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# Synthesis and Properties of 9,9′−(C$_{12}$H$_{25}$)$_2$−Fluorene Substituted Corrole Monomer and its Bridged Dimer

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*Herein, the low symmetric 9,9'-(C$_{12}$H$_{25}$)$_2$-fluorene substituted corrole monomer and its bridged dimer are reported. The electronic structure investigation was carried out to confirm the electronic influence of 9,9'-(C$_{12}$H$_{25}$)$_2$-fluorene unit for corrole monomer and dimer. Solvent-dependent spectroscopic investigation explained the possible inner NH tautomerism.*

**Keywords**: Corrole dimers, molecular chirality, electronic structure, spectroscopy.

# Синтез и свойства 9,9′−(C$_{12}$H$_{25}$)$_2$−флуорензамещенного коррола и его мостикового димера

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*В работе сообщается о низкосимметричном 9,9'-(C$_{12}$H$_{25}$)$_2$-флуорензамещенном корроле и его мостиковом димере, исследовано влияние 9,9'-(C$_{12}$H$_{25}$)$_2$-флуорена на электронную структуру мономера и димера коррола, на основании спектральных исследований в различных растворителях рассматривается возможность внутренней NH таутомерии.*

**Ключевые слова**: Корролы, димеры, молекулярная хиральность, электронная структура, спектроскопия.

Synthesis and Properties of 9,9'-(C$_{12}$H$_{25}$)$_2$-Fluorene Substituted Corrole
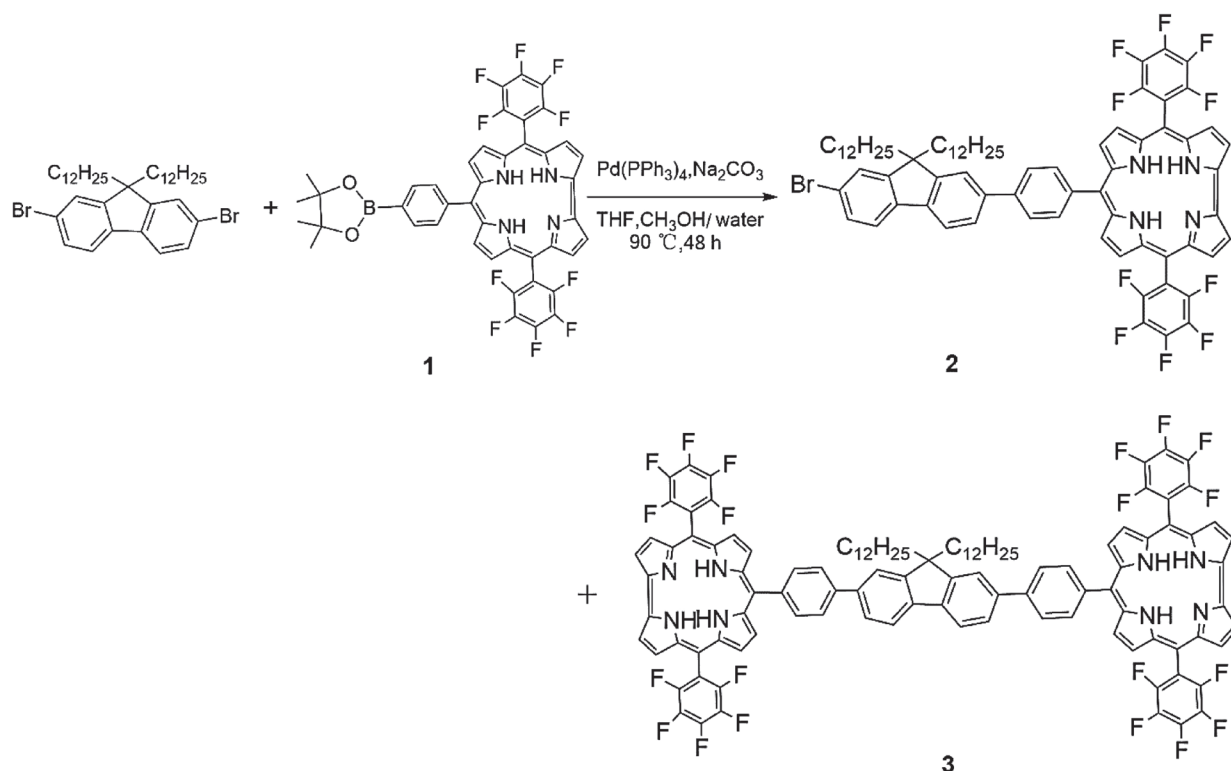
## Introduction

