

## A<sub>2</sub>B Type Cu(III)–Triarylcorroles: Synthesis and Tunable Electrocatalyzed Hydrogen Evolution Behaviors

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*The synthesis of three low symmetry A<sub>2</sub>B type Cu(III)-triarylcorroles with meso-arylsubstituents that provide push-pull electron-donating and electron-withdrawing properties is reported. An analysis of the structure-property relationships for the optical and redox properties has been carried out. The results demonstrate that A<sub>2</sub>B type Cu(III)-corroles are highly effective catalysts for hydrogen evolution, and the electrochemically catalytic properties could be facilely modulated by the electron withdrawing/donating ability of meso-substituent at B-positions.*

**Keywords:** A<sub>2</sub>B corrole, electronic structure, spectroscopy, electrochemistry, electrocatalysis.

## Сu(III)–Триарилкорролы A<sub>2</sub>B типа: синтез и регулируемое электрокатализируемое выделение водорода

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*В статье сообщается о синтезе трех низкосимметричных «пуш-пул» Cu(III)-триарилкорролов A<sub>2</sub>B типа с электронодонорными и электроноакцепторными мезо-арилзаместителями. Проведен анализ взаимосвязи структуры и оптических и окислительно-восстановительных свойств. Результаты показывают, что Cu(III)-корролы A<sub>2</sub>B типа являются высокоэффективными катализаторами выделения водорода, а электрохимические каталитические свойства возможно регулировать введением электроноакцепторных/донорных заместителей в положения B.*

**Ключевые слова:** A<sub>2</sub>B коррол, электронная структура, спектроскопия, электрохимия, электрокатализ.

### Introduction

The world's population growth accompanied by its corresponding high energy demands and environmental concerns necessitated scientist to find an alternative renewable and sustainable energy carrier either than fossil.<sup>[1-2]</sup> Molecular hydrogen is considered the ideal energy carrier for chemical energy conversion and other process.<sup>[3-4]</sup> It is an attractive and clean fuel candidate for sustainable

energy storage and transport. Electrochemical evolution of hydrogen through water splitting has for decades received tremendous attention worldwide. It proved to be the cleanest form of energy with zero emission of carbonaceous substances. However, the existence of a large overpotential in electrocatalysis process makes it urgent to design highly active electrocatalysts for the hydrogen evolution reaction. After decades of research, molecular catalysts from earth-abundant transition metals such as Cu, Mn, Ni, Co and Fe<sup>[5-8]</sup>

have proven to be the best choice over Pt. Despite recent achievements from molecular catalysts, high efficiency and durability in highly acidic and basic media could not be guaranteed owing to insufficient binding affinity of metals to ligands. This phenomenon arises when the coordination sites of nitrogen or oxygen in the molecular complex gets protonated under highly acidic condition thereby expelling the metal. Also, in highly basic media, the metal ions could get attracted and be pulled by the hydroxide ions.<sup>[9–10]</sup>

Corroles are structural analogs of porphyrins that have a direct pyrrole-pyrrole bond and an extra NH proton in their inner core, which are perhaps best known in a manner that results in lower molecular symmetry and more intense absorption in the longer wavelength portion of the visible region. In recent years, increased energy demands and serious environmental concerns, have made research on clean energy sources one of the most important tasks for modern society.<sup>[11–13]</sup> Hydrogen gas is an ideal energy storage carrier for the next generation of renewable energy systems, but the emergence of efficient hydrogen evolution reactions (HERs) to enable the formation of hydrogen gas from water will determine whether this clean energy world will emerge.<sup>[14–19]</sup> In addition, the modulation of electrochemical reactions has recently been achieved through molecular electrochemical catalysis by singly or doubly electrochemically reduced metallo-porphyrins and metallo-corroles, and the catalytic efficiency can be modulated by the symmetric and asymmetric introduction of various substituents.<sup>[9,20–22]</sup> The key advantage of using corroles is that a trianionic ligand is formed when a *meso*-carbon is removed from the porphyrin structure, which stabilizes the higher oxidation states of first-row transition metals, thus enhancing their utility for electrocatalytic reactions.<sup>[23–26]</sup> One of the most effective structural modifications with corroles is the push-pull strategy, which involves the introduction of both electron-donating (push) and withdrawing (pull) substituents onto the molecule through an A<sub>2</sub>B type pattern in the *meso*-aryl groups. This has been shown to enable significant modifications to the electronic structures of coordinated macrocyclic compounds including metallo-porphyrins, phthalocyanines and corroles.<sup>[27–29]</sup> In this study, the synthesis, optical spectroscopy, and electrochemistry of a series of push-pull Cu(III)-triarylcorroles (**3a–c**) is reported (Scheme 1) along with their hydrogen evolution reactions (HERs).

