz, 1H, 10-*m*, 4-CH₃Ph), 6.13 (d, $J = 8.2$ Hz, 1H, 8-*o*, 4-CF₃Ph), 5.93 (d, $J = 7.8$ Hz, 1H, 10-*o*, 4-CH₃Ph), 5.48 (d, $J = 7.8$ Hz, 1H, 10-*m*, 4-CH₃Ph), 2.07 (s, 3H, 5-*p*, 4-CH₃Ph), 1.97 (s, 1H, -OH), 1.86 (s, 3H, 15-*p*, 4-CH₃Ph), 1.68 (s, 3H, 10-*p*, 4-CH₃Ph). ¹⁹F NMR (C₆D₆, 60°C): δ -62.58 (s, 3F), -62.72 (s, 9F), -62.88 (s, 3F), -62.95 (s, 3F), -63.06 (s, 3F), -63.32 (s, 3F). MS (HR-ESI major isotopomer): $M^+ = 1738.42$ (expt), 1738.42 (calcd).

Undecaarylisocorrole H₂[(CF₃)₈Me₃(10-OH)]. UV-vis (CH₂Cl₂): λ_{\max} , nm ($\epsilon \times 10^{-4}$, M⁻¹ cm⁻¹): 458 (1.86), 658 (0.26). ¹H NMR (C₆D₆, 600 MHz, δ in ppm): δ 7.46 (d, $J = 8.3$ Hz, 2H, 10-*o*, 4-CH₃Ph), 6.95 (d, $J = 8.1$ Hz, 4H, 12-*m*, 4-CF₃Ph), 6.80 (d, $J = 8.2$ Hz, 4H, 18-*m*, 4-CF₃Ph), 6.77 (d, $J = 8.1$ Hz, 2H, 10-*m*, 4-CH₃Ph), 6.72 (d, $J = 8.3$ Hz, 4H, 18-*o*, 4-CF₃Ph), 6.68 (d, $J = 8.0$ Hz, 4H, 17-*m*, 4-CF₃Ph), 6.68 (b, 12-*o*, 4-CF₃Ph), 6.62 (d, $J = 8.0$ Hz, 4H, 13-*m*, 4-CF₃Ph), 6.40 (d, $J = 7.9$ Hz, 4H, 17-*o*, 4-CF₃Ph), 6.30 (d, $J = 8.0$ Hz, 4H, 13-*o*, 4-CF₃Ph), 6.28 (d, $J = 7.9$ Hz, 4H, 15-*o*, 4-CH₃Ph), 5.86 (d, $J = 7.8$ Hz, 4H, 15-*m*, 4-CH₃Ph), 2.39 (s, 1H, -OH), 1.98 (s, 3H, 10-*p*, 4-CH₃Ph), 1.80 (s, 6H, 5,15-*p*, 4-CH₃Ph). ¹⁹F NMR (CDCl₃): δ -63.06 (s, 6F), -63.15 (s, 6F), -63.19 (s, 6F), -63.54 (s, 6F). MS (HR-ESI major isotopomer): $M^+ = 1738.42$ (expt), 1738.42 (calcd).

Single-crystal X-ray diffraction analysis of Undecaarylisocorrole H₂[(CF₃)₈Me₃(5-OH)]. X-ray data for H₂[(CF₃)₈Me₃(5-OH)] 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 700 Plus low temperature apparatus on the goniometer head of a Bruker D8 diffractometer equipped with a APEX-II CCD detector. Diffraction data were collected with synchrotron radiation monochromated using silicon(111) to a wavelength of 0.7749(1)Å. An approximate full-sphere of data was collected using a ω scans with scan rates of 3 seconds per 0.5 degree with $2\theta = -36^\circ$. 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. The hydrogen atoms on the nitrogen and oxygen atoms were found in the Fourier difference map and allowed to ride on their respective N or O atoms. Additional crystallographic information has been summarized in Table

1 and full details can be found in the crystallographic information file provided in the Supplementary Information.

