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Ferrocenyl-based thioethers and sulphones as optical, and electrochemical sensors for the differential detection of Hg^{2+} and Cu^{2+} ions

Yufeng Liu[a], Jianfeng Hu[a,b], Qiang Teng[a], Hao Zhang[a,b,*]

[a] College of Chemical & Chemical Engineering, Inner Mongolia University, Hohhot, 010021, PR China
[b] Inner Mongolia Key Laboratory of Fine Organic Synthesis, Hohhot, 010021, PR China

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ABSTRACT

Two highly selective and sensitive ferrocenyl-based thioethers **4a** and **4b** as no nitrogen atom contained chemosensors were designed and synthesized by using an easy method. The thioethers **4a** and **4b** have shown excellent selective recognition toward Hg^{2+} through optical and electrochemical signals. The detection limit values can reach 6.93×10^{-7} M for **4a**-Hg^{2+} and 4.79×10^{-7} M for **4b**-Hg^{2+}. Moreover, ferrocenyl-based sulphone **5a** and **5b** which were oxidized through thioethers **4a** and **4b** have exhibited more selective recognition toward Cu^{2+} and the detection limit values can reach 5.22×10^{-7} M and 4.97×10^{-7} M. It was found that the colour of **5a** in solution changed obviously from colourless to green occurred only when Cu^{2+} ion was added to the solution of the ensemble which could be easily detected by the naked eye. The two kinds of chemosensors were not easily affected by the pH values.

1. Introduction

Though many metal ions, such as Li^+, Na^+, K^+ and Zn^{2+}, play very important roles in living system and affect human health [1–3], some heavy-metal ions are extremely harmful to the environment and human health [4]. For the reason, the development of selective chemosensors for heavy-metal ions has attracted much attention [5–9]. The Hg^{2+} ion, a highly toxic heavy metal, causes severe health problems such as immune/geno/neurotoxic defects due to its accumulating in the human body through the food chain. The Hg^{2+} ion can easily penetrate into the biomembranes and gets converted methyl mercury [10]. On the other hand, Cu^{2+} ion is an essential trace metal ions in the human body, which plays an important role in various environmental, chemical, and physiological systems. However, the excess Cu^{2+} ion may cause several neurological diseases, such as Parkinson's disease, epileptic seizures, Kidney and liver damages [11].

As a result, the design of new and simple Hg^{2+} and Cu^{2+} selective chemosensors is of great importance for the environment and human health [12]. To develop selective and sensitive chemosensors, various receptors for Hg^{2+} or Cu^{2+} have been reported [13–30]. One of the most elegant ways of achieving chemosensors design is to functionalize a receptor consisting of both selective recognition moieties and physical signal response moieties. The ferrocene moiety has often been attached to a receptor for its unique electrochemical signal in detection of different metal ions [31–39]. In the past few years, the ferrocenyl-based chemosensors containing nitrogen atom as electron donors have attracted considerable attention [40–48]. However, the selective recognition property of the nitrogen atom contained chemosensors were easily affected by the acidity of environmental systems [49]. Therefore, the discovery of new non-nitrogenous chemosensors is desirable. The sulphur atom containing organic compounds has been widely used as ligands in organometallic chemistry [50]. Recently, Finney and his co-workers introduced the sulphur atom into the pyrene derivatives as a new highly fluorescence sensor [49,51]. Whereas the ferrocene derivatives containing sulphur atom as an electron donor was rarely used as chemosensor, which may be due to the lack of excellent synthesis methods.

Inspired by the previous work [52,53], our research group has successfully synthesized various ferrocenyl-based thioethers. Depending on our mature method, two new simple ferrocenyl-based thioethers were obtained, and investigated their selective recognition properties toward the Hg^{2+} ion. Moreover, when the ferrocenyl-based thioethers was oxidized to ferrocenyl-based sul-

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* Corresponding author at: College of Chemical & Chemical Engineering, Inner Mongolia University, Hohhot, 010021, PR China.

E-mail addresses: haozhang@imu.edu.cn, zh_hjf@hotmail.com (H. Zhang).

