Graphical abstract

Improved synthetic protocols are presented for several free-base β -octabromo-*meso*-tris(*p*-X-phenyl)corroles (X = CF₃, NO₂, F, H, CH₃, and OCH₃), along with a synthesis of the heretofore inaccessible free-base β -octabromo-*meso*-tris(2,6-dichlorophenyl)corrole. The latter has also been complexed to provide the first iron octabromocorrole derivatives.

*Bioinorganic methods*Improved syntheses of β -octabromo-*meso*-triarylcorrole derivatives

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Abstract. In spite of significant applications as starting materials for a variety of metallocorrole derivatives, free-base β -octabromo-*meso*-triarylcorroles continue to be viewed as inaccessible. The reasons range from the need for tedious column-chromatographic purification to limitations of the reductive demetallation protocol for selected systems. Here we report that column chromatography may be entirely avoided for a number of β -octabromo-*meso*-tris(*p*-X-phenyl)corrole derivatives, where X = CF₃, NO₂, F, H, CH₃, and OCH₃; instead, analytically pure products may be obtained by recrystallization from chloroform/methanol. In addition, we have presented an optimized synthesis of the heretofore inaccessible, sterically hindered ligand β -octabromo-*meso*-tris(2,6-dichlorophenyl)corrole, H₃[Br₈TDCPC], via reductive demetallation of the corresponding Mn(III) complex. With our earlier report of tris(pentafluorophenyl)corrole, H₃[Br₈TPFPC], a comprehensive set of optimized synthetic protocols are thus in place for a good number of β -octabromo-*meso*-triarylcorrole ligands. Furthermore, we have illustrated the use of these ligands by synthesizing the iron complexes Fe[Br₈TDCPC]Cl and Fe[Br₈TDCPC](py)₂, of which the latter lent itself to single-crystal X-ray structure determination.

Introduction. Over a decade has elapsed since copper β -octabromo-*meso*-tris(*p*-X-phenyl)corroles, Cu[Br₈TpXPC] (X = CF₃, H, CH₃, OCH₃), were synthesized via direct bromination of β -unsubstituted copper triarylcorroles, Cu[TpXPC].¹ Subsequently, the reductive demetallation method also afforded octabrominated free-base corroles, H₃[Br₈TpXPC] (Figure 1).^{2,3} Since then, both copper and free-base octabromocorroles have seen important applications.⁴ Thus, the copper complexes have been derivatized to copper β -octakis(trifluoromethyl)-*meso*-triarylcorroles, Cu[(CF₃)₈TpXPC],⁵ and to copper undecaarylcorroles,⁶ both by means of palladium coupling reactions. The octabrominated free-base corroles were used to synthesize the first gold^{7,8} corroles and also unique diboron corroles,⁹ the latter differing markedly with respect to both chemical structure and conformation from β -unsubstituted diboron corroles.¹⁰ Despite these significant advances, applications of β -octabromo-*meso*-triarylcorroles have languished for a variety of reasons. In this study, we have addressed some of these problems and present protocols providing greatly improved access to several of these ligands.

Figure 1. Standard synthetic route to β -octabromo-*meso*-tris(*p*-X-phenyl)corrole derivatives.

Tedious column-chromatographic purification, a common bane of porphyrin chemistry, is also a problem for both $\text{Cu}[\text{Br}_8\text{TpXPC}]$ and $\text{H}_3[\text{Br}_8\text{TpXPC}]$ derivatives. A key result of this study is that, for $\text{X} = \text{CF}_3$, NO_2 , F , H , CH_3 , and OCH_3 , column chromatography may be largely or entirely averted, with analytically pure products obtained simply via recrystallization. Detailed protocols are given below for $\text{Cu}[\text{Br}_8\text{TPC}]$ and $\text{H}_3[\text{Br}_8\text{TPC}]$ (TPC = *meso*-triphenylcorrole).

