### **Supporting Information**

## Highly Reducible $\pi$ -Extended Copper Corroles

Pinky Yadav,<sup>a</sup> Muniappan Sankar,<sup>\*a</sup> Xiangyi Ke,<sup>b</sup> Lei Cong<sup>b</sup> and Karl M. Kadish<sup>\*b</sup>

<sup>a</sup>Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee-247667, India.

<sup>b</sup>Department of Chemistry, University of Houston, Houston, TX-77054, USA.

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#### **Experimental section**

#### Chemicals

Benzaldehyde, pyrrole, tributyl(phenylethynyl)stannane and Pd(PPh<sub>3</sub>)<sub>4</sub> were purchased from Alfa Aesar and used as received. Dichloromethane for synthesis was dried and distilled over CaH<sub>2</sub>. 1,4-dioxane was dried and distilled over Na metal and benzophenone. Synthesis of the Ag and free-base diphenylethynyl corroles were prepared following reported procedures.<sup>1</sup> 2,3,7,8,12,13,17,18-octabromo-5,10,15triphenylcorrole and 2,3,7,8,12,13,17,18-octabromo-5,10,15-tritolylcorrole were synthesized according to reported literature methods.<sup>2</sup> Crystals of CuTPC(PE)<sub>2</sub> 3 suitable for single crystal X-ray diffraction were obtained from slow diffusion of CH<sub>3</sub>OH into a CHCl<sub>3</sub> solution. The chloroform molecules are found to be disordered. Hence SOUEEZE procedure<sup>3</sup> was implemented in order to correct electron density contribution from disordered CHCl<sub>3</sub> molecules. The data is deposited at CCDC database (CCDC No 1532011). Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, anhydrous, ≥99.8%, EMD Chemicals Inc.) for electrochemistry were used as received. Benzonitrile (PhCN, reagentPlus, 99%) for electrochemistry was purchased from Sigma-Aldrich and freshly distilled over  $P_2O_5$  before use. Tetrahydrofuran (THF, for HPLC,  $\geq$ 99.9%) for electrochemistry was purchased from Sigma-Aldrich and freshly distilled using a Solvent System PS-MD-5-13-495 from Innovative Technology. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Sigma-Aldrich.

#### Instrumentation

UV-visible spectra of the neutral compunds was recorded using a Cary 100 spectrophotometer. All <sup>1</sup>H NMR measurements were performed using a Bruker

AVANCE 500 MHz or JEOL ECX 400 MHz spectrometer in CDCl<sub>3</sub>. MALDI-TOF mass spectra were measured using a Bruker UltrafleXtreme-TN MALDI-TOF/TOF spectrometer with 2-(4-hydroxyphenylazo)benzoic acid (HABA) as a matrix. Elemental analysis was carried out on Elementarvario EL III instrument. Cyclic voltammetry was carried out using an EG&G Princeton Applied Research (PAR) 173 potentiostat coupled to an EG&GPAR Model 175 Universal Programmer. Current-voltage curves were recorded on an EG&G PAR R-0151 X-Y recorder. A homemade three-electrode cell was used for cyclic voltammetry measurements and consisted of a glassy carbon working electrode, a platinum counter electrode and a homemade saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted bridge of low porosity, which contained the solvent/supporting electrolyte mixture. EPR spectra were recorded using broker spectrometer in toluene.

#### General synthetic procedure for synthesis of the di-phenylethynylcorroles

Cu metallation of free base phenylethynylcorroles were carried out as reported in the literature.<sup>4</sup> A Silica gel column was used to purify the target copper corroles using a 1:2 ratio of CHCl<sub>3</sub>/hexane compounds. **3** and **4** were synthesized in 80-90% yield.

