

β -Octabromo- and β -Octakis(trifluoromethyl)isocorroles: New Sterically Constrained Macrocyclic Ligands

Kolle E. Thomas,^[a] Christine M. Beavers,^[b] Kevin J. Gagnon,^[b] and Abhik Ghosh^{*[a]}

Presented herein is a study of the acid-induced demetalation of two sterically hindered copper corroles, Cu β -octabromo-*meso*-triphenylcorrole (Cu[Br₈TPC]) and β -octakis(trifluoromethyl)-*meso*-tris(*p*-methoxyphenyl)corrole (Cu[(CF₃)₈TpOMePC]). Unlike reductive demetalation, which affords the free-base β -octabromocorrole, demetalation of Cu[Br₈TPC] under non-reductive conditions (CHCl₃/H₂SO₄) resulted in moderate yields of free-base 5- and 10-hydroxy isocorroles. The isomeric free bases could be complexed to Co^{II} and Ni^{II}, affording stable

complexes. Only reductive demetalation was found to work for Cu[(CF₃)₈TpOMePC], affording a highly saddled, hydrated corrole, H₃[5-OH,10-H-(CF₃)₈TpOMePC], where the elements of water had added across C₅ and C₁₀. Interaction of this novel free base with Co^{II} resulted in Co[*iso*-10-H-(CF₃)₈TpOMePC], a Co^{II} 10-hydro isocorrole. The new metal complexes were all characterized by single-crystal X-ray diffraction analysis and, despite their sterically hindered nature, were found to exhibit almost perfectly planar isocorrole cores.

1. Introduction

Isocorroles are fascinating hybrid ligands that combine the dianionic character of porphyrins with the sterically constricted N₄ cavity of corroles (Figure 1). In addition, with significant absorption in the near-IR, they are of considerable interest as near-IR dyes for medical imaging. Traditionally, isocorroles have been synthesized from linear mono-, di-, and tetra-pyrrolic starting materials.^[1] Recently, Paolesse et al. showed that they could also be directly accessed from corroles. An attempt to synthesize a free-base β -octabromocorrole through the interaction of free-base *meso*-triarylcorrole and *N*-bromosuccinimide resulted instead in a free-base β -octabromoisocorrole, which, interestingly, aromatized to a corrole when complexed to Co^{III}.^[2] Subsequently, the same group synthesized β -unsubstituted *meso*-triarylisocorroles through DDQ oxidation of the corresponding free-base corroles.^[3] Attempts to demetalate silver corroles^[4] and to selectively brominate a β -nitrocorrole^[5] also afforded unexpected routes to isocorroles.

Reductive demetalation of Cu β -octabromocorroles with concentrated sulfuric acid and an excess of a reducing agent

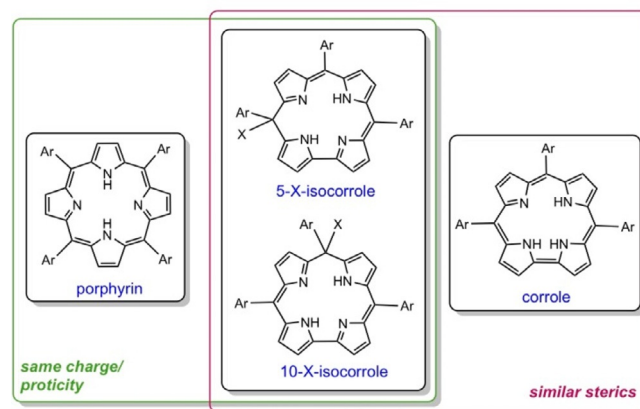


Figure 1. Isocorroles as hybrid ligands.

such as Fe^{II} or Sn^{II} finally provided a reliable route to free-base β -octabromocorroles.^[6] We also discovered that prolonged exposure to an acidic medium such as CHCl₃/H₂SO₄ without an added reductant resulted in moderate yields of 5- and 10-hydroxyisocorroles. Details of such a protocol have recently been published for undecaarylisocorroles.^[7] Presented herein are the results of our continued studies on sterically hindered isocorroles, including optimized protocols for the synthesis of 5/10-hydroxy- β -octabromo-*meso*-triphenylisocorrole, H₂[*iso*-5/10-OH-Br₈TPC], and its complexation to Co^{II} and Ni^{II}. Also presented are our first results on the demetalation of a copper β -octakis(trifluoromethyl)-*meso*-triarylcorrole. The various products obtained were characterized as far as possible with single-crystal X-ray crystallography; as discussed below, the results, a total of five X-ray structures (Table 1), provide substantial insights into the structural characteristics of isocorrole derivatives.

[a] Dr. K. E. Thomas, Prof. Dr. A. Ghosh
Department of Chemistry and
Center for Theoretical & Computational Chemistry
UiT—The Arctic University of Norway, 9037 Tromsø (Norway)
E-mail: abhik.ghosh@uit.no

[b] Dr. C. M. Beavers, Dr. K. J. Gagnon
Advanced Light Source, Lawrence Berkeley National Laboratory
Berkeley, CA 94720-8229 (USA)

Supporting Information and the ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/open.201700035>.

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Table 1. Crystallographic data for the compounds analyzed.

