

## Solid–State Synthesis, Spectroscopic and Electrochemical Properties of Symmetric $A_3$ Type Corroles with *meso*–3–Chloro–4–fluorophenyl Groups and Its $Co^{III}$ , $Mn^{III}$ and $Cu^{III}$ Complexes

Peng Zhang, Minzhi Li, Yu Jiang, Li Xu, Xu Liang,<sup>@1</sup> and Weihua Zhu<sup>@2</sup>

*School of Chemistry and Chemical Engineering, Jiangsu University, ZhenJiang 212013, China*

<sup>@1</sup>Corresponding author E-mail: [liangxu@ujs.edu.cn](mailto:liangxu@ujs.edu.cn)

<sup>@2</sup>Corresponding author E-mail: [sayman@ujs.edu.cn](mailto:sayman@ujs.edu.cn)

*Solid-state synthesis of  $A_3$  type 5,10,15-(3-chloro-4-fluorophenyl)corrole, and its  $Co^{III}$ ,  $Mn^{III}$  and  $Cu^{III}$  complexes having asymmetric meso-substituents were successfully synthesized and separated. Structural characterization by MS and  $^1H$  NMR and the spectroscopic properties by UV-vis, magnetic circular dichroism (MCD) spectra were investigated in this study. Electrochemical properties were also studied to in-depth understand the electronic structures of these corrole or metallo-corrole complexes.*

**Keywords:** Corrole, solid-state synthesis, spectroscopy, electrochemistry.

## Твердофазный синтез, спектральные и электрохимические свойства симметричного коррола $A_3$ типа с мезо–3–хлор–4–фторфенильными группами и его $Co^{III}$ , $Mn^{III}$ и $Cu^{III}$ комплексов

Пенг Жанг, Минжи Ли, Ю Джианг, Ли Ксу, Ксу Лианг,<sup>@1</sup> Вейхуа Жу<sup>@2</sup>

*Школа химии и химической инженерии, Университет Цзянсу, 212013 Чжэньцзян, Китай*

<sup>@1</sup>E-mail: [liangxu@ujs.edu.cn](mailto:liangxu@ujs.edu.cn)

<sup>@2</sup>E-mail: [sayman@ujs.edu.cn](mailto:sayman@ujs.edu.cn)

*Проведен твердофазный синтез 5,10,15-(3-хлоро-4-фторфенил)коррола  $A_3$  типа и его комплексов с  $Co^{III}$ ,  $Mn^{III}$  и  $Cu^{III}$  с асимметричными заместителями в мезо-положениях. Структура полученных соединений была подтверждена с помощью масс-спектрометрии и спектральных методов (ЭСР, спектроскопии  $^1H$  ЯМР и магнитного кругового дихроизма). Для более глубокого понимания электронной структуры полученного коррола и его металлокомплексов были изучены их электрохимические свойства.*

**Ключевые слова:** Коррол, твердофазный синтез, спектроскопия, электрохимия.

## Introduction

The porphyrinoid complexes have received the considerable amount of attention in recent years, since their optical and biological properties could lead to applications as functional dyes in a number of different high-technology fields, such as organic solar cells, photodynamic therapy, heat absorbers, and organic catalysis.<sup>[1]</sup> Corroles, the porphyrin analogues with a direct pyrrole-pyrrole bond and an extra N-H proton on the inner ligand perimeter, are best known for forming the basic structure of vitamin B<sub>12</sub>.<sup>[2]</sup> In recent decades, there has been a strong research focus on the use of corroles as functional ligands, largely due to their ability to stabilize higher oxidation states of the coordinated metals, which can be applied as potential catalysts such as: Cr(V), Fe(IV), Co(IV), and even Mn(V) or Co(V).<sup>[3]</sup> On the other hand, high-valence metallo-corrole complexes applied for combined photodynamic therapy (PDT) and bioimaging applications in living cells has recently been explored.<sup>[4]</sup> Recently, the synthesis of corrole is mainly focused on the acid-catalyzed reaction by Gryko,<sup>[5a-5d]</sup> or solid-state Al<sub>2</sub>O<sub>3</sub> supported reaction was also succeeded by Collman.<sup>[5e]</sup> However, in spite of research interests of corroles, the number of either spectroscopic or electrochemical investigations on the electronic structure of free base corroles and their metallo-complexes have been limited. Especially, the corrole analogues having asymmetric *meso*-substituents were less studied and reported previously. All these advantages promoted us to synthesize new corrole analogues containing asymmetric *meso*-substituents. In this paper, asymmetric 3-chloro-4-fluorobenzaldehyde was selected as the key starting materials to synthesis free base corrole via solid-state synthetic procedure. Spectroscopic properties studied by UV-vis absorptions, magnetic circular dichroism (MCD) spectrums and the electronic structures of these corrole analogues were also in-depth studied by cyclic voltammetry measurements.