## Experimental

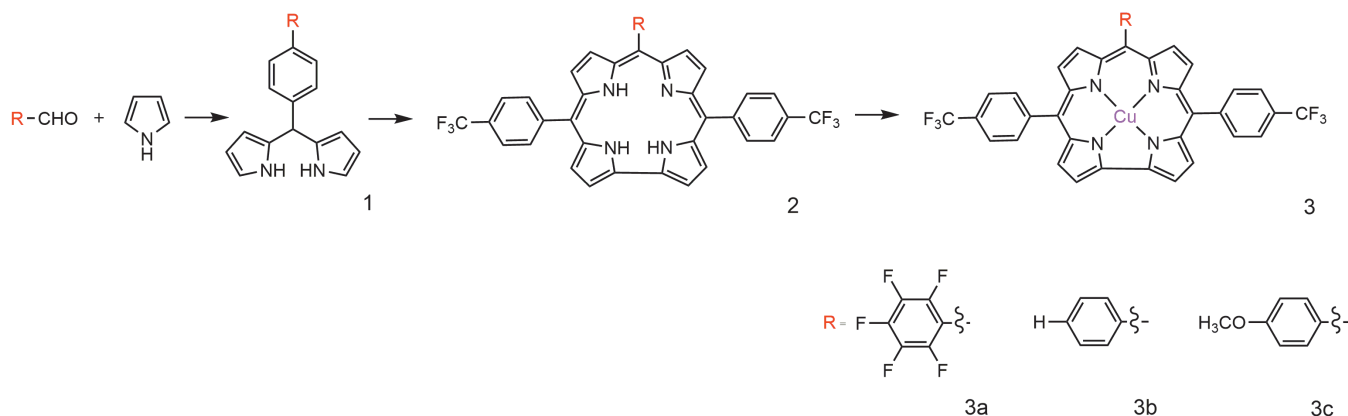
### General Considerations

<sup>1</sup>H NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400.03 MHz). Residual solvent peaks were used to provide internal references for the <sup>1</sup>H NMR spectra ( $\delta$ =7.26 ppm for CDCl<sub>3</sub>). All reagents and solvents used were of reagent grade and were used as received unless noted otherwise. Cyclic voltammetry was carried out on a Chi-730D electrochemistry station with a three-electrode cell. A glassy carbon disk, a platinum wire and an Ag/AgCl electrode were used as the working, counter and reference electrodes, respectively. The UV and visible regions of the electronic absorption spectra were recorded with an HP 8453A diode array spectrophotometer, while a Shimadzu UV-3600 plus instrument was used for measurements in the NIR region. An inert nitrogen atmosphere was introduced during all of the electrochemical measurements, which were carried out at room temperature. A JASCO J-815 spectrodichromometer equipped with a JASCO permanent magnet (1.6 tesla) was used to measure magnetic circular dichroism (MCD) spectra. Spectra were recorded using both parallel and antiparallel fields. The conventions recommended by Piepho and Schatz are used to describe the sign of the Faraday terms, so the sign of the B<sub>0</sub> terms matches that of the MCD signal.