Compound	H ₂ [<i>iso</i> -5-OH-Br ₈ TPC]	Co ^{II} [<i>iso</i> -10-OH-Br ₈ TPC](PPh ₃)	Ni ^{II} [<i>iso</i> -5-OH-Br ₈ TPC]	H ₂ [5-OH,10-H-(CF ₃) ₈ TPOMePC]	Co ^{II} [<i>iso</i> -10-H-(CF ₃) ₈ TPOMePC]
Chemical formula	C ₈₁ H ₄₉ Br ₁₆ Cl ₃ N ₈ O ₂	C ₇₃ H ₄₉ Br ₈ N ₄ OPCo	C ₁₅₃ H ₆₉ Br ₃₂ Cl ₁₅ N ₁₆ O ₄ Ni ₄	C ₄₈ H ₂₆ F ₂₄ N ₄ O ₄	C ₄₈ H ₂₂ F ₂₄ O ₃ N ₄ Co
Formula mass	2551.19	1727.34	5518.95	1178.73	1217.62
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Orthorhombic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 1	<i>P</i> -1	<i>Pbca</i>
λ [Å]	0.61992	0.7749	0.9537	0.93221	0.7749
<i>a</i> [Å]	14.4512(5)	12.2904(6)	14.4643(6)	12.3913(8)	12.2005(3)
<i>b</i> [Å]	14.5377(5)	13.8275(7)	14.5129(6)	13.3041(7)	25.9102(7)
<i>c</i> [Å]	21.5890(8)	19.5628(9)	22.0745(10)	15.3611(8)	28.2726(7)
α [°]	95.609(2)	76.253(3)	73.459(2)	67.137(3)	90
β [°]	101.915(2)	80.009(3)	76.456(2)	85.025(4)	90
γ [°]	113.646(2)	83.493(3)	66.8599(19)	82.537(4)	90
<i>Z</i>	2	2	1	2	8
<i>V</i> [Å ³]	3981.9(3)	3171.4(3)	4045.2(3)	2311.8(2)	8937.5(4)
Temperature [K]	100(2)	100(2)	100(2)	100(2)	100(2)
Density [g cm ⁻³]	2.128	1.809	2.266	1.693	1.810
Meas. reflections	73 287	55 091	84 466	30 220	175 802
Unique reflections	19 760	18 561	19 417	10 371	17 022
Parameters	1075	793	2082	741	735
Restraints	240	0	799	0	7
<i>R</i> _{int}	0.0697	0.0469	0.0653	0.0436	0.0429
θ range [°]	1.362–24.411	2.240–33.073	2.075–39.542	1.889–37.386	1.714–36.589
<i>R</i> ₁ , <i>wR</i> ₂ all data	0.0584, 0.1512	0.0336, 0.0740	0.0636, 0.1770	0.0670, 0.2135	0.0331, 0.0889
<i>S</i> (GooF) all data	1.044	1.048	1.030	1.024	1.049
Max/min res.	2.881/–1.980	0.810/–0.951	5.539/–2.087	0.361/–0.372	0.919/–0.764
dens. [e Å ⁻³]					

2. Results and Discussion

2.1. β-Octabromo-*meso*-triphenylisocorrole Derivatives

As shown in Figure 2, demetalation of Cu β-octabromo-*meso*-triphenylcorrole, Cu[Br₈TPC], with CHCl₃/H₂SO₄ resulted in

moderate yields of the isomers H₂[*iso*-5-OH-Br₈TPC] and H₂[*iso*-10-OH-Br₈TPC] in approximately 2 h.^[8] Both could be efficiently complexed to Co^{II} or Ni^{II} in about 1 h or less. Single-crystal X-ray structures were obtained for H₂[*iso*-5-OH-Br₈TPC] (Figure 3), Co^{II}[*iso*-10-OH-Br₈TPC](PPh₃) (Figure 4), and Ni^{II}[*iso*-5-OH-Br₈TPC] (Figure 5). The structures exhibit short metal–nitrogen distan-

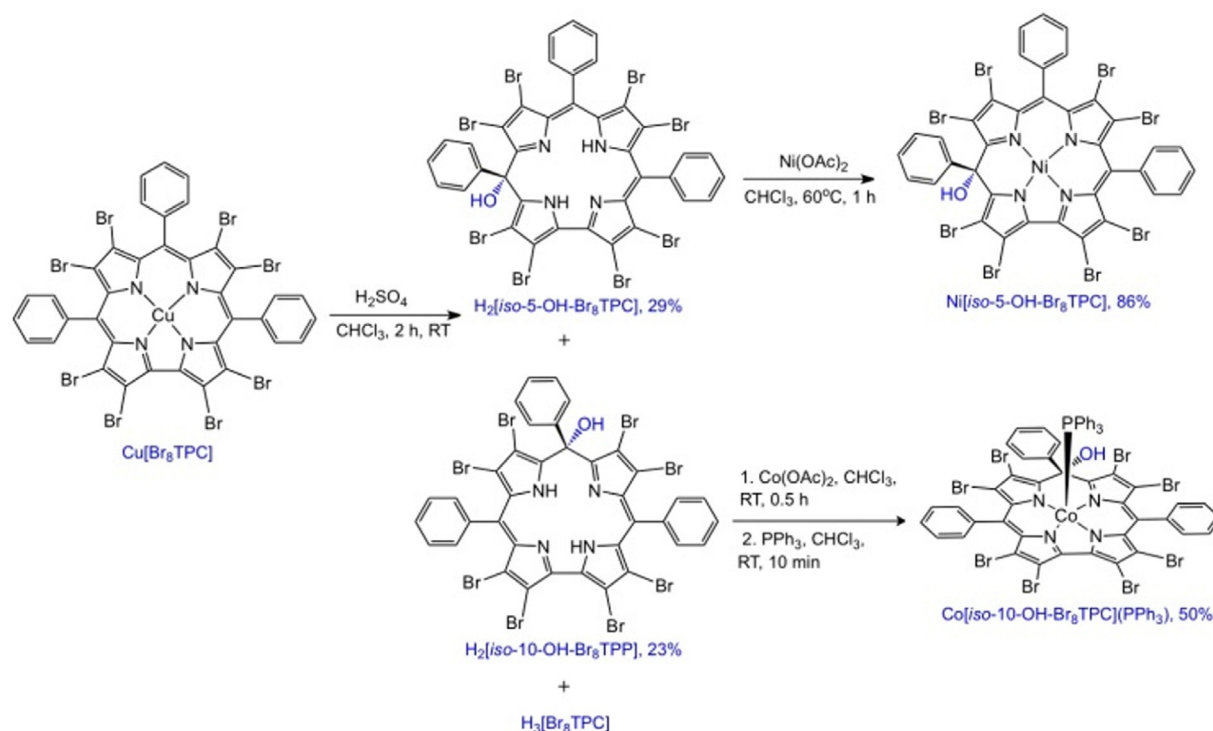


Figure 2. Demetalation of Cu[Br₈TPC] and complexation of the resulting 5- and 10-hydroxy isocorroles to Co^{II} and Ni^{II}.