## Experimental

### Chemicals

Analytical pure *N,N*-dimethylmethanamide (DMF) for electrochemical measurements was purchased from the Aladdin Reagent Company of Shanghai, and freshly distilled before use. All other chemicals and solvents were analytical pure grade and were purchased from the Shanghai Guoyao Company. All solvents were dried and distilled prior to use.

### Materials and Instruments

Cyclic voltammetry was performed in a three-electrode cell using a Chi-730C electrochemistry station. A glassy carbon disk electrode was utilized as the working electrode while a platinum wire and a saturated calomel electrode (SCE) were employed as the counter and reference electrodes, respectively. The working and counter electrodes were made from platinum mesh and the reference electrode was an SCE. The working and reference electrodes were placed in one compartment while the counter electrode was placed in the other. UV-visible absorption spectra were recorded with a HP 8453A diode array spectrophotometer.

All of the electrochemical measurements were carried out under a nitrogen atmosphere. Magnetic circular dichroism (MCD) spectra were measured with a JASCO J-820 equipped with a 1.6 T (tesla) permanent magnet by using both the parallel and anti-parallel fields. The conventions of Piepho and Schatz are used to describe MCD intensity and the Faraday terms.<sup>[7]</sup> MALDI-TOF mass spectra (MS) were collected using Bruker Daltonics autoflex II MALDI-TOF MS spectrometer. <sup>1</sup>H NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (operating at 400.13 MHz) using the residual solvent as an internal reference for <sup>1</sup>H ( $\delta$ =7.26 ppm for CDCl<sub>3</sub> and 5.32 ppm for CD<sub>2</sub>Cl<sub>2</sub>).

**Synthesis of 5,10,15-(3-chloro-4-fluorophenyl)corrole (1).** Neutralized Al<sub>2</sub>O<sub>3</sub> (3 g) was added to a mixture of 10 mL CH<sub>2</sub>Cl<sub>2</sub> solution of 3-chloro-4-fluorobenzaldehyde (1.59 g, 10 mmol). Freshly distilled pyrrole (0.90 mL, 13 mmol) was slowly added and heated again at 60 °C for 4h under N<sub>2</sub> after fully removed of CH<sub>2</sub>Cl<sub>2</sub>. After cooled to the room temperature, 25 mL CH<sub>2</sub>Cl<sub>2</sub> was added to the same mixture and the Al<sub>2</sub>O<sub>3</sub> was removed by filtration. Then, chronail (1.00 g, 40 mmol) was added to solution and stirred at 50 °C for 1h. Purification performed on the silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>:hexane = 1:1) and finally recrystallized from CH<sub>2</sub>Cl<sub>2</sub> and hexane to give 5,10,15-(3-chloro-4-fluorophenyl)corrole **1** (330 mg, 14.5 %). *m/z* (MALDI-TOF-mass) 685.63 (Calcd. [M+H]<sup>+</sup>=684.94). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\max}$  nm: 414 (136000), 571 (10700), 613 (7800), 644 (7800). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K)  $\delta_{\text{H}}$  ppm: 9.03 (2H, br s), 8.88 (2H, br s), 8.59 (4H, br s), 8.42 (2H, br s), 8.22 (2H, br s), 8.04 (1H, br s), 7.64 (4H, br s), -2.79 (3H, br s).