Another difficulty in this area is that the original reductive demetallation procedure fails for certain copper β -octabromocorroles. Thus, we failed to efficiently demetallate copper tris(pentafluorophenyl)corrole, $\text{Cu}[\text{TPFPFC}]$, and its β -octabromo derivative, $\text{Cu}[\text{Br}_8\text{TPFPFC}]$. Taking a cue from another early demetallation protocol by Chang and coworkers,¹¹ where manganese corroles were demetallated with $\text{SnCl}_2/\text{CH}_2\text{Cl}_2/\text{HCl}$, we successfully demetallated $\text{Mn}[\text{Br}_8\text{TPFPFC}]$ in up to 86% yield.³ Recently, we have also reported a high-quality single-crystal X-ray structure of the free base $\text{H}_3[\text{Br}_8\text{TPFPFC}]$.¹²

In the same vein, Dehaen and coworkers failed to cleanly demetallate copper β -octabromo-*meso*-tris(2,6-dichlorophenyl)corrole, $\text{Cu}[\text{Br}_8\text{TDCPC}]$, with SnCl_2/HCl in 2:1 acetonitrile/dichloromethane, obtaining partially debrominated free-base corroles instead.¹³ The same conditions did lead to demetallation of $\text{Cu}[\text{Cl}_8\text{TDCPC}]$, albeit in poor yield (20%).¹³ Thus, as of today, the highly desirable, sterically hindered ligand $\text{H}_3[\text{Br}_8\text{TDCPC}]$ has not been reported. Here we report an optimized protocol for the synthesis of this ligand via demetallation of the corresponding manganese complex, $\text{Mn}[\text{Br}_8\text{TDCPC}]$, which has been recently reported by Gross and coworkers (Figure 2).¹⁴

Figure 2. Synthesis of free-base and iron Br₈TDCPC derivatives.

Finally, to illustrate the use of H₃[Br₈TDCPC] as a ligand, we describe its conversion to two iron complexes – Fe[Br₈TDCPC]Cl and Fe[Br₈TDCPC](py)₂ (py = pyridine; see Figure 2). These are the first examples of iron β -octabromocorroles. The latter complex also lent itself to single-crystal X-ray structure determination, as described below.

Experimental section. Materials. Unless otherwise mentioned, all reagents and solvents were obtained from Sigma-Aldrich. Silica gel (DAVISIL[®] LC150A 35-70 μ m) was used as the stationary phase in all flash chromatographic purification. The β -unsubstituted free bases H₃[TpXPC]¹⁵ and H₃[TDCPC]¹⁵ and the corresponding copper complexes¹ were prepared as previously described. The Cu complexes Cu[TDCPC] and Cu[Br₈TDCPC] were synthesized according to Dehaen and coworkers.¹³ The Mn complexes Mn[TDCPC]¹⁶ and Mn[Br₈TDCPC]¹⁴ were synthesized according to procedures reported by Gross and coworkers. The analytical data for all known compounds mentioned below were fully consistent with published literature values.^{1,15}

Instrumentation. UV-visible spectra were recorded on an HP 8453 spectrophotometer. All NMR spectra (400 MHz for ¹H and 376 MHz for ¹⁹F) were recorded on a Mercury Plus Varian spectrometer at 298K in THF-*d*₈. The ¹H NMR spectra were referenced to $\delta = 3.58$ ppm (residual protons in THF-*d*₈) and the ¹⁹F NMR spectra were referenced to 2,2,2-trifluoroethanol-

d_3 ($\delta = -77.8$). High Resolution Mass Spectra (HRMS) were recorded on an LTQ Orbitrap XL spectrometer.

Synthesis and purification of Cu[Br₈TPC]. The synthetic procedure employed is slightly modified relative to that reported earlier.¹ To Cu[TPC] (0.105 g, 0.179 mmol) dissolved in CHCl₃ (50 mL) was added dropwise a solution of 275 μ L (5.34 mmol) of liquid bromine dissolved in CHCl₃ (20 mL) over a period of 30-40 minutes, followed by stirring for 1 h, all at room temperature. Pyridine (474 μ L) dissolved in CHCl₃ (20 mL) was then added dropwise over a period of 30-40 minutes, followed by stirring for an additional hour. The reaction was stopped by washing the reaction mixture twice with 20% w/v sodium metabisulfite (Na₂S₂O₅, 90 mL). The organic layer was dried with anhydrous sodium sulfate, filtered, and rotary-evaporated to dryness. The entire procedure was repeated 5 times.

The crude Cu[Br₈TPC] thus obtained could be purified with column chromatography on silica gel, with eluents of gradually increasing polarity, ranging from 1:1 CH₂Cl₂/hexane through pure CH₂Cl₂ to pure CHCl₃. Evaporation of the brown bands resulted in a 52% yield of Cu[Br₈TPC]. In all, the column chromatography required about 1 L of CH₂Cl₂ and 2 L of CHCl₃.