#### 3,17-diphenylethynyl-5,10,15-tripenylcorrolatocopper(II) cation radical (3)

<sup>1</sup>H NMR in CDCl<sub>3</sub> (400 MHz): δ(ppm) 8.18 (s, 2H, β-pyrrole-H), 7.61 (s, 4H, *meso-*phenyl-H), 7.48 (s, 12H, β- pyrrole-H and *meso-*phenyl-H), 7.21 (asym. d, 7H, J = 4.0 Hz, *meso-*phenyl-H and β- phenyl-H), 7.10 (d, 2H, J = 4.0 Hz, β- phenyl-H), 7.00 (dd, 4H, J = 4, 8 Hz, β- phenyl-H) MALDI/TOF-MS (m/z): found 787.76, calcd.

[M+H]<sup>+</sup> 787.19. Anal. calcd. for C<sub>53</sub>H<sub>31</sub>N<sub>4</sub>Cu: C, 80.85; H, 3.97; N, 7.12. Found: C, 80.71; H, 3.90; N, 7.15%.

#### 3,17-diphenylethynyl-5,10,15-tritolylcorrolatocopper(II) cation radical (4)

<sup>1</sup>H NMR in CDCl<sub>3</sub> (400 MHz): δ(ppm) 8.13 (s, 2H, β-pyrrole-H), 7.53 (d, 4H, J = 8 Hz, *meso*-phenyl-H), 7.45 (d, J = 8 Hz, 2H, *meso*-phenyl-H), 7.31-7.20 (m, 14H, β-pyrrole-H, *meso*-phenyl-H and β- phenyl-H), 7.15 (d, 2H, J = 8.0 Hz, β- phenyl-H), 7.01-6.99 (m, 4H, β- phenyl-H), 2.43(s, 3H, -CH<sub>3</sub>-H), 2.35(s, 6H, -CH<sub>3</sub>-H). MALDI/TOF-MS (m/z): found 829.74, calcd.  $[M+H]^+$  829.24. Anal. calcd. for C<sub>56</sub>H<sub>37</sub>N<sub>4</sub>Cu: C, 81.09; H, 4.50; N, 6.75. Found: C, 81.20; H, 4.62; N, 6.72%.

#### General synthetic procedure for β-octa-phenylethynylcorroles

Cu(Br<sub>8</sub>)TXC (0.060 g) was dissolved in 30 mL of distilled 1,4-dioxane and purged with Ar gas for 15 minutes. To this, tributyl(phenylethynyl)stannane (12 equiv.) in 2 mL of degassed 1,4-dioxane was added dropwise. Finally, Pd(PPh<sub>3</sub>)<sub>4</sub> (20 mol%) was added and reaction mixture heated to 75 °C for 60 minutes under Ar atmosphere. After completion of the reaction, the solvent was removed by vacuum distillation. The crude product was dissolved in CHCl<sub>3</sub> (5 mL) and purified on a silica column.

# 2,3,7,8,12,13,17,18-octaphenylethynyl-5,10,15-triphenylcorrolatocopper(II) cation radical (5)

Purification was carried out using a  $CHCl_3$ /hexane mixture (1:1, v/v) as eluent. The desired product was recrystallized using a  $CHCl_3$ /hexane mixture (1:5, v/v). The yield was 65%.

1H NMR in CDCl<sub>3</sub> (500 MHz): δ (ppm) 7.85 (d, 3H, J = 7.15 Hz, *meso*-phenyl-H), 7.78 (d, 1H, J = 7.15 Hz, *meso*-phenyl-H), 7.56 (d, 2H, J = 7.45 Hz, *meso*-phenyl-H), 7.48 (d, 5H, J = 7.30 Hz, *meso*-phenyl-H), 7.43 (d, 2H, *meso*-phenyl-H), 7.40 (d, 4H, β-pyrrole PE-H and *meso*-phenyl-H), 7.25-7.22 (m, 6H, β-pyrrole PE-H), 7.21-7.11 (m, 20H β-pyrrole PE-H), 7.10-7.04 (m, 12H, β-pyrrole PE-H). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (nm) ( $\epsilon \times 10^{-3}$  L mol<sup>-1</sup> cm<sup>-1</sup>) 496 (68.7), 621 (16.9), 732 (4.19). MALDI/TOF-MS (m/z): found 1388.944 [M+H]<sup>+</sup>, calcd. 1388.39. Anal. calcd. for C<sub>101</sub>H<sub>55</sub>N<sub>4</sub>Cu: C, 87.39; H, 3.99; N, 4.04. Found: C, 87.57; H, 4.06; N, 4.19%.