**Synthesis of Co(III)PPh<sub>3</sub>-5,10,15-(3-chloro-4-fluorophenyl)corrole (2a).** H<sub>3</sub>-5,10,15-(3-chloro-4-fluorophenyl)corrole **1** (68 mg, 0.1 mmol) was dissolved in a 40 mL of methanol/CH<sub>2</sub>Cl<sub>2</sub> (1:1) mixture containing triphenylphosphine (131 mg, 0.5 mmol, 5.0 eq) and Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (190 mg, 0.75 mmol). The mixture was slowly increased to 60 °C and kept for 1.5h. After removal of the solvent, purification by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>:hexane = 1:1), and recrystallization (CH<sub>2</sub>Cl<sub>2</sub>/hexane) to give the pure Co(III)-5,10,15-(3-chloro-4-fluorophenyl)corrole **2a** (92 mg, 92.0%). *m/z* (MALDI-TOF-mass) 740.14 (Calcd. [M]<sup>+</sup>=739.85). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\max}$  nm: 385 (43500), 410 (34800), 556 (9500), 582 (6700). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K)  $\delta_{\text{H}}$  ppm: 8.82 (2H, d, *J*=3.6 Hz), 8.45 (2H, d, *J*=4.8 Hz), 8.20 (2H, d, *J*=4.4 Hz), 8.09 (2H, d, *J*=4.4 Hz), 7.52~7.47 (m, PPh<sub>3</sub>), 7.17 (4H, br s), 6.76 (5H, br s).

**Synthesis of Mn(III)-5,10,15-(3-chloro-4-fluorophenyl)corrole (2b).** H<sub>3</sub>-5,10,15-(3-chloro-4-fluorophenyl)corrole **1** (68 mg, 0.1 mmol) was dissolved in 20 mL of distilled DMF mixture containing Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (183 mg, 0.75 mmol), and the mixture was heated at 110 °C for 30 mins. After removal of DMF under low pressure, the purification was carried by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>), alumina gel chromatography (CH<sub>2</sub>Cl<sub>2</sub>:ethylacetate = 4:1) and the target compound was obtained after recrystallization by CH<sub>2</sub>Cl<sub>2</sub> and hexane to give the pure Mn(III)-5,10,15-(3-chloro-4-fluorophenyl)corrole **2b** (76 mg, 69.0%). *m/z* (MALDI-TOF-mass) 735.20 (Calcd. [M]<sup>+</sup>=735.85). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\max}$  nm: 404 (37500), 428 (35600), 495(11100), 570(7500), 644 (8800).

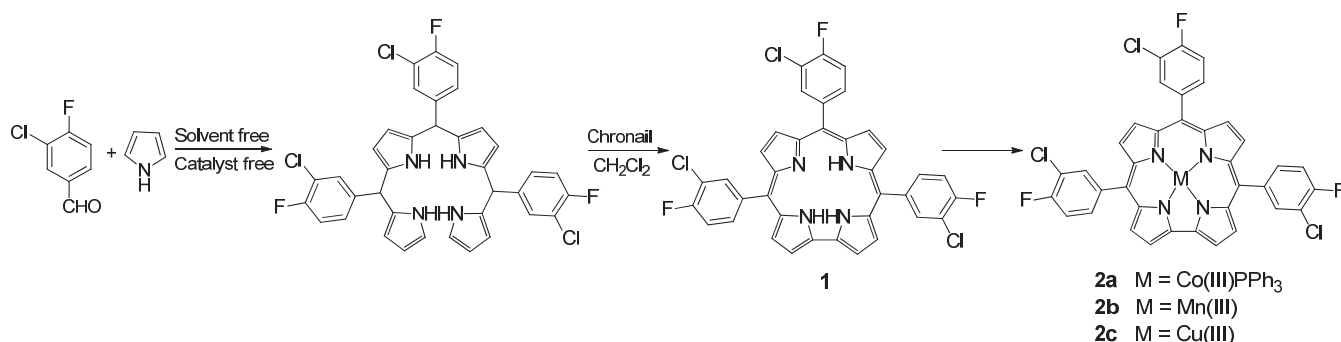
**Synthesis of Cu(III)-5,10,15-(3-chloro-4-fluorophenyl)corrole (2c).** H<sub>3</sub>-5,10,15-(3-chloro-4-fluorophenyl)corrole **1** (136 mg, 0.2 mmol) was dissolved in a 40 mL methanol/CH<sub>2</sub>Cl<sub>2</sub> (1:1) mixture containing Cu(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (200 mg, 1 mmol), and the mixture was refluxed at 60 °C for 2h. After removal of the solvent, the purification was carried by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>), alumina gel chromatography (CH<sub>2</sub>Cl<sub>2</sub>:ethylacetate = 4:1) and recrystallization (CH<sub>2</sub>Cl<sub>2</sub> and hexane to give the pure Cu(III)-5,10,15-(3-chloro-4-fluorophenyl)corrole **2c** (112 mg, 75.0%). *m/z* (MALDI-TOF-mass) 744.60 (Calcd. [M]<sup>+</sup>=744.50). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\max}$  nm: 410 (60100), 540 (4200), 620 (2700). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K)  $\delta_{\text{H}}$  ppm: 7.90 (2H, d, *J*=4.0 Hz), 7.78 (2H, d,