The time-consuming and solvent-wasting nature of the column chromatography prompted us to investigate recrystallization as an alternative method of purification. In the final, successful protocol, crude Cu[Br₈TPC], obtained from all 5 preparations, was combined and redissolved in a minimum volume of CHCl₃ and layered with an equal volume of methanol. The precipitated Cu[Br₈TPC] was filtered after 1-2 days, washed with methanol, and dried to give a combined yield of 0.556 g of the final product (51% relative to 0.525 g Cu[TPC], i.e. from all 5 batches). Although this product is suitable for further chemical transformations, a second recrystallization was carried out to yield 0.505 g of analytically pure product (46% relative to 0.525 g Cu[TPC]), which was characterized as previously reported.^{1,15}

Synthesis and purification of H₃[Br₈TPC]. Demetallation of Cu[Br₈TPC] was carried out essentially according to the original literature procedure for reductive demetallation.² A 50-mL round-bottomed flask equipped with a magnetic stirrer was charged with Cu[Br₈TPC] (63 mg, 0.052 mmol) and anhydrous FeCl₂ (31.1 mg, 0.245 mmol). Concentrated H₂SO₄ (2 mL) was added dropwise under stirring. The solution was alternately stirred for 30 min and sonicated for 30 min for a total of 2 h. The reaction mixture was then quenched with distilled water, washed 3-4 times with saturated aqueous NaHCO₃, and extracted with CHCl₃. The organic phase was dried with anhydrous Na₂SO₄ and filtered and the filtrate was rotary-evaporated to dryness.

The original method of purification involved column chromatography with 1:1 CH₂Cl₂/hexane as eluent.² This process was both tedious and required large quantities of solvent. In the new method, crude H₃[Br₈TPC] was dissolved in a minimum volume of CHCl₃ and layered with an equal volume of methanol. After standing for 1-2 days, the solution was filtered to yield purified H₃[Br₈TPC] in 53% yield (32 mg). A second recrystallization yielded the analytically pure free base (29 mg), which was characterized as previously reported.^{1,15}

*Synthesis and purification of para-substituted Cu[Br₈TpXPC] (X = CH₃, OCH₃, CF₃ and F).*¹ Copper β -octabromo-meso-triarylcorroles with *para*-X-substituted *meso* aryl groups could also be effectively purified by the recrystallization method described above. The optimum CHCl₃/methanol ratios, however, varied somewhat with X, being 1:2 for X = F and 1:3 for X = CH₃, OCH₃, and CF₃. The times required for crystallization were also somewhat longer, i.e. at least 2 days, compared with Cu[Br₈TPC].

For X = NO₂, exposure to methanol led to decomposition of the Cu[Br₈T(*p*-NO₂-P)C]. Fortunately, recrystallization could be achieved over a period of 2 days by layering a saturated CHCl₃ solution with an equal volume of hexane.

Full spectroscopic details of the Cu[Br₈TpXPC] derivatives with X = F and NO₂ have not been published to date and accordingly are presented below.

Characterization of Cu[Br₈TpFPc]. Yield 72%. UV-vis (CH₂Cl₂): λ_{max} , nm ($\epsilon \times 10^{-4}$, M⁻¹cm⁻¹): 445 (10.19), 649 (0.65). ¹H NMR: δ 7.58 (dd, 4H, 5,15-*o* or -*m*, 4-FPh), 7.52 (dd, 2H, 10-*o* or -*m*, Ph), 7.28 – 7.17 (overlapping triplets, 4H, *J* = 8.8 Hz, 5,15-*m* or -*o* and 2H, *J* = 8.8 Hz, 10-*m* or -*o* Ph). ¹⁹F NMR (THF-*d*₈): δ -110.81 to -110.93 (m, 1F, 10-*p*-F, Ph); -110.99 to -111.11 (m, 2F, 5,15-*p*-F, Ph). MS (ESI⁻, major isotopomer): M⁻ = 1271.3785 (expt), 1271.3706 (calcd).

Characterization of Cu[Br₈TpNO₂PC]. Yield 98.5%. UV-Vis (CH₂Cl₂): λ_{max} , nm ($\epsilon \times 10^{-4}$, M⁻¹cm⁻¹): 439 (7.15), 644 (0.67). ¹H NMR: δ 8.36 (d, 4H, ³*J* = 8Hz, 5,15-*m* or -*o*, 4-NO₂Ph); 8.31 (d, 2H, ³*J* = 8Hz, 10-*m* or -*o*, 4-NO₂Ph); 7.82 (d, 4H, ³*J* = 8 Hz, 5,15-*o* or -*m*, 4-NO₂Ph); 7.76 (d, 2H, ³*J* = 8Hz, 10-*o* or -*m*). MS (ESI⁻, major isotopomer): [M]⁻ = 1352.3518 (expt), 1352.3542 (calcd). Elemental analysis: 33.23% C (calcd 32.84%), 1.22% H (calcd 0.89%), 7.49% N (calcd 7.24%).

