

Synthesis and Characterization of Novel Mercapto-end Ferrocenyl Derivatives with Schiff Base Linkage

Hai Feng SONG¹, Miao CHEN^{2*}, Yong Min LIANG¹, Ling SHI¹, Guo Sheng HUANG^{1*}

¹ National Laboratory of Applied Organic Chemistry, Lanzhou University

² Lanzhou Institute of Physical Chemistry, Chinese Academic of Sciences
Lanzhou 730000

Abstract: Novel ferrocenyl derivatives of *p*-(10-mercaptodecyloxy) benzal 4-ferrocenylaniline have been prepared and characterized by element analysis, ¹H NMR, and FAB-MS. Cyclic voltammetry has been used to characterize the self-assembled monolayers formed from the compounds on the gold electrodes.

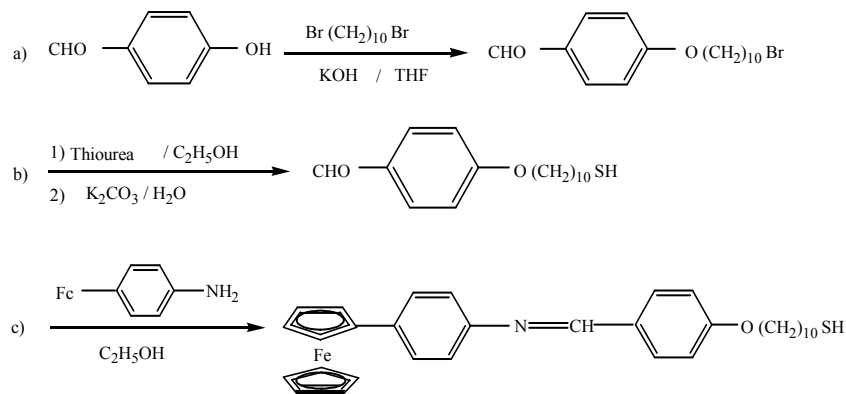
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Self-assembled monolayers (SAMs) have been gotten great attentions over the past decades because their considerable technological and scientific capabilities for electronic and optical devices, chemical sensors, lubricants, model biological membranes, electron-transfer barrier and catalysts^{1, 2}. SAMs of ω -ferrocenylalkanethiol on gold or other surfaces like Si or ITO have been studied for these systems could be considered as models for the formation of electronic devices by self-assembly³⁻⁸. In their work, the ferroceny-tailed SAMs containing N=N or CH=CH bond have been studied in detail. But the ferrocenyl derivatives with C=N bond (Schiff base) are rarely reported. Because of the novel structure and promising use of Schiff base derivatives containing ferrocenyl group, particularly in the field of liquid crystal⁹, we recently prepared a novel ferrocenyl Schiff base derivatives to enlarge the family of SAMs. This mercapto-end ferrocenyl derivatives were assembled on Au electrode, cyclic voltammetry has been used to characterize the SAMs formed from them.

All solvents were purified by standard methods. Reagent-grade chemicals were used without further purification. FAB-MS and ¹H NMR were recorded on VG ZBA-HS and DRX-300MHz instrument. Elemental analysis was performed with Elementar Vario EL.

The synthesis path of the compounds was divided into three steps, which are presented in **Scheme 1** as follows:

* E-mail: miaochen@lsl.ac.cn; gshuang@mx.nthu.edu.tw

Scheme 1 Synthetic paths of the compounds**Experimental***Synthesis of p-(10-bromodecyloxy) benzaldehyde ():*

0.5 g KOH was dissolved in 20 mL THF, then 3 g (10 mmol) of 1,10-dibromodecane and 0.6 g (5 mmol) of *p*-hydroxybenzaldehyde were added at once. After refluxing for 12 hrs, the product was extracted with dichloromethane and the organic layer was dried over Mg₂SO₄, solvent removed in vacuum. The residue was purified by column chromatography (hexane:ethyl acetate=8:1) to yield 0.8 g (47%). MS (FAB) *m/z*: 341 (M+1). ¹HNMR (CD₃Cl) δ_{ppm}: 1.84 ~ 1.90 (m, 16H, 8×CH₂), 3.43 (t, 2H, J=6.3Hz, CH₂Br), 3.88 (t, 2H, J=6.5Hz, OCH₂), 7.02 (d, 2H, J=9Hz, Ar), 7.80 (d, 2H, J=9Hz, Ar), 9.78 (s, 1H, CHO).