Corrole and their derivatives with a direct linked C–C chemical bond resulting in the ring-contracted molecular structure and novel optical and electrochemical properties have received the considerable attention in recent years.[1–2] Also, the three inner N–H protons can support corrole stabilizing metallic and/or non-metallic ions at the higher oxidation states, such as Fe(III), Co(III), Pt(IV), P(V).[3] On the other hand, although the first synthesis of corroles was reported in 1964, the complicated synthetic procedure and low yield have been a great challenge for further investigations.[4] Right now, the synthetic corrole chemistry is rapidly increased for both methodology and their functionalization. For example, corrole and its derivatives could be functionalized from both *meso-* and *β*-positions, and further ring-fusion and expansion are also effective strategies.[5] In addition, to create corrole oligomer system is an important branch for synthetic corrole chemistry, in which not only corrole could be used as a special substituent, but also the electron transfer could be modulated in a good manner.[6] As reported previously, corrole oligomers could be constructed through directly covalent link, functional bridging unit, large-size metal ion, and even metallic-μ-bridged linkage.[7] Despite of the novel molecular structure of corrole oligomers, their electronic structure and potential applications are also attractive due to the unprecedented electron and/or charge transfer are always observed to provide very interesting properties. In particular, covalently linked corrole oligomers have been appeared extremely attractive properties compared with similar porphyrin oligomers. Besides these, various corroles have been explored as catalysts, pigments for artificial photosynthesis and solar cells, sensors, and so on.[8] For example, the face-to-face porphyrin-corrole hybrids as well as corrole dimers as promising models of a catalyst for the four-electron reduction of oxygen to water.[9] Thus, all these advantages have promote us to design and synthesize new corrole oligomers, especially corrole dimers to investigate the electronic interactions between different corrole rings. Considering fluorine unit has been widely used as an efficient electron transferring bridging unit, we expect to understand the electron transfer when two corrole rings are covalently bridged by fluorine unit.[10] Herein, the synthesis, characterization and the electronic structure investigations of 9-(C$_{12}$H$_{25}$)$_2$-fluorene substituted corrole monomer and its bridged dimer, as well as their molecular tautomerision will be discussed.

## Experimental

### General

$^1$H NMR spectra were recorded on a Bruker AVANCE 600 spectrometer (600 MHz). Residual solvent peaks were used to provide internal references (δ = 7.26 ppm for CDCl$_3$). All reagents and solvents used were used as received unless noted otherwise. Cyclic voltammetry (CV) 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. An inert nitrogen atmosphere was introduced during all of the electrochemical measurements, which were carried out at room temperature. The UV and visible regions of the electronic absorption spectra were recorded with an HP 8453A diode array spectrophotometer. A JASCO J-815 spectrodichrometer equipped with a JASCO permanent magnet (1.6 tesla) was used to measure



**Scheme 1.** Synthetic procedure of 9,9'-(C$_{12}$H$_{25}$)$_2$-fluorene substituted H$_3$ corrole monomer **2** and its bridged dimer **3**.

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 $B_0$ terms matches that of the MCD signal.

*Supporting Information (SI)* is available at *https://macroheterocycles.isuct.ru/en/mhc191176l*.