Recrystallization of H₃[Br₈TpXPC]. Purification of the *para*-substituted free bases H₃[Br₈TpXPC] by means of recrystallization was somewhat less efficient, relative to H₃[Br₈TPC]. A good strategy leading to analytically pure octabromocorrole free bases involved

an initial column chromatography followed by crystallization from CHCl_3 /methanol (or CHCl_3 /hexane), as described above.

Synthesis of $\text{H}_3[\text{Br}_8\text{TDCPC}]$. Two different syntheses of $\text{H}_3[\text{Br}_8\text{TDCPC}]$ are described below, with the first clearly much more successful than the second.

Demetallation of $\text{Mn}[\text{Br}_8\text{TDCPC}]$. Into a 25-mL round-bottomed flask were placed $\text{Mn}[\text{Br}_8\text{TDCPC}]$ (20 mg, 0.014 mmol) and 10 equiv anhydrous FeCl_2 (17.9 mg, 0.14 mmol, Sigma-Aldrich). Concentrated H_2SO_4 (95-97%, 2.5 mL, Merck) was added. The mixture was then stirred at room temperature. The progress of the reaction was monitored by taking very small amounts of the reaction mixture into a small vial, adding distilled water, extracting with CH_2Cl_2 , washing once with saturated aqueous NaHCO_3 , and monitoring with UV-vis spectroscopy, followed by TLC and comparing with the starting material. After 1.5 h, the reaction was quenched by carefully pouring the mixture into distilled H_2O (300 mL), followed by extraction with CH_2Cl_2 . The green organic phase was washed once with distilled water and then twice with saturated aqueous NaHCO_3 . The organic phase was dried with anhydrous Na_2SO_4 and filtered and the filtrate was rotary-evaporated to dryness. The residue was chromatographed on a silica gel column with *n*-hexane/ CH_2Cl_2 (5:1, followed by 1:1) as eluent to afford the pure free base. Yield: 14.45 mg (75%). UV-vis (CH_2Cl_2) λ_{max} , nm ($\epsilon \times 10^{-4}$, $\text{M}^{-1}\text{cm}^{-1}$): 441 (4.70), 590 (0.73), 624 (0.49), 677 (0.42). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.56-7.66 (m, 9H, aryl), 0.85 (brs, 3H, NH). MS (HR-ESI, major isotopomer): $[\text{M}]^+ = 1364.27$ (expt), 1364.26 (calcd).

Demetallation of $\text{Cu}[\text{Br}_8\text{TDCPC}]$. Into a 25-mL round-bottomed flask were placed $\text{Cu}[\text{Br}_8\text{TDCPC}]$ (5.5 mg, 0.00386 mmol) and 5 equiv of anhydrous FeCl_2 (2.45 mg, 0.0193 mmol, Sigma-Aldrich). Concentrated H_2SO_4 (95-97%, 2 mL, Merck) was added. The mixture was alternately stirred and sonicated at 50 °C. The progress of the reaction was monitored by UV-vis spectroscopy. After 4 h the reaction mixture was cooled down to r. t. and the reaction was quenched by pouring the mixture into 300 mL distilled H_2O , then extracted with CH_2Cl_2 . The green organic phase was washed once with distilled water and then twice with saturated aqueous NaHCO_3 . The organic phase was dried with anhydrous Na_2SO_4 , filtered and rotary-evaporated to dryness. The residue obtained was chromatographed on a silica gel column first with 5:1 *n*-hexane/ CH_2Cl_2 to get the recovered $[\text{Cu}[\text{Br}_8\text{TDCPC}]$, then with 2:1 *n*-hexane/ CH_2Cl_2 to collect 0.7 mg of the pure free-base in 14% yield.

