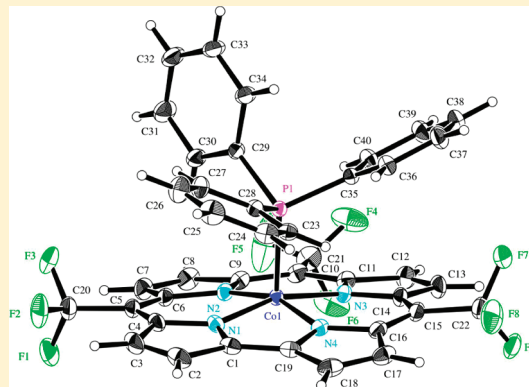


Corroles Cannot Ruffle

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S Supporting Information

ABSTRACT: X-ray structures of $\text{Co}^{\text{III}}[(\text{CF}_3)_3\text{Cor}](\text{PPh}_3)$ [$(\text{CF}_3)_3\text{Cor}$ = *meso*-tris(trifluoromethyl)corrolato] and $\text{Cu}[(\text{CF}_3)_4\text{Por}]$ [$(\text{CF}_3)_4\text{Por}$ = *meso*-tetrakis(trifluoromethyl)porphyrinato] revealed planar and highly ruffled macrocycle conformations, respectively, in line with analogous observations for a handful of other *meso*-perfluoroalkylated porphyrins and corroles reported in the literature. To gain insights into the difference in conformational behavior, we evaluated DFT (BP86-D/TZP) ruffling potentials for a variety of corrole complexes, as well as their porphyrin analogues. The calculations led us to conclude that corrole derivatives, in essence, cannot ruffle.



INTRODUCTION

Since corroles became available via one-pot syntheses some 15 years ago,¹ their chemistry has grown explosively and in certain respects has begun to rival that of their better known congeners, the porphyrins.² In our laboratory, we have focused on fundamental aspects of metallocorroles, particularly on the question of ligand noninnocence^{3,4} as well as on the substituent-sensitive electronic absorption spectra of certain metallocorroles.⁵ Recently, we have sought to better understand the structural chemistry of corroles, using a combined experimental⁵ (X-ray crystallography) and theoretical⁶ (mostly DFT, but also *ab initio*^{6d}) approach. One of our more interesting findings is that copper corroles, even sterically unhindered ones, are *inherently* saddled; i.e., the pyrrole rings are alternately tilted relative to the mean N_4 plane.⁵ In this study, we sought to find and characterize a *ruffled* corrole.

At present, the Cambridge Structural Database contains over 200 crystal structures of corrole derivatives, a rather small number compared to the number of structurally characterized porphyrins. Certain trends are nevertheless starting to emerge, which suggest, interestingly, that the structural chemistry of metallocorroles is rather different from that of metalloporphyrins. Thus, in contrast to porphyrins, for which significant non-planar distortions are common,⁷ the majority of metallocorroles exhibit essentially planar macrocycle frameworks (although the metal may reside somewhat outside the mean corrole plane).⁸ Several five-coordinate corrole complexes exhibit distinct doming,^{2,9} but strong saddling is rare, being largely limited to copper and silver corroles,^{5,10} and strong ruffling, where the pyrrole rings are alternately twisted about the $\text{M}-\text{N}$ bonds, is unknown.

Intrigued by this apparent difference between porphyrins and corroles, we set out to find an example of a ruffled corrole derivative. The most common factor that leads to ruffling in porphyrins is a small coordinated metal ion, most notably low-spin $\text{Ni}(\text{II})$, but also low-spin $\text{Fe}(\text{III})$.⁷ This, however, is not a productive approach to ruffled corroles, because nearly all metallocorroles already have short $\text{M}-\text{N}$ distances (~ 1.9 Å). Another strategy that leads to ruffling in porphyrins involves bulky *meso*-substituents such as *t*-butyl, trifluoromethyl, and other perfluoroalkyl groups. This is the approach we have chosen here for corroles, arguing that *meso*-tris(trifluoromethyl)corrole derivatives should be among the most likely to exhibit a ruffled macrocycle. Toward this end, we solved single-crystal X-ray structures of $\text{Co}^{\text{III}}[(\text{CF}_3)_3\text{Cor}](\text{PPh}_3)$ [$(\text{CF}_3)_3\text{Cor}$ = *meso*-tris(trifluoromethyl)corrolato] and $\text{Cu}[(\text{CF}_3)_4\text{Por}]$ [$(\text{CF}_3)_4\text{Por}$ = *meso*-tetrakis(trifluoromethyl)porphyrinato]. Although we failed to find any evidence of a ruffled corrole, the X-ray structures afford a number of insights into the structural chemistry of corroles. The experimental studies were also supplemented by extensive DFT calculations of porphyrin and corrole potential energy surfaces. Together, the experimental and computational results indicate that strong ruffling is virtually impossible for corrole derivatives.

