Ferrocenyl-based thioethers and sulphoneas as optical, and electrochemical sensors for the differential detection of Hg²⁺ and Cu²⁺ ions

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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 $6.93 \times 10^{-7} \text{ M}$ for **4a**- Hg^{2+} and $4.79 \times 10^{-7} \text{ M}$ 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 $5.22 \times 10^{-7} \text{ M}$ and $4.97 \times 10^{-7} \text{ M}$. 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.

Keywords: ferrocenyl, thioether, sulphone, optical signals, electrochemical signals

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 sulphones, 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 and 1, 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 μ M in CH₃CN containing 0.1 M [(n-C₄H₉)₄NPF₆] as supporting electrolyte and the scan rate was 0.1 V s⁻¹. The UV-vis spectra were carried out in CH₃CN solutions at c = 10 μ M or 20 μ M.

2.2. Instrumentation

All NMR experiments were carried out on a Bruker Avance 500 spectrometer using CDCl₃ and CD₃CN 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 and DPV measurements were carried out on the Metrohm Autolab B. V.

2.3. Synthetic procedures

Synthesis of chemosensor **4a**

The 2-naphthalenethiol **3a** (80.1 mg, 0.5 mmol), tosylhydrazine **2a** (99.1 mg, 0.25 mmol), K₂CO₃ (103.7 mg, 0.75 mmol) were suspended in dioxane (3 mL) in a 25 ml Schlenk tube under nitrogen. The solution was stirred at 110°C for 24 h. Then the reaction mixture was allowed to cool to room temperature, and diluted with 20 mL of CH₂Cl₂. The organic phase was washed with saturated brine, dried with MgSO₄ and filtered. The solvents were evaporated under reduced pressure and the residue was purified by column chromatography on silica gel and elution with hexane to afford yellow oil **4a** (67.0 mg, 72%): ¹H NMR (500 MHz, CDCl₃) δ 7.82 (s, 1H), 7.80 - 7.75 (m, 1H), 7.72 (m, 2H), 7.48 - 7.39 (m, 3H), 4.24 (q, *J* = 6.8 Hz, 1H), 4.17 (m, 1H), 4.14 (s, 5H), 4.10 (m, 1H), 4.06 (m, 1H), 4.03 (m, 1H), 1.65 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 133.6, 132.8, 132.4, 131.7, 130.5, 128.2, 127.7, 127.5, 126.4, 126.1, 90.8, 68.7, 68.0, 67.8, 67.7, 66.2, 43.6, 21.3. HRMS (ESI-TOF) *m/z*: [M]⁺ calcd for C₂₂H₂₀FeS 372.0635; Found: 372.0633.

Synthesis of chemosensor **4b**

The chemosensor **4b** was also prepared by the same method for **4a** and the amounts used were 2 times except **2b**. The residue was purified by column chromatography on silica gel and elution with hexane to afford yellow oil **4b** (64.2 mg, 46%): ¹H NMR (500 MHz, CDCl₃) δ 7.81 (s, 2H), 7.79 - 7.76 (m, 2H), 7.73 - 7.69 (m, 4H), 7.46 - 7.40 (m, 6H), 4.26 (m, 2H), 4.20 - 4.16 (m, 1H), 4.16 - 4.09 (m, 5H), 4.09 - 4.06 (m, 1H), 4.06 - 4.00 (m, 1H), 1.63 (d, *J* = 6.8 Hz, 3H), 1.62 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 133.6, 132.7, 132.6, 132.4, 131.8, 131.7, 130.5, 130.4, 128.2, 128.2, 127.7, 127.5, 126.4, 126.1, 91.2, 91.2, 68.9, 68.9, 68.8, 68.7, 68.64, 68.5, 66.9, 66.7, 43.5, 43.4, 21.5, 21.4. HRMS (ESI-TOF) *m/z*:

[M]⁺ calcd for C₃₄H₃₀FeS₂ 558.1138; Found: 558.1142.