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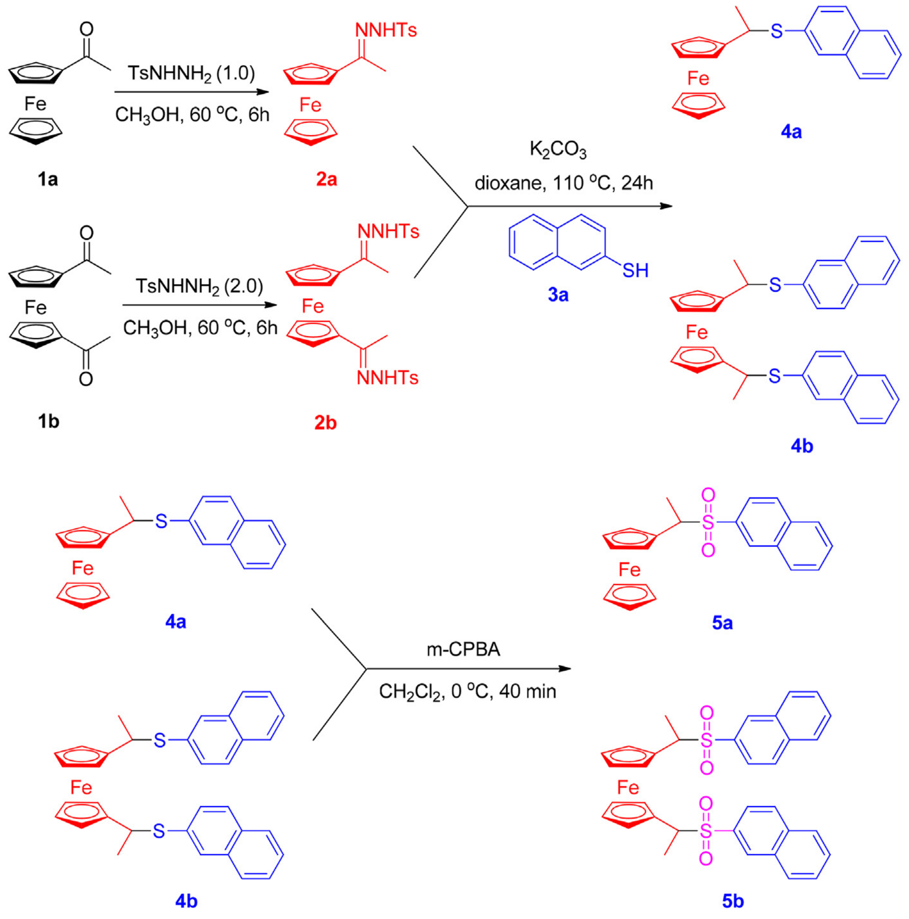

Scheme 1. Synthesis of ferrocenyl-based thioethers **4a**, **4b** and ferrocenyl-based sulphones **5a**, **5b**.

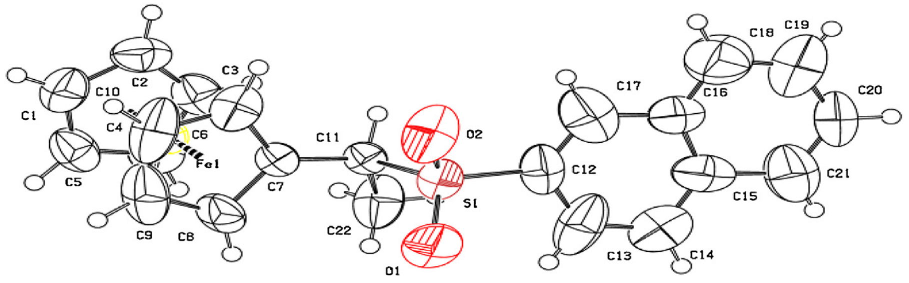

Fig. 1. X-ray structure of compound **5a**. Selected bond lengths (Å) and angles (deg): S1-O1 1.416(5), S1-O2 1.421(5), S1-C12 1.759(7), S1-C11 1.804(5), C11-C22 1.510(8), O1-S1-O2117.7(4), O1-S1-C12 106.3(4), O2-S1-C12 108.9(4), O1-S1-C11 109.3(3), O2-S1-C11 108.3(3), C12-S1-C11 105.8(3).

phones, they showed different selective recognition property. Compared with the thioether binding with Hg^{2+}, the sulphone tended to bind with Cu^{2+}.

2. Experimental

2.1. Materials and methods

All reagents were used as received from commercial sources, unless the 1-ferrocenyl ketone-derived *N*-tosylhydrazone and1, 1′-ferrocenyl di-ketone-derived *N*-tosylhydrazone were prepared as described in the literature [54]. All solvents were purified following standard literature procedures. For chromatography, 200–300 mesh silica gel (Qingdao, China) was employed. The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed with a conventional three-electrode configuration consisting of glassy carbon as the working electrode, platinum as an auxiliary electrode, and Ag/Ag^+ as a reference electrode. The concentration of the sample solutions was 100 μM in CH_3CN containing 0.1 M $[(n\text{-}C_4H_9)_4NPF_6]$ as supporting electrolyte and the scan rate was 0.1 V s^{-1}. The UV–vis spectra were carried out in CH_3CN solutions at c = 10 μM or 20 μM.

2.2. Instrumentation

All NMR experiments were carried out on a Bruker Avance 500 spectrometer using $CDCl_3$ and CD_3CN as the solvents with tetramethylsilane as the internal standard. Chemical shift values (δ) are given in parts per million. HRMS (ESI-TOF) spectra were recorded on a Bruker QTOF mass instrument. Melting points were determined with melting points apparatus and are uncorrected. The UV–vis spectra were recorded with UV-2700 (Shimadzu). The CV