$J=4.4$  Hz), 7.64–7.61 (5H, m), 7.53–7.49 (1H, m), 7.37–7.29 (5H, m), 7.26 (2H, d,  $J=4.8$  Hz).

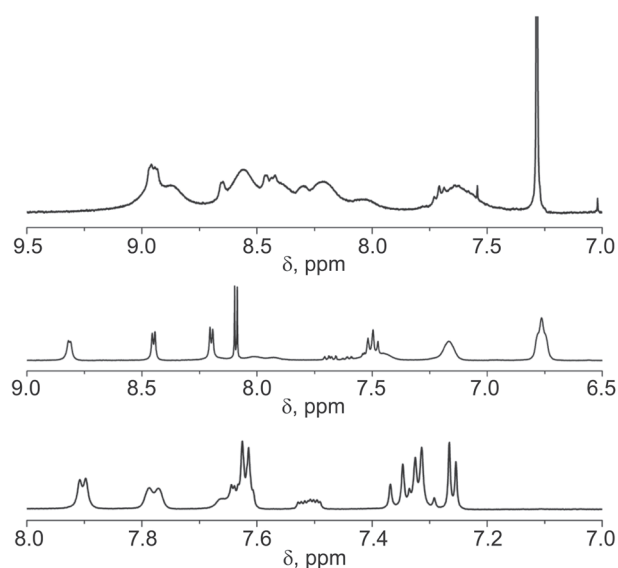
## Results and Discussion

### Synthesis and Characterization

The synthetic procedure is shown in Scheme 1. The solid-state synthetic procedure using  $\text{Al}_2\text{O}_3$  supported materials promoted that the less of acid media produced a simple purification system. The MALDI-TOF-mass spectra of **1** reveals a strong parent peak at  $m/z=685.63$  (Calcd  $[\text{M}+\text{H}]^+=684.94$ ), providing direct evidence that the target  $\text{H}_3$ -5,10,15-(3-chloro-4-fluorophenyl)corrole **1** was successfully obtained. Similar MALDI-TOF-mass peaks were also observed in the case of metallo-corroles **2a**, **2b** and **2c**. The proton signals which appeared in the  $^1\text{H}$  NMR spectra of **1** was similar with that of regular triarylcorrole from literatures.<sup>[5]</sup> The uncertain proton integration value of  $\text{PPh}_3$  of **2a** is probably due to the partial removal of the axial ligands during the purification or measurement.  $^1\text{H}$  NMR spectra of **1**, **2a** and **2c** are shown in Figure 1.



**Scheme 1.** Synthesis of  $\text{H}_3$ -5,10,15-(3-chloro-4-fluorophenyl)corrole **1**, and its metal complexes **2**.

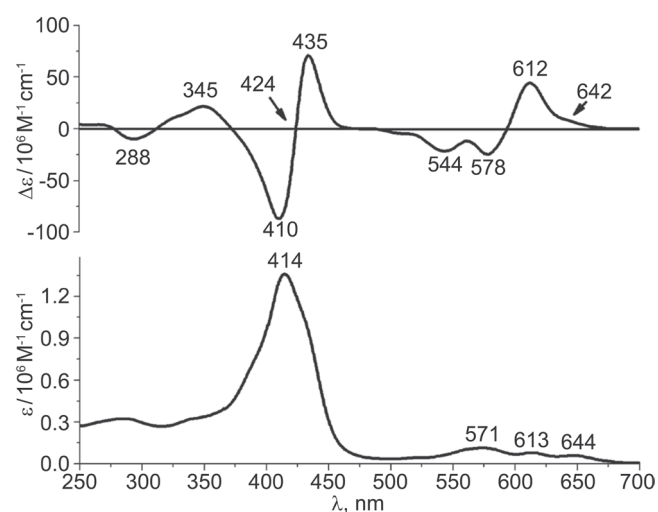


**Figure 1.**  $^1\text{H}$  NMR spectra of **1** (up) in  $\text{CDCl}_3$ , **2a** (middle) and **2c** (bottom) in  $\text{CD}_2\text{Cl}_2$ .