**Synthesis of Cu(III)-5,15-(*p*-trifluoromethylphenyl)-10-(pentafluorophenyl)corrole **3a**.** H<sub>3</sub>-5,15-(*p*-trifluoromethylphenyl)-10-(pentafluorophenyl)corrole **2a** was synthesized according to the procedure reported in literature.<sup>[22]</sup> A 25 mL CH<sub>2</sub>Cl<sub>2</sub>/MeOH (v:v=1:4) mixture of H<sub>3</sub>-triarylcorrole **2a** (0.05 mmol, 0.0308 g) was refluxed at 75 °C for 45 mins. After removal of organic solvent, the pure compound was obtained through silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) and recrystallization. Yield: 82 % (35.2 mg). *m/z* (MALDI-TOF-MS) 873.25 (Calcd. 873.17 [M]<sup>+</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K)  $\delta_{\text{H}}$  ppm: 8.41–8.30 (1H, m), 7.93 (3H, dd, *J*<sub>1</sub>=22.5 Hz, *J*<sub>2</sub>=8.9 Hz), 7.87–7.76 (3H, m), 7.72 (2H, dd, *J*<sub>1</sub>=15.1 Hz, *J*<sub>2</sub>=7.0 Hz), 7.56 (2H, dd, *J*<sub>1</sub>=18.0 Hz, *J*<sub>2</sub>=4.1 Hz), 7.37–7.30 (3H, m), 7.22–7.01 (2H, m).

**Synthesis of Cu(III)-5,15-(*p*-trifluoromethylphenyl)-10-phenylcorrole **3b**.** The general synthetic procedure was same as it was used in the synthesis of **3a**, except 5,15-(*p*-trifluoromethylphenyl)-10-phenylcorrole was used instead. Yield: 86.3 % yield (0.0282 g). *m/z* (MALDI-TOF-MS) 783.30 (Calcd. 783.14 [M]<sup>+</sup>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298K)  $\delta_{\text{H}}$  ppm: 7.88 (5H, d, *J*=8.3 Hz), 7.82–7.73 (5H, m), 7.70–7.56 (6H, m), 7.55–7.43 (5H, m).

**Synthesis of Cu(III)-5,15-(*p*-trifluoromethylphenyl)-10-(*p*-methoxyphenyl)corrole **3c**.** The general synthetic procedure was the same as it was used in the synthesis of **3a**, except 5,15-(*p*-trifluoromethylphenyl)-10-(*p*-methoxyphenyl)corrole



**Scheme 1.** Synthesis of Cu(III)triarylcorroles **3a–c**.

was used instead. Yield: 80.8 % (32.8 mg).  $m/z$  (MALDI-TOF-MS) 813.33 (Calcd. 813.14  $[M]^+$ ).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 298K)  $\delta_{\text{H}}$  ppm: 7.86 (5H, d,  $J=8.2$  Hz), 7.74 (5H, dd,  $J_1=18.0$  Hz,  $J_2=7.2$  Hz), 7.56 (5H, dd,  $J_1=11.2$  Hz,  $J_2=8.4$  Hz), 7.30 (5H, dt,  $J_1=7.3$  Hz,  $J_2=3.6$  Hz), 7.00 (4H, d,  $J_1=8.6$  Hz), 3.93 (3H, d,  $J_1=6.5$  Hz).

## Results and Discussion

### Synthesis and Structural Characterization

The free base corrole compounds (**2a-c**) were synthesized by reaction of *meso-p*-trifluoromethyl-dipyrromethane **1** and the appropriate aryl-aldehyde (Scheme 1) according to the literature procedures.<sup>[22]</sup> Cu(III)-corroles (**3a-c**) were then synthesized by a metalation reaction of **2a-c**, and were purified by silica gel column chromatography and recrystallization. MALDI-TOF mass for **3a** revealed an intense parent peak at  $m/z=873.25$  (Calcd.  $[M]^+=873.17$ ) providing direct evidence that the Cu(III)-5,15-(*p*-trifluoromethylphenyl)-10-(pentafluoromethylphenyl)corrole was prepared successfully. Similar parent peaks were also observed for **3b-c**. The proton signals for the *meso*-substituents and pyrrole rings in the  $^1\text{H NMR}$  spectra (Figure 1) of **3a** mainly lie beyond 7.00 ppm, which could be assigned as protons from *meso*-aryl-substituents and  $\beta$ -protons. Similar peaks have been observed for Cu(III)-corroles **3b-c** that indicated the target compounds were successfully obtained and isolated.