Synthesis of Fe[Br₈TDCPC]Cl. Iron insertion into free-base H₃[Br₈TDCPC] was carried out essentially according to the procedure reported by Gross and coworkers.^{17,18} Free-base H₃[Br₈TDCPC] (0.030 g, 0.022 mmol) and anhydrous FeCl₂ (0.056 g, 0.44 mmol, 20 equiv) were dissolved in dry DMF (25 mL) under argon. The mixture was heated to reflux and the reaction mixture was monitored by thin-layer chromatography. After the solution had been refluxed for 40 min, no more starting material was detected with thin-layer chromatography and heating was discontinued. Upon cooling to room temperature, the reaction mixture was rotary evaporated to dryness. The residue was dissolved in diethyl ether and chromatographed on a short column of silica gel with diethyl ether as eluent. After the evaporation of the diethyl ether, the product was dissolved in CH₂Cl₂, washed twice with 2.0 M aqueous HCl, and then twice with water. The organic phase was dried with anhydrous Na₂SO₄, followed by rotary evaporation of the solvent. After chromatography on a short column of silica gel with CH₂Cl₂ as eluent, pure Fe[Br₈TDCPC]Cl was obtained in 92% yield (0.029 g, 0.020 mmol). UV-vis (CH₂Cl₂) λ_{max} , nm ($\epsilon \times 10^{-4}$, M⁻¹cm⁻¹): 419 (4.31), 566 (0.68). ¹H NMR (400 MHz, CDCl₃) δ 10.56 (s, 1H, 10-*para*), 9.16 (s, 4H, 5,15-*meta*), 8.32 (s, 2H, 5,15-*para*), -4.52 (s, 2H, 10-*meta*). MS (HR-ESI, major isotopomer: [M – Cl]⁺ = 1416.30 (expt), 1416.29 (calcd).

Synthesis of Fe[Br₈TDCPC](py)₂. Iron insertion was carried out exactly as described above for Fe[Br₈TDCPC]Cl. Thus, free-base H₃[Br₈TDCPC] (0.030 g, 0.022 mmol) and anhydrous FeCl₂ (0.056 g, 0.44 mmol, 20 equiv) were dissolved in dry DMF (25 mL) under argon. The reaction mixture was heated to reflux and monitored by TLC. Heating was discontinued after no more starting material could be detected by TLC, in about 40 min. After rotary evaporation of the solvent, the residue was dissolved in diethyl ether and chromatographed on a short column of silica gel with diethyl ether as eluent. The iron-corrole dietherate (characterized only by means of mass spectrometry) thus obtained was dissolved in a minimum volume of diethyl ether/*n*-heptane containing a few drops of pyridine. Crystallization over several hours led to Fe[Br₈TDCPC](py)₂ in 90% yield (0.031 g, 0.0198 mmol). X-ray quality crystals were obtained by recrystallization of Fe[Br₈TDCPC](py)₂ by diffusion of *n*-heptane into a concentrated benzene solution (over 3-4 weeks). UV-vis (CH₂Cl₂): λ_{max} , nm ($\epsilon \times 10^{-4}$, M⁻¹cm⁻¹) 425 (6.71), 573 (1.14), 780 (0.37). ¹H NMR (400 MHz, CDCl₃): δ 9.59 (s, 2H), 7.61 (s, 4H), 7.41 (s, 3H). (The axial pyridines exhibited complex dynamic behavior in the ¹H NMR and could not be readily assigned.) MS (HR-ESI, major isotopomer): [M]⁺ = 1575.26 (expt), 1575.49 (calcd).

X-ray structure determination of Fe[Br₈TDCPC](py)₂. X-ray data were collected on beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. A 115 x 110 x 10 μm^3 green plate 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 an APEXII CCD detector. Diffraction data were collected for synchrotron radiation monochromated with silicon(111) to a wavelength of 0.9322(1) Å. An approximate full-sphere of data was collected with 0.3° ω scans. The structure was 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. Key crystal data are as follows. Empirical formula: C_{56.44}H_{33.05}Br₈Cl₆FeN₆; formula weight: 1703.04. Crystal system: monoclinic. Space group P2₁/n. Unit cell dimensions: $a = 16.316(5)$ Å, $b = 18.168(5)$ Å, $c = 19.625(6)$ Å, $\alpha = 90^\circ$, $\beta = 94.533(4)^\circ$, $\gamma = 90^\circ$, and $V = 5799(3)$ Å³. Reflections collected: 40077; independent reflections: 6091 [R(int) = 0.0858]. Final R indices [I > 2 σ (I)]: R1 = 0.0597, wR2 = 0.1207. R indices (all data): R1 = 0.0969, wR2 = 0.1388. Additional details may be obtained from the crystallographic information file provided as Supporting Information.

