Corroles That "Click": Modular Synthesis of Azido- and Propargyl-Functionalized Metallocorrole Complexes and Convergent Synthesis of a Bis-corrole Scaffold

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Ⓢ Supporting Information

ABSTRACT: Bis-corroles have been prepared through a convergent synthesis using a copper-catalyzed azide−alkyne cycloaddition. Synthesis of the final homo- and heterobimetallic complexes has been achieved in three to four steps from commercially available materials in good overall yield. *Meso*-substituted corroles functionalized with a single azido or propargyl group were used as key starting materials. $(C_6F_5)_2(p$-$O(CH_2CCH)Ph)$corroleH$_3$ (**1**) and $((C_6F_5)_2(m$-$CH_2N_3)Ph)$-corroleH$_3$ (**3**) were metalated with copper or iron and attached by Huisgen azide−alkyne cycloaddition ("click" reaction) first to small substrates and then to each other, demonstrating a convergent synthesis of bimetallic bis-corrole molecules.
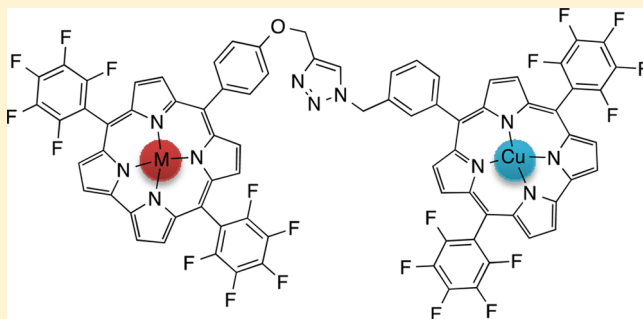
INTRODUCTION

Interest in conjugated metallomacrocycles has rapidly increased in recent years, due to their close analogy to biological porphyrinoid systems and their potential application to real-world problems. Lanthanide phthalocyanines have exhibited single-molecule magnetism that may prove useful in molecular switches.[1−5] Porphyrins have been used recently as high-quantum-yield sensitizers in solar cells,[6] in nonlinear optics,[7] and in molecular-scale electroluminescence,[8] among many other applications. While less studied than their 20-membered-ring counterparts, metallocorrole complexes[9] have demonstrated excellent activity as oxygen reduction catalysts with potential applications in fuel cells,[10−13] as well as other catalytic activity for small-molecule/ion activation[14,15] and detection of environmental toxins.[16,17] Additionally, iron corroles have been shown to catalytically lower cholesterol levels and may be used to prevent heart disease,[18] in addition to both gallium and phosphorus corroles being used as fluorescent reporters for tumor detection and treatment due to their high quantum yields.[19,20]

As potential applications of conjugated macrocycles and their metal complexes become increasingly prevalent, the question of how to practically incorporate these molecules into devices, drugs, and sensors is often what limits the next step in their development. Unattached small-molecule catalysts are impractical in a fuel cell or battery and need to be affixed to an electrode; interest in the use of corrole as an oxygen reduction

catalyst was an early motivator for this research.[11] Imaging agents and metal-based drugs are more effective if attached to a biomolecule that provides targeted delivery to the site of interest.[21] Methods for covalently attaching corroles to other substrates have been reported in the literature,[22] but none have seen widespread application.

Huisgen azide−alkyne cycloaddition,[23−25] or "click" chemistry, has demonstrated utility both in surface attachment of small molecules[26−31] and in targeted delivery in biological systems.[30,32−35] In particular, both surfaces and biomolecules are easily functionalized with azido groups, and so couplings with alkynyl-functionalized small molecules are of great utility.[36−40] The reaction takes place under mild conditions and is tolerant of a wide range of functional groups. This makes it ideal for attachment reactions of porphyrinoids, which are often fragile with regard to strongly oxidizing conditions. The fact that the "click" reaction, when optimized, occurs in quantitative yield is also an important attribute, considering both the possibility of unreacted starting materials compromising device functionality and the high value of porphyrinoids as a substrate. Indeed, several examples of azido- and alkynyl-functionalized porphyrins have been used for click reactions in the literature.[41−44] Further examples also exist where porphyrinoids have been attached to a surface by way of a

"clicked" axial ligand.[42] One example of a corrole functionalized with an azido group was reported in 2005 as a synthetic intermediate;[45] this corrole has very recently been metalated with gallium and attached to a BODIPY dye by way of Huisgen azide−alkyne cycloaddition to demonstrate bidirectional fluorescence resonance energy transfer.[46] In addition, one example of a corrole-functionalized with an alkynyl group has been reported;[47,48] while it was not used for "click" chemistry, this species was used for a cross-coupling reaction between corrole and coumarin units in order to study the optical properties of the dyad.

One of the major advantages of the Gryko "A₂B" synthesis of corroles[49] is that it allows more straightforward access to conjugated macrocycles with a single *meso* substituent with unique properties. In contrast, porphyrins with one unique *meso* substituent[50] (*meso*-substituted A₃B porphyrins) are often prepared by statistical synthesis, and existing examples of alkynyl-substituted porphyrins have multiple alkynyl groups,[41] creating the potential for a complex mixture of molecular environments when these are attached to a surface.

Preparation of bisporphyrinoids is similarly challenged by the use of statistical syntheses and is further plagued by compounding low yields. Although several groups have prepared interesting bis-corrole, bis-porphyrin, and porphyrin−corrole bimetallic complexes and demonstrated their activity as small-molecule activation catalysts,[10,51,52] the reported yields are poor. In these unique cases the rigid backbone of these complexes is important to their reactivity and may not allow for the use of "click" chemistry. However, convergent synthesis where two corroles are assembled separately and then attached gives much better overall yields, as well as allowing for separate coordination of two different metals to produce a heterobimetallic complex.

Here we present the synthesis of two corrole ligands functionalized with propargyl and azido groups, respectively. These corroles are metalated with copper and iron and then attached to small-molecule test substrates by Huisgen azide−alkyne cycloaddition as a proof of concept. Finally, homobimetallic (Cu₂) and heterometallic (CuFe) bis-corrole molecules are prepared in good yields by the same "click" reaction.

■ EXPERIMENTAL SECTION

General Considerations. Reactions were performed either using standard Schlenk and N₂-atmosphere glovebox techniques or under ambient conditions on the laboratory bench, as noted. As much as possible, flasks for synthesis were covered with aluminum foil to reduce exposure to light throughout the procedures. When required, solvents were dried by passing through a column of activated alumina and degassed with nitrogen[53] or using a Phoenix solvent drying system commercially available from JC Meyer Solvent Systems.

Purity of products was estimated by NMR spectroscopy, assuming that aliphatic impurities, when not identifiable, had a molecular weight of 100 and that a peak integrating to 1 in the ¹H NMR spectrum (relative to a corrole aromatic peak of area 2) had one equivalent of impurity to one equivalent of corrole. In general this will overestimate the concentration of impurity, and so the results given are conservative and represent a minimum limit on purity and yield. Aromatic impurities were compared to impurities observed in the ¹⁹F NMR spectrum (where compounds were assumed to have a 1:1 mass ratio to the corrole product) and in this case were assumed to be redundant.

Instrumentation. All NMR spectra were obtained at ambient temperature in deuterated solvents using Bruker AVB-400 or AVQ-400 spectrometers at the University of California, Berkeley, or on 400, 500, or 600 MHz NMR instruments at the Organic Chemistry

Institute, Polish Academy of Sciences. UV−visible spectra were determined with a Varian Cary 50 UV−vis spectrophotometer using a 1 mm quartz cell. Mass spectral data (ESI-MS, positive mode) were obtained at the University of California, Berkeley, Microanalytical Facility. Melting points were determined using sealed capillaries and are uncorrected.

5-Pentafluorophenyldipyrromethane[54] and 4-propargyloxybenzalde-hyde[55] were prepared according to literature procedures. 5,15-Bis(pentafluorophenyl)-10-(4-methoxyphenyl)corrole ((C₆F₅)₂(*p*-OMePh)corroleH₃; **4**) was prepared according to a previously reported procedure.[49]

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), triethylbenzyl-lammonium chloride (TEBA), and copper(I) acetate were purchased from TCI and used as received. Sodium azide was purchased from Acros and used as received. Copper(II) acetate, benzyl azide, and propargyl alcohol were purchased from Aldrich and used as received. 3-Bromomethylbenzaldehyde, 2-(2-azidoethoxy)ethan-1-ol, and iron-(II) bromide (bis(THF)) were obtained from commercial sources and used as received. Tetraethylammonium tetrafluoroborate (TEABF₄) was purchased from Fluka and used as received. Tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) was purchased from Oakwood Products, Inc., and was purified by dissolving in ethyl acetate, precipitating with pentane, filtering, and drying *in vacuo* overnight.