RESULTS

The X-ray structure of $\text{Co}^{\text{III}}[(\text{CF}_3)_3\text{Cor}](\text{PPh}_3)$, shown in Figure 1a, reveals an essentially planar macrocycle. Except for an

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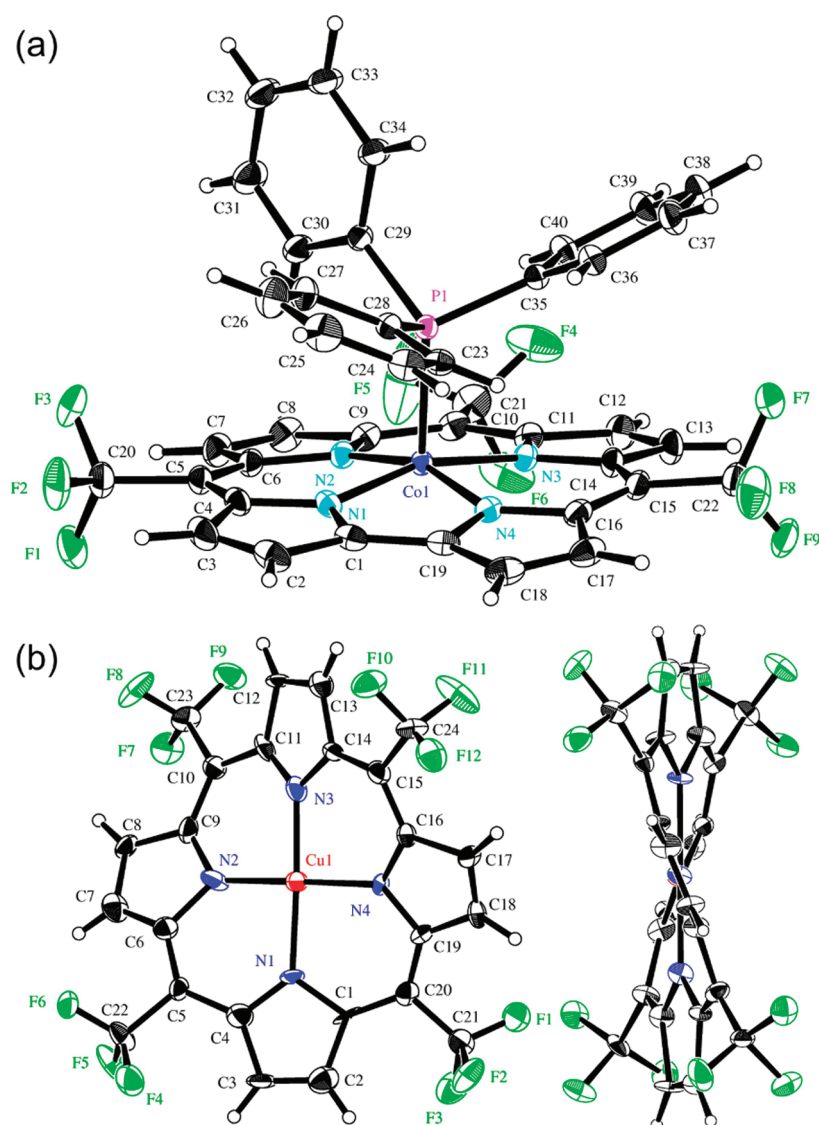


