Straightforward Synthesis of Ferrocenyl-based Thioether and Application as Chemosensor for Hg²⁺ ion

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ABSTRACT

A simple and efficient strategy of constructing ferrocene-based thioether ligands through metal-free reductive coupling of thiols with *N*-tosylhydrazones bearing a ferrocenyl group has been developed. This method features metal-free, good functional group tolerance, and readily available starting materials. Moreover, the compound **3k** as a novel chemosensor has shown excellent recognition towards Hg²⁺ ion *via* optical and electrochemical signals. Quantification of the absorption titration analysis shows that the detection limit was 9.56×10^{-7} M for **3k**-Hg²⁺.

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1. Introduction

Ferrocene derivatives have shown an improved application in organometallic chemistry,¹⁻⁴ materials science,⁵⁻⁷ catalysis,^{8,9} electrochemistry¹⁰⁻¹² and bioorgano-metallic chemistry^{13,14} since their discovery in 1951. As they contain the ferrocene/ferrocenium pair transformation, ferrocene derivatives have unique properties in electrochemistry.^{15,16} Because of this property, many ferrocenyl-based chemosensors have been synthesized.¹⁷⁻²⁴ In the past few years, the ferrocenyl-based chemosensors containing N or O as electron donors have attracted considerable attention.²⁵⁻³³ However, ferrocenyl-based thioethers were very rarely used as chemosensors, which may be due to only a few methods to synthesize ferrocenyl-based thioethers.

We all know the classical method to synthesize thioethers is the Williamson reaction.³⁴ In recent years, many new methods have been developed. Among them, transition metal-catalyzed hetero-cross-coupling (C–S) between aryl³⁵⁻⁴⁵ or alkyl halides and thiols may be the most popular method. In addition, the metal free catalyzed reaction involving the addition of a thiol to an alkene is also a special method.⁴⁶⁻⁴⁸ These methods have proven to be highly effective in such coupling reactions, but it is still difficult to obtain ferrocenyl-based thioethers. Therefore, there is a great need to develop new methods to synthesize ferrocenyl-based thioethers. As a new type of carbene precursor, *N*-tosylhydrazones received more attention for scholars.⁴⁹⁻⁵³ Recently, Valdes and Peng have developed a novel metal-free carbon–oxygen bond-forming reaction *via* the metal-free

reductive coupling of alcohols or phenols with tosylhydrazones.^{54,55} Inspired by their work, we reported the synthesis of two new types of ferrocenyl-based thioethers. By using this method, which is simple, efficient and low cost, 1-substituted and 1,1'-disubstituted ferrocenyl-based thioethers could be synthesized in moderate to good yields. The reaction can also tolerate various functional groups.

With these compounds in hand, we chose **3k** containing benzimidazolyl as chemosensor and studied its recognition performance. Through the optical and electrochemical selectivity experiments, the chemosensor **3k** showed excellent recognition towards Hg²⁺ ion. Because of the famous minamata disease, almost everyone know the Hg²⁺ ion is an extremely toxic heavy metal. In fact, the accumulating Hg²⁺ ion in human body through the food chain could really cause severe health problems, such as immune, geno and neurotoxic defects.⁵⁶ As a result, the design of new and simple Hg²⁺ selective chemosensors is of great importance for the environment and human health.⁵⁷⁻⁵⁸

2. Results and discussion

2.1. Synthesis of Ferrocenyl-based Thioethers Ligands

At the outset of the investigation, we employed 4-chlorobenzenethiol (**1a**) and *N*-tosylhydrazone (**2a**) derived from 1-acetylferrocene as the substrates to optimize the reactions (Table 1). We observed that the desired product **3a** was obtained in 79% yield, when **1a** (1.5 equiv.) and **2a** (1.0 equiv.) reacted with K₂CO₃ (3.0 equiv.) in dioxane at 110 °C for 24 hours (Table 1, entry 1). Since the *N*-tosylhydrazone (**2a**) did not react

completely, the increase of **1a** led to the improvement of the yield (85%) (entries 2 and 3). 3.0 equivalents K_2CO_3 was adequate for the reaction (entries 3, 4 and 5). Dioxane was found to be the most suitable solvent, and the reaction also played smoothly in N,N'-dimethylformamide (DMF), tetrahydrofuran (THF) (entries 8 and 9). A low yield was obtained when toluene, acetonitrile (CH_3CN) or dichloroethane (DCE) was used as the solvent (entries 6, 7 and 10). Ultimately, we chose dioxane which had a high boiling point as the solvent because the high temperature may be good to the reaction. We also screened the effect of bases, but lower yields were obtained with other bases (entries 11-15). Finally, the optimum conditions were identified as dioxane at 110 °C, with inexpensive K_2CO_3 as the base.