Synthesis and Characterization of Compounds 1−15. *5,15-Bis(pentafluorophenyl)-10-(4-propargyloxyphenyl)corrole.* (C₆F₅)₂(*p*-O(CH₂CCH)Ph)corroleH₃ (**1**) was prepared according to a modified literature procedure.[49] 5-Pentafluorophenyldipyrromethane (3.12 g, 10 mmol) and 4-propargyloxybenzaldehyde (0.80 g, 5 mmol) were dissolved in methanol (500 mL). Concentrated hydrochloric acid (36%, 25 mL) was combined with 500 mL of distilled water, and the acid solution was added to the methanol solution while stirring, immediately producing a peach-colored suspension. The mixture was stirred for 1 h at room temperature and then extracted with chloroform. The organic extracts were combined, washed twice with water, dried over sodium sulfate, filtered, and diluted with chloroform to 1.25 L. DDQ (3.4 g, 15 mmol) was added, and the reaction mixture was stirred overnight at room temperature. The solution was concentrated to 200 mL by rotary evaporation, then filtered through a short silica gel column (1:1 CH₂Cl₂/hexanes). The combined eluents were concentrated to dryness. Column chromatography on silica gel (1:1 CH₂Cl₂/hexanes, R_f = 0.62 in 1:1 CH₂Cl₂/hexanes) provided the corrole with a minor impurity, which appears as a yellow spot on the TLC plate. This impurity is removed by recrystallization of the solid from hexanes, which is repeated until the yellow spot disappears, yielding a purple solid (950 mg, 97% est. purity, 23% yield). ¹H NMR (500 MHz, CDCl₃): δ 9.09 (d, *J* = 4.5 Hz, 2H), 8.71 (t, *J* = 4.3 Hz, 4H), 8.56 (d, *J* = 3.0 Hz, 2H), 8.11 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 5.5 Hz, 2H), 4.96 (d, *J* = 2.5 Hz, 2H, OC*H₂*CCH), 2.68 (t, *J* = 2.3 Hz, 1H, OCH₂CC*H*), −2.70 (br s, 3H, N*H*). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 197.7, 157.6, 147.1, 145.1, 140.7, 138.9, 136.9, 135.6, 134.6, 127.8, 125.3, 117.6, 114.0, 113.8, 112.9, 78.8, 75.9, 56.1. ¹⁹F NMR (470 MHz, CDCl₃): δ −137.9 (d, *J* = 18.8 Hz), −152.9 (s), −161.8 (t, *J* = 17.9 Hz). UV−vis (nm): 409, 561, 614. ESI-MS (+): calcd 761.13937 for C₄₀H₁₈F₁₀O₁N₄H, obsd 761.14109. Mp: decomposition above 350 °C.

5,15-Bis(pentafluorophenyl)-10-(3-bromomethylphenyl)corrole. ((C₆F₅)₂(*m*CH₂Br)Ph)corroleH₃ (**2**) was prepared according to a modified literature procedure.[49] 5-Pentafluorophenyldipyrromethane (1.56 g, 5 mmol) and 3-bromomethylbenzaldehyde (0.50 g, 2.5 mmol) were dissolved in methanol (250 mL). Concentrated hydrochloric acid (36%, 12.5 mL) was combined with 250 mL of distilled water, and the acid solution was added to the methanol solution while stirring, immediately producing a peach-colored suspension. The mixture was stirred for 1 h at room temperature and then extracted with chloroform. The organic extracts were combined, washed twice with water, dried over sodium sulfate, filtered, and diluted with chloroform to 1 L. DDQ (1.7 g, 7.5 mmol) was added, and the reaction mixture was stirred overnight at room temperature. The solution was concentrated to 200 mL by rotary evaporation, then filtered through

a short silica gel column (1:1 CH$_2$Cl$_2$/hexanes). The combined eluents were concentrated to dryness. Column chromatography on silica gel (1:1 CH$_2$Cl$_2$/hexanes, R_f = 0.54 in 1:1 CH$_2$Cl$_2$/hexanes) and subsequent concentration of the combined fractions yielded the pure product as a purple microcrystalline solid (380 mg, 96% est. purity, 18% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ 9.12 (d, J = 4.2 Hz, 2H), 8.72 (dd, J = 18.4, 4.8 Hz, 4H), 8.58 (d, J = 4.7 Hz, 2H), 8.24 (m, 1H), 8.15−8.08 (m (dt, unresolved), 1H), 7.82−7.77 (m, 1H), 7.77−7.71 (m, 1H), 4.78 (s, 2H, CH_2N$_3$), −2.76 (br s, 3H, NH). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 147.1, 145.1, 142.8, 141.8, 140.7, 138.9, 137.0, 136.9, 135.1, 134.7, 128.4, 127.8, 125.8, 117.5, 114.0, 112.6, 33.5. ^{19}F NMR (470 MHz, CDCl$_3$): δ −137.1 (dd, J = 24.0, 8.0 Hz), −152.5 (t, J = 21.2 Hz), −160.95 (td, J = 22.8, 7.8 Hz). UV−vis (nm): 409, 561, 612. ESI-MS (+): calcd 799.05497 for C$_{38}$H$_{17}$Br$_1$F$_{10}$N$_4$, pbserved 799.05352. Mp: decomposition above 350 °C.

5,15-Bis(pentafluorophenyl)-10-(3-azidomethylphenyl)corrole. ((C$_6$F$_5$)$_2$(m-CH$_2$N$_3$)Ph)corroleH$_3$ (**3**) was prepared using 5,15-bis(pentafluorophenyl)-10-(3-bromomethylphenyl)corrole (**2**) (150 mg, 0.188 mmol) dissolved in dry dimethylformamide (30 mL). Sodium azide (13.4 mg, 0.207 mmol) and triethylbenzyl ammonium chloride (TEBA) (4.3 mg, 0.019 mmol) were added, and the reaction mixture was stirred overnight at room temperature.[56] The reaction was monitored by thin-layer chromatography (silica gel, 1:1 CH$_2$Cl$_2$/hexanes). The reaction volume was diluted to 75 mL with chloroform. The organic phase was washed twice with water and dried over sodium sulfate, and the solvent removed by rotary evaporation. The solid was dissolved in 10 mL of CH$_2$Cl$_2$, and the solvent again removed by rotary evaporation to ensure complete removal of the dimethylformamide. Column chromatography on silica gel (1:1 CH$_2$Cl$_2$/hexanes, R_f = 0.49 in 1:1 CH$_2$Cl$_2$/hexanes) and subsequent concentration of the combined fractions yielded the pure product as a purple microcrystalline solid (106 mg, 92% est. purity, 69% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ 9.10 (d, J = 4.0 Hz, 2H), 8.71 (d, J = 4.0 Hz, 2H), 8.67 (d, J = 4.5 Hz, 2H), 8.56 (d, J = 2.5 Hz, 2H), 8.13 (m, 2H), 7.78 (m, 1H), 7.72 (m, 1H), 4.61 (s, 2H, CH_2N$_3$), −2.80 (br s, 3H, NH). ^{13}C{^{1}H} (125 MHz, CDCl$_3$): δ 162.3, 147.1, 145.1, 142.8, 141.9, 140.7, 136.9, 135.3, 134.5, 131.2, 128.8, 127.8, 125.8, 121.8, 117.6, 114.0, 112.6, 96.9, 54.8. ^{19}F NMR (470 MHz, CDCl$_3$): δ −137.9 (d, J = 18.8 Hz), −152.9 (s), −161.8 (t, J = 17.9 Hz). UV−vis (nm): 409, 561, 613. ESI-MS (+): calcd 761.1313 for C$_{38}$H$_{17}$F$_{10}$N$_7$, obsd 761.1307. Mp: decomposition above 350 °C.

Copper(III) 5,15-Bis(pentafluorophenyl)-10-(4-propargyloxyphenyl)corrole. (C$_6$F$_5$)$_2$(p-O(CH$_2$CCH)Ph)corroleCu (**5**) was prepared according to a modified literature procedure.[57] 5,15-Bis(pentafluorophenyl)-10-(4-propargyloxyphenyl)corrole ((C$_6$F$_5$)$_2$(p-O(CH$_2$CCH)Ph)corroleH$_3$) (50 mg, 0.066 mmol) was dissolved in CH$_2$Cl$_2$ (10 mL) under ambient conditions. Copper(II) acetate (36 mg, 0.197 mmol) was suspended in methanol (5 mL), and the suspension added to the corrole solution. An additional 5 mL of methanol was used in three portions to rinse residual copper(II) acetate into the reaction mixture. The reaction was allowed to stir 30 min at room temperature and was monitored by thin-layer chromatography (silica gel, 1:1 CH$_2$Cl$_2$/hexanes). Upon completion, the solvent was removed by rotary evaporation and the resulting solid purified by column chromatography (silica gel, 1:4 CH$_2$Cl$_2$/hexanes, R_f = 0.75 in 1:1 CH$_2$Cl$_2$/hexanes). The product was isolated as a purple-brown solid (50 mg, 80% est. purity, 74% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.95 (d, J = 4.0 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 4.2 Hz, 2H), 7.26 (d, J = 5.7 Hz, 2H), 7.21 (d, J = 4.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 4.80 (d, J = 2.4 Hz, 2H), 2.59 (t, J = 2.3 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 158.4, 150.4, 149.6, 146.1, 145.0, 144.1, 142.6, 140.9, 139.0, 136.8, 132.6, 132.1, 129.8, 122.8, 114.6, 112.0, 78.3, 75.9, 55.9. ^{19}F NMR (470 MHz, CDCl$_3$): δ −137.1 (dd, J = 23.6, 7.9 Hz), −152.5 (t, J = 18.8 Hz), −161.0 (td, J = 22.6, 7.9 Hz). UV−vis (nm): 399, 427, 548. ESI-MS (+): calcd 821.0455 for C$_{40}$H$_{15}$Cu$_1$F$_{10}$N$_4$O$_1$H, obsd 821.0496. Mp: decomposition above 350 °C.