# 2,3,7,8,12,13,17,18-octaphenylethynyl-5,10,15-tritolylcorrolatocopper(II) cation radical (6)

Purification was carried out using a CHCl<sub>3</sub>/hexane mixture (1:1, v/v) as eluent. The desired product was recrystallized from a  $CHCl_3$ /hexane mixture (1:5, v/v). The yield was 72%. <sup>1</sup>H NMR in CDCl<sub>3</sub> (400 MHz):  $\delta$  (ppm) 7.75 (d, 3H, J = 8 Hz, mesophenyl-H), 7.67 (d, 2H, J = 8 Hz, meso-phenyl-H), 7.41 (d, 4H, J = 4 Hz, mesophenyl-H), 7.28-7.26 (m, 3H, meso-phenyl-H), 7.23 (d, 7H, J = 8 Hz,  $\beta$ -pyrrole PE-H), 7.23-7.09 (m, 21H, β-pyrrole PE-H), 7.08-7.03 (m, 12H, β-pyrrole PE-H), 2,22 (s, 6H, meso-phenylCH<sub>3</sub>-H), 2.17 (s, 3H, meso-phenylCH<sub>3</sub>-H). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  (nm) ( $\epsilon \times 10^{-3}$  L mol<sup>-1</sup> cm<sup>-1</sup>) 508(74.8), 620(15.3), 729(5.2). MALDI/TOF-MS (m/z): found 1432.61  $[M+2H]^+$ , calcd. 1432.19. Anal. calcd. for C<sub>104</sub>H<sub>61</sub>N<sub>4</sub>CuO•0.5H<sub>2</sub>O: C, 86.79; H, 4.34; N, 3.89. Found: C, 86.82; H, 4.40; N, 4.30%.



Figure S1. <sup>1</sup>H NMR spectrum of CuTPC(PE)<sub>2</sub> 3 in CDCl<sub>3</sub> at 298 K.



Figure S2. <sup>1</sup>H NMR spectrum of CuTTC(PE)<sub>2</sub> 4 in CDCl<sub>3</sub> at 298 K.



**Figure S3.** <sup>1</sup>H NMR spectrum of CuTPC(PE)<sub>8</sub> **5** in CDCl<sub>3</sub> at 298 K.



Figure S4. <sup>1</sup>H NMR spectrum of CuTTC(PE)<sub>8</sub> 6 in CDCl<sub>3</sub> at 298 K.



Figure S5. MALDI-TOF mass spectrum of CuTPC(PE)<sub>2</sub> 3 using HABA matrix.



Figure S6. MALDI -TOF mass spectrum of CuTTC(PE)<sub>2</sub> 4 using HABA matrix.



Figure S7. MALDI-TOF mass spectrum of CuTPC(PE)<sub>8</sub> 5 using HABA matrix.



Figure S8. MALDI-TOF mass spectrum of CuTTC(PE)<sub>8</sub> 6 using HABA matrix.



**Figure S9.** Front view (left) and side view (right) of two independent molecules (one in red color and another one is in blue color) of crystal structure of  $CuTPC(PE)_2$  **3**.



Figure S10. Crystal packing diagram of corrole CuTPC(PE)<sub>2</sub> 3.