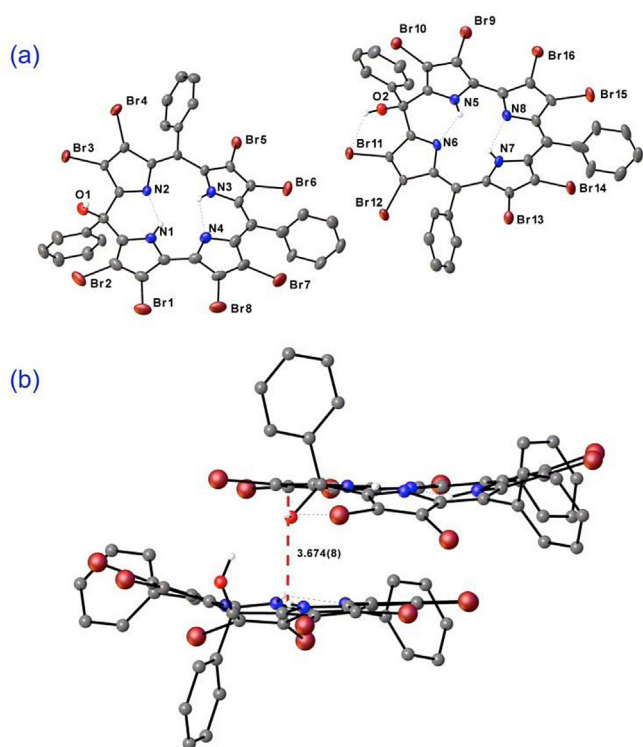


Figure 3. Two views of the X-ray structure of the free-base isocorrole $H_2[iso-5-OH-Br_8TPC]$.

ces and essentially planar isocorrole cores. Like corroles, isocorroles thus appear to be strongly resistant to nonplanar distortions,

which is thought to be a consequence of the rigidity of the C1–C19 pyrrole–pyrrole linkage and its resistance to both twisting and pyramidalization. Both metalloisocorrole structures exhibit intramolecular hydrogen bonding involving the *meso*-OH groups and intermolecular metal– β -bromine interactions (Figure 4 and Figure 5). Finally, the new isocorroles exhibit fairly strong near-IR absorption (Figure 6), which may promise application as a near-IR dye in medical imaging and/or photodynamic therapy.

2.2. β -Octakis(trifluoromethyl)-*meso*-triarylisocorrole Derivatives

Although copper^[9] and gold^[10] β -octakis(trifluoromethyl)-*meso*-tris(*p*-X-phenyl)corrole derivatives, $M[(CF_3)_8TpXPC]$ ($M = Cu, Au$), were synthesized in one of our laboratories a few years ago, a useful demetalation procedure for the complexes has so far proved elusive. Reported herein is the first such demetalation, carried out under reductive conditions on the complex $Cu[(CF_3)_8TpOMePC]$, and the complexation of the resulting free base to cobalt(II). As shown in Figure 7, the demetalation occurs with a twist: the metal-free product obtained in high yield is not an isocorrole, but rather a hydrated corrole, with the elements of water added across C_5 and C_{10} , whereas the Co^{II} complex is a 10-hydro isocorrole. The X-ray structure of the free-base product, denoted here as $H_3[5-OH,10-H-(CF_3)_8TpOMePC]$, revealed a strongly saddled macrocyclic core, clearly a result of exceptional steric crowding owing to the three central NH groups and the peripheral substituents (Fig-

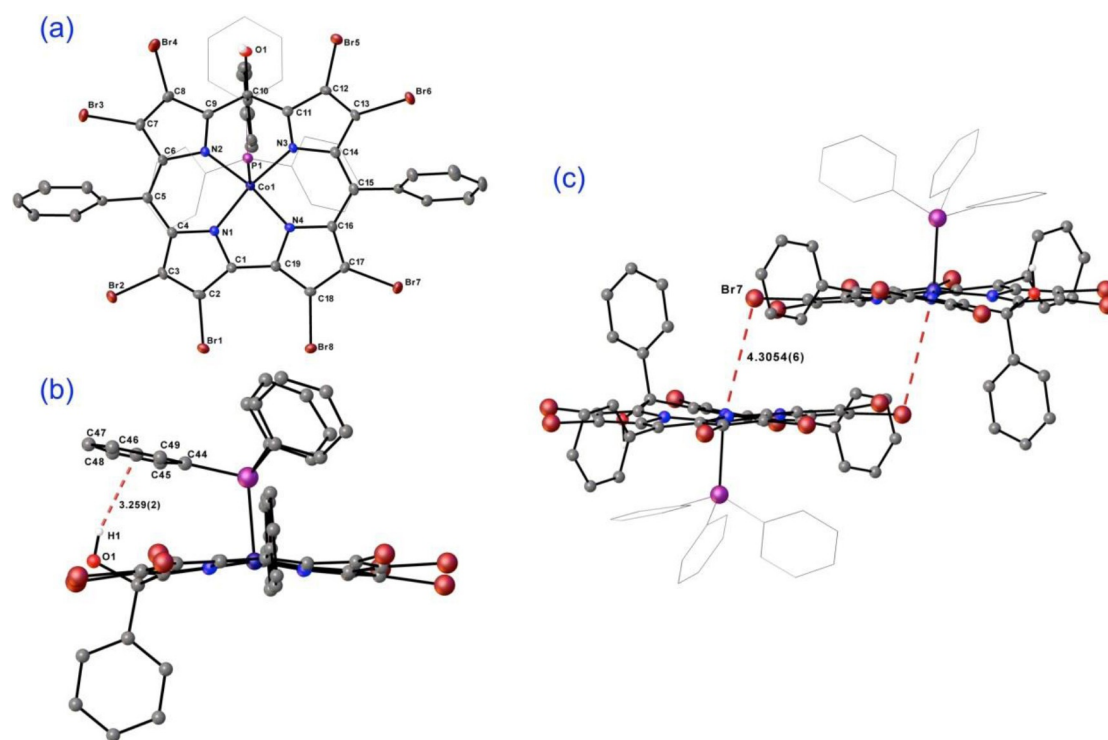


Figure 4. X-ray structure of $Co^{II}[iso-10-OH-Br_8TPC](PPh_3)$: a) top view, b) side-view showing 10-OH... $\pi(PPh_3)$ hydrogen bonding, and c) side view showing stacking and Co...Br interactions (Å). Selected distances: Co(1)–N(1) 1.887(2), Co(1)–N(2) 1.930(2), Co(1)–N(3) 1.927(2), Co(1)–N(4) 1.881(2), and Co(1)–P(1) 2.3837(7) Å.