Copper(III) 5,15-Bis(pentafluorophenyl)-10-(3-azidomethylphenyl)corrole. ((C$_6$F$_5$)$_2$(m-CH$_2$N$_3$)Ph)corroleCu (**6**) was prepared according to a modified literature procedure.[57] 5,15-Bis(pentafluorophenyl)-10-(3-azidophenyl)corrole ((C$_6$F$_5$)$_2$(m-(CH$_2$N$_3$)Ph)corroleH$_3$) (82 mg, 0.108 mmol) was dissolved in CH$_2$Cl$_2$ (12 mL) under ambient conditions. Copper(II) acetate (58 mg, 0.323 mmol) was suspended in methanol (6 mL), and the suspension added to the corrole solution. An additional 6 mL of methanol was used in three portions to rinse residual copper(II) acetate into the reaction mixture. The reaction was allowed to stir 30 min at room temperature and was monitored by thin-layer chromatography (silica gel, 1:1 CH$_2$Cl$_2$/hexanes). Upon completion, the solvent was removed by rotary evaporation, and the resulting solid was purified by column chromatography (silica gel, 1:1 CH$_2$Cl$_2$/hexanes, R_f = 0.70 in 1:1 CH$_2$Cl$_2$/hexanes). The product was isolated as a brown solid (77 mg, 88% est. purity, 77% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.97 (d, J = 4.0 Hz, 2H), 7.59−7.48 (m, 4H), 7.42 (d, J = 4.3 Hz, 2H), 7.24−7.16 (m, 4H), 4.44 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 150.3, 149.5, 146.2, 144.9, 144.1, 142.6, 140.5, 138.8, 136.8, 135.6, 132.1, 130.3, 128.9, 126.6, 122.9, 111.7, 54.5. ^{19}F NMR (470 MHz, CDCl$_3$): δ −141.8 (ddd, J = 32.7, 23.3, 7.2 Hz), −157.1 (t, J = 21.2 Hz), −165.6 (tdd, J = 22.8, 15.3, 7.7 Hz). UV−vis (nm): 406, 547. ESI-MS (+): calcd 821.0452 for C$_{38}$H$_{14}$Cu$_1$F$_{10}$N$_7$, obsd 821.0460. Mp: decomposition above 350 °C.

Copper(III) 5,15-Bis(pentafluorophenyl)-10-(4-methoxyphenyl)-corrole. (C$_6$F$_5$)$_2$(p-OMePh)corroleCu (**7**) was prepared according to a modified literature procedure.[57] 5,15-Bis(pentafluorophenyl)-10-(4-methoxyphenyl)corrole ((C$_6$F$_5$)$_2$(p-OMePh)corroleH$_3$; **4**) (200 mg, 0.272 mmol) was dissolved in CH$_2$Cl$_2$ (50 mL) under ambient conditions. Copper(II) acetate (148 mg, 0.815 mmol) was suspended in methanol (20 mL), and the suspension added to the corrole solution. An additional 30 mL of methanol was used in three portions to rinse residual copper(II) acetate into the reaction mixture. The reaction was allowed to stir 30 min at room temperature and was monitored by thin-layer chromatography (silica gel, 1:1 CH$_2$Cl$_2$/hexanes). Upon completion, the solvent was removed by rotary evaporation, and the resultant solid was purified by column chromatography (silica gel, 1:1 CH$_2$Cl$_2$/hexanes). The product was isolated as a brown solid (203 mg, 82% est. purity, 77% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.90 (br s, 2H) 7.52 (d, J = 8.0 Hz, 2H, C$_6$H$_2$H$_2$-OMe), 7.33 (br s, 2H), 7.06 (br s, 4H), 6.98 (d, J = 8.0 Hz, 2H, C$_6$H$_2$H$_2$-OMe), 3.88 (s, 3H, OCH_3). ^{19}F NMR (376 MHz, CDCl$_3$): δ −136.2 (d, J = 18.8 Hz, 4F), −151.6 (t, J = 20.7 Hz, 2F), −160.1 (quintet, J = 11.3 Hz, 4F). UV−vis (nm): 399, 430, 549. ESI-MS (+): calcd 796.0377 for C$_{38}$H$_{15}$Cu$_1$F$_{10}$O$_1$N$_4$, obsd 796.0379. Mp: decomposition above 350 °C.

Iron(III) 5,15-Bis(pentafluorophenyl)-10-(4-propargyloxyphenyl)-corrole Bis(diethyl ether). (C$_6$F$_5$)$_2$(p-O(CH$_2$CCH)Ph)corroleFe-(Et$_2$O)$_2$ (**8**) was prepared according to a modified literature procedure.[58] 5,15-Bis(pentafluorophenyl)-10-(4-propargyloxyphenyl)-corrole ((C$_6$F$_5$)$_2$(p-OMePh)corroleH$_3$) (200 mg, 0.263 mmol) was dissolved in dry dimethylformamide (30 mL) under nitrogen on a Schlenk line. Iron(II) bromide(bis(THF)) (1.89 mg, 5.26 mmol) was placed in another nitrogen-filled Schlenk flask, and the corrole solution transferred by cannula. The resulting mixture was refluxed overnight at 110 °C, and the reaction monitored by thin-layer chromatography (silica gel, 1:1 CH$_2$Cl$_2$/hexanes). Dimethylformamide was removed under reduced pressure at 60 °C, and the resulting solid was triturated twice with diethyl ether, which was subsequently removed under reduced pressure to ensure complete removal of the dimethylformamide. The compound was purified by column chromatography (silica gel, 100% diethyl ether), and the combined organic fractions were concentrated to 50 mL. Hydrazine (32 μL, 1.0 mmol) was added, and the remaining solvent was removed under reduced pressure on a Schlenk line to give the product as a red-brown solid (130 mg, 84% est. purity, 44% yield). ^{1}H NMR (400 MHz, C$_6$D$_6$, 23 °C): 19.73 (br s), 7.49 (br s), 5.90 (br s), 3.27 (br), 1.11 (br s, Et$_2$O), 0.90 (br s), 0.16 (br s, Et$_2$O), −2.98 (br s), −58.78 (br s), −110.23 (br s). ^{19}F NMR (376 MHz, C$_6$D$_6$, 23 °C): δ −95.3 (br s, *ortho*-F), −149.7 (s, *para*-F), −155.2 (s, *meta*-F). UV−vis (nm): 381, 551. ESI-MS (+): calcd 813.0430 for C$_{40}$H$_{15}$F$_{10}$Fe$_1$N$_4$O$_1$, obsd 813.0457. Mp: decomposition above 350 °C.

Iron(III) 5,15-Bis(pentafluorophenyl)-10-(4-methoxyphenyl)-corrole Bis(diethyl ether). $(C_6F_5)_2(p\text{-OMePh})corroleFe(Et_2O)_2$ (**9**) was prepared according to a modified literature procedure.[58,59] 5,15-Bis(pentafluorophenyl)-10-(4-methoxyphenyl)corrole $((C_6F_5)_2(p\text{-OMePh})corroleH_3;$ **4**) (74 mg, 0.1 mmol) was dissolved in dry dimethylformamide (30 mL) under nitrogen on a Schlenk line. Iron(II) bromide (720 mg, 2.0 mmol) was placed in another flask under nitrogen, and the corrole solution transferred by cannula. The resulting mixture was refluxed for 6 h at 110 °C, and the reaction monitored by thin-layer chromatography (silica gel, 1:1 CH_2Cl_2/hexanes). Dimethylformamide was removed under reduced pressure at 60 °C, and the resulting solid was triturated twice with diethyl ether, which was subsequently removed under reduced pressure to ensure complete removal of the dimethylformamide. The solid was extracted with diethyl ether and filtered by cannula, and the solvent was removed quickly under alternating nitrogen and vacuum to give a brown solid (82 mg, 93% est. purity, 87% yield). ^{1}H NMR (400 MHz, C_6D_6, 23 °C): δ 8.68 (s), 7.73 (s), 6.18 (br s), 3.73 (s), 2.37 (s), 1.89 (s), 0.30, (s), −0.97 (br s), −34.35 (br s), −46.23 (br s), −104.68 (br s). ^{19}F NMR (376 MHz, C_6D_6, 23 °C): δ −100.5 (br s, *ortho-F*), −149.5 (s, *para-F*), −155.7 (s, *meta-F*). UV−vis (nm): 376. ESI-MS (+): calcd 789.0430 for $C_{38}H_{15}F_{10}Fe_1N_4O_1$, obsd 789.0432. Mp: decomposition above 350 °C.

