A₂B Type Cu(III)–Triarylcorroles: Synthesis and Tunable Electrocatalyzed Hydrogen Evolution Behaviors

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The synthesis of three low symmetry A₂B 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 A₂B 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: A₂B corrole, electronic structure, spectroscopy, electrochemistry, electrocatalysis.

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.[1-2] Molecular hydrogen is considered the ideal energy carrier for chemical energy conversion and other process.[3-4] 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[5-8]...
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.[9-10]

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.[11-13] 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.[14-19] In addition, the modulation of electrochemical reactions has recently been achieved through molecular electrocatalysis 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.[9,20-22] 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 and durability in highly acidic and basic media could not be 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 spectrophotometer 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 Pieplo and Schatz are used to describe the sign of the Faraday terms, so the sign of the B0 terms matches that of the MCD signal.

Synthesis of Cu(III)-5,15-(p-trifluoromethylphenyl)-10-(pentafluorophenyl)corrole 3a. H3-5,15-(p-trifluoromethylphenyl)-10-(pentafluorophenyl)corrole 2a was synthesized according to the procedure reported in literature.[22] A 25 mL CHCl3/MeOH (v:v=1:4) mixture of H3-triarylcorrole 2a (0.05 mmol, 0.0308 g) was refluxed at 75 ℃ for 45 mins. After removal of organic solvent, the pure compound was obtained through silica gel column chromatography (CHCl3) and recrystallization. Yield: 82 % (35.2 mg). m/z (MALDI-TOF-MS) 783.30 (Calcd. 783.14 [M]+) and were used as received unless noted otherwise. Experimental General Considerations 1H NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400.03 MHz). Residual solvent peaks were used to provide internal references for the 1H NMR spectra (δ=7.26 ppm for CDCl3). All reagents and solvents used were of reagent grade and were used as received. 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 spectrophotometer 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 Pieplo and Schatz are used to describe the sign of the Faraday terms, so the sign of the B0 terms matches that of the MCD signal.

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Synthesis of Cu(III)-5,15-(p-trifluoromethylphenyl)-10-(pentafluorophenyl)corrole 3b. The general synthetic procedure was as described in the synthesis of 3a, except 5,15-(p-trifluoromethylphenyl)-10-phenylcorrole was used instead. Yield: 86.3 % (0.0282 g). m/z (MALDI-TOF-MS) 873.25 (Calcd. 873.17 [M]+). 1H NMR (CD3Cl, 298 K) δH ppm: 7.82–7.73 (5H, m), 7.72 (2H, dd, J=4.1 Hz), 7.37–7.30 (3H, m), 7.22–7.01 (2H, 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
was used instead. Yield: 80.8 % (32.8 mg). \( m/z \) (MALDI-TOF-MS) 813.33 (Calcd. 813.14 [M])

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,[22] 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 \(^1\)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 ML\( ^{±0} \), \( ±1 \), \( ±2 \), \( ±3 \), \( ±4 \), \( ±5 \), \( ±6 \), \( ±7 \) sequence in ascending energy terms that is determined by the angular nodal properties. Since the HOMO and LUMO have ML valence nodal properties. Since the HOMO and LUMO have ML values of \( ±4 \) and \( ±5 \), respectively, Gouterman’s 4-orbital model predicts the presence of an allowed B transition (\( AM_{1}^{±1} \)) at high energy and a forbidden Q-transition (\( AM_{1}^{±9} \)) 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 \( 3d_{z}^{±2} \) 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 ([NtBu][ClO4]; TBAP). The redox potentials (\( E^{\frac{1}{2}} \)) 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 \( E^{\frac{1}{2}} = 0.08 \text{ V} \) (in \( o \)DCB), which can be assigned to the \([\text{Cu(III)}\text{Corrole}]^{−}\) cation. In addition, when the solvent polarity has been increased, the clear positive shift of the 1\text{st} and 3\text{rd} reductive potentials, and the negative shift of the 1\text{st} 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\text{nd} 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](https://example.com/image1.png)

**Figure 1.** \(^1\)H NMR spectra of 3a-c in CDCl₃ at 298 K.
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Figure 2. UV-Vis absorption (bottom) and magnetic circular dichroism spectra of Cu(III)-corroles 3a-c in CH₂Cl₂.

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. | \(E_{\frac{1}{2}}^{\text{Ox}}\) / V | \(E_{\frac{1}{2}}^{\text{Red}}\) | \(E_{\frac{1}{2}}^{\text{Red}^\text{II}}\) | \(E_{\frac{1}{2}}^{\text{Red}^\text{III}}\) |
|-----|-------------------------------|-----------------|----------------|----------------|
| 3a  (PhCN) / V | 0.76 | 0.02 | -1.16 | -1.85 |
| 3b  (PhCN) / V | 0.85 | -0.08 | -1.74 | - |
| 3c  (PhCN) / V | 0.79 | -0.09 | -1.82 | - |
| 3a  (oDCB) / V | 0.87 | -0.08 | -1.12 | -1.73 |
| 3b  (oDCB) / V | 0.94 | -0.07 | -1.78 | - |
| 3c  (oDCB) / V | 0.89 | -0.09 | -1.76 | - |

the \(\text{B-meso-aryl} \) ring is increased, a positive shift of the \(E_{\frac{1}{2}}\) values were all observed when PhCN was used, but less to no changes were observed in the case of oDCB 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 (\(i_{\text{cat}}\)) 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.

The kinetic reactivity (\(i_{\text{cat}}/i_p\)) 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)/CuII and CuII/CuI reduction couples. When the concentration of TFA is increased from 1.0–10.0 eq., there is a clear increase in the icat values that is related to the electron-withdrawing ability of the \(B\)-position \(\text{meso-}\)substituent, which demonstrates that the electronic structure of A,B type corroles has a significant influence on HER catalysis. In the case of 3a, the complex with the most strongly electron-withdrawing \(B\)-position, \(\text{meso-}\)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 \(\text{meso-}\)substituent in this order.

Conclusion

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