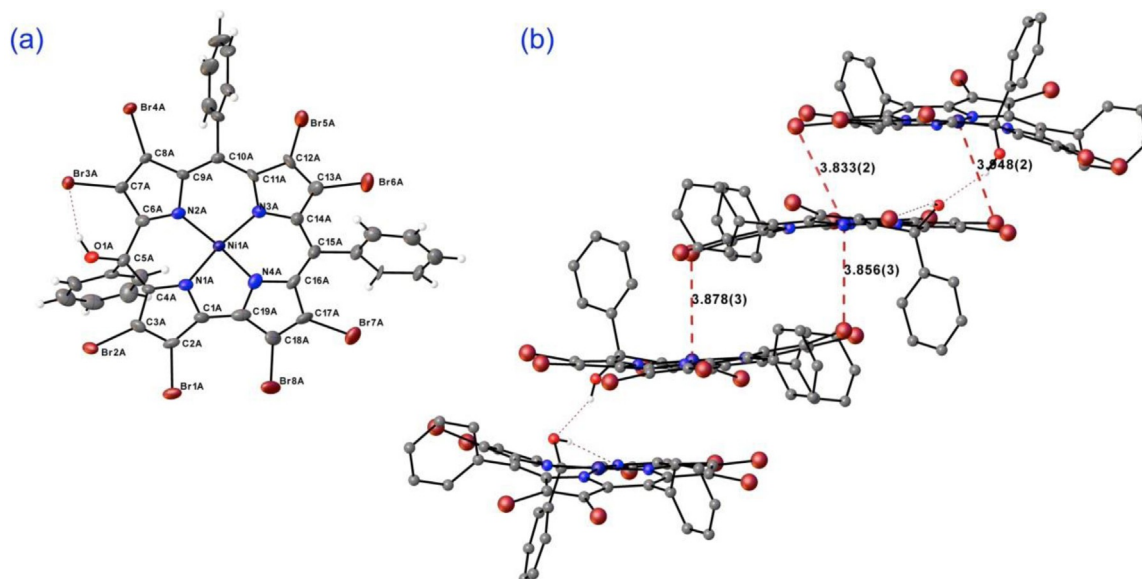


Figure 5. X-ray structure of Ni^{II}[*iso*-5-OH-Br₈TPC]: a) top view and b) side view showing stacking and Ni...Br interactions (Å). Selected distances: Ni(1A)–N(1A) 1.851(11), Ni(1A)–N(2A) 1.904(10), Ni(1A)–N(3A) 1.920(10), and Ni(1A)–N(4A) 1.863(11) Å.

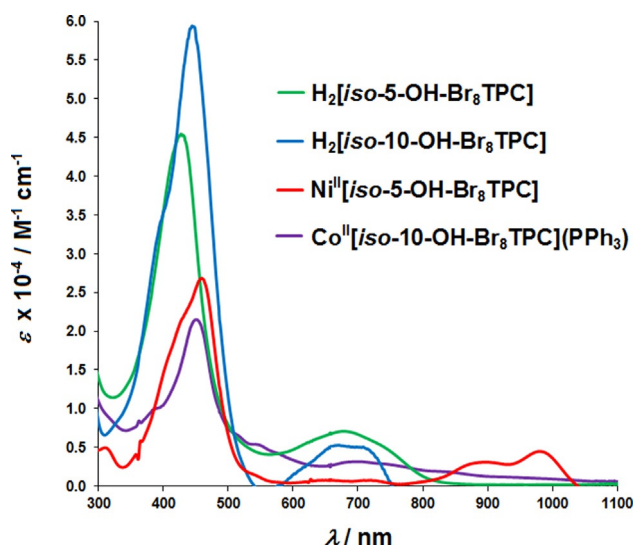


Figure 6. UV/Vis spectra of *iso*-5/10-OH-Br₈TPC derivatives.

ure 8a).^[11] The X-ray structure of the Co^{II} complex, denoted here as Co[*iso*-10-H-(CF₃)₈TpOMePC], on the other hand, was found to exhibit a planar isocorrole core (Figure 8b), with intermolecular Co...OMe interactions (Figure 8c). Like other isocorrole derivatives, Co[*iso*-10-H-(CF₃)₈TpOMePC] was also found to exhibit a strong near-IR feature (λ_{\max} = 707 nm) (Figure 9).

3. Conclusions

Optimized protocols have been developed for the demetalation of the sterically hindered copper corroles Cu[Br₈TPC] and Cu[(CF₃)₈TpOMePC]. Although 5- and 10-hydroxyisocorroles were obtained as the major products of demetalation of Cu[Br₈TPC] under nonreductive conditions, Cu[(CF₃)₈TpOMePC]

could only be demetalated under reductive conditions and the major product turned out to be a unique 5-hydroxy-10-hydro corrole, that is, a free-base hydrated corrole. The free-base ligands could all be complexed to Co^{II} and/or Ni^{II} to afford stable metalloisocorroles. X-ray structures of the metal complexes exhibited short metal–nitrogen bonds and essentially isocorrole cores. The stability and robustness of both the free-base ligands and metalloisocorroles reported here appear to foreshadow a bright future for isocorroles as transition-metal ligands. The strong near-IR absorption of isocorroles also promises applications as near-IR dyes, notably in medicinal applications such as photodynamic therapy.

Experimental Section

Materials

All reagents and solvents were used as purchased. 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 chromatographic plates (20×20 cm; 0.5 mm thick, Merck), were used for further purification where relevant. The starting materials Cu[Br₈TPC]^[12] and Cu[(CF₃)₈TpOMePC]^[9a] were synthesized as previously described.

Instrumentation

UV/Vis spectra were recorded on an HP 8453 spectrophotometer in CH₂Cl₂. All NMR spectra were obtained on a Mercury Plus Varian spectrometer at 298 K. ¹H NMR spectra were recorded in CD₂Cl₂ (referenced to 5.30 ppm) or in 1,1,2,2-[D₂]tetrachloroethane [(CDCl₂)₂], referenced to 5.91 ppm at 400 MHz. ¹⁹F NMR spectra were referenced to 2,2,2-trifluoroethanol-*d*₃ (δ = –77.8 ppm) at 376 MHz. High-resolution electrospray ionization (HR-ESI) mass spectra were recorded on an LTQ Orbitrap XL spectrometer.