## Syntheses

*2-(5,15-Dipentafluorophenyl-10-phenylcorrole)-7-bromo-9-(C_{12}H_{25})_2-fluorene,* **2**. 2,7-Dibromo-9,9'-(C_{12}H_{25})_2-fluorene (65.0 mg, 0.10 mmol), H^3-10-benzoboronicpinacalester-5,15-pentafluorophenylcorrole (165 mg, 0.20 mmol), Na_2CO_3 (380 mg, 3.6 mmol), and Pd(PPh_3)_4 (23.0 mg, 0.02 mmol) were dissolved in a mixed solution (THF/CH_3OH/H_2O; 25mL/10mL/10mL), and refluxed at 90 °C under Ar in the absence of light for 48 h. After washing with saturated NH_4Cl solution, the solution was extracted by CH_2Cl_2 (40 mL×3). After removal of organic solvent, the residue was finally obtained by passing through silica gel column chromatography (CH_2Cl_2/hexane = 4:1; v:v) to give the pure blue-purple solid state compound in a 16 % yield (21.1 mg). HR-ESI-mass: Calcd. for $C_{74}H_{71}BrF_{10}N_4$: 1285.4702, found: 1285.4689 [M+H]+. ^1H NMR (600 MHz, CDCl_3) $\delta_H$ ppm: 9.13 (d, $J$ = 4.20 Hz, 2H), 8.83 (d, $J$ = 4.80 Hz, 2H), 8.74 (d, $J$ = 7.80 Hz, 2H), 8.59 (d, $J$ = 3.60 Hz, 2H), 8.30 (d, $J$ = 7.80 Hz, 2H), 8.09 (d, $J$ = 7.80 Hz, 2H), 7.91–7.87 (m, 3H), 7.66 (d, $J$ = 8.40 Hz, 1H), 7.54 (t, $J$ = 8.40 Hz, 2H), 2.26–2.03 (m, 5H), 1.24 (d, $J$ = 28.20 Hz, 45H), 0.89 (t, $J$ = 7.20 Hz, 5H). ^13C NMR (150 MHz, CDCl_3) $\delta_C$ ppm: 153.34, 151.37, 147.03, 147.00, 146.96, 145.35, 140.77, 140.33, 140.02, 139.84, 139.79, 138.85, 138.72, 138.67, 137.16, 137.08, 136.99, 135.24, 131.46, 130.11, 129.00, 126.19, 127.86, 126.45, 126.30, 126.08, 125.50, 121.58, 121.23, 120.33, 117.64, 114.09, 113.13, 55.69, 40.44, 31.96, 29.63, 26.94, 23.87, 22.68, 14.08.

*2,7-(5,15-Dipentafluorophenyl-10-phenylcorrole)-9,9'-(C_{12}H_{25})_2-fluorene 3.* The corrole dimer **3** was isolated from the reaction mixture of **2** as a blue-purple solid state compound in a 35 % yield (68.0 mg). HR-ESI-mass: Calcd for $C_{111}H_{86}F_{20}N_8$: 1910.6656, found: 1910.6606 [M]+. ^1H NMR (600 MHz, CDCl_3) $\delta_H$ ppm: 9.10 (d, $J$ = 4.20 Hz, 4H), 8.86 (d, $J$ = 4.80 Hz, 4H), 8.77 (d, $J$ = 4.20 Hz, 4H), 8.59 (s, 4H), 8.32 (d, $J$ = 7.80 Hz, 4H), 8.15 (d, $J$ = 7.80 Hz, 4H), 8.03 (d, $J$ = 8.40 Hz, 2H), 7.99 (s, 4H), 2.30 (t, $J$ = 7.20 Hz, 4H), 1.32–1.24 (m, 40H), 0.91 (t, $J$ = 6.60 Hz, 6H). ^13C NMR (150 MHz, CDCl_3) $\delta_C$ ppm: 152.13, 147.02, 145.40, 140.96, 140.57, 140.22, 139.73, 138.86, 135.28, 127.90, 126.12, 121.70, 117.70, 117.63, 114.12, 113.19, 55.66, 40.75, 31.91, 30.27, 29.74, 29.37, 22.66, 14.05.

## Results and Discussion

The synthetic route used to prepare the 9,9'-(C_{12}H_{25})_2-fluorene substituted corrole monomer **2** and its bridged dimer **3** is given in Scheme 1. H_3-10-benzoboronicpinacalester-5,15-pentafluorophenylcorrole was prepared as the key precursor according to the reported procedure,[11] and the corrole monomer **2** and dimer **3** were synthesized from Suzuki coupling reaction. Repeated purification by silica gel column chromatography gave **2** and **3** in the 16 % and 35 % yields, respectively. High-resolution-ESI mass spectra of **2** (Figure S1, see ESI) revealed the parent ion peaks at $m/z$ = 1285.4689 (calcd for $C_{74}H_{71}BrF_{10}N_4$, [M+H]+ = 1285.4702) and of **3** at $m/z$ = 1910.6606, (Calcd for $C_{111}H_{86}F_{20}N_8$, [M]+ = 1910.6656) provided the direct evidences that corrole monomer **2** and dimer **3** were clearly observed (Figure S4, see *SI*). The ^1H NMR spectra of compounds **2** and **3** (Figures S2, S5, see *SI*) showed proton signals

ascribed to the aromatic protons in the range 7.52–9.13 ppm. The protons from long alkyl chain -C_{12}H_{25} could be assigned from 0.77–2.14 ppm. Also, these compounds also were confirmed by ^13C NMR signals from both aromatic region and long alkyl chains (Figures S3, S6, see *SI*).