Undecaarylisorcorrole H₂[H₈Me₃(5-OH)]. Into a 50 mL round-bottomed flask, 12 mg (0.0097 mmol) of Cu[H₈Me₃] was added and dissolved in 2 mL of CH₂Cl₂. Subsequently, 2 mL of concentrated H₂SO₄ (95-97%, Merck) was added. The mixture was stirred and sonicated at room temperature. The progress of the reaction was monitored by ESI mass spectrometry. After 2 hours the reaction was quenched by pouring the mixture into 300 mL distilled H₂O and then extracted with CHCl₃. The brown organic phase was washed once with distilled water and once with saturated aqueous NaHCO₃. Upon washing with NaHCO₃ the color of organic phase changed from brown to green. The organic phase was dried with anhydrous Na₂SO₄, filtered and evaporated under vacuum. The residue obtained was chromatographed on a silica gel column with CH₂Cl₂/5%-MeOH. The product was further purified by PLC with 1:2 *n*-hexane/CH₂Cl₂. The olive-green band at the bottom of the plate was pure H₂[H₈Me₃(5-OH)]. Yield: 5.6 mg, 48%. UV-vis (CH₂Cl₂): λ_{max}, nm (ε × 10⁻⁴, M⁻¹ cm⁻¹): 439 (0.69), 689 (0.15). ¹H NMR (C₆D₆, 600 MHz, δ in ppm): δ 8.22 (d, *J* = 7.8 Hz, 2H, 5-*o*, 4-CH₃Ph), 7.07 (d, *J* = 7.2 Hz, 2H, 3-*o*, Ph), 7.04 (d, *J* = 8.1 Hz, 2H, 5-*m*, 4-CH₃Ph), 7.03 (o, 7-*o*, Ph), 7.0 (b, 1H, 10-*o*, 4-CH₃Ph), 6.94 (d, *J* = 7.2 Hz, 2H, 2-*o*, Ph), 6.94 (o, 7-*p*, Ph), 6.86 (t, *J* = 7.5 Hz, 2H, 3-*m*, Ph), 6.81 (d, *J* = 7.2 Hz, 1H, 3-*p*, Ph), 6.77 (o, 7-*m*, Ph), 6.73 (o, 7-*m*, Ph), 6.66 (o, 7-*o*, Ph), 6.56 (t, *J* = 6.8 Hz, 2H, 2-*m*, Ph), 6.56 (o, 15-*o*, 4-CH₃Ph), 6.55 (o, 8-*m*, Ph), 6.51 (12-*m*, Ph), 6.48 (o, 15-*m*, 4-CH₃Ph), 6.43 (o, 8-*m*, Ph), 6.37 (b, 1H, 10-*m*, 4-CH₃Ph), 6.23 (b, 1H, 10-*o*, 4-CH₃Ph), 5.56 (b, 1H, 10-*m*, 4-CH₃Ph), 2.52 (s, 1H, -OH), 2.08 (s, 3H, 5-*p*, 4-CH₃Ph), 1.82 (s, 3H, 15-*p*, 4-CH₃Ph), 1.68 (s, 3H, 10-*p*, 4-CH₃Ph). MS (HR-ESI major isotopomer): M⁺ = 1193.52 (expt), 1193.52 (calcd).

Undecaarylisorcorrole H₂[(CF₃)₈H₃(5-OH)]. To a solution of Cu[(CF₃)₈H₃] (25 mg, 0.014 mmol) in CH₂Cl₂ (7.0 mL) was added dropwise 1 mL H₂SO₄ (95-97%) and the resulting suspension was stirred for 30 min. The mixture was poured into cold, distilled water and extracted with CH₂Cl₂. The green organic phase was washed once with distilled H₂O and once with saturated aqueous NaHCO₃, dried with anhydrous Na₂SO₄, and filtered. After concentration to a minimum volume, the organic phase was chromatographed on a silica gel column with 1:1 hexane/CH₂Cl₂, whereupon the isocorrole isomers eluted as a green band. PLC with 3:2 hexane/CH₂Cl₂ yielded the 5-OH-isocorrole (17mg, 0.01, 71.6%) as the first intense green band. Free base H₃[(CF₃)₈H₃] (1.8 mg, 7%) followed as a second, thinner green band, closely followed by a third, bright green band containing the 10-OH-isocorrole (2.5 mg, 11%). The latter two

products were not fully characterized because of the small quantities obtained so analytical data are only reported for the 5-OH isomer. UV-Vis (CH₂Cl₂): λ_{\max} , nm ($\epsilon \times 10^{-4}$, M⁻¹cm⁻¹): 433 (4.30), 681 (0.98). ¹H NMR (C₆D₆): δ 8.0 (d, 2H, 5-*o*, Ph), 7.20 (m, 1H, 7-*m*, 4-CF₃Ph), 7.15 (t, 2H, 5-*m*, Ph); 7.05 - 7.0 (m, 3H, 5-*p*, Ph and 3-*m*, 4-CF₃Ph), 6.82 (d, 2H, 3-*o*, 4-CF₃Ph), 6.75 (d, 1H, 10-*o*, Ph), 6.75- 6.56 {m, 7-*m* (1H, 4-CF₃Ph), 2-*o*, *m* (4H, 4-CF₃Ph), 8-*m* (1H, 4-CF₃Ph), 7-*o* (1H, 4-CF₃Ph), 15-*m* (2H, Ph)}, 6.54 (d, 1H, 8-*m*, 4-CF₃Ph), 6.42 (d, 1H, 7-*o*, 4-CF₃Ph), 6.40 – 6.25 {m, 15-*p* (1H, Ph), 10-*m* (1H, Ph), 8-*o* (2H, 4-CF₃Ph), 15-*o* (2H, Ph)}, 6.20 (t, 1H, 10-*p*, Ph), 6.10 (d, 1H, 8-*o*, 4-CF₃Ph), 6.0 (d, 1H, 10-*o*, Ph), 5.65 (t, 1H, 10-*m*, Ph). ¹⁹F NMR (C₆D₆)₂: δ -62.88 (s, 3F), -63.02 (s, 3F), -63.41 to -63.46 (m, 3F), -63.48 (s, 6F), -63.53 (s, 3F), -63.61 (s, 3F), -63.71 to -63.76 (m, 3F). HRMS (ESI⁺, major isotopomer): [M + H]⁺ = 1696.3692 (expt), 1696.3708 (calcd). Elemental analysis. Found (calcd) : C, 65.86 (65.88); H, 3.20 (2.97), N, 3.27 (3.30).