Synthesis of p-(10-mercaptodecyloxy) benzaldehyde ()

Thiourea (0.38 g, 5 mmol) was added to 10 mL of ethanol and water (10:1) at 50 °C under Ar atmosphere. *p*-(10-Bromodecyloxy) benzaldehyde (0.34g, 1mmol) was added to the solution after 5 mins, and the solution was stirred for 6 hrs. The solution was cooled to room temperature, and an aqueous solution (2 mL) containing K₂CO₃ (1.1 g) was added. The solution was then refluxed for 2 hrs. The product was extracted with ethyl ether, and the organic layer was dried over Mg₂SO₄, solvent was removed *in vacuo*. The residue was purified by column chromatography (hexane:ethyl acetate=6:1) to yield 0.17 g (58 %). MS (FAB) *m/z*: 295 (M+1). ¹HNMR (DMSO-*d*₆) δ_{ppm}: 1.24 ~ 1.75 (m, 16H, 8×CH₂), 2.20 (t, 1H, J=7.6Hz, SH), 2.48 (m, 2H, CH₂S), 4.05 (t, 2H, J=6.5Hz, OCH₂), 7.05 (d, 2H, J=8.7Hz, Ar), 7.87 (d, 2H, J=8.7Hz, Ar), 9.78 (s, 1H, CHO).

Synthesis of p-(10-mercaptodecyloxy) benzal 4-ferrocenylaniline ()

p-(10-Mercaptodecyloxy) benzaldehyde (0.15 g, 0.5 mmol) was stirred with *p*-ferrocenylaniline (0.14 g, 0.5 mmol) in ethanol for 0.5 hr in the presence of small amount of acetic acid at room temperature. The precipitates were collected and recrystallized from hexane, finally the orange powder was yielded: 0.22 g (80 %). MS (FAB) *m/z*: 553 (M⁺).

Figure 1 Cyclic voltammograms of SAMs from **III** modified Au electrode in 0.1 mol/L NaClO₄ (pH=7) (The Scan rate was 5, 20, 50 mV/s, respectively.)

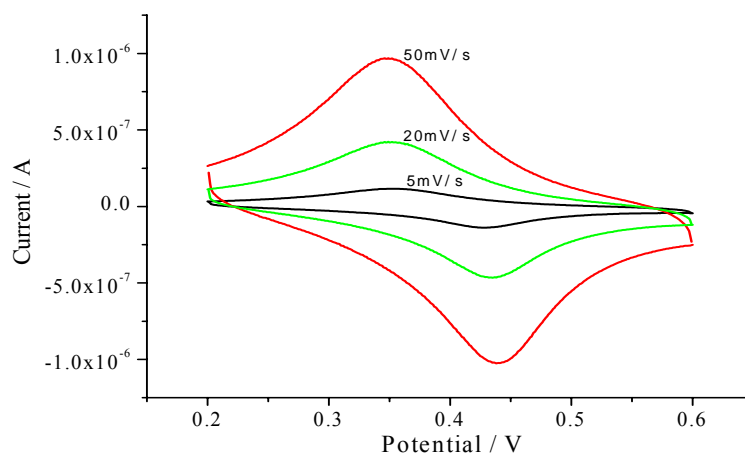
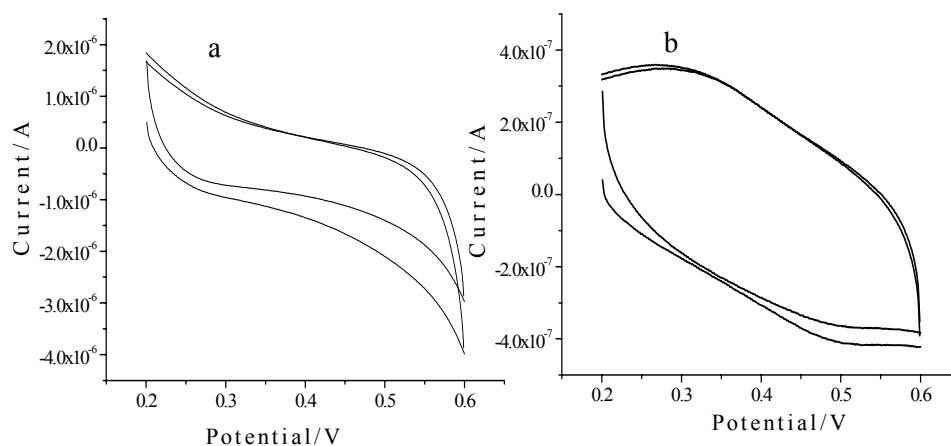