Electronic absorption spectroscopy is one of the most useful methods for characterizing corroles and their analogues due to the presence of intense $\pi \rightarrow \pi^*$ bands in the visible region. The optical spectroscopy of corroles can be understood based on a consideration of perturbations to an $M_L$ = 0, ±1, ±2, ±3, ±4, ±5, ±6 and ±7 sequence in ascending energy terms for the orbital angular momentum quantum number for the MOs of a $D_{15h}$ symmetry parent hydrocarbon perimeter. The HOMO and LUMO have $M_L$ = ±4 and ±5, respectively, and are linked by forbidden and allowed $\Delta M_L$ = ±9 and ±1 transitions, which are associated with the *Q*- and *B*-bands of Gouterman's 4-orbital model,[12] respectively, that are observed in the 500–600 and 400–450 nm regions of corrole spectra. The absorption spectrum of **2** in low-polar CH_2Cl_2 contains a single intense *B*-band at 411 nm with an unclear shoulder band at slightly longer wavelength region, while three relatively intense bands are observed in the *Q*-band region at 568, 613 and 640 nm. Corrole dimer **3** revealed similar absorption properties at *Q*-band region, but a clear shoulder band was observed at *B*-band region, at 427 nm. The clear split of the Soret band absorption of corrole **3** could be explained as the strong electron coupling interaction between two corrole rings through bridged 9,9'-(C_{12}H_{25})_2-fluorene unit. These corrole derivatives could also emit, corrole monomer **2** and dimer **3** have similar fluorescent peaks (Figure S7, see *SI*) at λ = 653, 710 nm for **2** and λ = 652, 708 nm for **3**, respectively.

In addition, magnetic cicular dichroism (MCD) spectra can be analyzed on the basis of the three Faraday terms.[13] The low-symmetry of corroles dictates that only Faraday $B_0$ terms are observed (Figure 1). In this context, Michl's perimeter model can be used to analyze the properties of the corrole π-system on the basis of the MCD spectroscopy. The +/– sign sequence in ascending energy terms observed in the Faraday $B_0$ terms in the *Q*-band region of the MCD spectra clearly identifies a weaker shoulder of intensity at *ca.* 640 nm to the red of the main absorption band at *ca.* 613 nm as also being electronic in origin due to the symmetry-induced split of the *Q*-band into *x*- and *y*-polarized components. This is the pattern typically observed for corroles, since the separation of the MOs derived from the LUMO of the parent perimeter (ΔLUMO value) is smaller than that of those derived from the HOMO level (ΔHOMO value). As would normally be anticipated, a +/– sign sequence can also be identified for the main bands in the *B*-region. It is noteworthy that marked changes are observed in the absorption spectra of **2** and **3** when the solvent polarity is increased by using DMF (Figure 2, Table 1). Similar spectral changes are also observed when spectra are measured in DMSO and PhCN, and few changes were observed when THF was used. In the normalized absorption spectrum recorded for **2** in different solvents, the *B*-band lies further to red at 428 nm with a shoulder of intensity at 445 nm, and relatively intense bands are observed in the *Q*-band region at 595 and 645 nm. Similar trends are observed in the spectra of **3**. It has been
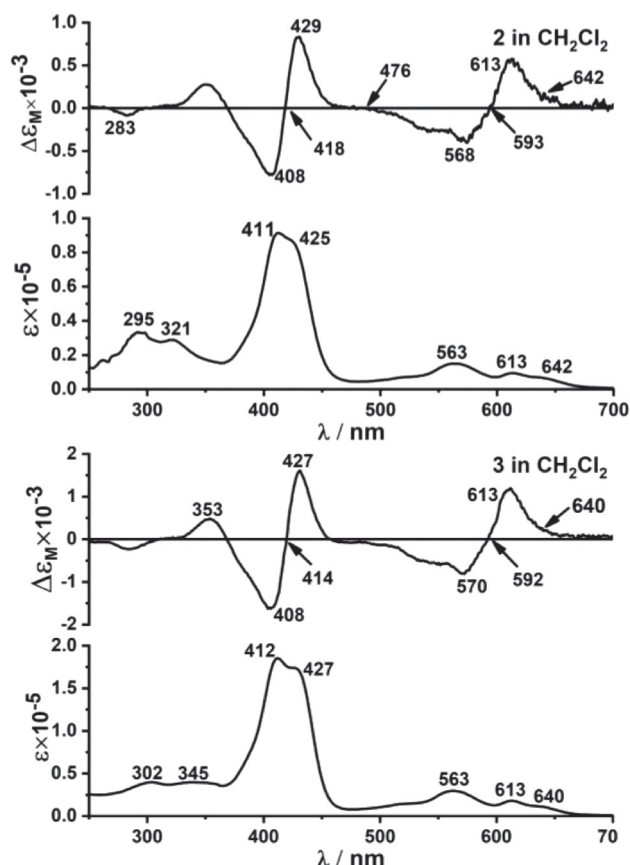
**Figure 1.** Magnetic circular dichroism (up) and UV-Vis absorption (bottom) spectra of **2** and **3** in CH$_2$Cl$_2$.