Synthesis of chemosensor **5a**

The m-Chloroperbenzoic acid (75 %, 117.0 mg, 0.508 mmol) was added to a solution of **4a** (86.1mg, 0.231mmol) in CH₂Cl₂ (5 mL) at 0 °C. After 40 minutes, the reaction mixture was concentrated and purified by column chromatography on silica gel and elution with ethyl acetate/ hexane (1/3 v/v) to afford light red solid **5a** (65.4 mg, 70%): mp: 141.5 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.11 (s, 1H), 7.87 (d, *J* = 7.8, 4.5 Hz, 2H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 8.6, 1.5 Hz, 1H), 4.20 (s, 1H), 4.11 (d, *J* = 1.7 Hz, 3H), 4.08 (d, *J* = 12.2 Hz, 6H), 3.92 (s, 1H), 1.75 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 135.2, 133.2 131.8, 131.5, 129.4, 129.1, 128.4, 127.9, 127.4, 124.5, 81.3, 70.8, 68.8, 68.6, 67.1, 62.6, 14.1. HRMS (ESI-TOF) *m/z*: [M]⁺ calcd for C₂₂H₂₀FeO₂S 404.0533; Found: 404.0576.

Synthesis of chemosensor **5b**

The chemosensor **5b** was also prepared by the same method for **5a** and the amounts used were 2 times. After 40 minutes, the reaction mixture was concentrated and purified by column chromatography on silica gel and elution with ethyl acetate/ hexane (1/1 v/v) to afford light red solid **5b** (58.5 mg, 56%): mp: 201.5 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.07 (s, 2H), 7.89 - 7.78 (m, 6H), 7.60 (d, *J* = 31.9, 7.3 Hz, 4H), 7.47 - 7.36 (m, 2H), 4.09 - 3.96 (m, 8H), 3.90 (s, 1H), 3.85 (s, 1H), 1.65 (d, *J* = 7.0 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 135.3, 132.9, 131.8, 131.5, 129.3, 128.5, 127.94 (s), 127.52 (s), 124.34 (s), 82.09 (s), 77.36 (s), 77.10 (s), 76.85 (s), 71.73 (s), 71.50 (s), 69.90 (s), 69.59 (t, *J* = 15.4 Hz), 67.78 (s), 67.54 (s), 62.17 (s), 14.18 (d, *J* = 12.0 Hz). HRMS (ESI-TOF) *m/z*: [M+Na]⁺ calcd for C₃₄H₃₀FeNaO₄S₂ 645.0833; Found: 645.0829.

3. Results and Discussion

3.1. Synthesis and characterisation

The ferrocenyl-based thioethers **4a** and **4b** were obtained from the following literature procedures with some modification [52,53]. As shown in Scheme 1, the precursors **2a** and **2b** both undergo insertion into S-H bond of 2-naphthalenethiol **3a** to generate compound **4a** and **4b** in 72% and 46% yields, respectively. The ferrocenyl-based sulphones **5a** and **5b** were prepared through oxidizing the corresponding thioethers **4a** and **4b** [51]. As shown in Scheme 1, the compound **4a** and **4b** were oxidized by m-chloroperbenzoic acid to form the compound **5a** and **5b** in 70% and 56% yields. Compounds **4a**, **4b**, **5a** and **5b** have been characterized by HRMS (ESI-TOF) spectrometry, ¹H NMR and ¹³C NMR spectroscopy. Furthermore, the solid-state structure of **5a** was confirmed by X-ray structure analysis (Fig. 1) and was in full agreement with spectroscopic data. The metal cations recognition properties of the chemosensors have been established by UV-vis spectroscopic, ¹H NMR titration, and electrochemical studies.

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 ($\text{\AA}$) and angles ($^\circ$): 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-O2 117.7(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).