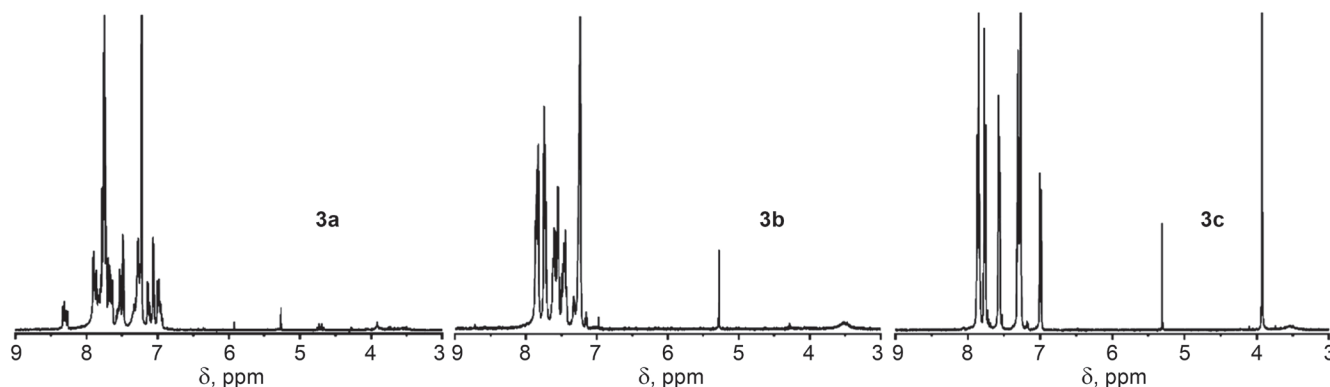
### Optical Spectroscopy

The electronic structures and optical spectra of porphyrinoids can be readily rationalized using Gouterman's 4-orbital model and Michl's perimeter model. The  $\pi$ -MOs associated with the 15 atom 18  $\pi$ -electron inner ligand perimeter are arranged in an  $\text{ML}=0, \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \pm 6, \pm 7$  sequence in ascending energy terms that is determined by the angular nodal properties. Since the HOMO and LUMO have ML values of  $\pm 4$  and  $\pm 5$ , respectively, Gouterman's 4-orbital model predicts the presence of an allowed B transition ( $\Delta\text{ML}=\pm 1$ ) at high energy and a forbidden Q-transition ( $\Delta\text{ML}=\pm 9$ ) at low energy. The B-bands of **3a-c** can be readily assigned to the intense band in the 400–410 nm region and the shoulder of absorbance to high energy, since there is an intense pair of oppositely-signed Faraday  $B_0$  terms in the MCD spectra