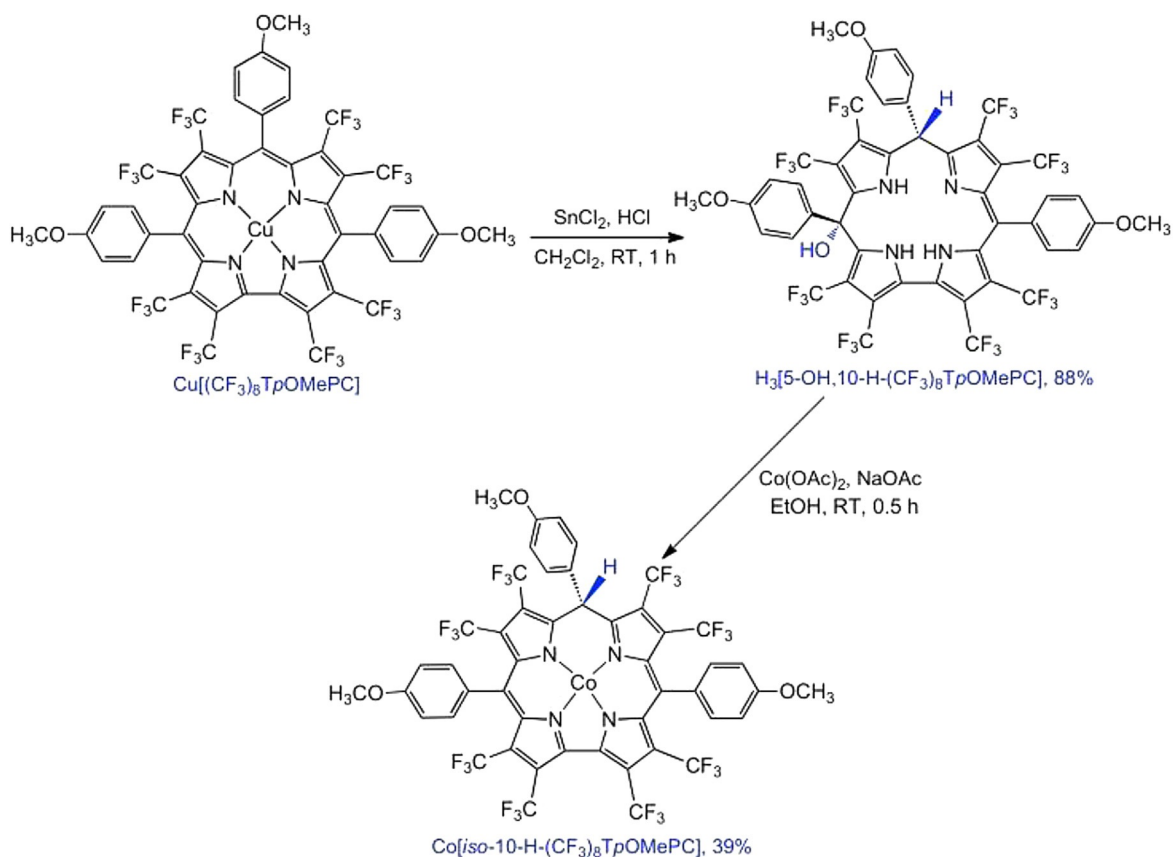


Figure 7. Reductive demetalation of $\text{Cu}[(\text{CF}_3)_8\text{TpOMePC}]$ and complexation of the resulting free base to Co^{II} .

Synthesis of $\text{H}_2[\text{iso-5-OH-Br}_8\text{TPC}]$ and $\text{H}_2[\text{iso-10-OH-Br}_8\text{TPC}]$

To a pre-sonicated and stirred solution of $\text{Cu}[\text{Br}_8\text{TPC}]$ (62 mg, 0.051 mmol) in CHCl_3 (10 mL) was added concentrated H_2SO_4 (95–97%, 6 mL) in a dropwise manner over 6 min. The resulting suspension was stirred and sonicated alternately over 2 h. The green suspension obtained was shaken with distilled H_2O (100 mL \times 2) and extracted with CHCl_3 . The organic phase was washed with saturated aqueous NaHCO_3 , dried over anhydrous Na_2SO_4 , and filtered. The filtrate was concentrated to a minimum volume and chromatographed on a silica gel column with *n*-hexane/ CH_2Cl_2 (7:3) to yield impure green $\text{H}_3[\text{Br}_8\text{TPC}]$ (14 mg) and bright green $\text{H}_2[\text{iso-10-OH}(\text{Br}_8\text{TPC})]$, closely followed by the 5-isomer. Crystallization from 2:1 $\text{CH}_3\text{OH}/\text{CHCl}_3$ yielded the pure 10-isomer (13.6 mg, 22.7%), whereas crystallization from 2:1 *n*-hexane/ CHCl_3 yielded the pure 5-isomer (17.4 mg, 29.1%). $\text{H}_2[\text{iso-5-OH-Br}_8\text{TPC}]$: UV/Vis (CH_2Cl_2): λ_{max} nm ($\epsilon \times 10^{-4}$, $\text{M}^{-1} \text{cm}^{-1}$): 431 (4.52), 677 (0.71). $^1\text{H NMR}$ $\{(\text{CDCl}_3)_2\}$: δ 13.91 (s, 1H, NH); 12.63 (bs, 1H, NH); 7.70–7.60 (m, 2H); 7.52–7.16 (m, 15H); 3.44 (s, 1H, OH). HRMS (ESI⁺, major isotopomer): $[\text{M} + \text{H}]^+ = 1174.4923$ (expt), 1174.4944 (calcd). Elemental analysis: Found (calcd) : C, 36.07 (37.86); H, 1.55 (1.54), N, 4.34 (4.77).

$\text{H}_2[\text{iso-10-OH-Br}_8\text{TPC}]$: UV/Vis (CH_2Cl_2): λ_{max} nm ($\epsilon \times 10^{-4}$, $\text{M}^{-1} \text{cm}^{-1}$): 444 (5.94), 669 (0.53), 707 (0.51). $^1\text{H NMR}$ $\{(\text{CDCl}_3)_2\}$: δ 13.60 (s, 2H, NH); 7.67–7.61 (m, 2H); 7.51–7.45 (m, 2H); 7.45–7.38 (m, 4H); 7.29–7.22 (m, 7H); 3.75 (s, 1H, OH). HRMS (ESI⁺, major isotopomer): $[\text{M} + \text{H}]^+ = 1174.4961$ (expt), 1174.4944 (calcd).