3.2. UV-Visible Absorption Studies

The UV-vis spectra of **4a** and **4b** (Fig. 2) showed the absorption of 225 nm, 254 nm and 310 nm produced by $\pi\text{-}\pi^*$ charge transfer (CT) transition of naphthyl. To evaluate the selectivity, we carried out the

UV-vis absorption test of **4a** and **4b** in the presence of various metal salts Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , Ag^+ , and Hg^{2+} ions. As shown in the Fig. 2a, upon addition of Hg^{2+} , the spectra of **4a** exhibited obvious changes of the absorption band. The absorption band at 225 nm decreased, the absorption band at 254 nm increased with 4 nm blue shifted and the absorption band at 310 nm increased. Similar results were observed for **4b** (Fig. 2b).

As the UV-vis titration spectra (Fig. 3a, 3b) of **4a** and **4b** with Hg^{2+} (0-0.5 equiv or 0-1.0 equiv) shown, the well defined isosbestic point at 237 nm for **4a**- Hg^{2+} and **4b**- Hg^{2+} indicate the presence of a unique complexing equilibrium with **4a** and **4b**, respectively. The insert figure of Fig. 3a Job's plot of **4a** with Hg^{2+} indicated the formation of 2:1 complexes, but for **4b** with Hg^{2+} (Fig. 3b), the formation was 1:1 complexes which was further confirmed by ESI-MS, where peaks at m/z 766.5943 in the mass spectra (Fig. S3). As the well known Benesi-Hilderbrand (BH) equation [55] shows the binding constant (K) values were $2.50 \times 10^{13} \text{ M}^{-2}$ for **4a**- Hg^{2+} and $5.00 \times 10^4 \text{ M}^{-1}$ for **4b**- Hg^{2+} (Figs. S1a, S2a). The detection limit values could reach $6.93 \times 10^{-7} \text{ M}$ for **4a**- Hg^{2+} and $4.79 \times 10^{-7} \text{ M}$ for **4b**- Hg^{2+} (Figs. S1b, S2b). Notably, from the detection limit values, **4b** exhibited higher sensitivity toward Hg^{2+} than **4a**, which may due to two receptor units in **4b**.

Fig. 2. UV-vis absorption spectra of **4a** (a) and **4b** (b) observed upon addition of 1 equiv of various metal ions in CH_3CN (20 μM).

Fig. 3. UV-vis absorption titration spectra of **4a** (a) and **4b** (b) with $\text{Hg}(\text{ClO}_4)_2$ in CH_3CN (10 μM).

For the ferrocenyl-based sulphones **5a** and **5b**, we also studied their selectivity and sensitivity. The UV-vis absorption spectra (Fig. 4a) of **5a** in the presence of various metal ions showed the single selectivity towards Cu^{2+} . The same selectivity result was observed for **5b** (Fig. 4b). Obvious changes of

the absorption band had been achieved. The absorption band at 225 nm decreased, other absorption bands increased, two new absorption bands appeared at 256 nm and 285 nm. In addition, a new small absorption band appeared at 640 nm which may lead the color of the solution changes from colorless to green (Fig. 5). The changes in the absorption spectra are accompanied by dramatic color changes which allow the potential for “naked eye” detection. The UV-vis titration spectra (Fig. 6a, 6b) of **5a** and **5b** with Cu^{2+} (0-1.0 equiv or 0-2.0 equiv) exhibited the absorption band gradually increased. The insert figures of Figs. 6a and 6b Job's plots of **5a** and **5b** with Cu^{2+} indicated the formation of 1:1 and 1:2 complexes, respectively. For **5a**, the stoichiometry of the complexes was further confirmed by ESI-MS, where peak at m/z 467.3803 in the mass spectra (Fig. S6). According to the Benesi-Hilderbrand (BH) equation of **5a** and **5b** with Cu^{2+} , the binding constant (K) values were $5.74 \times 10^4 \text{ M}^{-1}$ for **5a**- Cu^{2+} and $9.12 \times 10^4 \text{ M}^{-1}$ for **5b**- Cu^{2+} (Figs. S4a, S5a). The detection limit values could reach $5.22 \times 10^{-7} \text{ M}$ for **5a**- Cu^{2+} and $4.97 \times 10^{-7} \text{ M}$ for **5b**- Cu^{2+} (Figs. S4b, S5b). These datum of **5a** and **5b** also indicate the 1,1'-disubstituted ferrocene-based derivative has better recognition performance than the 1-substituted ferrocene-based derivative.

