

## Electronic Supplementary Information

# Reductive demetallation of Cu-corroles - A new protective strategy towards functional free-base corroles

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### 1. General experimental methods

NMR spectra were acquired on commercial instruments (Bruker Avance 300 MHz, Bruker AMX 400 MHz or Bruker AMX 600 MHz) and chemical shifts ( $\delta$ ) are reported in parts per million (ppm) referenced to tetramethylsilane (Me<sub>4</sub>Si) (<sup>1</sup>H) or the carbon signal of deuterated solvents (<sup>13</sup>C). *J* values are given in Hz. Mass spectra were run using a Thermo Finnigan LCQ Advantage apparatus (ESI). UV–vis spectra were taken on a Perkin-Elmer Lambda 20 Spectrometer. For column chromatography 70-230 mesh silica 60 (E. M. Merck) was used as the stationary phase. Chemicals received from commercial sources were used without further purification.

### 2. Experimental and characterization data

**General procedure for the Cu-metallation of Fb *meso*-triarylcorroles:** To a solution of the respective Fb corrole (0.1 mmol) in THF (15 mL), anhydrous Cu(OAc)<sub>2</sub> (54 mg, 0.3 mmol, 3 equiv) was added and the mixture was stirred at rt under Ar for 10 min. THF was removed under reduced pressure and the Cu-corroles were obtained in pure form as brown-red solids after flash column chromatography (silica, eluent CH<sub>2</sub>Cl<sub>2</sub>–heptane mixtures).

**Copper 10-(4-aminophenyl)-5,15-bis(2,4,6-trimethylphenyl)corrole (1b):** Yield 90%;  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>)/nm 393 (log  $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 4.915), 432 (4.846), 512 (4.152), 613 (3.845);  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 7.94 (2 H, br s, H <sub>$\beta$</sub> ), 7.40 (2 H, d, *J* 7.8, H<sub>ph</sub>), 7.36 (2 H, br s, H <sub>$\beta$</sub> ), 7.27 (2 H, d, *J* 4.3, H <sub>$\beta$</sub> ), 7.20 (2 H, br s, H <sub>$\beta$</sub> ), 7.01 (4 H, s, H<sub>mesit</sub>), 6.75 (2 H, d, *J* 7.8, H<sub>ph</sub>), 3.86 (2 H, br s, NH), 2.39 (6 H, s), 2.05 (12 H, s);  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>) 149.0, 147.2, 144.4, 143.7, 138.3 (br), 137.6, 134–132 (br), 130.8 (CH), 128.2 (CH<sub>mesit</sub>), 121.1 (CH), 114.4 (CH), 21.3 (CH<sub>3</sub>), 19.9 (CH<sub>3</sub>); *m/z* (ESI+) 686.6 [M + H]<sup>+</sup>.

**Copper 10-(4-cyanophenyl)-5,15-bis(2,4,6-trimethylphenyl)corrole (2b):** Yield 95%;  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>)/nm 403 (log  $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 4.849), 534 (3.845), 599sh (3.540);  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 7.97 (2 H, br s, H <sub>$\beta$</sub> ), 7.79 (2 H, d, *J* 8.2, H<sub>ph</sub>), 7.71 (2 H, d, *J* 8.2, H<sub>ph</sub>), 7.37 (2 H, d, *J* 3.7, H <sub>$\beta$</sub> ), 7.18 (2 H, br s, H <sub>$\beta$</sub> ), 7.06–6.98 (6 H, m, H<sub>mesit</sub>/H <sub>$\beta$</sub> ), 2.39 (6 H, s), 2.05 (12 H, s);  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>) 149.0, 144.5, 144.0, 137.9, 132.7, 132.1 (CH), 131.7 (CH), 128.7, 128.3 (CH<sub>mesit</sub>), 128.0, 125.7 (CH), 121.6 (CH), 118.9, 112.3, 21.4 (CH<sub>3</sub>), 19.9 (CH<sub>3</sub>); *m/z* (ESI+) 695.3 [M + H]<sup>+</sup>.

