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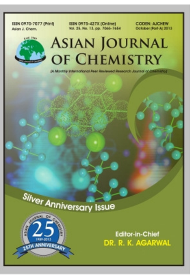

NOTE

Synthesis and Electrochemical Properties of Ferrocene Formylated Curcumin

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Ferrocene formylated curcumin was synthesized from ferrocene monocarboxylic acid and curcumin. Its structure was characterized by MS, IR and ^1H NMR. The voltammetric behaviour of the new compound was investigated, appearing a pair of well defined redox wave at oxidation potential 0.768 V and reduction potential 0.219 V, respectively in the range of 0-1.0 V. The experimental result showed that curcumin had a great influence on the reversibility of the ferrocene, changing its oxidation peak position by the bridge of ester bond. It could have great current change in the range of 0-1.0 V, which is possible to be used as molecular level electronic switch.

Key Words: Curcumin, Ferrocenecarboxylate, Cyclic voltammetry.

Curcumin is consisted by the two *o*-methylphenols and a β-diketone, belonging to the polyphenol, having a unique conjugated structure. It is well known that curcumin can be used for a variety of pharmaceuticals (such as the treatment of arthritis drugs like antivirus, antitumor), an antiinflammatory pharmaceutical agents and oral treatment of diabetes[1]. Curcumin is noteworthy due to its unique chemical structure. It is a strong antioxidant and can be used for inhibiting lipid peroxidation, scavenging superoxide radicals, nitrogen dioxide-induced free radicals[2]. The coordation between curcumin carbonyl and copper ions improves its ability to reduce free radical[3]. Structural modification for curcumin and synthetic curcumin derivatives are attracting many to study its unique electrochemical properties[4].

In recent years, inorganic molecular devices showed unique electrochemical properties[5]. Designed synthesis of inorganic molecular devices is becoming research focus. In particular, by introduction of a stable molecular conjugation system of macromolecules into regulate the reduction and oxidation potential. Due to good electrochemical properties and unique sandwich structure of ferrocene, the macromolecules of ferrocene-containing conjugated system by covalent bonding showed active redox electronic coupling sensor. Specifically, porphyrin labeled by ferrocene through acetylene was found to be a good electron transport system, having potential as an electronic switch[6]. Through the same method, sulfur-containing aromatics which was labeled by ferrocene, appearing a good reversibility of the redox potential by cyclic voltammetry[7]. The study of ester of covalently linked ferrocene-curcumin has not been reported by now.

In this study, ferrocene formylated curcumin is synthesized from the ferrocene acylation of curcumin, getting its electrochemical properties by the use of cyclic voltammetry in DMF. The experimental results show that curcumin has a larger impact on the reversibility of the ferrocene through the ester, changing in the oxidation peak position, providing research ideas of oxidation molecular level device.

Ferrocenecarboxylate (Suzhou Highfine, Biotechnology Co., Ltd. AR); column chromatography silica gel (Qingdao Marine Chemical Factory, 200 μm); curcumin (Sinopharm Chemical Reagent AR); chemical reagents were of analytical grade (twice distilled, no water); Agilent1100 liquid chromatography-G1969A time-of-flight mass spectrometry; AVATAR360 Fourier transform infrared spectrometer (Nicolet); the AMX 500 NMR spectrometer (a Bruker); XT4-100A micro melting point analyzer (temperature control type. Beijing Tech electro-optical instrument factory); electrochemical workstation (CHI440 Shanghai Chen hua instrument Co., Ltd.).

Synthesis of chlorocarbonyl ferrocene: Under anhydrous conditions, the 0.01 mol ferrocenecarboxylate is suspended in 75 mL of anhydrous toluene in multiple; add 0.015 mol PCl_5 slowly; stir for 3 h, the reaction solution becomes black and reappear at the bottom of a black precipitate gradually. Steam toluene; re-distillation to obtain ferrocene chloride by petroleum ether get a crimson liquid, dark red crystals, weigh[8].

Synthesis of ferrocene formylated curcumin: Weigh the 1 mmol curcumin dissolving in 100 mL round bottom flask with 35 mL chloroform; 1.2 mmol chlorocarbonyl ferrocene dissolves in 10 mL chloroform, stirs, adds to a round bottom flask; adds a catalytic amount of triethylamine; reacts 20 h, the colour of solution gradually deepens; washes over the column, dries (dropping process, kept cold) and get light red solid (m.p. 186-187 ºC)[8,9].

Electrochemical experiments: Glassy carbon electrode as working electrode, saturated calomel electrode as the reference electrode, platinum wire electrode as the counter electrode, the compound dissolve in DMF-methanol (the ratio of 1:1) making 0.5 mmol L^{-1} of solution; adding saturated KCl as the supporting electrolyte, cyclic voltammetry, scans rate of 10 mV s^{-1} scan range of 0-1.0 V.