Figure 2 Electrochemical response of SAMs from **III** modified Au electrode in (a) 0.1 mol/L KOH (pH=13) and (b) 0.1 mol/L HClO₄ (pH=1)



¹H NMR (DMSO-d₆) δ_{ppm}: 1.24 ~ 1.70 (m, 16H, 8×CH₂), 2.19 (t, 1H, J=7.5Hz, SH), 2.47 (m, 2H, CH₂S), 4.00 (s, 5H, Cp), 4.02 (t, 2H, J=6.8Hz, OCH₂), 4.32 (s, 2H, Cp), 4.77 (s, 2H, Cp), 7.03 (d, 2H, J=8.5Hz, Ar), 7.16 (d, 2H, J=8.5Hz, Ar), 7.54 (d, 2H, J=7.6Hz, Ar), 7.85 (d, 2H, J=7.6Hz, Ar), 8.55 (s, 1H, CH=N). Anal. Calcd for C₃₃H₃₉NOSFe: C, 71.61; H, 7.05; N, 2.53. Found: C, 71.43; H, 7.08; N, 2.50.

Electrochemical measurement was conducted in a three-electrodes cell with a CHI660A electrochemical workstation (USA). Calomel electrode and Pt foil were used as reference and counter electrodes, respectively. A gold disk electrode (CHI 101) was employed as the working electrode, which was subjected to the same pretreatment procedure before each experiment¹⁰. The polished gold electrode (with 0.05 μm Al₂O₃)

was rinsed with water. Thereafter, it was cleaned thoroughly with 1:1 nitric acid, 1:1 methylcyanide and distilled water, respectively. The cleaned gold electrode was dried by N₂ stream, then put into the 0.1 mol/L methylcyanide solution of product **III** and self-assembled for 24 hrs. After assembling, the modified electrodes were rinsed with methylcyanide and dried under a stream of purified N₂. The electrochemistry of the SAMs of **III** modified Au electrodes was tested by cyclic voltammetry in 0.1 mol/L NaClO₄, 0.1 mol/L KOH and 0.1 mol/L HClO₄ aqueous solutions respectively, as shown in **Figure 1**, **Figure 2a** and **Figure 2b**.

In each cyclic voltammogram, the electrode potential was cycled between 0.2V and 0.6V. In **Figure 1**, the peak potential was almost independent of the scan rate, v , and the ratio of the anodic and cathodic peak current (i_{pa}/i_{pc}) was unity (≈ 1) at a given v . The peak currents increased linearly with v in a range of 0.02V/s to 1.5V/s. These data illustrate that the CV peaks were in fact derived from surface - confined species¹¹, that is, the ferrocene Schiff base derivatives were assembled on the Au electrode. One electron reversible oxidation of surface-confined ferrocenyl (Fc/Fc⁺) tail group was observed. The currents did not decrease after repeated cycling in methyl-cyanide solution, demonstrating that the ferrocene SAMs were stable with respect to the potential cycling.

The electron transfer rate of these SAMs can be estimated from the redox peak separation E_p . The experimental E_p values independent of the scan rates obtained from the **Figure 1** showed that the electron transfer was relatively fast. However, the E_p values of Fc/Fc⁺ was about 80 mV implied that the presence of large conjugated Schiff base part shared the electron energy of the ferrocene part in these SAMs systems¹¹.

The redox peaks of Fc/Fc⁺ disappeared in 0.1 mol/L KOH (pH=13, **Figure 2a**) and HClO₄ (pH=1, **Figure 2b**). These findings illustrate that the Schiff base compounds were unstable in the strong alkaline or acidic solution, and the ferrocenyl tail group were apart from the SAMs on the Au electrode.

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