Discussion. Our key findings may be summarized as follows.

Even by the standards of porphyrin and corrole chemistry, where column chromatography is the standard method of purification, the column chromatography of many Br₈TpXPC derivatives is unusually tedious.² The compounds ‘tail’ badly and accordingly purification demands both long times and prodigious quantities of solvent. In the new protocols outlined above, we have completely averted column-chromatographic purification for all Cu[Br₈TpXPC] (X = CF₃, NO₂, F, H, CH₃, and OCH₃) derivatives. Recrystallization was found to work effectively for all such complexes, saving a lot of both time and solvent. Recrystallization was also found to be valuable for the purification of the corresponding free bases H₃[Br₈TpXPC].

We have presented optimized procedures for the synthesis of the new, sterically hindered free-base corrole, H₃[Br₈TDCPC], and for its complexation to iron. The two iron complexes reported are the first examples of iron octabromocorroles. Applications in areas such as biomimetic catalysis of atom and group transfer reactions may now be expected.¹⁹ A few interesting physical properties of the new iron complexes are pointed out below.

Extensive ^1H NMR, DFT and *ab initio* computational studies have established that FeCl triarylcorroles are generally best described as an intermediate-spin $S = 3/2$ Fe(III) center antiferromagnetically coupled to a corrole $^{\bullet 2-}$ radical leading to an overall $S = 1$ ground state.^{20,21,22,23,24} Walker and coworkers, however, have emphasized that the nature of the spin coupling is sensitive to the displacement of the iron above the corrole N_4 plane. Thus, for the undecasubstituted complex octamethyltriphenylcorrolatoiron chloride, $\text{Fe}[\text{Me}_8\text{TPC}]\text{Cl}$, the spin coupling is ferromagnetic, leading to an unusual $S = 2$ ground state. **At this point, the spin state of $\text{Fe}[\text{Br}_8\text{TDCPC}]\text{Cl}$ (i.e., $S = 1$ or 2) has not been determined; such a determination will be carried out and reported in due course.**

Figure 3 depicts the thermal ellipsoid plot for $\text{Fe}[\text{Br}_8\text{TDCPC}](\text{py})_2$. The Fe-N distances involving the anionic corrole nitrogens, averaging around 1.91 Å, are shorter than those involving the axial pyridines, which average around 2.02 Å. These distances are typical of low-spin Fe(III) complexes with all-nitrogen coordination and similar to those found for $\text{Fe}[\text{TDCPC}](\text{py})_2$. An interesting feature of the present structure is that the 2,6 C-H bonds on the axial pyridines act as hydrogen bond donors toward the chlorines of the 5,15-dichlorophenyl groups. As shown in Figure 4, the $\text{C-H}\cdots\text{Cl}$ hydrogen bond distances all lie in the range 3.54-3.82 Å. Despite the low energies associated with such interactions, the presence of four such interactions per molecule apparently stabilize the observed conformation, where the two axial pyridines and the 5,15-dichlorophenyl groups are all roughly coplanar.

Figure 3. Thermal ellipsoid plot for $\text{Fe}[\text{Br}_8\text{TDCPC}](\text{py})_2$. Selected distances: Fe1-N1 1.893(9) Å; Fe1-N2 1.934(10) Å; Fe1-N3 1.930(9) Å; Fe1-N4 1.884(10) Å; Fe-N_{py} 2.032(9) Å.

Figure 4. C-H...Cl hydrogen bonding interactions in $\text{Fe}[\text{Br}_8\text{TDCPC}](\text{py})_2$.

Concluding remarks. As a result of this work, improved syntheses are now available that afford near-gram quantities of several free-base β -octabromo-*meso*-triarylcorroles, including $\text{H}_3[\text{Br}_8\text{TpXPC}]$ ($\text{X} = \text{CF}_3$, NO_2 , F , H , CH_3 , and OCH_3) and ~100 mg of the sterically hindered ligand $\text{H}_3[\text{Br}_8\text{TDCPC}]$. To this list may be added the perhalogenated ligand $\text{H}_3[\text{Br}_8\text{TPFPC}]$, which we reported in our earlier work.³ Furthermore, we have illustrated the use of these ligands by synthesizing the first iron octabromocorroles. We look forward to seeing additional applications of these ligands in the synthesis of new reagents, catalysts, and materials with novel properties.

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