General procedure: Synthetic route shown in Fig. 1.

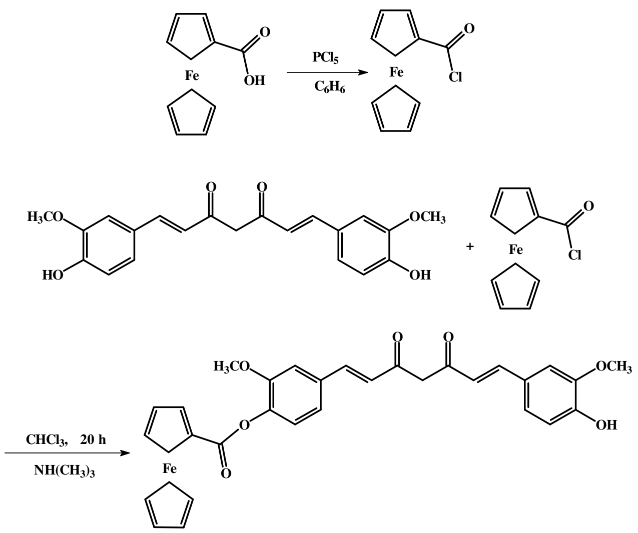

Fig. 1. Synthesis of ferrocene formylated curcumin

Detection method: Determinaton of molecular mass: Ferrocene formylated curcumin ($M + H^+$): 581.12. IR data: ν cm^{-1}: 3310 (O-H),1722(C=O, curcumin),1622 (C=O, ester carbonyl base), 1513, 1449 (Ar), 1267 (C-O). ^1H NMR data: δ: 3.97 (s, 6H, OCH_3-4'), 4.16 (s, 2H, C4-H), 6.10 (s, 2H, C2, C-6) 4.41-4.98 (m, 9H, ferrocene) 7.22-7.30 (m, 6H, Ar-H), 7.36 (s, 2H, C7-H), 9.82 (s, 1H, ph-OH)($CDCl_3$).

The results of electrochemical performance of the product by cyclic voltammetry method is shown in Fig. 2.

Ferrocene groups have a high degree of electron-rich characteristics of sandwich-type structure and aromaticity, thermal stability and good reactivity. The voltammetric behaviour of the new compound was investigated, appearing a pair of well defined redox wave at oxidation potential 0.768 V and reduction potential 0.219 V, respectively, in the range of 0-1.0 V. The peak separation (Δp) is 0.549 V. The peak current ratio (pa/pc) is1.78. The cyclic voltammetry data indicated that the acylated ferrocene had good electron transport ability in solution.

The peak of oxidation of product becomes lower compared ferrocene (oxidation potential 0.768 V and reduction potential 0.219 V, respectively[10]), showing that it is easier to lose electron. This may be caused by a big p-π conjugated system formed from the ester between cyclopentadienyl and curcumin. The p-π conjugated system increased the ring electron density and stabled ferrocene oxidation state. However, upon oxidation

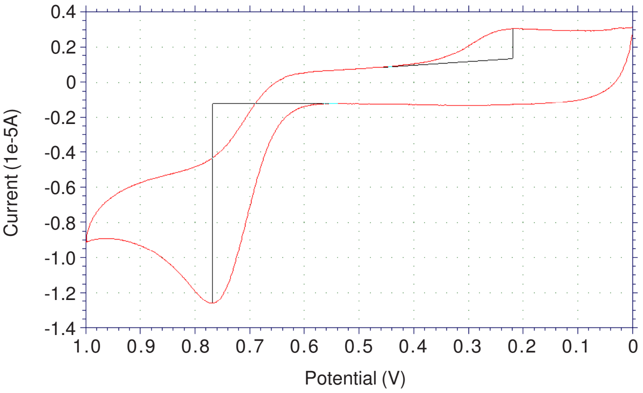

Fig. 2. Cyclic voltammogram of ferrocene formylated curcumin

of ferrocene to ferrocenium ion in ester bridged conjugates by using oxidizing agent, the compounds exhibited decent current due to elimination of the possibility of electron transfer. Thus, the ester bridged conjugates can be used as on/off current switches which will be explored in due course of time.

The ability of electron transfer by ester bond is not strong than by acetylene, which may cause reversible variation. The specific mechanism remains to be studied.

Conclusion

The voltammetric behaviour of the new compound is investigated, appearing a pair of well defined redox wave at oxidation potential 0.768 V and reduction potential 0.219 V, respectively, in the range of 0-1.0 V. Curcumin had a larger impact on the reversibility of the ferrocene through the ester, changing in the oxidation peak position. The ester bridged conjugates can be used as on/off current switches which will be explored in due course of time.

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