Synthesis of $\text{Ni}^{\text{II}}[\text{iso-5-OH-Br}_8\text{TPC}]$

To a solution of $\text{H}_2[\text{iso-5-OH-Br}_8\text{TPC}]$ (20 mg, 0.017 mmol) in CHCl_3 (20 mL) maintained at 50 °C, was added $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (23 mg, 5 equiv) dissolved in CH_3OH (3 mL) in a dropwise manner over 5 min, whereupon the mixture turned from bottle green to olive green. After stirring for 1 h at 60 °C, TLC (with 3:2 *n*-hexane/ CH_2Cl_2) indicated full consumption of the starting material. The mixture was then evaporated to dryness and the residue chromatographed on a silica gel column. Initial elution with 3:2 *n*-hexane/ CH_2Cl_2 resulted in the removal of a pale-yellow impurity. Gradual increase of solvent polarity to pure CH_2Cl_2 yielded the nickel isocorrole product as a brown band. The pure complex (18 mg, 85.6%) was obtained by crystallization from 1:1 $\text{CHCl}_3/\text{CH}_3\text{OH}$. UV/Vis (CH_2Cl_2): λ_{max} nm ($\epsilon \times 10^{-4}$, $\text{M}^{-1} \text{cm}^{-1}$): 459 (2.68), 892 (0.31), 982 (0.44). $^1\text{H NMR}$ $\{(\text{CDCl}_3)_2\}$: δ 7.88–7.83 (m, 2H,); 7.44–7.24 (m, 10H); 7.19–7.04 (m, 3H); 3.29 (s, 1H, OH). HRMS (ESI⁺, major isotopomer): $[\text{M}]^+ = 1229.4049$ (expt), 1229.4056 (calcd). Elemental analysis: Found (calcd): C, 35.61 (36.11); H, 1.66 (1.31), N, 4.16 (4.55). Cubic crystals of X-ray quality were grown by slow evaporation of a chloroform solution layered with an equal volume of *n*-hexane.

Synthesis of $\text{Co}^{\text{II}}[\text{iso-10-OH-Br}_8\text{TPC}](\text{PPh}_3)$

To a solution of $\text{H}_2[\text{iso-10-OH-Br}_8\text{TPC}]$ (20 mg, 0.017 mmol) in CHCl_3 (10 mL), was added $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (84 mg, 10 equiv) dissolved in CH_3OH (2 mL) in a dropwise manner, whereupon the mixture changed from bright green to brown. After stirring for 30 min, the mixture was evaporated to dryness and the residue was chromato-

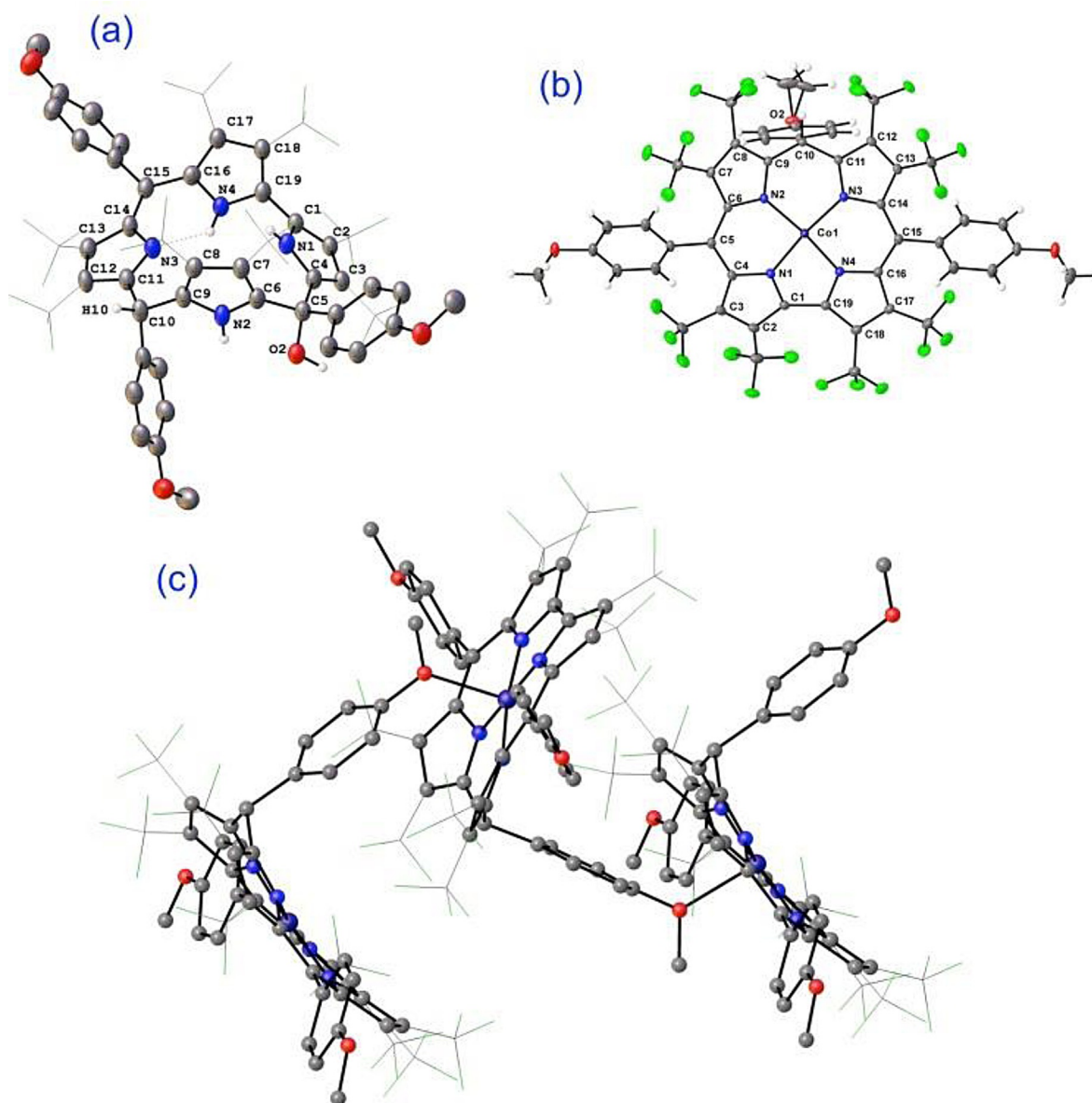


Figure 8. Thermal ellipsoid plots of a) $H_3[5\text{-OH},10\text{-H-(CF}_3)_8\text{TpOMePC}]$ and b) $\text{Co}[iso\text{-}10\text{-H-(CF}_3)_8\text{TpOMePC}]$. c) Intermolecular interactions of $\text{Co}[iso\text{-}10\text{-H-(CF}_3)_8\text{TpOMePC}]$. Selected distances for $\text{Co}[iso\text{-}10\text{-H-(CF}_3)_8\text{TpOMePC}]$: $\text{Co}(1)\text{-N}(1)$ 1.8730(8), $\text{Co}(1)\text{-N}(2)$ 1.9053(8), $\text{Co}(1)\text{-N}(3)$ 1.9071(8), $\text{Co}(1)\text{-N}(4)$ 1.8730(8), and $\text{Co}(1)\text{-O}(2)$ 2.2921(8) Å.