### Spectroscopic Properties

The optical spectroscopy of corroles can be described in terms of perturbations to an  $M_L=0, \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \pm 6, \pm 7$  sequence of MOs associated with the parent  $\text{C}_{15}\text{H}_{15}^{3-}$  perimeter for the 15-atom 18- $\pi$ -electron system of the inner ligand perimeter. Moffitt<sup>[6]</sup> and Michl<sup>[7]</sup> demonstrated that when the symmetry of aromatic and heteroaromatic  $\pi$ -systems are lowered by perturbations to the structure, the alignments of the nodal patterns of the MOs of the parent perimeter are retained. This can be used to predict the effect of structural perturbations on the relative energies of the frontier  $\pi$ -MOs. The HOMO and LUMO of the parent  $\text{C}_{15}\text{H}_{15}^{3-}$  perimeter for corroles have  $M_L=\pm 4$  and  $\pm 5$  properties, respectively. By analogy with Gouterman's four-orbital model it can be demonstrated that this leads to allowed  $B$  and forbidden  $Q$  bands based on allowed  $\Delta M_L=\pm 1$  and forbidden  $\Delta M_L=\pm 9$  transitions.

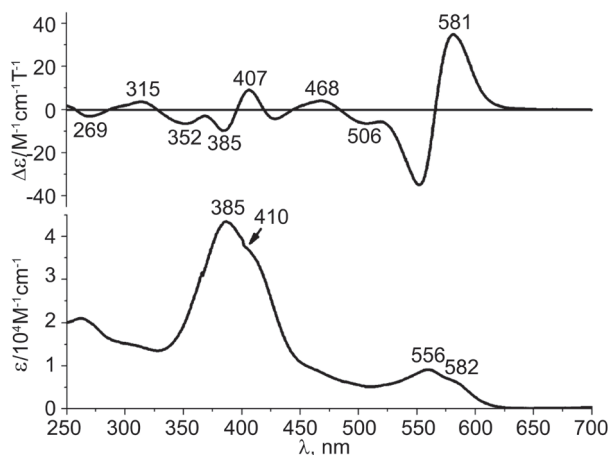
UV-visible absorption spectroscopy is one of the most useful methods for characterizing porphyrins and their analogues. The UV-vis absorption spectra of  $\text{H}_3$ -5,10,15-(3-chloro-4-fluorophenyl)corrole **1** (Figure 2, bottom) reveal an intense Soret band absorptions at 414 nm, and three



**Figure 2.** UV-vis absorption (bottom) and MCD spectra (top) of  $\text{H}_3$ -Corrole **1** in  $\text{CH}_2\text{Cl}_2$ .

weak  $Q$  band absorptions at 571, 613 and 644 nm. The additional information provided by the MCD technique<sup>[8]</sup> is derived from three highly characteristic spectral features, the Faraday  $A_1$ ,  $B_0$ , and  $C_0$  terms.<sup>[9]</sup> The oppositely signed coupled pair of Faraday  $B_0$  terms observed at 410 (negative) and 435 nm (positive) at the Soret band region, 544 (negative), 578 (negative), 612 (positive), 644 nm (positive) at the  $Q$  band region. Based on the intensity and the sign of the MCD signals of **1**,  $Q_x(0-0)$ ,  $Q_x(0-1)$ ,  $Q_y(0-0)$ ,  $Q_y(0-1)$  bands were assigned to the  $B_0$ -terms observed at 644, 612, 578, 544 nm in non-polar solvent  $\text{CH}_2\text{Cl}_2$ , respectively. The observed positive sign of the low energy  $Q_x$  band and negative sign for higher energy  $Q_y$  band in the positive-positive-negative-negative manners are uncharacteristic of porphyrinoids and indicative of the larger energy difference between the LUMO and LUMO+1 orbitals ( $\pi^*$  orbitals) the HOMO and HOMO-1  $\pi$  MOs ( $\pi$  orbitals). In the spectra of low symmetry porphyrinoids, pairs of coupled oppositely signed Faraday  $B_0$  terms replace the derivative-shaped  $A_1$ -terms that are observed in the spectra of radially symmetric metal porphyrinoid complexes.<sup>[8]</sup>