Copper(III) 5,15-Bis(pentafluorophenyl)-10-(4-oxymethyl-(1-ethoxyethanol-1,2,3-triazol-4-yl)phenyl)corrole. $(C_6F_5)_2(p\text{-O-}(CH_2(C_2HN_3(CH_2CH_2OCH_2CH_2OH)))Ph)corroleCu$ (**10**) was prepared as follows. Copper(III) 5,15-bis(pentafluorophenyl)-10-(4-propargyloxyphenyl)corrole (**5**) (150 mg, 0.182 mmol) and 2-(2-azidoethoxy)ethan-1-ol (26 mg, 0.201 mmol) were placed in a dry 250 mL Schlenk flask. The flask was evacuated and filled with argon three times, and dry CH_2Cl_2 (50 mL) was added by cannula. Copper(I) acetate (catalytic, approximately 5 mg) was added, and the suspension was stirred for 30 min at room temperature.[60] The reaction was monitored by thin-layer chromatography (silica gel, 1:1 CH_2Cl_2/hexanes). The solution was extracted twice with water to remove excess azide. The combined extracts were dried over sodium sulfate and filtered, and the solvent was removed by rotary evaporation. The resultant solid was purified by column chromatography (silica gel, 95:5 CH_2Cl_2/MeOH). The resulting solid was further purified by dry column vacuum chromatography (99:1 CH_2Cl_2/MeOH). The product was isolated as a brown solid (92 mg, 93% est. purity, 49% yield). ^{1}H NMR (600 MHz, CDCl₃): δ 7.94 (d, J = 4.0 Hz, 2H), 7.87 (s, 1H, N_3C_2H), 7.54 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 4.3 Hz, 2H), 7.26 (d, J = 4.7 Hz, 2H), 7.21 (d, J = 4.5 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 5.31 (s, 2H, Ph-O-CH_2), 4.61 (t, J = 5.0 Hz, 2H), 3.96−3.91 (m, 2H), 3.75−3.68 (m, 2H), 3.61−3.56 (m, 2H), 1.26 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, CDCl₃): δ 159.1, 149.6, 145.0, 144.1, 138.6, 136.9, 132.5, 132.1, 129.8, 124.0, 122.8, 114.5, 72.5, 69.3, 62.2, 61.7, 50.4. ^{19}F NMR (470 MHz, CDCl₃): δ −141.8 (dd, J = 24.0, 8.1 Hz), −157.2 (d, J = 23.5 Hz), −165.8 (td, J = 22.5, 7.7 Hz). UV−vis (nm): 399, 429, 549. ESI-MS (+): calcd 951.1077 for $C_{44}H_{24}Cu_1F_{10}N_7O_1$, obsd 951.1073. Mp: decomposition above 350 °C.

Copper(III) 5,15-Bis(pentafluorophenyl)-10-(4-oxymethyl-(1-benzyl-1,2,3-triazol-4-yl)phenyl)corrole. $(C_6F_5)_2(p\text{-O-}(CH_2(C_2HN_3(CH_2C_6H_5)))Ph)corroleCu$ (**11**) was prepared as follows. Copper(III) 5,15-bis(pentafluorophenyl)-10-(4-propargyloxyphenyl)corrole (**5**) (25 mg, 0.030 mmol) and benzyl azide (15 mg, 0.100 mmol) were placed in a dry 25 mL Schlenk flask. The flask was evacuated and filled with nitrogen three times, and dry CH_2Cl_2 (5 mL) was added by cannula. Copper(I) acetate (catalytic, approximately 1 mg) was added, and the suspension was stirred for 30 min at room temperature.[60] The reaction was monitored by thin-layer chromatography (silica gel, 1:1 CH_2Cl_2/hexanes). The solution was extracted twice with water to remove excess azide. The combined extracts were dried over sodium sulfate and filtered, and the solvent was removed by rotary evaporation. The product was purified by dry column vacuum chromatography (silica gel, 98:2 CH_2Cl_2/MeOH), and the solvent was removed under vacuum to give a brown microcrystalline solid (25 mg, 86% est. purity, 72% yield). ^{1}H NMR (400 MHz, CDCl₃): δ 7.93 (d, J = 4.4 Hz, 2H), 7.71 (dt, J = 7.4,3.7

Hz, 1H), 7.57−7.50 (m, 2H), 7.46−7.12 (m, 11H), 7.08 (d, J = 8.0 Hz, 2H), 5.56 (s, 2H), 5.30 (s, 2H). ^{19}F NMR (376 MHz, CDCl₃): δ −136.2 (dd, J = 24.0, 8.0 Hz), −151.6 (t, J = −22.6 Hz), −160.1 (td, J = 23.0, 7.9 Hz). UV−vis (nm): 400, 430, 550. ESI-MS (+): calcd 954.1095 for $C_{47}H_{22}Cu_1F_{10}N_7O_1H$, obsd 954.1107. Mp: decomposition above 350 °C.

Iron(III) 5,15-Bis(pentafluorophenyl)-10-(4-oxymethyl-(1-benzyl-1,2,3-triazol-4-yl)phenyl)corrole Bis(diethyl ether). $(C_6F_5)_2(p\text{-O-}(CH_2(C_2HN_3(CH_2C_6H_5)))Ph)corroleFe(Et_2O)_2$ (**12**) was prepared as follows. Iron(III) 5,15-bis(pentafluorophenyl)-10-(4-propargyloxyphenyl)corrole bis(diethyl ether) (33 mg, 0.034 mmol) and benzyl azide (5 mg, 0.038 mmol) were placed in a dry 25 mL Schlenk flask. The flask was evacuated and filled with nitrogen three times, and dry CH_2Cl_2 (5 mL) was added by cannula. Copper(I) acetate (catalytic, approximately 1 mg) was added, and the resulting suspension was stirred for 15 min at room temperature.[60] The reaction was monitored by thin-layer chromatography (silica gel, 1:1 CH_2Cl_2/hexanes). The solution was extracted twice with water to remove excess azide. The combined extracts were dried over sodium sulfate and filtered, and the solvent was removed by rotary evaporation. The solid was purified by dry column vacuum chromatography (silica gel, 1:1 diethyl ether/hexanes). The product was dissolved in diethyl ether, and 5 μL of hydrazine was added. The solvent was removed by slow evaporation under a stream of nitrogen to isolate the compound as a brown solid (22 mg, 89% est. purity, 52% yield). ^{1}H NMR (400 MHz, C_6D_6, 23 °C): δ 10.65 (br s), 9.58 (br s), 9.23 (br s), 8.65 (br s), 5.48 (br s), 4.98 (br s), 3.85 (br s), 3.21 (br s), 1.35 (br s, Et₂O), 0.27 (br s), 0.05 (br s, Et₂O), −38.24 (br s), −50.08 (br s), −107.74 (br s). ^{19}F NMR (376 MHz, C_6D_6, 23 °C): δ −92.9 (br s, *ortho-F*), −150.2 (s, *para-F*), −155.5 (s, *meta-F*). UV−vis (nm): 410, 561. ESI-MS (+): calcd 947.1148 for $C_{47}H_{22}F_{10}Fe_1N_4O_7H$, obsd 947.1153. Mp: decomposition above 350 °C.

Copper(III) 5,15-Bis(pentafluorophenyl)-10-(3-methynyl-(4-methanol-1,2,3-triazol-1-yl)phenyl)corrole. $((C_6F_5)_2(m\text{-}CH_2N_3C_2H\text{-}(CH_2OH))Ph)corroleCu$ (**13**) was prepared as follows. Copper(III) 5,15-bis(pentafluorophenyl)-10-(3-azidomethylphenyl)corrole (30 mg, 0.037 mmol) and propargyl alcohol (2.5 mg, 0.045 mmol) were placed in a dry 25 mL Schlenk flask. The flask was evacuated and filled with argon three times, and dry CH_2Cl_2 (5 mL) was added by cannula. Copper(I) acetate (catalytic, approximately 1 mg) was added, and the resulting suspension was stirred overnight at room temperature.[60] The reaction was monitored by thin-layer chromatography (silica gel, 1:1 CH_2Cl_2/hexanes). After completion, the solvent was removed by rotary evaporation, and the resulting solid was purified by column chromatography (silica gel, 98:2 CH_2Cl_2/MeOH, R_f = 0.32 in 98:2 CH_2Cl_2/MeOH) to yield a brown solid (14 mg, 94% est. purity, 41% yield). ^{1}H NMR (500 MHz, CDCl₃): δ 7.97 (d, J = 4.2 Hz, 2H), 7.60−7.40 (m, 6H), 7.23−2.10 (m, 5H), 5.60 (s, 2H), 4.79 (s, 2H), 2.22 (br s, 1H). ^{13}C{^{1}H} NMR (125 MHz, CDCl₃): δ 149.6, 148.1, 146.2, 144.2, 142.6, 140.6, 138.8, 136.8, 134.9, 131.9, 131.2, 130.4, 129.2, 127.0, 125.3, 123.0, 121.6, 111.6, 108.5, 56.7, 53.9. ^{19}F NMR (470 MHz, CDCl₃): δ −136.9 to −137.2 (m), −152.2 (t, J = 21.2 Hz), −160.8 (qd, J = 21.7, 8.0 Hz). UV−vis (nm): 304, 548. LR-MS: calcd 878.1 for $C_4H_{24}Cu_1F_{10}N_7O_1$, obsd 878.1. Mp: decomposition above 350 °C.