graphed on a silica gel column with 3:7 *n*-hexane/ CH_2Cl_2 as the eluent to yield $\text{Co}^{\text{II}}[iso\text{-}10\text{-OH-Br}_8\text{TPC}]$ as a brown band (16.8 mg, 80.2%). UV/Vis (CH_2Cl_2): λ_{max} nm ($\epsilon \times 10^{-4}$, $\text{M}^{-1} \text{cm}^{-1}$): 443 (5.14), 574 (0.87), 736 (0.72), 938 (0.29). HRMS (ESI⁺, major isotopomer): $[M]^+ = 1230.4076$ (expt), 1230.4037 (calcd). To the $\text{Co}^{\text{II}}[iso\text{-}10\text{-OH-Br}_8\text{TPC}]$ (15 mg, 0.012 mmol) dissolved in CHCl_3 (10 mL), was then added triphenylphosphine (16 mg, 5 equiv) and the mixture was stirred for 10 min. The mixture was filtered and evaporated to dryness to yield $\text{Co}^{\text{II}}[iso\text{-}10\text{-OH-Br}_8\text{TPC}](\text{PPh}_3)$ as a brown solid (9 mg, 50%). UV/Vis (CH_2Cl_2): λ_{max} nm ($\epsilon \times 10^{-4}$, $\text{M}^{-1} \text{cm}^{-1}$): 451 (2.15), 697 (0.32). HRMS (ESI⁺, major isotopomer): $[M]^+ = 1492.4956$ (expt), 1492.4959 (calcd). Vapor diffusion of *n*-hexane into a saturated benzene solution of the product led within 10 days to rectangular dark-red crystals suitable for X-ray analysis.

Synthesis of $H_3[5\text{-OH},10\text{-H-(CF}_3)_8\text{TpOMePC}]$

To a solution of $\text{Cu}[(\text{CF}_3)_8\text{TpOMePC}]$ (30 mg, 0.024 mmol) in CH_2Cl_2 (5 mL), was added anhydrous SnCl_2 (46 mg, 10 equiv), followed by dropwise addition of concentrated HCl (37%, 1 mL). After stirring for 1 h, the purple suspension obtained was washed twice with distilled water and once with saturated aqueous NaHCO_3 . The orange CH_2Cl_2 phase was dried over Na_2SO_4 , filtered, evaporated to a minimum volume, and chromatographed on a silica gel column. Elution with 1:1 *n*-hexane/ CH_2Cl_2 led to a brown band identified with HR-ESI as the detrifluoromethylated product $H_3[(\text{CF}_3)_7\text{TpMeOPC}]$ (1.2 mg), whereas 2:3 *n*-hexane/ CH_2Cl_2 resulted in $H_3[5\text{-OH},10\text{-H-(CF}_3)_8\text{TpOMePC}]$ as an orange band (25 mg, 88%). UV/Vis (CH_2Cl_2): λ_{max} nm ($\epsilon \times 10^{-4}$, $\text{M}^{-1} \text{cm}^{-1}$): 486 (2.57). ¹H NMR (CD_2Cl_2): δ 11.44 (s, 1H, NH); 8.75 (s, 1H, NH); 7.57 (s, 1H, NH); 7.43 (d, 2H, 5,15-o or m); 7.29 (d, 2H,10-o or m); 7.07 (d, 2H, 5,15-o or

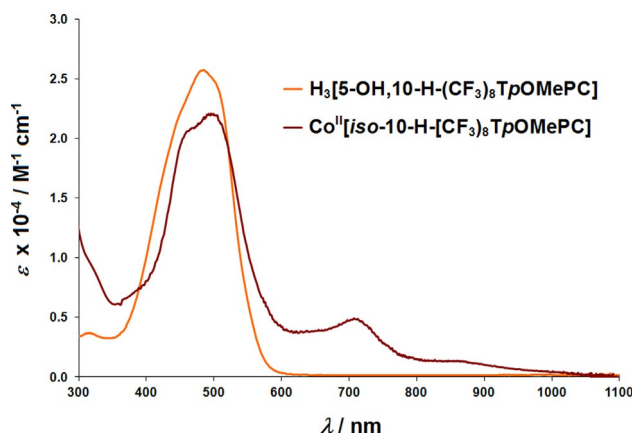


Figure 9. UV/Vis spectra of partially saturated $(\text{CF}_3)_8\text{TpOMePC}$ derivatives.

m); 7.02–6.95 (overlapping *d*, 4H, 5,15-*o* or *m*); 6.88 (*d*, 2H, 10-*o* or *m*); 6.30 (*s*, 1H, 10-*meso*, H); 3.91 (*s*, 3H, 10-*p-OMe*, Ph); 3.80 (*s*, 6H, 5,15-*p-OMe*, Ph); 3.40 (*s*, 1H, 5-*meso*, OH). ^{19}F NMR: δ –51.70 (*q*, 3F); –52.64 to –52.89 (*m*, 9F); –54.78 (*q*, 3F); –55.91 to –56.11 (*m*, 3F); –56.80 to –57.0 (*m*, 3F); –57.12 (*q*, 3F). HRMS (ESI⁺, major isotopomer): $[\text{M} + \text{H}]^+ = 1179.1660$ (expt), 1179.1644 (calcd). Elemental analysis. Found (calcd): C, 49.93 (48.91); H, 2.52 (2.22), N, 4.65 (4.75). Diffusion of a saturated CH_2Cl_2 solution of the latter product into *n*-hexane yielded orange needles suitable for X-ray analysis.