**Copper 10-(4,6-dichloro-2-methylsulfanylpyrimidin-5-yl)-5,15-bis(2,4,6-trimethylphenyl)corrole (3b):** Yield 94%. Spectral and physical properties concur with previously published data.<sup>6b,\*</sup>

**Copper 5,10,15-tris(2,6-dichlorophenyl)corrole (4b):** Yield 85%. Spectral and physical properties concur with previously published data.<sup>7g</sup>

**Copper 10-(4-nitrophenyl)-5,15-bis(2,4,6-trimethylphenyl)corrole (5b):** Yield 95%;  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>)/nm 397 (log  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  4.804), 451sh (4.513), 538sh (3.900), 599 (3.630);  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.35 (2 H, d, *J* 8.2, H<sub>ph</sub>), 7.96 (2 H, br s, H <sub>$\beta$</sub> ), 7.77 (2 H, d, *J* 8.2, H<sub>ph</sub>), 7.37 (2 H, br s, H <sub>$\beta$</sub> ), 7.19 (2 H, br s, H <sub>$\beta$</sub> ), 7.04 (2 H, d, *J* 3.7, H <sub>$\beta$</sub> ), 7.01 (4 H, s, H<sub>mesit</sub>), 2.39 (6 H, s), 2.05 (12 H, s);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>) 148.9, 147.9, 144.5, 144.0, 140.9, 137.9, 132.7, 131.9 (CH), 128.6, 128.3 (CH), 128.0, 123.5 (CH), 121.6 (CH), 21.4 (CH<sub>3</sub>), 19.9 (CH<sub>3</sub>); *m/z* (ESI<sup>+</sup>) 716.4 [M + H]<sup>+</sup>.

**Copper 5,10,15-tris(pentafluorophenyl)corrole (6b):** Yield 91%. Spectral and physical properties concur with previously published data.<sup>7d,g</sup>

**3,3'-Bis-[copper-5,10,15-tris(pentafluorophenyl)corrole] (7b):** Spectral and physical properties concur with previously published data.<sup>7g</sup>

**General procedure for the demetallation of Cu-*meso*-triarylcorroles:** To a solution of the respective Cu-corrole (0.05 mmol) in acetonitrile–dichloromethane (2–1; 15 mL), SnCl<sub>2</sub>·2H<sub>2</sub>O (113 mg, 0.5 mmol, 10 equiv) was added and the resulting mixture was stirred for 10 min at rt under Ar. Subsequently, concentrated aqueous HCl (1 mL) was added and stirring was continued for 10 min at rt under Ar. The completion of the demetallation process was monitored by ESI-MS and TLC. The mixture was diluted with diethyl ether, washed with water till neutral, dried over Na<sub>2</sub>SO<sub>4</sub> and the drying agent was filtered off. The solvent was evaporated under reduced pressure and the pure Fb corroles were obtained as purple solids after flash column chromatography (silica, eluent CH<sub>2</sub>Cl<sub>2</sub>–heptane mixtures).

**10-(4-Aminophenyl)-5,15-bis(2,4,6-trimethylphenyl)corrole (1a):** Yield 96%. Spectral and physical properties concur with previously published data.<sup>11,12</sup>

**10-(4-Cyanophenyl)-5,15-bis(2,4,6-trimethylphenyl)corrole (2a):** Yield 85%. Spectral and physical properties concur with previously published data.<sup>9</sup>

**10-(4,6-Dichloro-2-methylsulfanylpyrimidin-5-yl)-5,15-bis(2,4,6-trimethylphenyl)corrole (3a):** Yield 94%. Spectral and physical properties concur with previously published data.<sup>6b</sup>

**5,10,15-Tris(2,6-dichlorophenyl)corrole (4a):** Yield 87%. Spectral and physical properties concur with previously published data.<sup>9b,15</sup>

**5,10,15-Tris(pentafluorophenyl)corrole (6a):** Yield 54%. Spectral and physical properties concur with previously published data.<sup>9b,15</sup>

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\* The inserted reference numbers are identical to those mentioned in the manuscript.