The metal coordinated corrole analogues generally exhibit different shape of the absorptions of the UV-vis spectra compared with free-base corroles, due to the metal-ligand or the ligand-metal transition interaction was occurred in these coordinated corrole complexes. Co(III)PPh<sub>3</sub> corrole **2a** (Figure 3, bottom) exhibits intense Soret band absorptions at 386 nm with an extra shoulder band at around 410 nm, and two  $Q$  bands appeared at 556 and 582 nm, respectively. The decreased number of the  $Q$  bands of **2a** can be assigned as the change of the molecular symmetry via metal-coordination. The MCD spectra of compound **2a** (Figure 3, up) in  $\text{CH}_2\text{Cl}_2$  are revealed by the Faraday  $B_0$ -terms in the corresponding MCD spectra centered at 385 (negative) and 410 nm (positive) at the Soret band region, 556 (negative), 582 nm (positive) at the  $Q$  band region. The MCD spectra of **2a** reveal intense signals in the  $Q$  band region and weak signals in the Soret band region, that is different from the regular free-base corrole and its analogues, probably due to the intramolecular metal-ligand transitions. The Mn(III)-coordinated corrole **2b** (Figure 4, bottom) reveals broader

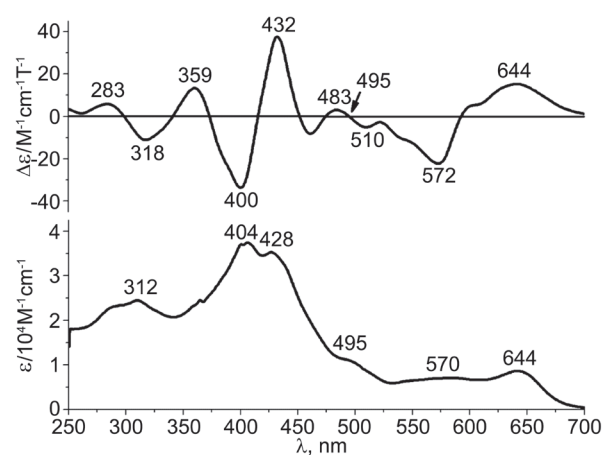


**Figure 3.** UV-vis absorption (bottom) and MCD spectra (top) of Co(III)PPh<sub>3</sub>-Corrole **2a** in  $\text{CH}_2\text{Cl}_2$ .

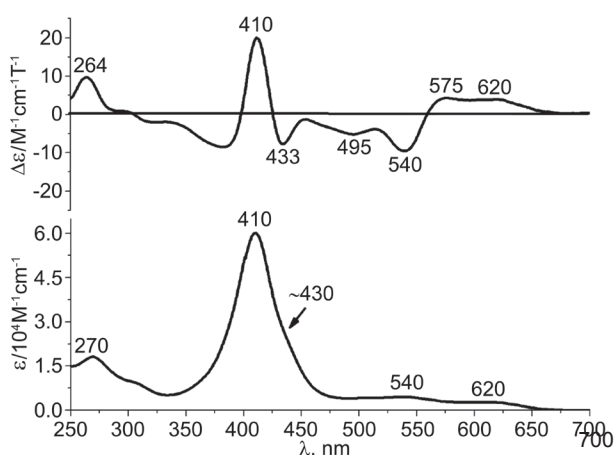
region of absorptions in the UV-vis spectrum. Two Soret band absorptions appeared at 408, 428 nm, and two  $Q$  band absorptions appeared at 570, 640 nm, respectively. The MCD spectra of compound **2b** (Figure 4, up) in  $\text{CH}_2\text{Cl}_2$  are revealed by the Faraday  $B_0$ -terms in the corresponding MCD spectra centered at 400 (negative) and 432 nm (positive) at the Soret band region, 572 (negative), 644 nm (positive) at the  $Q$  band region. The Cu(III)-coordinated corrole **2c** (Figure 5, bottom) reveals intense Soret band at 410 nm, where a shoulder band appeared at around 430 nm. Two weak  $Q$  band absorptions were appeared at 540, and 620 nm. The MCD spectra of compound **2c** (Figure 5, up) in  $\text{CH}_2\text{Cl}_2$  are revealed by the Faraday  $B_0$ -terms in the corresponding MCD spectra centered at 410 (positive) and 433 nm (negative) at the Soret band region, 540 (negative), 575 nm (positive), 620 nm (positive) at the  $Q$  band region.