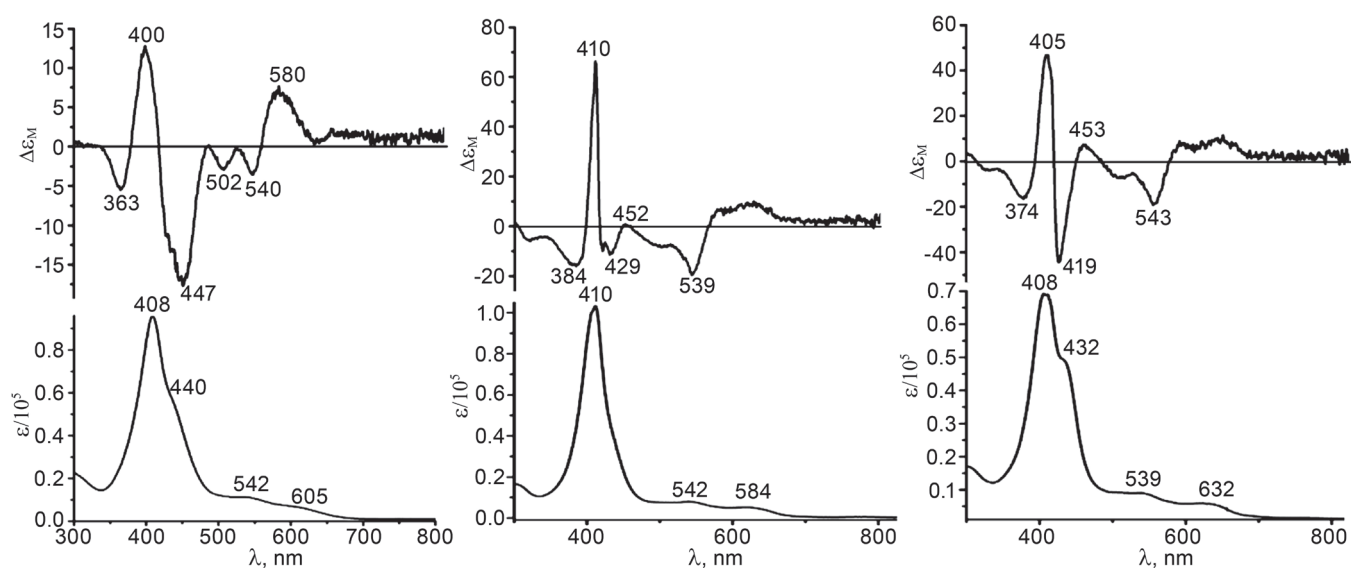
(Figure 2) which lie at *ca.* 408 nm for **3a**, 410 nm for **3b**, 408 and 432 nm for **3c**, respectively. The analysis of the weaker bands in the Q-band region (500–700 nm) is complicated by the presence of ligand-to-metal charge transfer (LMCT) bands, since the LUMO is previously predicted to be associated primarily with the  $3d_{x^2-y^2}$  orbital of the central metal ion. Upon increasing electron donating ability at *meso-B*-position, the red-shift of the Q-band absorptions were clearly observed at  $\lambda=542, 582$  nm for **3a**;  $\lambda=542, 605$  nm for **3b**;  $\lambda=542, 642$  nm for **3c**. On the other hand, the observed  $-/+$  sequences on the MCD spectra indicated difference on the energy split as a  $\Delta\text{HOMO}<\Delta\text{LUMO}$  manner.