1-[(10-(3-Methylenephenyl))-5,15-bis(pentafluorophenyl)copper-(III)corrole]-4-[(10-(4-oxymethylene))-5,15-bis(pentafluorophenyl)-copper(III)corrole]triazole. $Cu(corrole((C_6F_5)_2(Ph))\text{-}p\text{-O}(CH_2)\text{-}(C_2HN_3)(CH_2)\text{-}m\text{-}(Ph(C_6F_5)_2corrole)Cu)$ (**14**) was prepared as follows. Copper(III) 5,15-bis(pentafluorophenyl)-10-(4-propargyloxyphenyl)corrole (25 mg, 0.030 mmol) and copper(III) 5,15-bis(pentafluorophenyl)-10-(3-azidomethylphenyl)corrole (25 mg, 0.030 mmol) were combined in a dry Schlenk flask under nitrogen. Dry CH_2Cl_2 (5 mL) and copper(I) acetate (catalytic, approximately 3 mg) were added, and the reaction was stirred overnight at room temperature.[60] The reaction was monitored by thin-layer chromatography (silica, 1:1 CH_2Cl_2/hexanes). The solvent was removed by rotary evaporation, and the resulting solid was purified by column chromatography (silica gel, 1:1 CH_2Cl_2/hexanes, ramped to 100% CH_2Cl_2, ramped to 95:5 CH_2Cl_2/MeOH). The solvent was

Scheme 1. Preparation of (a) Propargyl-, (b) Azido-, and (c) Methoxy-Functionalized Metallocorroles
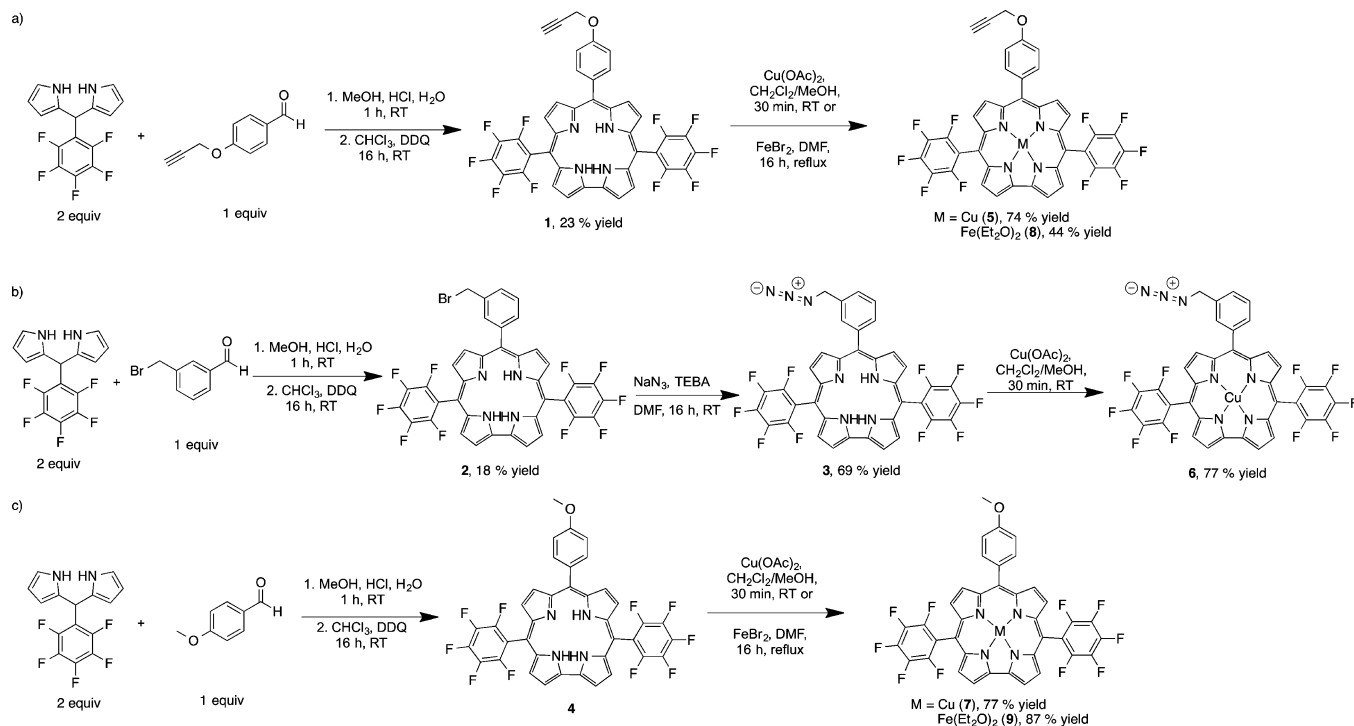
removed under vacuum to give a brown microcrystalline solid (45 mg, 93% est. purity, 84% yield). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.04 (m, 4H), 7.75 (s, 1H), 7.62−7.40 (m, 10H), 7.24 (q, J = 5.1 Hz, 6H), 7.17 (d, J = 4.6 Hz, 2H), 7.08 (d, J − 8.3 Hz, 2H), 5.66 (s, 2H), 5.26 (s, 2H). ^{19}F NMR (376 MHz, CD$_2$Cl$_2$): δ −137.1 to −137.4 (m), −152.4 to −152.8 (m), −160.8 to −161.2 (m). UV−vis (nm): 402, 550. ESI-MS (+): calcd 1664.0727 for C$_{78}$H$_{29}$Cu$_2$F$_{20}$N$_{11}$O$_1$Na$_1$, obsd 1664.0732; calcd 1680.0466 for C$_{78}$H$_{29}$Cu$_2$F$_{20}$N$_{11}$O$_1$K$_1$, obsd 1680.0468. Mp: decomposition above 350 °C.

1-[(10-(3-Methylenephenyl))-5,15-bis(pentafluorophenyl)copper-(III)corrole]-4-[(10-(4-oxymethylene))-5,15-bis(pentafluorophenyl)-iron(III)corrole(bis(acetonitrile))]triazole. Fe(CH$_3$CN)$_2$(corrole-((C$_6$F$_5$)$_2$(Ph))-p-O(CH$_2$)(C$_2$HN$_3$)(CH$_2$)-m-(Ph(C$_6$F$_5$)$_2$corrole)Cu) (15) was prepared as follows. Iron(III) 5,15-bis(pentafluorophenyl)-10-(4-propargyloxyphenyl)corrole bis(diethyl ether) (24 mg, 0.025 mmol) and copper(III) 5,15-bis(pentafluorophenyl)-10-(3-azidomethylphenyl)corrole (21 mg, 0.025 mmol) were combined in a dry Schlenk flask under nitrogen. Dry CH$_2$Cl$_2$ (5 mL) and copper(I) acetate (catalytic, approximately 3 mg) were added, and the reaction was stirred overnight at room temperature.[60] The reaction was monitored by thin-layer chromatography (silica, CH$_2$Cl$_2$/hexanes). The solvent was removed by rotary evaporation, and the resultant solid was purified by column chromatography (silica gel, 1:1 CH$_2$Cl$_2$/hexanes, ramped to 100% CH$_2$Cl$_2$, ramped to 95:5 CH$_2$Cl$_2$/MeOH). The solvent was removed under vacuum, the solid was dissolved in acetonitrile, and 5 µL of hydrazine was added. The solvent was degassed with nitrogen and then removed under vacuum on the Schlenk line to produce a brown solid (26 mg, 90% est. purity, 54% yield). ^{1}H NMR (400 MHz, CD$_3$CN, 23 °C): δ 8.01−7.94 (m), 7.75 (d, J = 4 Hz), 7.65−7.40 (m), 7.1−4.6 (very br s), 5.81 (br s), 5.44 (s), 4.49 (s), 3.85 (s), 3.60 (s), 3.50 (s), 1.81 (s), 1.28 (s), −1.62 (br s), −12.20 (br s), −32.12 (br s), −83.08 (br s). ^{19}F NMR (376 MHz, CD$_3$CN, 23 °C): δ −117.7, −140.5, −158.0, −163.7, −165.2. UV−vis (nm): 403, 552. ESI-MS (+): calcd 1635.0955 for C$_{78}$H$_{30}$Cu$_1$F$_{20}$Fe$_1$N$_{11}$O$_1$, obsd 1635.1101. Mp: decomposition above 350 °C.