### Electrochemical Properties

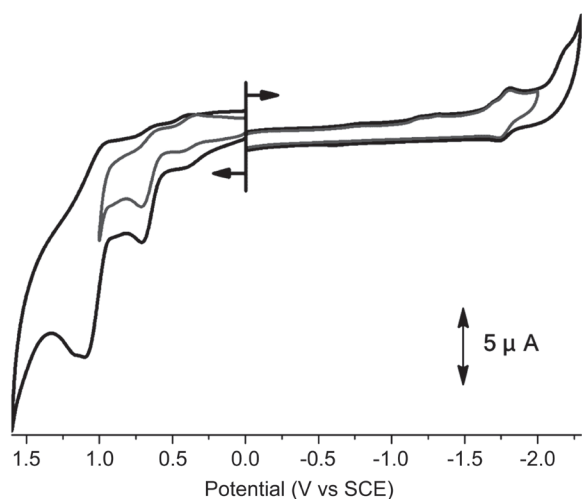
In order to in-depth understand the electronic structure of H<sub>3</sub>-corrole **1** (Figure 6) and its metallo-coordinated



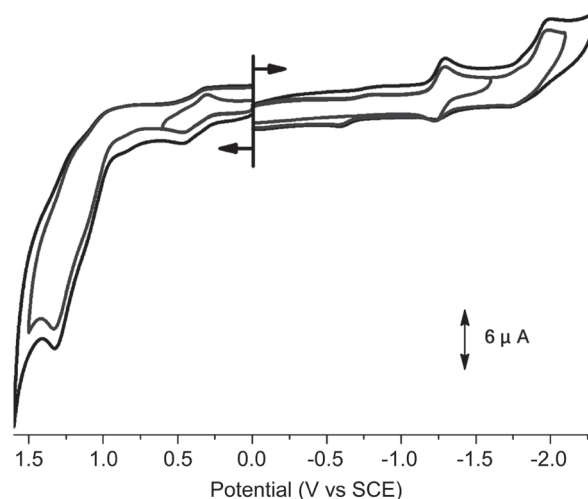
**Figure 4.** UV-vis absorption (bottom) and MCD spectra (top) of Mn(III)-Corrole **2b** in  $\text{CH}_2\text{Cl}_2$ .



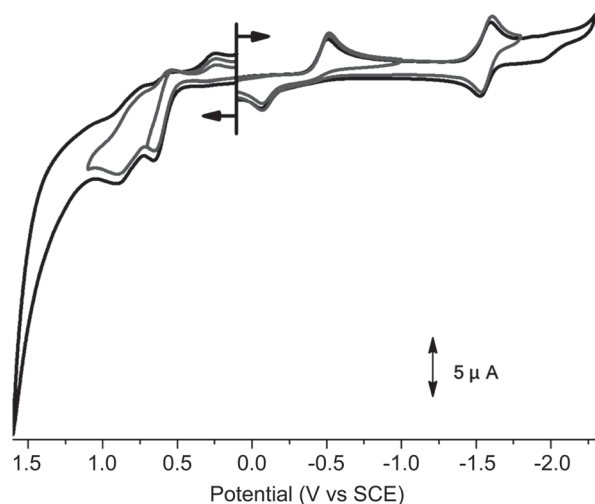
**Figure 5.** UV-vis absorption (bottom) and MCD spectra (top) of Cu(III)-Corrole **2c** in  $\text{CH}_2\text{Cl}_2$ .