Synthesis of $\text{Co}^{\text{II}}[\text{iso-10-H-(CF}_3)_8\text{TpOMePC}]$

To an orange solution of $\text{H}_3[5\text{-OH,10-H-(CF}_3)_8\text{TpOMePC}]$ (20 mg, 0.017 mmol) in absolute ethanol (5 mL), was added anhydrous sodium acetate (78.4 mg, 22 equiv) and the suspension stirred for 5 min, upon which it turned orange–red. Cobalt acetate (31.6 mg, 7.5 equiv) was then added and, after stirring for 30 min, the resulting green suspension was rotary evaporated to dryness. The obtained green residue was chromatographed on a silica gel column. Elution with pure CH_2Cl_2 resulted in the pure cobalt isocorrole product as an orange–brown band. Subsequent elution with 5:1 $\text{CH}_2\text{Cl}_2/\text{MeOH}$ resulted in several green bands. These were combined and rotary evaporated to yield a brown residue, which, according to HR-ESI, was largely the impure product. Preparative TLC of the combined pure and impure fractions with 2:3 *n*-hexane/ CH_2Cl_2 yielded the pure product $\text{Co}^{\text{II}}[\text{iso-10-H-(CF}_3)_8\text{TpOMePC}]$ (8 mg, 39%) as the first brown band. UV/Vis (CH_2Cl_2): λ_{max} nm ($\epsilon \times 10^{-4}$, $\text{M}^{-1} \text{cm}^{-1}$): 496 (2.21), 707 (0.49). HRMS (ESI⁺, major isotopomer): $[\text{M}]^+ = 1217.0685$ (expt), 1217.0635 (calcd). Diffusion of a saturated benzene solution of the complex into *n*-hexane yielded brown needles suitable for X-ray analysis.

X-ray Crystallographic Analysis

X-ray data 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 cold nitrogen stream provided by an Oxford Cryostream 700 Plus low temperature apparatus on the goniometer head of a Bruker D8 diffractometer. An APEXII CCD detector was generally used, except for $\text{Co}^{\text{II}}[\text{iso-10-OH-Br}_8\text{TPC}](\text{PPh}_3)$, where a PHOTON100 CMOS detector operating in shutterless mode was employed. Diffraction data were collected by synchrotron radiation monochromated

using silicon(111) to wavelengths of 0.7749(1) Å for the two Co complexes, 0.9537(1) Å for $\text{Ni}^{\text{II}}[\text{iso-5-OH-Br}_8\text{TPC}]$, 0.61992(1) Å for $\text{H}_2[\text{iso-5-OH-Br}_8\text{TPC}]$, and 0.93221(1) Å for $\text{H}_3[5\text{-OH,10-H-(CF}_3)_8\text{TpOMePC}]$. In all cases, an approximate full-sphere of data was collected by using 0.3° ω scans. The structures were solved by intrinsic phasing (SHELXT) and refined by using full-matrix least squares on F^2 (SHELXL-2013/4). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on all carbon atoms were geometrically calculated and refined as riding atoms. Any hydrogen atoms located on oxygen or nitrogen atoms were found in the Fourier difference map, their distances fixed, and allowed to refine with a riding model. Additional crystallographic information has been summarized in Table 1 and full details can be found in the crystallographic information files provided as Supporting Information.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: corroles • isocorroles • macrocyclic ligands • near-infrared • single-crystal X-ray crystallography

- [1] a) G. Hohlneicher, D. Bremm, J. Wytko, J. Bley-Esrich, J.-P. Gisselbrecht, M. Gross, M. Michels, J. Lex, E. Vogel, *Chem. Eur. J.* **2003**, *9*, 5636–5642; b) M. Hoffmann, B. Cordes, C. Kleeberg, P. Schweyen, B. Wolfram, M. Bröring, *Eur. J. Inorg. Chem.* **2016**, 3076–3085; c) J.-I. Setsune, A. Tsukajima, J. Watanabe, *Tetrahedron Lett.* **2006**, *47*, 1817–1820; d) J.-I. Setsune, A. Tsukajima, J. Watanabe, *Tetrahedron Lett.* **2007**, *48*, 1531–1535; e) J.-I. Setsune, A. Tsukajima, N. Okazaki, *J. Porphyrins Phthalocyanines* **2009**, *13*, 256–265; f) D. L. Flint, R. L. Fowler, T. D. LeSaulnier, A. C. Long, A. Y. O'Brien, G. R. Geier III, *J. Org. Chem.* **2010**, *75*, 553–563; g) R. Costa, G. R. Geier III, C. Ziegler, *Dalton Trans.* **2011**, *40*, 4384–4386.
- [2] R. Paolesse, S. Nardis, F. Sagone, R. G. Khoury, *J. Org. Chem.* **2001**, *66*, 550–556.
- [3] a) S. Nardis, G. Pomarico, F. R. Fronczek, M. G. H. Vicente, R. Paolesse, *Tetrahedron Lett.* **2007**, *48*, 8643–8646; b) G. Pomarico, X. Xiao, S. Nardis, R. Paolesse, F. R. Fronczek, K. M. Smith, Y. Fang, Z. Ou, K. M. Kadish, *Inorg. Chem.* **2010**, *49*, 5766–5774; c) S. Nardis, G. Pomarico, F. Mandoj, F. R. Fronczek, K. M. Smith, R. Paolesse, *J. Porphyrins Phthalocyanines* **2010**, *14*, 752–757.
- [4] M. Stefanelli, J. Shen, W. Zhu, M. Mastroianni, F. Mandoj, S. Nardis, Z. Ou, K. M. Kadish, F. R. Fronczek, K. M. Smith, R. Paolesse, *Inorg. Chem.* **2009**, *48*, 6879–6887.
- [5] L. Tortora, S. Nardis, F. R. Fronczek, K. M. Smith, R. Paolesse, *Chem. Commun.* **2011**, *47*, 4243–4245.
- [6] C. Capar, K. E. Thomas, A. Ghosh, *J. Porphyrins Phthalocyanines* **2008**, *12*, 964–967.
- [7] J. Capar, J. Zonneveld, S. Berg, J. Isaksson, K. J. Gagnon, K. E. Thomas, A. Ghosh, *J. Inorg. Biochem.* **2016**, *162*, 146–153.
- [8] The source of the *meso*-OH groups has not been investigated in this study. Earlier ^{18}O labeling studies on undecaarylisocorroles, however, strongly suggest that the OH group originates from atmospheric dioxygen as opposed to water.^[7]

- [9] a) K. E. Thomas, I. H. Wasbotten, A. Ghosh, *Inorg. Chem.* **2008**, *47*, 10469–10478; b) K. E. Thomas, J. Conradie, L.-K. Hansen, A. Ghosh, *Eur. J. Inorg. Chem.* **2011**, 1865–1870.
- [10] K. E. Thomas, C. M. Beavers, A. Ghosh, *Mol. Phys.* **2012**, *110*, 2439–2444.
- [11] Note that the addition of the 5-OH and 10-H occurs in a stereoselective manner, presumably reflecting the combined steric requirements of the various peripheral substituents.
- [12] I. H. Wasbotten, T. Wondimagegn, A. Ghosh, *J. Am. Chem. Soc.* **2002**, *124*, 8104–8116.

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