### Electrochemistry

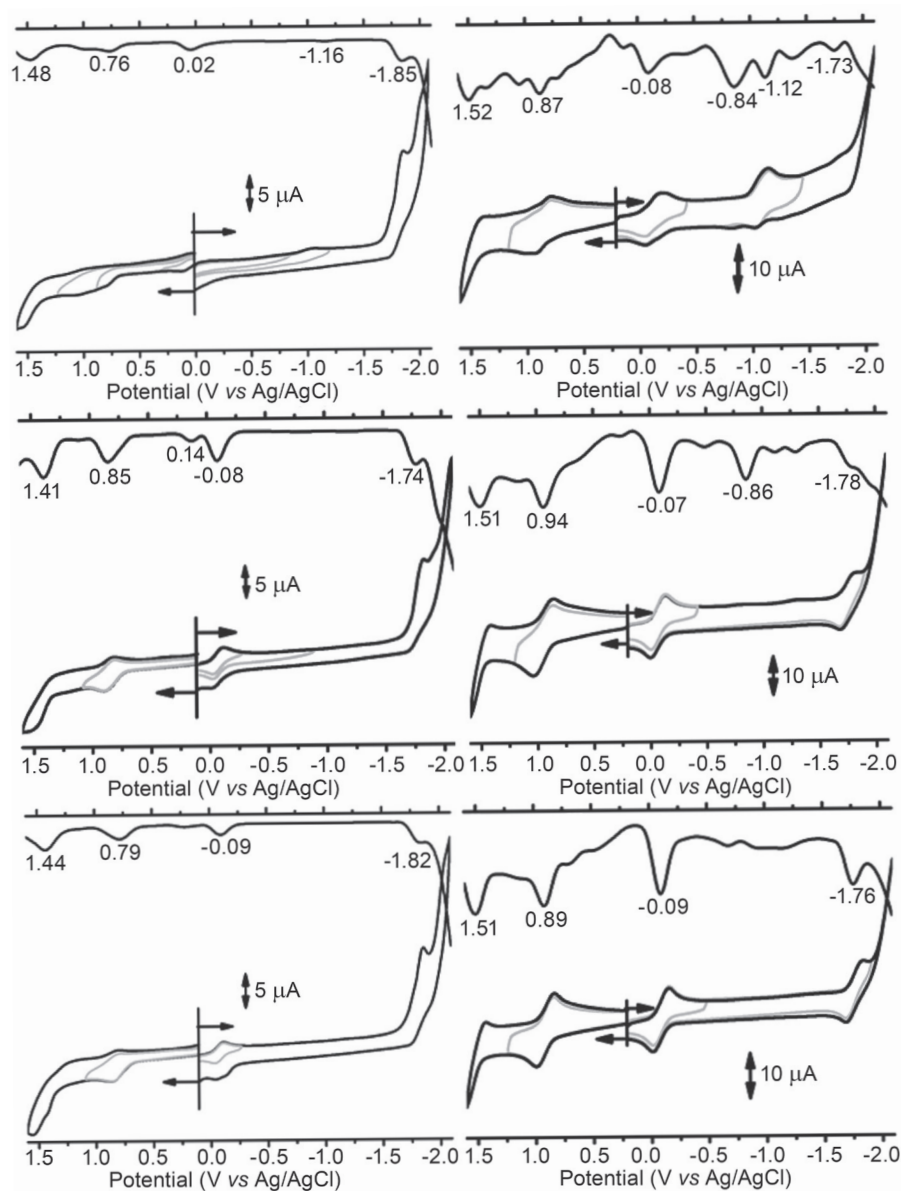
To gain further insight into the electronic structures of Cu(III)-corrole **3a-c** and the effect of solvent polarity on the electrochemical properties, CV and DPV measurements were carried out in the low polar *o*-dichlorobenzene (*o*DCB) and high polar PhCN containing 0.1 M tetra-*n*-butylammonium perchlorate ( $[\text{NtBu}]\text{ClO}_4$ ; TBAP). The redox potentials ( $E_{1/2}$ ) values derived from both CV and DPV measurements (Figure 3 and Table 1). When electron-donating ability of *meso*-substituents at *B*-positions of Cu(III)-corroles is increased in an order of **3a-c**, there is a theoretical increase in the electron density of the metallo-corrole  $\pi$ -conjugation system, thereby leading to significantly difficult reduction and more easier oxidation. The cyclic voltammogram for **3a** consists of a reversible first reduction step at  $E_{1/2}=-0.08$  V (in *o*DCB), which can be assigned to the  $[\text{Cu(III)Corrole}]/[\text{Cu(II)Corrole}]$ , and following with the reduction from pentafluorophenyl ring and the corrole themselves, at  $E_{1/2}=-1.12$  and  $-1.73$  V, respectively. On the other hand, the 1<sup>st</sup> oxidation curve which is observed at  $E_{1/2}=0.87$  V could be clearly assigned as the ring oxidation from  $[\text{Cu(III)Corrole}]$  to  $[\text{Cu(III)Corrole}]^+$  cation. In addition, when the solvent polarity has been increased, the clear positive shift of the 1<sup>st</sup> and 3<sup>rd</sup> reductive potentials, and the negative shift of the 1<sup>st</sup> oxidative potential were observed that indicate the solvent polarity has a large influence on the electronic structure of Cu(III)-corrole complexes. The mirror influence on the 2<sup>nd</sup> reductive potential curve could be attributed the electronic structure of pentafluoro-ring itself. On the other hand, when the electron-donating ability on



**Figure 1.**  $^1\text{H NMR}$  spectra of **3a-c** in  $\text{CDCl}_3$  at 298 K.



**Figure 2.** UV-Vis absorption (bottom) and magnetic circular dichroism spectra of Cu(III)-corroles **3a-c** in  $\text{CH}_2\text{Cl}_2$ .