Synthesis of gold β -octakis(*p*-trifluoromethylphenyl)-*meso*-triphenylcorrole,

Au[(CF₃)₈H₃]. Gold(III) acetate (11 mg, 5 equiv) was added to a green solution of a mixture of the isomeric isocorroles H₂[(CF₃)₈H₃(5/10-OH)] (15 mg, 0.009mmol) pyridine (5.0 mL). After overnight stirring, the resulting reddish-brown suspension was evaporated and the residue eluted through silica gel with 7:3 hexane/CH₂Cl₂, yielding the gold undecaarylcorrole as the first red band (7 mg, 41.5%). Vapour diffusion of hexane into a CH₂Cl₂ solution yielded tiny rectangular needles of x-ray quality in approximately a month. UV-Vis (CH₂Cl₂): λ_{\max} , nm ($\epsilon \times 10^{-4}$, M⁻¹cm⁻¹): 434 (6.08), 544 (0.58). 580 (2.0). ¹H NMR (600 MHz, (CDCl₂)₂): δ 7.29 (d, *J* = 8.2 Hz, 4H, 2,18-*o*,4-CF₃Ph), 7.15 (d, 4H, 5, 15-*o*, Ph), 7.09 (d, 2H, 10-*o*, Ph), 7.05 (d, *J* = 8.1 Hz, 4H, 3,17-*o*, 4-CF₃Ph), 7.02 (d, *J* = 8.1 Hz, 4H, 2,18-*m*,4-CF₃Ph), 6.96 (d, *J* = 7.9 Hz, 4H, 3,17-*m*, 4-CF₃Ph), 6.93 – 6.89 (m, 8H, 7, 8, 12,13-*m*, 4-CF₃Ph), 6.87 (d, *J* = 8.0 Hz, 4H, 7,13-*o*, 4-CF₃Ph), 6.82 (d, *J* = 7.9 Hz, 4H, 8,12-*o*, 4-CF₃Ph), 6.74 (t, *J* = 7.7 Hz, 2H, 5,15-*p*, Ph), 6.65 (t, *J* = 7.6 Hz, 1H, 10-*p*, Ph), 6.49 (t, *J* = 7.7 Hz, 4H, 5,15-*m*, Ph), 6.41 (t, *J* = 7.7 Hz, 2H, 10-*m*, Ph). ¹⁹F NMR (CDCl₃): δ -63.31 (s, 12F); -63.42 (s, 6F); -63.49 (s, 6F). HRMS (ESI⁺, major isotopomer): [M]⁺ = 1873.3112 (expt), 1873.3110 (calcd). Elemental analysis. Found (calcd) : C, 59.90 (59.63); H, 2.77 (2.53), N, 3.11 (2.99).

Single-crystal X-ray diffraction analysis of the gold undecaarylcorrole Au[(CF₃)₈H₃].

X-ray data for Au[(CF₃)₈H₃] were collected on beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. A red tablet with dimensions 50 x 40 x 15 μm^3 was mounted on a MiTeGen[®] kapton loop and placed in a 100(2) K nitrogen cold stream provided by an Oxford Cryostream 700 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 with synchrotron radiation monochromated using silicon(111) to a wavelength of 0.7749(1) Å. An approximate full-sphere of data was collected using a combination of ϕ and ω scans with scan speeds of 1 second per degree for the ϕ scans, and 1 and 3 seconds per degree for the ω 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 full details can be found in the crystallographic information file provided in the Supporting Information.

Supporting information. UV-vis, ^1H NMR, and high-resolution mass spectra (42 pages); crystallographic information files for $\text{H}_2[(\text{CF}_3)_8\text{Me}_3(5\text{-OH})]$ and $\text{Au}[(\text{CF}_3)_8\text{H}_3]$.

Acknowledgement. This work was supported by the of the Research Council of Norway (FRINATEK project 231086, AG) and the Advanced Light Source, Berkeley, California (CMB, KJG). The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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- (a) A. B. Alemayehu, L.-K. Hansen, A. Ghosh, *Inorg. Chem.* 49 (2010) 7608–7610.
- (b) K. E. Thomas, H. Vazquez-Lima, Y. Fang, Y. Song, K. J. Gagnon, C. M. Beavers, K. M. Kadish, A. Ghosh, *Chem. Eur. J.* 21 (2015) 16839–16847.
- [31] I. H. Wasbotten, T. Wondimagegn, A. Ghosh, *J. Am. Chem. Soc.* 124 (2002) 8104–8116.