**Table 1.** Normalized UV-Vis absorption spectra data of **2** and **3** in various solvents.

| | Solvent | Soret band (nm) | | Q-band (nm) | | |
|---|---|---|---|---|---|---|
| | DMF | 425 | 443 | 547 | 586 | 629 |
| | DMSO | 428 | 444 | 544 | 587 | 629 |
| 2 | THF | 420 | – | 569 | 611 | 646 |
| | PhCN | 432 | 446 | 549 | 590 | 631 |
| | CH$_2$Cl$_2$ | 411 | 425 | 563 | 613 | 642 |
| | DMF | 426 | 446 | 547 | 588 | 628 |
| | DMSO | 426 | 447 | 550 | 586 | 628 |
| 3 | THF | 421 | – | 522 | 568 | 613 |
| | PhCN | 430 | 448 | 551 | 588 | 631 |
| | CH$_2$Cl$_2$ | 412 | 427 | 563 | 613 | 640 |

and its bridged dimer **3**, their electrochemistry was also investigated, and $E_{1/2}$ values are derived from both CV and DPV characterizations (Figure 3). The 9,9'-(C$_{12}$H$_{25}$)$_2$-fluorene substituted corrole monomer **2** has two reversible ring oxidations and reductions at $E_{1/2}$ = 1.03 V and 0.25 V, and $E_{1/2}$ = –1.06 and –1.61 V, respectively. Also, slightly changed electrochemical properties were also observed in the case of 9,9'-(C$_{12}$H$_{25}$)$_2$-fluorene bridged corrole dimer **3**. As shown in Figure 3, slightly changed two reversible ring oxidations and reductions at $E_{1/2}$ = 1.06 V and 0.26 V, and $E_{1/2}$ = –1.06 and –1.60 V, respectively. The slightly positive shift of the oxidation curves **3** compared with **2** could be explained as the influence of bridged 9,9'-(C$_{12}$H$_{25}$)$_2$-fluorene unit on the charge separation of corrole ring itself. Due to the limit of potential windows, the electrochemical signals of 9,9'-(C$_{12}$H$_{25}$)$_2$-fluorene itself was not observed.

## Conclusions

In summary, the low symmetric 9,9'-(C$_{12}$H$_{25}$)$_2$-fluorene substituted corrole monomer and its bridged dimer were successfully synthesized, isolated and fully characterized by $^1$H, $^{13}$C NMR spectroscopy and high-resolution mass spectrometry. Their photophysical and electrochemical properties also were investigated by spectroscopy including
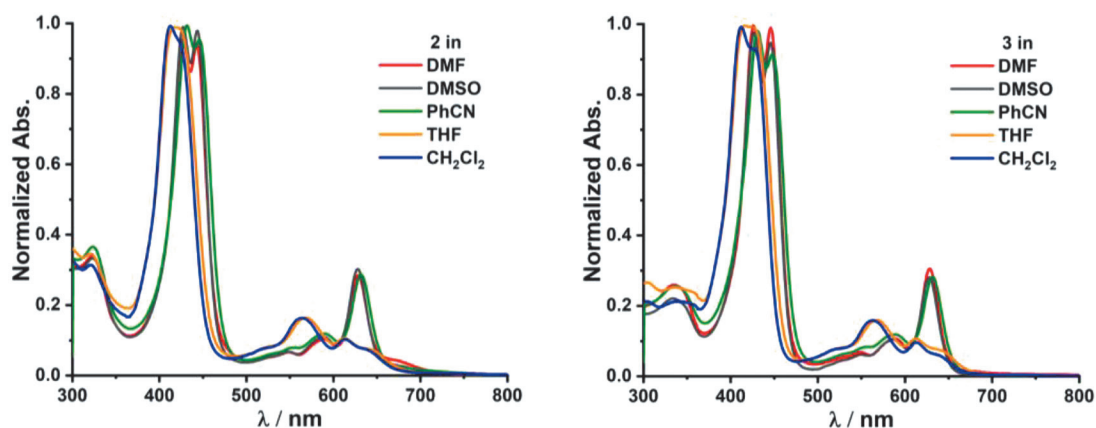
reported previously by Ziegler and us that a significant splitting is observed in the B-band region in polar solvents, such as DMF, that is not observed in a low-polar solvent, such as CH$_2$Cl$_2$, THF. The observed solvent-dependent spectroscopic changes of 9,9'-(C$_{12}$H$_{25}$)$_2$-fluorene substituted corrole monomer and its bridged dimer could be explained as two may reasons: the self-tautomerism of inner protons of corrole rings, as well as N-basicity and thermodynamic stability of two tautomers.[14]