Figure 1. ORTEPs (20% thermal ellipsoids). (a) $\text{Co}^{\text{III}}[(\text{CF}_3)_3\text{Cor}](\text{PPh}_3)$. Distances (Å): Co–N1, 1.875(2); Co–N2, 1.8847(17); Co–N3, 1.886(2); Co–N4, 1.873(2); and Co–P, 2.2034(6). (b) $\text{Cu}[(\text{CF}_3)_4\text{Por}]$ (“top” and “side” views). Distances (Å): Cu–N1, 1.988(9); Cu–N2, 1.931(14); Cu–N3, 1.931(12); and Cu–N4, 1.977(10). Dihedrals (deg): C4–N1–N3–C11, $-44.6(16)$; C1–N1–N3–C14, $-39.6(15)$; C6–N2–N4–C19, $45.4(14)$; and C9–N2–N4–C16, $37.6(15)$.

interesting corrole–corrole stacking interaction (not shown), the structure is otherwise unremarkable. The X-ray structures of $\text{Re}[(\text{CF}_3)_3\text{Cor}](\text{O})$ ¹¹ and $\text{Ga}[(n\text{-C}_3\text{F}_7)_3\text{Cor}](\text{py})$ ¹² (py = pyridine) also exhibit planar corrole ligands, although the metal ions in these cases exhibit somewhat larger out-of-plane displacements. In contrast, the *meso*-perfluoroalkylated metalloporphyrin $\text{Zn}[(n\text{-C}_3\text{F}_7)_4\text{Por}](\text{py})$,¹³ as well as the β -octabrominated complex, $\text{Ni}[\text{Br}_8(n\text{-C}_3\text{F}_7)_4\text{Por}]$,¹⁴ features a strongly ruffled macrocycle, and the same is found here for $\text{Cu}[(\text{CF}_3)_4\text{Por}]$ (Figure 1b). Thus, seen from a porphyrin perspective, the absence of ruffling in $(\text{CF}_3)_3\text{Cor}$ complexes^{11,12} is striking.

These results suggest that ruffling is highly unfavorable for corroles, a conclusion that is fully supported by DFT calculations (see Experimental Section for details). Potential energy curves were obtained for ruffling and saddling by a series of constrained optimizations, where the ruffling or saddling dihedral (defined in Figure 2a) was constrained to specific values, while all other

geometry parameters were fully optimized. Figure 2b presents DFT ruffling potentials for $\text{Co}^{\text{III}}[\text{Cor}](\text{PH}_3)$, $\text{Co}^{\text{III}}[(\text{CF}_3)_3\text{Cor}](\text{PH}_3)$, $\text{Cu}(\text{Por})$, and $\text{Cu}[(\text{CF}_3)_4\text{Por}]$. The results confirm what is observed crystallographically: viz., whereas *meso*- CF_3 groups lead to a strongly ruffled minimum for a porphyrin, they fail to ruffle a metallocorrole.

Very small central ions such as Si^{IV} , P^{V} , and As^{V} lead to strong ruffling in porphyrins.¹⁵ For corroles, although a few P^{V} complexes have been synthesized,¹⁶ only one has been structurally characterized, viz., $[\text{P}(\text{EMC})(\text{OH})]\text{Cl}$, where EMC = 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole.^{16b} We therefore evaluated DFT ruffling potentials for $\text{P}(\text{Cor})\text{F}_2$, $[\text{P}(\text{Cor})(\text{OH})]^+$, $\text{As}(\text{Cor})\text{F}_2$, $[\text{As}(\text{Cor})(\text{OH})]^+$, and $[\text{P}(\text{Por})\text{F}_2]^+$ (Figure 2c), arguing that the corroles in this series should be among the most likely to exhibit ruffled conformations. A planar minimum, however, was found for each of the corrole derivatives, in agreement with the crystal structure of $[\text{P}(\text{EMC})(\text{OH})]\text{Cl}$, in