**Table S1**. Crystal structure data of CuTPC(PE)2 3.

	$CuTPC(PE)_2 (3)$				
Empirical Formula	$C_{53}H_{31}CuN_4$				
Formula wt.	787.36				
Crystal system	Triclinic				
Space group	P-1				
<i>a</i> (Å)	16.7756(6)				
<i>b</i> (Å)	17.1514(5)				
<i>c</i> (Å)	18.3118(6)				
α (°)	117.549(3)				
β(°)	109.011(3)				
γ(°)	97.510(3)				
Volume (Å <sup>3</sup> )	4160.4(3)				
Ζ	4				
D <sub>cald</sub> (mg/m <sup>3</sup> )	1.257				
$\lambda$ (Å)	0.71073				
T (°C)	150(2) K				
No. of total reflns.	26671				
No. of indepnt. reflns.	15766				
R	0.0770				
R <sub>w</sub>	0.2607				
GOOF	0.986				
CCDC No	1532011				



**Figure S11.** Variable temperature <sup>1</sup>H NMR spectra of CuTPC **1** in  $C_6D_6$  showing the aromatic region of the spectrum.



**Figure S12.** Variable temperature <sup>1</sup>H NMR spectra of CuTTC **2** in  $C_6D_6$  showing the aromatic region of the spectrum.



**Figure S13.** Variable temperature <sup>1</sup>H NMR spectra of CuTPC(PE)<sub>2</sub> **3** in C<sub>6</sub>D<sub>6</sub> showing the aromatic region of the spectrum.



Figure S14. Variable temperature <sup>1</sup>H NMR spectra of CuTPC(PE)<sub>8</sub> 5 in  $C_6D_6$  showing the aromatic region of the spectrum.



**Figure S15.** Variable temperature <sup>1</sup>H NMR spectra of CuTTC(PE)<sub>8</sub> **6** in C<sub>6</sub>D<sub>6</sub> showing the aromatic region of the spectrum.



Figure S16. EPR spectra of corroles 1-6 at (a) 100 K and (b) 293 K in toluene.



Figure S17. EPR spectra of corroles 1-6 in toluene at 353 K.



Figure S18. EPR spectra of chemically oxidized corroles 1-6 in toluene at 100 K.



Figure S19. EPR spectra of chemically reduced corroles 1-6 in toluene at 100 K.



**Figure S20.** Cyclic voltammograms of **2**, **4** and **6** in  $CH_2Cl_2$  at 20 °C, with 0.1 M TBAP. Scan rate = 0.1 V/sec.



Figure S21. Cyclic voltammograms of 1, 3 and 5 in  $CH_2Cl_2$  (a) at 20 °C and (b) -60° C, with 0.1 M TBAP. Scan rate = 0.1 V/sec.



Figure S22. Cyclic voltammograms of 2, 4 and 6 in PhCN at 20 °C, with 0.1 M TBAP. Scan rate

= 0.1 V/sec.



Figure S23. Cyclic voltammograms of 1, 3 and 5 in PhCN at 20 °C, with 0.1 M TBAP. Scan rate = 0.1 V/sec.



**Figure S24.** Cyclic voltammograms of **2**, **4** and **6** in THF at 20 °C, with 0.1 M TBAP. Scan rate = 0.1 V/sec.

Oxidation # of Reduction Solvent Macrocycle Cor # 2<sup>nd</sup> 4<sup>th</sup>  $1^{st}$  $1^{st}$ 2<sup>nd</sup> 3<sup>rd</sup> PE  $CH_2Cl_2$ CuTTC 0 2 1.36 0.73 -0.20 2 0.76 4 1.28 -0.07 -1.72 -1.85 8 6 1.42 0.94 0.10 -1.26 -1.69 CuTPC 0 1 1.38 0.75 -0.18 2 3 1.32 0.70 -0.07 -1.67 8 5 1.38 0.97 0.10 -1.24 -1.69<sup>a</sup> PhCN CuTTC 0 1.37 0.70 -0.21 2 2 4 1.39 0.78 -0.09 -1.78 8 6 1.47 0.97 0.10 -1.28 -1.71 CuTPC 0 1.44 0.76 -0.16 1 2 3 1.41 0.82 -0.05 -1.75 8 5 1.50 0.99 0.10 -1.26 -1.67 THF CuTTC 0 2 0.80 -0.14 -1.96 -2.57<sup>a</sup> 2 4 0.86 0.00 -1.67 -1.82 -2.17<sup>a</sup> 8 6 1.01 0.16 -1.23 -1.67 -1.85 CuTPC 0 1 0.85 -0.10 -1.96 -2.52<sup>a</sup> 2 3 0.88 0.03 -1.64 -2.16

**Table S2.** Half-wave potential (V *vs.* SCE) for the investigated copper corroles in  $CH_2Cl_2$  and PhCN, and THF, scan rate = 0.1V/s at 20°C.