**3,3'-Bis-[5,10,15-tris(pentafluorophenyl)corrole] (7a)**: Yield 43%. Spectral and physical properties concur with previously published data.<sup>16c</sup>

### **S<sub>N</sub>Ar/demetallation sequence**

**Copper 10-[4,6-bis(4-*tert*-butylphenoxy)-2-methylsulfanylpyrimidin-5-yl]-5,15-bis(2,4,6-trimethylphenyl)corrole (8b)**: To a solution of Cu-corrole **3b** (75 mg, 95  $\mu\text{mol}$ , 1 equiv) in DMF (10 mL) were added 4-*tert*-butylphenol (86 mg, 0.57 mmol, 6 equiv) and Cs<sub>2</sub>CO<sub>3</sub> (279 mg, 0.86 mmol, 9 equiv) and the mixture was heated overnight (14 h) at 120 °C under an Ar atmosphere. DMF was evaporated in vacuum and the resulting residue was dissolved in diethyl ether, washed with distilled water and the organic fraction was dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was evaporated under reduced pressure and the pure Cu-corrole **8b** (97 mg, 81%) was obtained as a red-brown solid after column chromatographic purification (silica, eluent CH<sub>2</sub>Cl<sub>2</sub>-heptane, 7-3).  $\lambda_{\text{max}}$  (CH<sub>2</sub>Cl<sub>2</sub>)/nm 265 (log  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  4.597), 400 (4.829), 538 (3.880);  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 7.95 (2 H, br s, H $_{\beta}$ ), 7.35-7.22 (10 H, m), 7.04 (4 H, s, H<sub>mesit</sub>), 6.91 (4 H, d, *J* 9.1), 2.41 (6 H, s), 2.20 (3 H, s, SMe), 2.08 (12 H, s), 1.26 (18 H, s);  $\delta_{\text{C}}$ (75 MHz, CDCl<sub>3</sub>) 171.1, 150.6, 148.6, 148.0, 143.7, 137.7, 132.0 (CH), 128.3 (CH), 126.3, 125.9 (CH), 125.2, 121.1 (CH), 120.8 (CH), 34.5, 31.6 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>), 20.0 (CH<sub>3</sub>), 14.1 (S-CH<sub>3</sub>); *m/z* (ESI+) 1015.4 [M + H]<sup>+</sup>.

Under identical conditions (50 mg scale), bis-substituted Fb corrole **8a** was obtained in 29% yield.

**10-[4,6-Bis(4-*tert*-butylphenoxy)-2-methylsulfanylpyrimidin-5-yl]-5,15-bis(2,4,6-trimethylphenyl)corrole (8a)**: According to the general demetallation procedure: Yield 90%;  $\lambda_{\text{max}}$  (CH<sub>2</sub>Cl<sub>2</sub>)/nm 265 (log  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  4.372), 408 (5.137), 427 (5.040), 566 (4.321), 600 (4.070), 633 (3.586);  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.78 (2 H, d, *J* 3.7, H $_{\beta}$ ), 8.65 (2 H, d, *J* 4.6, H $_{\beta}$ ), 8.52 (2 H, d, *J* 4.6, H $_{\beta}$ ), 8.24 (2 H, d, *J* 3.7, H $_{\beta}$ ), 7.25 (4 H, s, H<sub>mesit</sub>), 7.14 (4 H, d, *J* 9.2), 6.89 (4 H, d, *J* 9.1), 2.60 (6 H, s), 2.35 (3 H, s, SMe), 1.94 (12 H, s), 1.15 (18 H, s);  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>) 170.7, 169.7, 150.8, 147.7, 139.4, 137.8, 135.8, 128.2 (CH), 127.7 (CH), 125.7 (CH), 125.2 (CH), 121.1 (CH), 114.7 (CH), 102.9, 96.3, 34.4, 31.4 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>), 14.3 (S-CH<sub>3</sub>); *m/z* (ESI+) 955.5 [M + H]<sup>+</sup>.