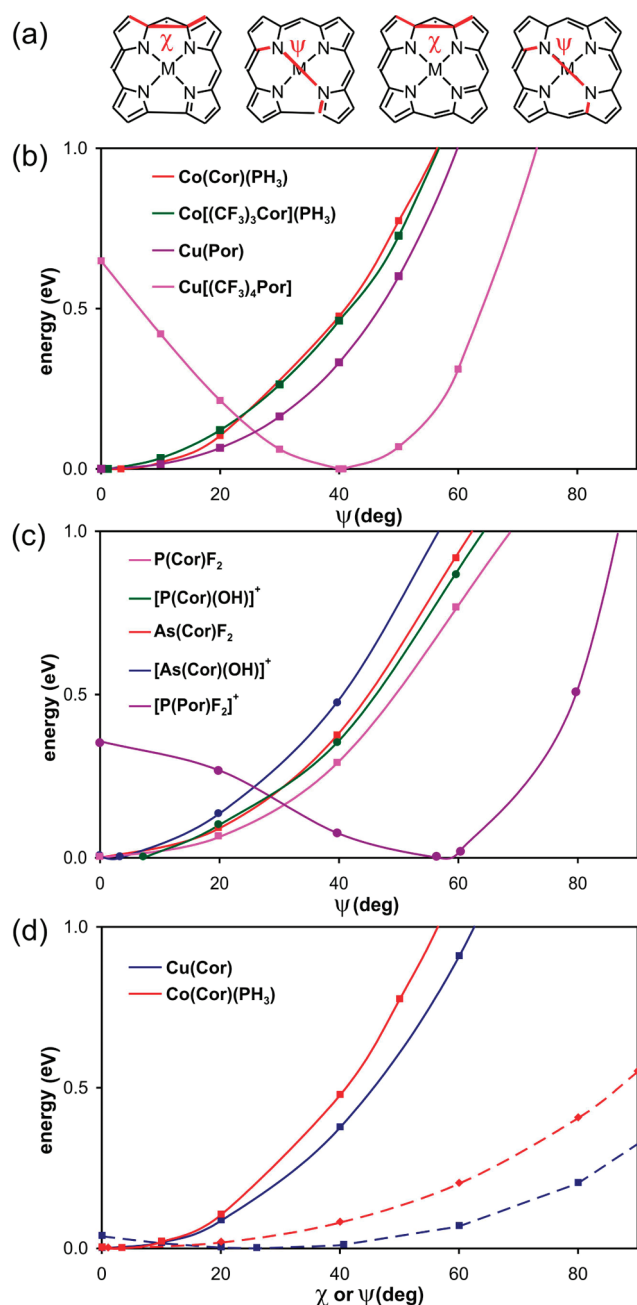


Figure 2. (a) Definition of ruffling (ψ) and saddling (χ) dihedrals. BP86-D/STO-TZP ruffling potentials for (b) Co and Cu porphyrins/corroles and for (c) P and As porphyrins/corroles. (d) Comparison of ruffling (solid lines) and saddling potentials (dotted lines).

contrast to $[P(Por)F_2]^+$, for which a highly ruffled geometry was obtained.¹⁵

To further exclude the possibility of ruffling in a metallocorrole, we also examined the bis-isocyanide complex $Fe^{III}(Cor)(PhNC)_2$. In analogous cationic iron(III) porphyrins, the axial isocyanide ligands strongly stabilize the two d_{π} orbitals, leading to a relatively unusual d_{xy}^1 ground state.¹⁷ Such d_{xy}^1 iron(III) porphyrins are generally strongly ruffled, because ruffling allows an otherwise symmetry-forbidden overlap between the iron d_{xy} orbital and the porphyrin a_{2u} HOMO. For $Fe^{III}(Cor)(PhNC)_2$, however, geometry optimization led to one of the isocyanide

ligands falling off the iron, and the remaining $Fe^{III}(Cor)(PhNC)$ complex had a relatively planar corrole ligand.

Finally, to obtain a “feel” for the energetics of ruffling versus saddling, we evaluated ruffling and saddling potentials for two different metallocorroles, $Cu(Cor)$ and $Co^{III}[Cor](PH_3)$. As shown in Figure 2d, for each molecule, the ruffling potential is much steeper than the saddling potential. Stated differently, corroles are much more deformable with respect to the saddling dihedral χ than with respect to the ruffling dihedral ψ (see Figure 2a).