In order to better understand the electronic structure of 9,9'-(C$_{12}$H$_{25}$)$_2$-fluorene substituted corrole monomer **2**



**Figure 2.** Normalized UV-Vis absorption spectra of **2** (left) and **3** (right) in DMF, DMSO, PhCN, THF and CH$_2$Cl$_2$ at room temperature.
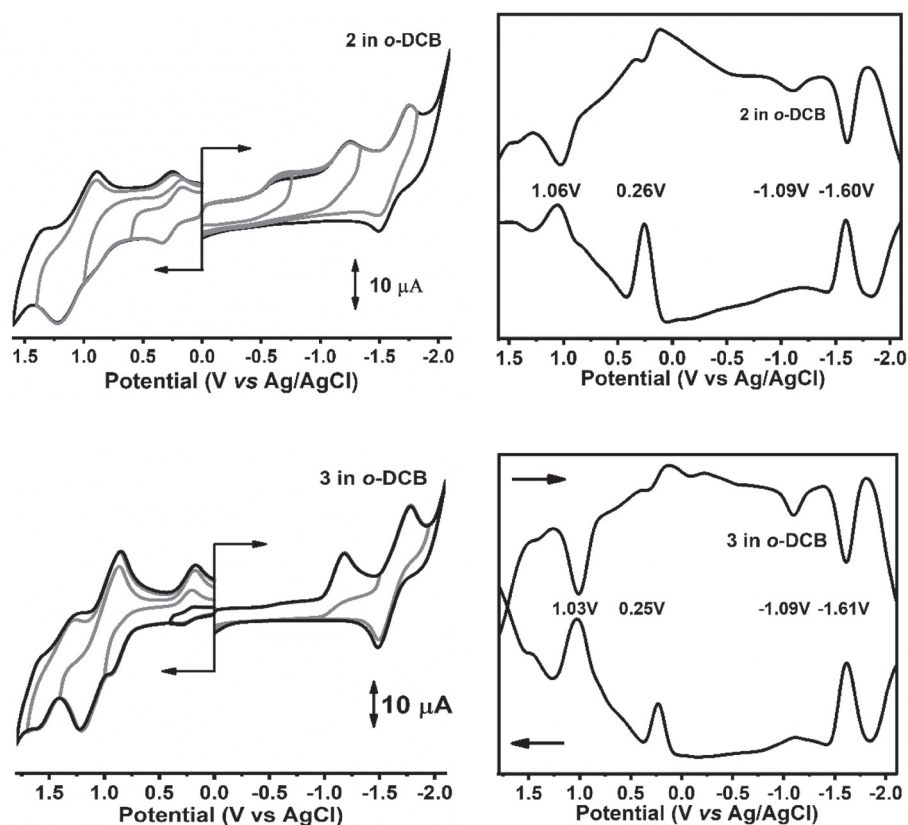
**Figure 3.** Electrochemical characterization of **2** (up panel) and **3** (bottom panel) in *o*-dichlorobenzene.

UV-Vis, fluorescence, magnetic circular dichroism (MCD), along with electrochemistry. Solvent-dependent spectroscopic investigation explained the two sets of possible inner NH tautomers which are likely to have similar energies. We can confirm that 9,9'-$(C_{12}H_{25})_2$-fluorene unit could be used as an efficient electron donating unit for corrole monomer and the efficient electron transferring unit for corrole dimer. Considering corrole derivatives have various advantages in high-tech field, the results may provide useful information for future investigation of corrole chemistry.

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