To check the practical application ability of **4a** and **5a**, we carried the UV-vis experiments of **4a** with Hg^{2+} and **5a** with Cu^{2+} in different pH solutions. As the Fig. 7 shown, the absorbance changes slightly, which illustrates that **4a** and **5a** still exhibited good recognition performance toward Hg^{2+} or Cu^{2+} in long pH ranges 4-10. Compared with nitrogen atom contained chemosensors, **4a** and **5a** were not easily affected by the pH values.

Fig. 4. UV-vis absorption spectra of **5a** (a) and **5b** (b) observed upon addition of 1 equiv of various metal ions in CH_3CN (10 μM).

Fig. 5. Visual features observed in CH_3CN of **5a** (300 μM) after addition of 5 equiv of various metal ions.

Fig. 6. UV-vis absorption titration spectra of **5a** (a) and **5b** (b) with $\text{Cu}(\text{ClO}_4)_2$ in CH_3CN (10 μM).

Fig. 7. The absorbance of chemosensor **4a** (10 μM) with $\text{Hg}(\text{ClO}_4)_2$ or without $\text{Hg}(\text{ClO}_4)_2$ (top) and **5a** (10 μM) with $\text{Cu}(\text{ClO}_4)_2$ or without $\text{Cu}(\text{ClO}_4)_2$ (bottom) in different pH solutions.

3.3. Electrochemical Studies

The electrochemical signal can be immediately read out [56-67], therefore chemosensors bearing a ferrocene moiety as a part of the sensing units have been broadly studied [68,69], due to the $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ redox couple has unique electrochemical signal. The metal recognition properties of **4a**, **4b**, **5a** and **5b** were evaluated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) analysis in CH_3CN solutions containing 0.1 M $[(n\text{-C}_4\text{H}_9)_4\text{NPF}_6]$ as the supporting electrolyte.

Ferrocenyl-based thioethers **4a** and **4b** both display one-electron-oxidation process at $E_{1/2} =$

0.559 and 0.584 V, respectively. No perturbation of the CV and DPV voltammograms of **4a** (Fig. 8a, 8b) and **4b** (Fig. 8c, 8d) were observed in the presence of various metal salts Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} and Ag^+ . However, as shown in the Fig. 9a, the original peak gradually migrated from $E_{1/2} = 0.559$ V to $E_{1/2} = 0.518$ V upon stepwise addition of Hg^{2+} , while a new irreversible peak appeared at 0.785V. The DPV titration experiment of **4a** with Hg^{2+} (Fig. 9b) shows the corresponding results. For the ferrocenyl-based sulphones **5a** and **5b** their one-electron-oxidation process at $E_{1/2} = 0.651$ V and 0.775 V. No obvious changes of the CV and DPV voltammograms of **5a** (Fig. 10a, 10b) and **5b** (Fig. 10c, 10d) were observed in the presence of various metal salts Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Hg^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} and Ag^+ . Yet, when the Cu^{2+} was added stepwise (Fig. 11a), the current obviously increased with $\Delta E_{1/2} = 15$ mV cathodic migration. Changes of the DPV titration experiment of **5a** with Cu^{2+} (Fig. 11b) confirmed the results of the CV titration experiment.

Fig. 8. Cyclic Voltammetry and Differential Pulse Voltammetry spectra of **4a** (a), (b) and **4b** (c), (d) observed upon addition of 1 equiv of various metal ions in CH_3CN (100 μM), containing 0.1 M $[(n\text{-C}_4\text{H}_9)_4\text{NPF}_6]$ as supporting electrolyte.

Fig. 9. Cyclic Voltammetry and Differential Pulse Voltammetry titration spectra of **4a** with $\text{Hg}(\text{ClO}_4)_2$ in CH_3CN (100 μM), containing 0.1 M $[(n\text{-C}_4\text{H}_9)_4\text{NPF}_6]$ as supporting electrolyte and scanned at 0.1 V s^{-1} .