DISCUSSION

The above results strongly suggest that corroles cannot ruffle, at least to any appreciable degree. To what extent is this conclusion supported by the more than 200 corrole crystal structures reported to date? A search of the Cambridge Structural Database did not reveal a single instance of a significantly ruffled corrole. In no case did the ruffling dihedrals exceed values of about 10° or so, compared with values of 30 – 50° that are routinely found for porphyrins. Nor did we find a case where the mean displacement of the corrole *meso* carbons above the N_4 plane exceeded 0.20 – 0.25 Å; indeed in an overwhelming majority of reported corrole crystal structures, the *meso* carbon displacements are far smaller. It is worth pointing out, however, that the term ruffling has occasionally been used simply to refer to any form of nonplanar distortion. Thus, although certain copper corroles have been described as ruffled, they are in fact better described as saddled. This is consistent with our proposal, now strongly supported by X-ray crystallography and DFT calculations, that copper corroles are *inherently* saddled.⁵ In other words, copper corroles are significantly saddled ($\chi = 30$ – 45°) even in the absence of sterically hindered substituents, although the latter do accentuate the saddling.

A final question worth considering is whether the very idea that strong ruffling is essentially impossible for corroles is a trivial one, a *fait accompli*. Given that ruffling involves pyramidalization of the C1–C19 bipyrrrole linkage (see Figure 1a for the atom numbering), it is not surprising, one might argue, that it is highly unfavorable. Indeed, mild pyramidalization of the bipyrrrolic double bond is observed for domed corroles; such pyramidalization, however, never translates to ruffling, i.e., alternate twisting of the pyrrole groups about the metal–nitrogen bonds. A similar argument might also be made for saddling, which entails twisting about the C1–C19 linkage, and yet medium to strong saddling is well-documented for copper corroles.^{5,16} Therefore, the finding that the energetic cost of saddling is considerably lower than that of ruffling (as shown in Figure 2d) is not trivial and, most likely, could not have been *a priori* predicted.

CONCLUSION

Combined use of X-ray structural studies and DFT calculations has proved to be a valuable approach in mapping out the structural chemistry of corroles,⁵ still a rather young field, relative to similar studies on porphyrins. In this work, based on the crystal structure of $Co^{III}[(CF_3)_3Cor](PPh_3)$ and a large set of DFT calculations inspired thereby, we have shown that strong ruffling is essentially impossible for corrole complexes. This is a negative but nontrivial conclusion; it is a major difference from porphyrin chemistry, where ruffling occurs widely and strongly modulates physical and chemical properties as well as biological function.⁷

With the above results in place, we are now in a position to comment on a large part of the conformational space of corrole complexes. The overall picture may be summarized as follows: (a) By and large, corrole complexes are relatively planar.² (b) Mild to moderate doming is also common for five-coordinate complexes.² (c) With a coordinated BHB group, even a kind of waved conformation has been observed,¹⁸ although this must be viewed as somewhat of a curiosity. (d) Saddling is uncommon, although copper corroles, which are inherently saddled, are an important exception. (e) Finally, as shown in this work, ruffling is impossible for corroles, except to a purely nominal degree.

EXPERIMENTAL SECTION

Materials. All reagents and solvents were used as purchased, except pyrrole, which was predried and distilled from CaH₂ at reduced pressure. 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 cm × 20 cm, 0.5 mm-thick, Merck) were used for final purification of the copper(II) tetrakis(trifluoromethyl)-porphyrin.

Instrumentation. Ultraviolet–visible spectra were recorded on an HP 8453 spectrophotometer with dichloromethane as the solvent. NMR spectra were recorded on a Mercury Plus Varian spectrometer (400 MHz for ¹H and 376 MHz for ¹⁹F) at room temperature in chloroform-*d*. Proton chemical shifts (δ) in parts per million were referenced to residual chloroform (δ = 7.2 ppm). Fluorine-19 chemical shifts (δ) in parts per million were referenced to 2,2,2-trifluoroethanol-*d*₃ (δ = −77.8 ppm). MALDI-TOF mass spectra were recorded on a Waters Micromass MALDI micro MX Mass Spectrometer using α-cyano-4-hydroxycinnamic acid (CHCA) as matrix.