### **Halogenation (S<sub>E</sub>Ar)/demetallation sequence**

**Copper 2,3,7,8,12,13,17,18-octabromo-5,10,15-tris(2,6-dichlorophenyl)corrole (9b)**: To a stirred solution of Cu-5,10,15-tris(2,6-dichlorophenyl)corrole (**4b**) (40 mg, 50.4  $\mu\text{mol}$ ) in CHCl<sub>3</sub> (20 mL), liquid Br<sub>2</sub> (116  $\mu\text{L}$ , 2.25 mmol, 45 equiv), dissolved in 8 mL of CHCl<sub>3</sub>, was added over a period of 15 min, and the resulting mixture was stirred for 5 h at rt. The work-up was performed according to Ghosh *et al.*,<sup>7d</sup> and the octabrominated Cu-corrole **9b** (32 mg, 44%) was obtained as a brownish solid after purification by column chromatography (silica, eluent CH<sub>2</sub>Cl<sub>2</sub>-heptane, 1-1).  $\lambda_{\text{max}}$  (CH<sub>2</sub>Cl<sub>2</sub>)/nm 294 (log  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  4.197), 429 (4.753), 571 (3.814);  $\delta_{\text{H}}$ (600 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 7.45-7.40 (3 H, m), 7.36 (4 H, dd, *J* 8.1 and 1.1), 7.33 (2 H, d, *J* 8.3);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>) 150.8, 148.2, 145.0, 136.6 (br), 132.9, 132.0 (CH), 131.8 (CH), 130.7, 128.4 (CH), 128.3 (CH), 121.7; *m/z* (ESI-) 1423.4 [M - H]<sup>-</sup>.

**Copper 2,3,7,8,12,13,17,18-octachloro-10-(4,6-dichloropyrimidin-5-yl)-5,15-bis(2,4,6-trimethylphenyl)corrole (11b)**: To a stirred solution of Cu-10-(4,6-dichloropyrimidin-5-yl)-

5,15-bis(2,4,6-trimethylphenyl)corrole **10b**<sup>6b</sup> (50 mg, 0.067 mmol) in *o*-dichlorobenzene (5 mL) at 140 °C under Ar, *N*-chlorosuccinimide (81 mg, 0.606 mmol, 9 equiv) was gradually added over a 3 h period, and the mixture was stirred at 90 °C overnight, after which complete conversion was checked via ESI-MS. The solution was evaporated to dryness and the crude residue was redissolved in diethyl ether, washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated in vacuum. The resulting crude product was purified by column chromatography (silica, eluent CH<sub>2</sub>Cl<sub>2</sub>-heptane, 1-1), affording octachlorinated Cu-corrole **11b** (31.5 mg, 46%) as a brownish solid.  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>)/nm 269 (log  $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 4.393), 290 (4.345), 417 (4.962), 527 (3.970);  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.89 (1 H, s, H<sub>pyrim</sub>), 7.03 (4 H, s, H<sub>mesit</sub>), 2.35 (6 H, s), 2.05 (12 H, s);  $\delta_{\text{C}}$ (100 MHz, CDCl<sub>3</sub>) 157.8 (CH<sub>pyrim</sub>), 146.4, 143.5-142.0 (br), 142.0-140.0 (br), 139.7, 128.9 (CH<sub>mesit</sub>), 127.3, 21.5 (CH<sub>3</sub>), 20.2 (CH<sub>3</sub>); *m/z* (ESI-) 1018.2 [M - H]<sup>-</sup>.

**2,3,7,8,12,13,17,18-Octachloro-10-(4,6-dichloropyrimidin-5-yl)-5,15-bis(2,4,6-trimethylphenyl)corrole (11a)**: According to a slightly adapted demetallation procedure: 10.0 mg Cu-corrole **11b**, 2 mL acetonitrile, 1 mL dichloromethane, 0.5 mL HCl (conc), 1 equiv SnCl<sub>2</sub>·2H<sub>2</sub>O (2.2 mg), 6 h reaction at rt, eluent CH<sub>2</sub>Cl<sub>2</sub>-heptane, 1-1: Yield 20% (1.9 mg), 70% recovery of Cu-corrole **11b**;  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>)/nm 430 (log  $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 4.960), 578 (3.997), 615 (3.805), 657 (3.687);  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 9.14 (1 H, s, H<sub>pyrim</sub>), 7.21 (4 H, s, H<sub>mesit</sub>), 2.57 (6 H, s), 1.88 (12 H, s);  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>)<sup>†</sup> 164.8, 158.0 (CH<sub>pyrim</sub>), 139.5, 138.6, 131.3, 128.9 (CH<sub>mesit</sub>), 125.7, 21.7 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>); *m/z* (ESI+) 957.3 [M + H]<sup>+</sup>.

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<sup>†</sup> Due to the small product quantity and the low abundance for several (quaternary) carbon atoms of triarylcorroles, not all required signals were observed in the <sup>13</sup>C spectrum of **11a**.

### 3. <sup>1</sup>H NMR spectra for the novel *meso*-triarylcopper(II) corroles