Cyclic Voltammetry of Compounds 7, 9, 14, and 15. Cyclic voltammetric measurements were performed with a Gamry Reference 600 potentiostat, using either 0.1 M tetraethylammonium tetrafluoroborate in acetonitrile or 0.1 M tetra-n-butylammonium tetrafluoroborate in CH$_2$Cl$_2$. A three-electrode cell was used, with a glassy carbon working electrode (3 mm diameter), a platinum mesh counter electrode, and a Ag/Ag$^+$ reference electrode. The reference electrode consisted of a silver wire in a solution of 0.01 M AgNO$_3$ and 0.1 M TEABF$_4$ in acetonitrile, separated from the bulk solution by a Vycor frit. Electrolyte solutions were deoxygenated with nitrogen for at least 10 min before any compounds were added and were kept under a blanket of nitrogen during analysis. Between measurements, the working electrode was polished with 0.05 µm alumina and rinsed with distilled water and acetonitrile.

All potentials are referenced to Ag/Ag$^+$ (0.01 M Ag$^+$). Potentials reproduced from other publications have been converted from SCE to Ag/Ag$^+$ by subtracting 298 mV.[61] All scans shown were taken at 100 mV/s, except for 15 (the Cu−Fe complex), which was not sufficiently soluble in acetonitrile (although solubility was better in acetonitrile than in CH$_2$Cl$_2$) and had to be measured at 500 mV/s to observe well-resolved peaks. Currents are reported as current densities, calculated using an electrode area of 0.071 cm^2. Arrows on the voltammograms (in the SI) indicate the direction of the first potential sweep.

RESULTS AND DISCUSSION

Previous research has emphasized the importance of electron-withdrawing *meso*-substituents on corrole ligands.[62] These make the first oxidation potential more positive[63] and enhance the stability of the corrole toward light and oxygen.[64] For this reason, we chose 5-(pentafluorophenyl)dipyrromethane as a key substrate. Combination of two equivalents of 5-(pentafluorophenyl)dipyrromethane and one equivalent of 4-propargyloxybenzaldehyde in a mixture of methanol and acidic water at room temperature was followed by extraction with chloroform and the addition of DDQ.[49] After stirring overnight at room temperature, column chromatography and recrystallization gave 5,15-bis(pentafluorophenyl)-10-(4-propargyloxyphenyl)corrole ((C$_6$F$_5$)$_2$(p-O(CH$_2$CCH)Ph)-corroleH$_3$; 1) as a purple crystalline solid in 23% yield (Scheme 1a).
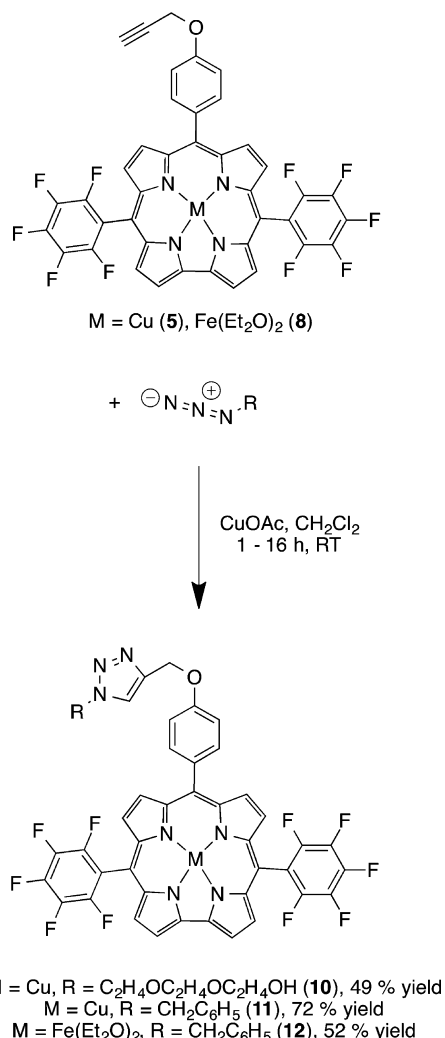
Following the same general procedure[49] 5,15-bis-(pentafluorophenyl)-10-(3-bromomethylphenyl)corrole ((C$_6$F$_5$)$_2$(m-(CH$_2$Br)Ph)corroleH$_3$; **2**) was prepared in 18% yield. The bromomethyl group was then converted to an azidomethyl group by reaction with sodium azide in the presence of triethylbenzyl ammonium chloride as a phase transfer catalyst.[56] This reaction was stirred overnight at room temperature, and after aqueous extraction and column chromatography 5,15-bis(pentafluorophenyl)-10-(3-azidomethylphenyl)corrole ((C$_6$F$_5$)$_2$(m-(CH$_2$N$_3$)Ph)-corroleH$_3$; **3**) was isolated as a purple crystalline solid in 69% yield (Scheme 1b). Free-base corroles **1**, **2**, and **3** have been characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopies, UV−visible spectroscopy, and ESI mass spectrometry (see Experimental Section). To our knowledge, these species constitute only the second example in each case of of alkynyl-functionalized[47] (propargyl) and azido-functionalized[45,46] corrole ligands.

Both **1** and **3**, in addition to the previously reported 5,15-bis(pentafluorophenyl)-10-(4-methoxyphenyl)corrole ((C$_6$F$_5$)$_2$(p-OMePh)corroleH$_3$; **4**), were reacted with copper-(II) acetate to form **5** (74% yield), **6** (77% yield), and **7** (77% yield), respectively (Scheme 1).[57] All three compounds have been characterized by ^{1}H and ^{19}F NMR spectroscopies (**5** and **6** were also characterized by ^{13}C NMR spectroscopy; see the SI), UV−visible spectroscopy, and ESI mass spectrometry (see the Experimental Section). **7** was prepared primarily as a reference compound for electrochemical characterization (see below).

Compounds **1** and **4** were reacted with iron(II) bromide in refluxing dimethylformamide under Schlenk conditions to produce **8** (44% yield) and **9** (87% yield), respectively (Scheme 1a).[58] Unlike for the analogous trisperfluorophenyl-corrole complexes, these compounds were sensitive to oxidation to a bis-iron(IV)-bridged μ-oxo species and required either anhydrous, air-free workup (**9**) or column chromatography followed by reduction with hydrazine in diethyl ether (**8**) to cleanly produce the paramagnetic iron(III) corrole species. Both compounds have been characterized by ^{1}H and ^{19}F NMR spectroscopies (see the SI), where their paramagnetically shifted peaks are diagnostic and match closely with those previously reported by Gross and co-workers for the paramagnetic high-spin iron(III) trisperflouorophenyl corrole bis(diethyl ether).[58] Specifically, the broad signal at −95.3 ppm in the ^{19}F NMR spectrum of **8** (−100.5 ppm in **9**) can be assigned to the *ortho*-fluorine atoms, while that at −149.7 ppm (−149.5 ppm in **9**) can be assigned to the *para*-fluorine and that at −155.2 ppm (−155.7 ppm in **9**) to the *meta*-fluorine atoms. Differentiation of these compounds from the bis-iron(IV)-bridged μ-oxo species is straightforward because the latter displays five inequivalent diamagnetically shifted signals in the ^{19}F NMR spectrum. There are slight differences between the chemical shifts of these compounds in both the ^{1}H and ^{19}F NMR spectra; these differences correspond to a very slight difference in UV−visible absorption maxima between **8** (381 nm) and **9** (376 nm). As these compounds differ only by a remote substituent (propargyl vs methoxy), the reasons for these differences are unclear; however they may relate to the slightly greater electronic-donating nature of the methoxy group and subsequent inductive electron donation by the 10-phenyl *meso* substituent to the corrole ring. These compounds were also characterized by ESI mass spectrometry (see the Experimental Section).

To test the reactivity of these species toward "click" chemistry and to ascertain that the presence of coordinated metals did not inhibit this reactivity, **5** was reacted with 2-(2-azidoethoxy)ethan-1-ol and **5** and **8** were both reacted with benzyl azide to produce **10** (49% yield), **11** (72% yield), and **12** (52% yield), respectively (Scheme 2).