Fig. 10. Cyclic Voltammetry and Differential Pulse Voltammetry spectra of **5a** (a), (b) and **5b** (c), (d) observed upon addition of 1 equiv of various metal ions in CH_3CN (100 μM), containing 0.1 M $[(n\text{-C}_4\text{H}_9)_4\text{NPF}_6]$ as supporting electrolyte.

Fig. 11. Cyclic Voltammetry and Differential Pulse Voltammetry titration spectra of **5a** with $\text{Cu}(\text{ClO}_4)_2$ in CH_3CN (100 μM), containing 0.1 M $[(n\text{-C}_4\text{H}_9)_4\text{NPF}_6]$ as supporting electrolyte and scanned at 0.1 V s^{-1} .

3.4. Binding Studies

To obtain the complexation evidence, ^1H NMR experiments were carried out in the CD_3CN solution. For ferrocenyl-based thioethers **4a** and **4b**, only the sulphur atom could act as the binding site. The significant changes in ^1H NMR titration spectra of **4a** with Hg^{2+} (Fig. 12) exhibited the complexation between **4a** and Hg^{2+} . Upon the addition of Hg^{2+} into the free receptor **4a**, the number of all proton peaks decreased, the tertiary carbon proton (Ha) and ferrocenyl proton (Hc) were mixed, and the methyl carbon (Hb) highfield shift: $\Delta\text{Hb} = 0.1 \text{ ppm}$. But for the ferrocenyl-based sulphone **5a**, the binding site may be the oxygen atom. The X-ray structure of **5a** (Fig. 1) showed the two oxygen atoms were at the different side with the methyl and naphthyl units. The big steric hindrance makes the sulphur atom and Cu^{2+} difficult to contact. However, the two bare oxygen atoms could easily contact with Cu^{2+} . For the reason, the two kinds of receptors showed different selectivity toward metal ions. The changes of the IR spectra of **5a** with Cu^{2+} (Fig. 14) also confirmed our assumption. The characteristic stretching frequency for the sulphone ($\text{O}=\text{S}=\text{O}$) unit at 1130 and 1330 cm^{-1} disappeared. Compared with the receptor **4a**, the similar changes in ^1H NMR titration spectra of **5a** with Cu^{2+} (Fig. 13) also exhibited the complexation between **5a** and Cu^{2+} . When the Cu^{2+} was added into the free receptor **5a**, similar changes were observed, and the methyl carbon (Hb) highfield shift: $\Delta\text{Hb} = 0.3 \text{ ppm}$, the ferrocenyl proton (Hc) downfield shift: $\Delta\text{Hc} = 0.2 \text{ ppm}$.

Fig. 12. Evolution of the ^1H NMR spectra of **4a** upon addition of 0.5 equiv Hg^{2+} in the CD_3CN solution. Insert: possible binding mode of metal ion with the receptor **4a**.

Fig. 13. Evolution of the ^1H NMR spectra of **5a** upon addition of 1.0 equiv Cu^{2+} in the CD_3CN solution. Insert: possible binding mode of metal ion with the receptor **5a**.

Fig. 14. The IR spectra of **5a** and **5a**-Cu²⁺ complex.

4. Conclusions

In conclusion, we have described two new and simple ferrocenyl-based thioethers as no nitrogen contained chemosensors **4a** and **4b**, which selectively bind with Hg²⁺ ion through optical and electrochemical signals. The 1,1'-disubstituted thioether **4b** has shown higher sensitivity than 1-substituted thioether **4a**. However, when the thioethers **4a** and **4b** were oxidized to sulphones **5a** and **5b**, they have exhibited more selective recognition toward Cu²⁺ ion. When Cu²⁺ ion was added into the solution of **5a**, the color changed from colorless to green, which allows its potential use for “naked eye” detection. The pH values changes (4-10) had no obvious effect on two kinds of chemosensors.

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