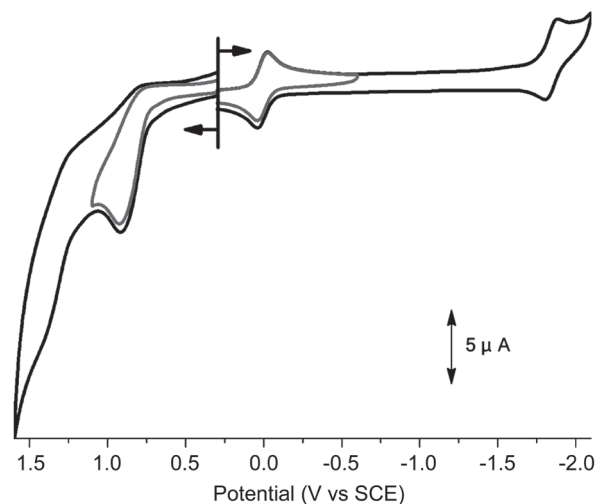
**Figure 6.** Cyclic voltammetry measurement of H<sub>3</sub>-corrole **1** in DMF containing 0.1 M TBAP, scan rate: 0.1 V/s.



**Figure 8.** Cyclic voltammetry measurement of Mn(III)-corrole **2b** in DMF containing 0.1 M TBAP, scan rate: 0.1 V/s.



**Figure 7.** Cyclic voltammetry measurement of Co(III)PPh<sub>3</sub>-corrole **2a** in DMF containing 0.1 M TBAP, scan rate: 0.1 V/s.



**Figure 9.** Cyclic voltammetry measurement of Cu(III)-corrole **2c** in DMF containing 0.1 M TBAP, scan rate: 0.1 V/s.

complexes **2a** (Figure 7), **2b** (Figure 8) and **2c** (Figure 9), respectively. Cyclic voltammetry measurements were carried out in DMF containing 0.1 M TBAP. H<sub>3</sub>-corrole **1** reveals a clear reversible redox at  $E_{1/2} = -1.70$  V which can be assigned as [H<sub>3</sub>-Corrole]/[H<sub>3</sub>-Corrole]<sup>-</sup> from the reduction of the corrole ring, and the oxidation part of **1** turned to be irreversible due to the decomposition of H<sub>3</sub>-corrole **1** during the oxidation processes of CV measurements. In the case of Co(III)PPh<sub>3</sub>-corrole **2a**, two reversible reduction processes were observed at  $E_{1/2} = -0.40$  and  $-1.48$  V, respectively. These two processes of **2a** can be assigned as [Co(III)-Corrole]<sup>+</sup>/[Co(II)-Corrole] and [Co(II)-Corrole]/[Co(II)-Corrole]<sup>-</sup>, respectively. The oxidation processes of **2a** are also irreversible. The Mn(III)-corrole **2b** also reveal two reversible reduction processes at  $E_{1/2} = -1.14$  V for [Mn(II)-Corrole]/[Mn(I)-Corrole]<sup>2-</sup> and  $E_{1/2} = -1.84$  V for ring reduction [Mn(I)-Corrole]<sup>2-</sup>/[Mn(I)-Corrole]<sup>3-</sup>, respectively. The oxidation processes of **2b** reveal only one reversible curve

at  $E_{1/2} = 0.34$  V assigned as [Mn(III)-Corrole]/[Mn(II)-Corrole]. Finally, the Cu(III)-corrole **2c** only reveals two reversible reduction  $E_{1/2} = 0.08$  and  $-1.75$  V, that can be assigned as [Cu(III)-Corrole]/[Cu(II)-Corrole] and ring reduction [Cu(II)-Corrole]/[Cu(II)-Corrole]<sup>2-</sup>. All electrochemistry results are similar with other A<sub>3</sub> type H<sub>3</sub>-*meso-p*-fluorophenylcorrole or H<sub>3</sub>-*meso-m*-chlorophenylcorrole and their metallo-complexes,<sup>[10]</sup> that indicate mirror effect of the unsymmetric introduction of fluoro- or chloro-substituents at *meso*-phenyl positions.

## Conclusions

In this paper, A<sub>3</sub> type 5,10,15-(3-chloro-4-fluorophenyl)corrole having asymmetric *meso*-3-chloro-4-fluorophenyl-substituents was successfully obtained via a solid-state synthetic procedure. The Co(III)PPh<sub>3</sub>,

Mn(III) and Cu(III) coordinated corrole complexes were also successfully synthesized and isolated for the first time. Spectroscopic properties were studied by UV-vis absorption and magnetic circular dichroism spectroscopy, as well as cyclic voltammetry measurements were carried out. Considering that development of new synthetic pathways and investigations on the electronic structures of corroles are very useful design and analysis of chromophores, our results in this research will offer useful information for the future corrole chemistry.

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