Scheme 2. Test Reactions to Confirm Reactivity of Propargyl-Functionalized Corroles 5 and 8 toward the "Click" Reaction with Small Substrates

M = Cu (**5**), Fe(Et$_2$O)$_2$ (**8**)

$+$ $^-$N$=$N$^+$$=$N·R

CuOAc, CH$_2$Cl$_2$
1 - 16 h, RT

M = Cu, R = C$_2$H$_4$OC$_2$H$_4$OC$_2$H$_4$OH (**10**), 49 % yield
M = Cu, R = CH$_2$C$_6$H$_5$ (**11**), 72 % yield
M = Fe(Et$_2$O)$_2$, R = CH$_2$C$_6$H$_5$ (**12**), 52 % yield
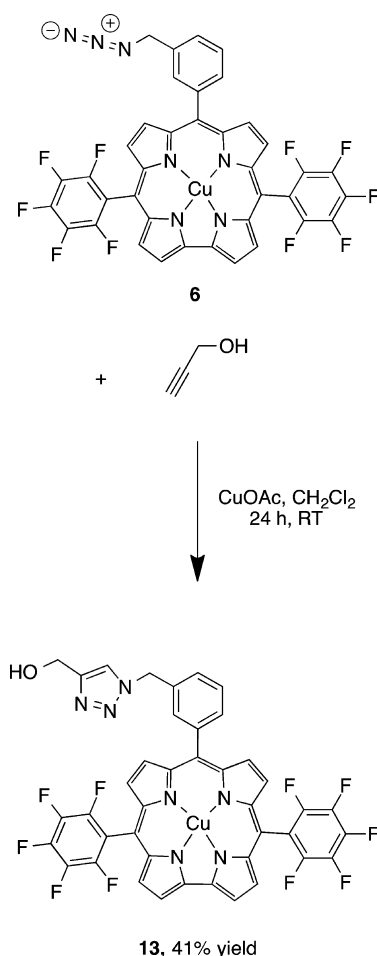
Similar to its precursor **8**, **12** was reacted with hydrazine in diethyl ether to cleanly isolate the iron(III) corrole species. To a similar end, **6** was reacted with propargyl alcohol to produce **13** (41% yield) (Scheme 3). In all cases copper(I) acetate, recently published as an excellent catalyst for azide−alkyne cycloaddition,[65] was used as a heterogeneous catalyst for this reaction, and the compounds were isolated by column chromatography. All three compounds were characterized by ^{1}H and ^{19}F NMR spectroscopies (and **10** by ^{13}C NMR spectroscopy; see the SI), UV−visible spectroscopy, and ESI mass spectrometry (see the Experimental Section). The paramagnetic NMR spectra of **12** are consistent with those observed for **8** and with those reported in the literature.[58]

It should be noted that initial attempts were also made to react the free-base corrole **1** with benzyl azide. These resulted in very low yields of **5** and **11** among a mixture of species,
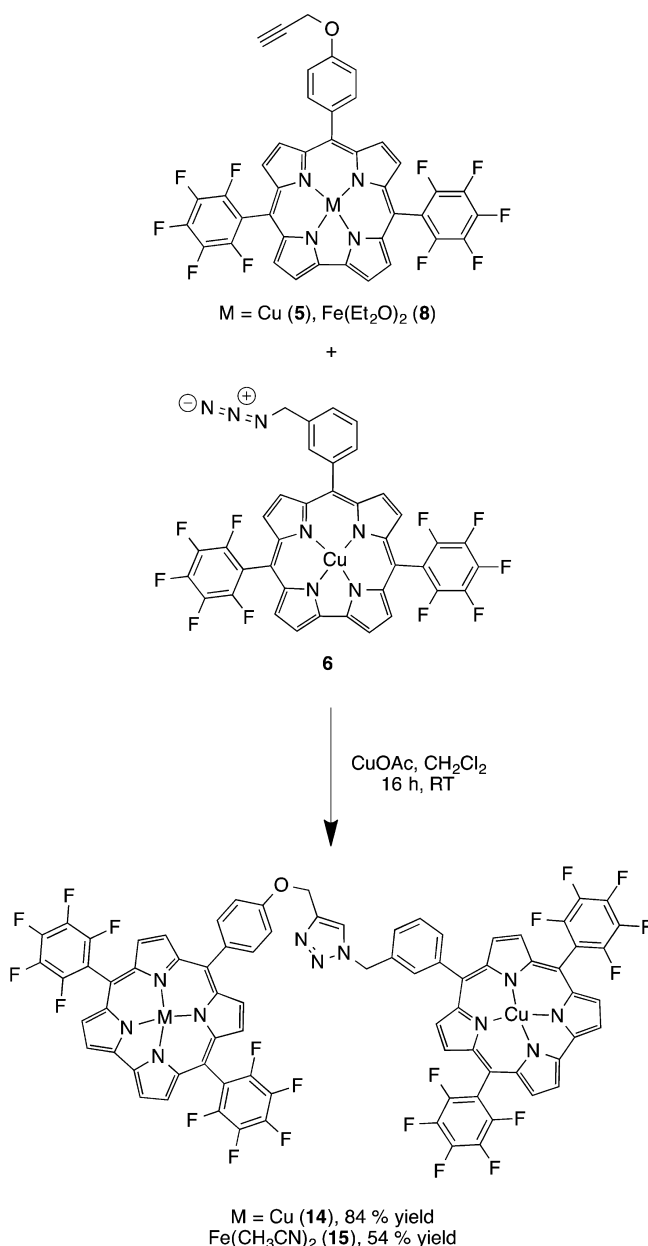
Scheme 3. Test Reactions to Confirm Reactivity of Azido-Functionalized Corrole 6 toward the "Click" Reaction with Small Substrates

Scheme 4. Synthesis of Homobimetallic (14) and Heterobimetallic (15) Bis-corrole Complexes by a "Click" Reaction

suggesting metalation of the free-base corrole by copper(I) acetate. However, there was no indication of substitution of iron with copper in reactions performed on **8**, indicating that metal exchange was not an issue in this case and that the presence of redox-active iron(III) and copper(III) species does not interfere with "click" reactivity.

Of greater interest than the ability to attach to small organic substrates was the question of whether azido- and alkynyl-derivatized corroles could be coupled with each other to produce bis-corrole bimetallic species. To this end, **5** and **6** were reacted in the presence of copper(I) acetate to produce bis-copper complex **14** in 84% yield (Scheme 4). The identity of this compound as a single molecule (as opposed to a mixture of the two starting materials) was confirmed by ESI-MS (see the Experimental Section). The ^{1}H and ^{19}F NMR spectra suggest that there is no significant interaction between the two corrole rings; unlike in several reported examples of "sandwich" species where the corroles are cofacial with metals and bridging ligands between them,[66–68] no unusual shifts of the β-pyrrolic hydrogen atoms or the $-C_6F_5$ fluorine atoms are observed. If the two rings interacted, then nonequivalency of the *ortho* and *meta* fluorine atoms would be expected, and those on the inside of the cofacial "sandwich" would be shifted upfield due to shielding by added effects of two anisotropic corrole rings. The ^{19}F NMR spectrum is notable in that it is clearly a superposition of two sets of $-C_6F_5$ peaks in nearly identical chemical

environments (Figure 1), consistent with two bis-perfluorinated copper(III) corroles that do not have any electronic communication. Figure 1 also shows enlarged regions (inset) for the *ortho*, *para*, and *meta* fluorine peaks for compounds **5**, **6**, and **14**. While the spectra cannot be overlaid directly due to differences in solvent and magnetic field strength, comparison of the complex peaks of **14** with those of its precursors shows that the spectrum is consistent with two corrole rings in diamagnetic environments. Additionally, the alkynyl proton observed in the ^{1}H NMR spectrum of **5** is not present in **14**, but an additional singlet that integrates to 1H is observed at 7.75 ppm in the aromatic region (which otherwise looks very much like a superposition of the spectra of **5** and **6**), consistent with formation of the triazole.