Synthesis of Free-Base 5,10,15-Tris(trifluoromethyl)-corrole. *a. From Trifluoroacetaldehyde Hydrate.* Trifluoroacetaldehyde hydrate (ca. 75% in water, 467 μL, 6 mmol, *d* = 1.49 g cm^{−3}; Alfa Aesar, tech grade) and trifluoromethanesulfonic acid (17 μL, 0.2 mmol; Fluka, >99%) were introduced into a 25 mL round-bottomed flask in that order. Pyrrole (420 μL, 6 mmol; Merck) was added, upon which the mixture changed from colorless to pale yellow. The mixture was then heated to 80 °C within 1 h and stirred at this temperature for an additional 4 h. During this period, the mixture became orange and finally brown. The brown liquid was allowed to cool to room temperature and dissolved in 10 mL of CH₂Cl₂. DDQ (681 mg, 3 mmol, Fluka; dissolved in 10 mL THF) was added and the suspension stirred for 15 min. The reaction mixture was diluted with 20 mL of *n*-hexane and filtered through silica gel on a Büchner filter (3.5 × 5.5 cm) and further down with small volumes of 1:1 *n*-hexane/CH₂Cl₂. The brown filtrate obtained was evaporated, and the residue was subjected to column chromatography on silica gel (20 cm in length) with 9:1 *n*-hexane/CH₂Cl₂ as eluent (1100 mL). After 2–3 bands of green impurities, the free base corrole was collected as the third purple band. The purple eluate was evaporated, and the residue was crystallized from 1:1 hexane/CH₂Cl₂ to yield 6.6 mg (0.65%) of the free-base corrole as tiny needles. UV–vis (CHCl₃), λ_{max} (nm), [(log ε (M^{−1} cm^{−1}))]: 397 (4.89) and 403 (4.88), 497 (3.47), 537 (3.80), 550 (3.85), 598 (3.61). ¹H NMR: δ 1.30–1.15 (m, 4H, β-H); 0.87–0.78 (m, 4H, β-H). ¹⁹F NMR: δ −38.60 to −39.20 (broad). MS (MALDI-TOF, major isotopomer): [M + H]⁺ = 503.08 (expt), 503.09 (calcd). Elemental analysis: 52.58% C (calcd 52.60%), 2.09% H (calcd 2.21%), 11.15% N (calcd 11.15%).

b. From Trifluoroacetaldehyde Methyl Hemiacetal. Trifluoroacetaldehyde methyl hemiacetal (574 μL, 6 mmol, Alfa Aesar) and trifluoromethanesulfonic acid (17 μL, 0.2 mmol, Fluka, >99.0%) were introduced into a 50 mL round-bottomed flask in that order. After stirring for 5 min, pyrrole (420 μL, 6 mmol, Merck) was added and the

mixture heated to 80 °C over the course of an hour. Stirring was continued at this temperature for an additional 4 h. The brown liquid thus obtained was cooled to room temperature and dissolved in 10 mL of CH₂Cl₂. DDQ (454 mg, 2 mmol, dissolved in 10 mL THF) was added, and the suspension was stirred for 20 min. Workup and purification were carried out as in part a to yield 6.0 mg (0.60%) of the free-base corrole as tiny purple needles.