<sup>a</sup>Peak potential.



**Figure S25.** Spectral changes obtained during 1<sup>st</sup> reduction and 1<sup>st</sup> oxidation of **2**, **4** and **6** in PhCN, 0.1M TBAP.

(a) CuTPC 1



**Figure S26.** Spectral changes obtained during 1<sup>st</sup> and 2<sup>nd</sup> reductions of **1**, **3** and **5** in THF, 0.1M TBAP.

Table S3. UV-vis spectral data of Cu corroles in their neutral and electroreduced forms in THF, 0.1 M TBAP.

Corrole	$\lambda$ (nm) ( $\epsilon \times 10^4$ M <sup>-1</sup> cm <sup>-1</sup> )											
Macrocycle	$[Cu^{ll}(Cor^{+})]^{0}$ (neutral)				[Cu <sup>ll</sup> (Cor)	] <sup>-</sup> (1 <sup>st</sup> Red)			[C	$u^{II}(Cor)]^{2-}(2^{nd} R)$	ed)	
TPC 1	409 (5.1)	542 (0.4)	626 (0.2)	432 (6.3)	542 (0.4)	575 (0.7)	608 (1.1)	435 (2.4)	610 (0.7)	697 (0.8)		
TTC 2	416 (12.3)	542 (0.9)	632 (0.5)	431(6.0)	542 (0.9)	575 (1.4)	609 (2.4)	433 (3.5)	609 (0.8)	697 (0.6)		
$TPC(PE)_2$ 3	425 (4.3)	576 (0.8)	665 (0.6)	448(3.6)	465 (3.7)	615 (1.5)	646 (2.0)	370 (2.3)	467 (2.0)	545 (0.9)	611 (0.9)	748 (1.9)
TTC(PE) <sub>2</sub> 4	430 (6.2)	576 (0.8)	665 (0.6)	446(5.2)	463 (4.8)	615 (2.4)	646 (3.0)	366 (3.0)	450 (3.2)	547 (1.20)	611 (1.7)	748 (2.6)
TPC(PE) <sub>8</sub> 5	496 (3.3)	626 (1.0)	738 (0.4)	534(3.0)	632 (1.1)	679 (1.0)	729 (0.8)	528 (1.7)	849 (0.8)			
TTC(PE) <sub>8</sub> 6	507(5.6)	623 (1.3)	740 (0.5)	527(5.2)	623 (1.3)	679 (1.7)	727 (1.2)	548 (2.2)	837(1.4)			



**Figure S27.** UV-vis spectral changes of CuTTC **2**, CuTTC(PE)<sub>2</sub> **4** and CuTTC(PE)<sub>8</sub> **6** upon oxidation with (tris(p-bormophenylammoniumyl)exachloroantimonate) in CH<sub>2</sub>Cl<sub>2</sub> at 298K. The single oxidized species are shown in red and represented as  $[2]^+$ ,  $[4]^+$  and  $[6]^+$ .



**Figure S28.** UV-vis spectral changes of corrole CuTPC **1**, CuTPC(PE)<sub>2</sub> **3** and CuTPC(PE)<sub>8</sub> **5** while addition of one electron oxidant (tris(*p*-bormophenyl)ammoniumyl hexachloroantimonate) in CH<sub>2</sub>Cl<sub>2</sub> (left) and one electron reductant (KO<sub>2</sub>) in CH<sub>3</sub>CN (right) at 298 K.

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