By a similar procedure, **8** and **6** were reacted in the presence of copper(I) acetate to generate the heterobimetallic copper-
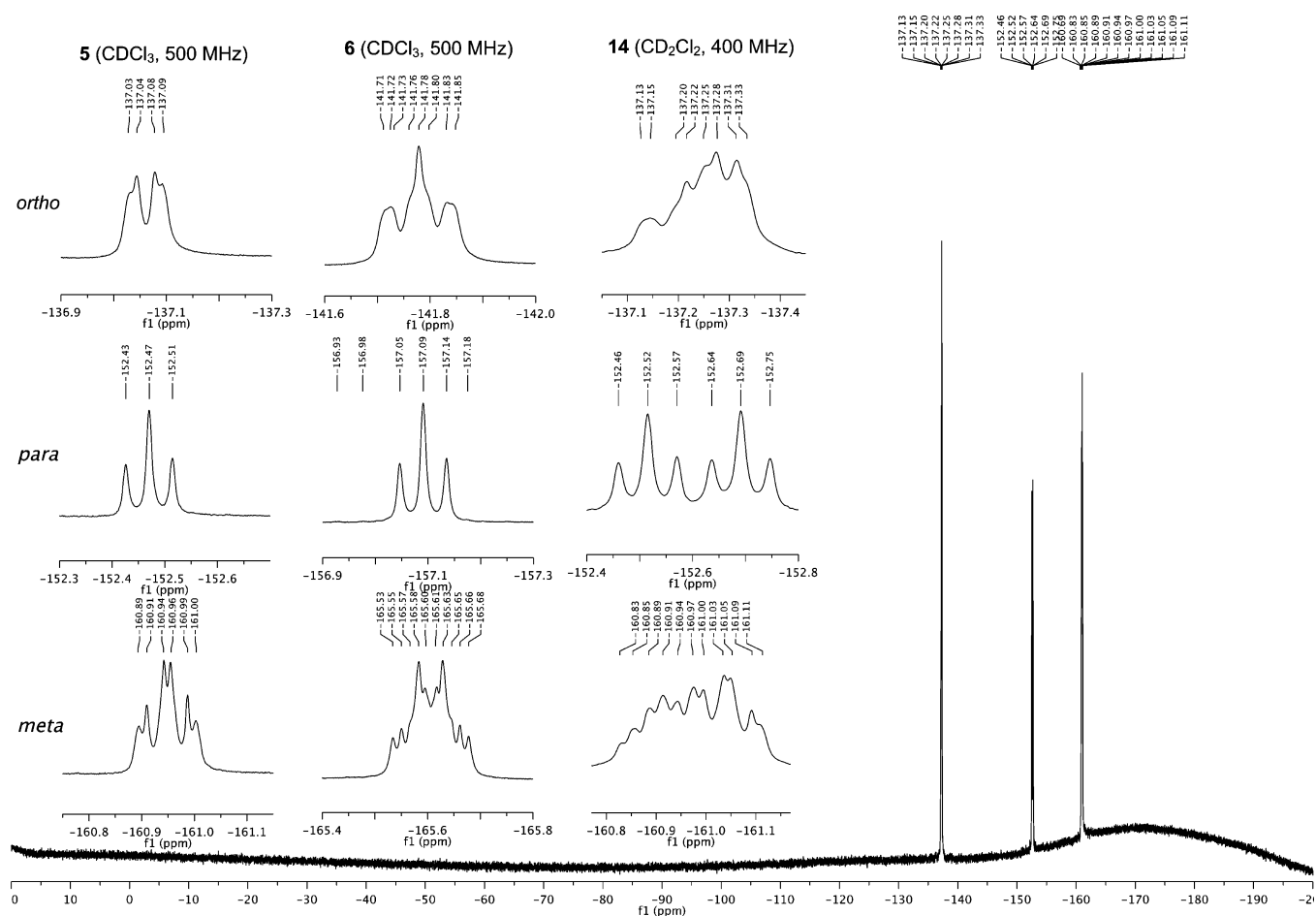
Figure 1. ^{19}F NMR spectrum of **14** (large spectrum), exhibiting typical chemical shifts for perfluorophenyl groups. Insets show *ortho*, *para*, and *meta* fluorine peaks for compounds **5**, **6**, and **14**.

(III) iron(III) bis-corrole complex **15** (54% yield). Analogous to the iron(III) complex **12**, hydrazine was added to convert the product cleanly to an iron(III) species; in this case acetonitrile was used as the coordinating solvent due to limited solubility of the larger molecule in diethyl ether. ^{1}H and ^{19}F NMR spectroscopies again suggest that there is minimal interaction between the two metal centers, although broad peaks from the paramagnetic iron(III) corrole do overlap the peaks of the copper corrole in the ^{1}H NMR spectrum, precluding accurate integration of the sharp peaks. The paramagnetically shifted peaks of the iron corrole in both the ^{1}H and ^{19}F NMR spectra of **15** are again consistent with those previously reported for an iron(III) corrole species.[58] In the ^{19}F NMR five peaks are observed (δ −117.7 (*ortho-F*-Fe(corrole)), −140.5 (*ortho-F*-Cu(corrole)), −158.0 (possibly two peaks, *para-F*'s), −163.7 (*meta-F*), −165.2 (*meta-F*)); it is likely that two peaks are superimposed at −158 ppm due to slight broadening of this peak; however integration is inaccurate in the presence of a paramagnetic metal center. The *meta*-fluorine peaks cannot be distinguished without more advanced NMR spectroscopic studies.

Both **14** and **15** were characterized by cyclic voltammetry, as were **7** and **9** for comparison. **14** shows a single reversible peak at −0.21 V vs Ag/Ag$^+$ in methylene chloride, corresponding to the Cu^{III}/Cu^{II} peaks of both copper centers (Figure S5, Table 1).[69] This peak is at essentially the same potential with double the current observed for **7** (−0.23 V vs Ag/Ag$^+$) and occurs at a

Table 1. Assignment of Peaks in Cyclic Voltammograms of 14 and 15 and Comparison to Reference Compounds^a

corrole (solvent)	reduction(s)	Cu^{III}/Cu^{II}	Fe^{III}/Fe^{IV}	ligand oxidation(s)
14 (CH$_2$Cl$_2$)		−0.21		0.74
15 (CH$_3$CN)^b		−0.19	0.04	0.6,^{b} 0.9^b
7 (CH$_2$Cl$_2$)		−0.23		0.73, 1.33,^{c} 1.53^c
7 (CH$_3$CN)		−0.22		0.62, 1.43^c
9 (CH$_2$Cl$_2$)	−0.69		−0.01	0.32, 1.00
9 (CH$_3$CN)	−0.76, −1.88		0.01	0.29, 0.84
Cu(tpfc) (CH$_2$Cl$_2$)[69]	−2.00	−0.09		0.82, 1.26
Cu(p-OMePh)$_3$corrole (CH$_2$Cl$_2$)[69]		−0.54		0.35, 1.01, 1.29
Fe(tpfc) (CH$_2$Cl$_2$)[58]	−1.08		0.44	(none reported)

^{a}All voltages calculated as $E_{pf} - E_{pr}$ at 0.1 V/s and reported in V vs Ag/Ag$^+$, unless otherwise indicated. E_{pf} = peak potential in the forward direction; E_{pr} = peak potential in the reverse direction. Voltages originally reported in SCE were converted to Ag/Ag$^+$ by subtracting 298 mV.[61] ^{b}Data for **15** collected at 0.5 V/s due to low solubility. Ligand oxidations were poorly resolved; peak potentials estimated. ^{c}Irreversible oxidations; reported as the oxidative peak potential.

potential 0.12 V more negative than the analogous peak in previously reported copper(III) tris(perfluorophenyl) corrole (Cu(tpfc)) and 0.33 V more positive than the previously

reported copper(III) tris(p-methoxyphenyl) corrole. These numbers are consistent with the corresponding electron-withdrawing and electron-donating natures of the corrole ligands in **7**, Cu(tpfc), and Cu(p-OMePh)$_3$corrole.[69] The voltammogram of **14** also shows a quasireversible peak at 0.74 V vs Ag/Ag$^+$ with an oxidative shoulder at 0.64 V (0.1 V/s) that merges with the main peak at higher scan rates. These peaks correspond to oxidation of the ligand and are again very similar to the corresponding ligand oxidation observed for **7** but with roughly double the current. The presence of a single peak for the Cu^{III}/Cu^{II} transition for **14** and the nearly identical ligand oxidations for both **14** and **7** suggest that there is no interaction or electronic communication between the two copper corroles in **14**, consistent with what is observed by NMR spectroscopy and consistent with the fact that a recently reported corrole–BODIPY dyad with click attachment exhibits only through-space and not through-bond fluorescence resonance energy transfer.[46]

Cyclic voltammetry of **15** in acetonitrile displays an oxidation and a reduction consistent with the presence of both copper and iron. The peak at −0.19 V vs Ag/Ag$^+$ corresponds to the Cu^{III}/Cu^{II} couple and that at 0.04 V corresponds to Fe^{III}/Fe^{IV};[58] these are essentially the same peaks observed for the two corresponding mononuclear species, **7** and **9** (Table 1). As is the case with the Cu^{III}/Cu^{II} peak, the Fe^{III}/Fe^{IV} couple occurs at a potential 0.40 V more negative than the analogous Fe^{III}/Fe^{IV} peak in Fe(tpfc).[58] It should be noted that the voltammograms of **14** and **15** were recorded in different solvents due to solubility limitations. Similarly to **14**, the voltammogram of **15** shows oxidative peaks corresponding to the oxidation of the ligand. Also analogous to **14**, there is no indication of interaction between the two metal centers, based on the fact that the metal oxidations and reductions are observed at essentially the same potentials as seen in the monometallic analogues.

CONCLUSION

In summary, we have demonstrated that bis-corroles possessing a flexible linker can be efficiently synthesized via Huisgen azide–alkyne cycloaddition chemistry. Our convergent strategy makes it possible to construct two building blocks independently and then to combine them in the final step. This methodology allows preparation of stable homo- and heterobimetallic complexes. Further studies are underway to demonstrate the utility of this reaction for attachment of corroles to larger substrates and surfaces.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Cyclic voltammograms of **7**, **9**, **14**, and **15** and NMR spectra of **1**–**3** and **5**–**15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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