**Figure 3.** CV and DPV measurements of **3a** (top), **3b** (middle) and **3c** (bottom) in PhCN (left) and *o*-dichlorobenzene (right) containing 0.1 M TBAP.



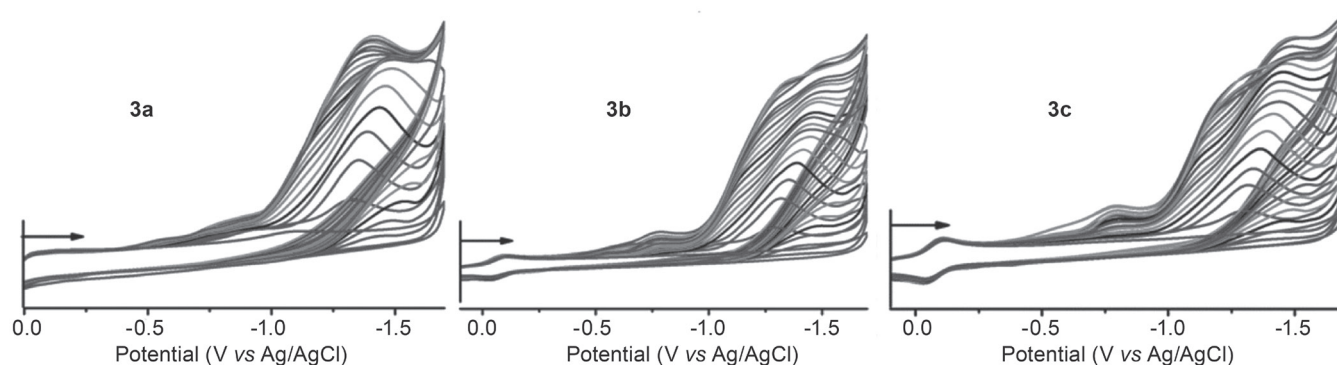
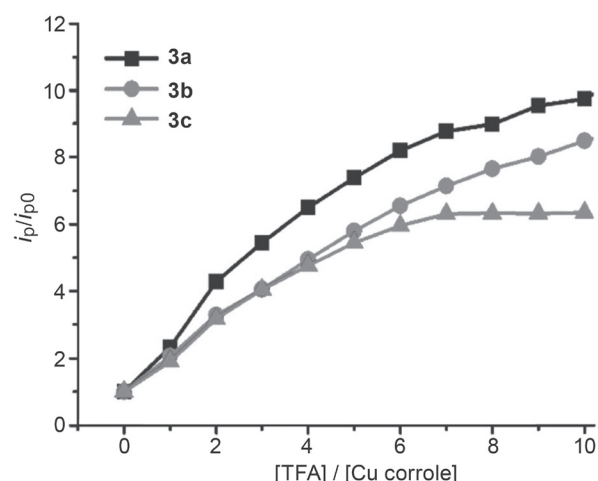
**Table 1.** Redox potential data of **3a-c** derived from CV and DPV measurements.