Synthesis of [5,10,15-Tris(trifluoromethyl)corrolato](triphenylphosphine)cobalt(III). Free-base 5,10,15-tris(trifluoromethyl)corrole (12.0 mg, 0.024 mmol) and anhydrous sodium acetate (44.7 mg, 0.526 mmol, 22 equiv) were dissolved in absolute ethanol (12.0 mL). After stirring for 5 min, Co(OAc)₂·4H₂O (44.7 mg, 0.179 mmol, 7.5 equiv) and triphenylphosphine (75.2 mg, 0.286 mmol, 12 equiv) were added in that order to the purple reaction mixture. Stirring was continued for an additional 20 min, when TLC indicated complete consumption of the free base. The reddish-brown reaction mixture was evaporated, and the residue was chromatographed on a silica gel column (31 cm × 3 cm) with 95:5 *n*-hexane/CH₂Cl₂ as eluent (700 mL) to yield the product as the first reddish-brown band. Yield: 14 mg (71.4%). Slow diffusion of a saturated benzene solution of the cobalt corrole into *n*-hexane gave brown X-ray quality crystals of Co^{III}[(CF₃)₃-Cor](PPh₃). UV–vis (CHCl₃), λ_{max} (nm), [(log ε (M^{−1} cm^{−1}))]: 369 (4.65) and 407 (4.75), 508 (3.71), 540 (3.64), 585 (3.97). ¹H NMR: δ 9.22–9.17 (m, 2H); 9.16–9.11 (m, 2H); 9.05 (d, 2H); 8.91–8.85 (m, 2H); 7.03–6.97 (qt, 3H, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.2 Hz, *para*-H of PPh₃); 6.63–6.55 (dt, 6H, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 3.2 Hz, *meta*-H of PPh₃); 4.28–4.18 (ddd, 6H, ³J_{HH} = 11.6 Hz, ⁴J_{HH} = 7.8 Hz, ⁵J_{HH} = 1.2 Hz, *ortho*-H of PPh₃). ¹⁹F NMR: δ −43.89 (t, 3F, ⁵J_{FF} = 3.0 Hz); −46.33 (t, 6F, ⁵J_{FF} = 2.6 Hz). MS (MALDI-TOF, major isotopomer): M⁺ = 819.21 (expt), 820.08 (calcd). Elemental analysis: 58.78% C (58.55% calcd), 2.75% H (calcd 2.83%), 6.81% N (calcd 6.83%).

Synthesis of [5,10,15,20-Tetrakis(trifluoromethyl)porphyrinato]copper(II). Trifluoroacetaldehyde hydrate (495 μL, 6 mmol), pyrrole (420 μL, 6 mmol), and trifluoromethanesulfonic acid (17 μL, 0.2 mmol, hissing upon addition) were introduced sequentially into a 25-mL round-bottomed flask. The mixture was heated to 75 °C over the course of an hour and allowed to stir for 4.5 h at this temperature. The orange-red gel thus obtained was allowed to cool to room temperature and then was dissolved in 5 mL of pyridine. Cu(OAc)₂·H₂O (600 mg, 3 mmol) was added to the red solution, and the mixture was stirred at 75 °C for 4 h. The resulting black viscous reaction mixture was evaporated. After the addition of 5 mL of CH₂Cl₂ (5 mL), the residue, now a slurry, was slowly vacuum-filtered through silica gel (3.5 cm thickness, 5.5 cm in diameter) on a Büchner funnel and washed down with 1:1 *n*-hexane/CH₂Cl₂. The purple and orange fractions of the filtrate were evaporated, and the residue thus obtained was chromatographed on a silica gel column (20 cm × 3 cm) with 5:1 *n*-hexane/CH₂Cl₂ as eluent, giving the copper porphyrin as the first purple eluate (15 mg). The last orange eluate after two additional purple impurity bands was the corresponding copper corrole (which is rather unstable and is not described here in depth). Further purification of the purple solid by preparative TLC with 4:1 *n*-hexane/CH₂Cl₂ as eluent yielded 13 mg (1.3%) of the pure copper porphyrin. Purple rectangular X-ray quality crystals were obtained by slow evaporation of a saturated CHCl₃ solution of the complex within 2–3 weeks. UV–vis (CHCl₃), λ_{max} (nm), [(log ε (M^{−1} cm^{−1}))]: 406 (5.28), 544 (3.84), 584 (4.27). MS (MALDI-TOF, major isotopomer): M⁺ = 642.86 (expt), 642.98 (calcd). Elemental analysis: 44.88% C (44.77% calcd), 1.21% H (calcd 1.25%), 8.62% N (calcd 8.70%).

Computational Methods. All calculations were carried out with the BP86¹⁹ exchange-correlation functional, with Grimme's dispersion corrections,²⁰ all as implemented in ADF 2009.²¹ An STO-TZP basis set was used throughout, as well as fine meshes for numerical integration of matrix elements and tight criteria for geometry optimization. Ruffling and saddling potentials were obtained via constrained optimizations,

where a given dihedral was constrained, while all other internal coordinates were optimized.

■ ASSOCIATED CONTENT

S Supporting Information. Details of synthesis, characterization, and X-ray analysis and CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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