No.	$E^{1/2}$ Ox <sup>I</sup>	$E^{1/2}$ Red <sup>I</sup>	$E^{1/2}$ Red <sup>II</sup>	$E^{1/2}$ Red <sup>III</sup>
<b>3a</b> (PhCN) / V	0.76	0.02	−1.16	−1.85 <sup>a</sup>
<b>3b</b> (PhCN) / V	0.85	−0.08	−1.74 <sup>a</sup>	—
<b>3c</b> (PhCN) / V	0.79	−0.09	−1.82 <sup>a</sup>	—
<b>3a</b> ( <i>o</i> DCB) / V	0.87	−0.08	−1.12	−1.73
<b>3b</b> ( <i>o</i> DCB) / V	0.94	−0.07	−1.78	—
<b>3c</b> ( <i>o</i> DCB) / V	0.89	−0.09	−1.76	—

the *B-meso*-aryl ring is increased, a positive shift of the  $E^{1/2}$  values were all observed when PhCN was used, but less to no changes were observed in the case of *o*DCB characterizations. The trend observed in the gaps between the first reduction and oxidation steps are consistent with the slight blue-shift of the main *Q* and *B*-bands that is observed spectroscopically and predicted in theoretical calculations. The enhanced electron donating ability of *meso*-substituents at *B*-positions results in a significant increase of the electron density of the Cu(III)-corrole  $\pi$ -system in a manner that results in a slight increase in the magnitude of the HOMO-LUMO gap.

### Electrocatalyzed Hydrogen Evolutions

Stability in acidic environments is an important consideration during the design of new HER catalysts. The stability of **3a-c** was evaluated in PhCN at high trifluoroacetic acid (TFA) concentrations (about 10.0 eq). Herein, TFA was selected due to their high ionizing properties in the organic solvent. Since negligible spectral changes are observed after the mixture was kept at dark for over 5h, it is certain to assume that complexes **3a-c** are suitable for use as HER catalysts. Upon addition of 1.0–20.0 eq. of TFA to solutions of **3a-c**, there is a slight increase in the peak current ( $i_{cat}$ ) at *ca.*  $E = -0.8$  V (Figure 4). The intensities of these peaks at around  $E = -1.4$  V are much stronger than those observed when only the Cu(III)-triarylcorroles and TFA are present in solution. It should be noted that a slight change in the potential values of **3a-c** were observed due to the protonation of the dimethylaminophenyl unit at the *B*-position.

**Figure 4.** Reductive electrochemical measurements of Cu(III)-corroles **3a-c** in the presence of 1.0–10.0 eq. of TFA in PhCN containing 0.1 M  $[NBu_4]^+ [ClO_4]^-$  (TBAP) as a supporting electrolyte.**Figure 5.** Plot of  $i_{cat}/i_p$  values of **3a-c** upon addition of 1.0–10.0 eq of TFA in PhCN containing 0.1 M TBAP, all values are derived from CV measurement.

The kinetic reactivity ( $i_{cat}/i_p$ ) and onset potentials can be used to evaluate the efficiency of the HERs (Figure 5). The addition of TFA to homogeneous solutions of **3a-c** in PhCN induces catalytic waves beyond the  $Cu^{III}/Cu^{II}$  and  $Cu^{II}/Cu^I$  reduction couples. When the concentration of TFA is increased from 1.0–10.0 eq., there is a clear increase in the  $i_{cat}$  values that is related to the electron-withdrawing ability of the *B*-position *meso*-substituent, which demonstrates that the electronic structure of  $A_2B$  type corroles has a significant influence on HER catalysis. In the case of **3a**, the complex with the most strongly electron-withdrawing *B*-position, *meso*-substitution was found to be the most efficient catalyst, followed in order of efficiency by **3b** and **3c** since there is an increase in the electron donating ability of the *B*-position *meso*-substituent in this order.

### Conclusion

Three *meso*-substituted low symmetric Cu(III)-corroles containing various *B meso*-substituents have been synthesized and characterized. A detailed analysis of the spectroscopic investigations including UV-Visible

absorption and MCD spectra, and electrochemical characterizations such as cyclic and differential pulse voltammetry measurements was carried out. The electronic structure investigation has been carried out to identify the main trends in the electronic structures and optical properties. It has been demonstrated that these Cu(III)-corroles are highly effective catalysts for hydrogen evolution, and the electrochemically catalytic properties could be facilely modulated by the electron withdrawing/donating ability of *meso*-substituent at *B*-positions.

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