Table 1. Optimization of conditions ^a

Entry	1a : 2a	Solvent (mL)	Base (equiv)	T (°C)	Yield (%) ^b
1	1.5:1.0	dioxane(3)	K_2CO_3 (3.0)	110	79
2	2.0:1.0	dioxane(3)	K_2CO_3(3.0)	110	85
3	3.0:1.0	dioxane(3)	K_2CO_3 (3.0)	110	87
4	2.0:1.0	dioxane(3)	K_2CO_3 (2.0)	110	73
5	2.0:1.0	dioxane(3)	K_2CO_3 (4.0)	110	74
6	2.0:1.0	toluene(3)	K_2CO_3 (3.0)	110	42
7	2.0:1.0	DCE(3)	K_2CO_3 (3.0)	110	trace
8	2.0:1.0	DMF(3)	K_2CO_3 (3.0)	110	81
9	2.0:1.0	THF(3)	K_2CO_3 (3.0)	110	84
10	2.0:1.0	CH_3CN (3)	K_2CO_3 (3.0)	110	49
11	2.0:1.0	dioxane(3)	Na_2CO_3 (3.0)	110	31
12	2.0:1.0	dioxane(3)	CS_2CO_3 (3.0)	110	27
13	2.0:1.0	dioxane(3)	LiO'Bu(3.0)	110	42
14	2.0:1.0	dioxane(3)	NaO'Bu(3.0)	110	38
15	2.0:1.0	dioxane(3)	KO'Bu(3.0)	110	33

^a Reactions were carried out with **1a** and **2a** in the presence of 3.0 equiv. of base at 110 °C under a N_2 atmosphere for 24 h. ^b Yield of the isolated product after chromatography.

With the optimized conditions, we investigated the scope of the reaction (Scheme 1). A series of thiophenols with **2a** were examined. The thiophenol bearing a halide group (F, Cl, Br) and alkyl group (Me) gave the desired products in excellent yields (**3a-e** and **3f**). Significantly, both *ortho*-, *meta*- and *para*-substituted thiophenols were afforded the corresponding products in good yields (**3a**, **3d**, **3e** and **3h-j**). The strong electron-donating groups were also tolerated well (**3h-j**). However, the thiophenols with strong electron-withdrawing group showed lower reactivity (**3g**). Notably, benzimidazolyl substituted thioether (**3k**) could also be obtained in moderate yield. In addition, benzyl mercaptane (**3l**) could be compatible with this

reaction in spite of low yield. A range of ferrocenyl ketone derived *N*-tosylhydrazones with different substitution patterns were also investigated. The substituent of tosylhydrazones had little effect on the reaction, and both alkyl groups or the aromatic group were all tolerated (**3m-p** and **3q**). The structure of compound **3a** was confirmed by the X-ray structural analysis (Figure 1).

Scheme 1. Metal-free reductive coupling of thiols with *N*-tosylhydrazones bearing a ferrocenyl group ^{ab}. ^a Reaction conditions: **1** (0.5 mmol), **2** (0.25 mmol), K_2CO_3 (3 equiv.), solvent (3 mL), 110 °C, 24 h. ^b Isolated yield.

Figure 1. X-ray structure of compound **3a**. Selected bond lengths (Å) and angles (deg): S1-C6 1.831(3), S1-C7 1.766(3), C1-C6 1.499(3), C6-C13 1.522(4), C1-C6-S1 103.93(15), C13-C6-S1 111.20(15), C7-C8 1.385(3), C7-C12 1.391(3), C8-C7-S1 124.76(17), C12-C7-S1 116.59(17).

Next, we further applied the system to 1,1'-ferrocenyl diketone-derived *N*-tosylhydrazone with various thiophenols. To our delight, the desired product **5a** could be obtained in 64% yield with the modified condition. The substrate scope of thiophenols was studied by using **4a**. Functional groups such as halogens (F, Cl, Br) and alkyl (Me) on the benzene ring could afford the corresponding products in good yields (**5a-e** and **5f**).

The steric bulk of the substitute had little effect on the reaction (**5a**, **5d** and **5e**). Furthermore other substituted *N*-tosylhydrazones bearing a ferrocenyl group also proceeded smoothly under the condition (**5k-n**). The reaction was not significantly affected by the substituent.

Scheme 2. Metal-free reaction of various thiols with 1,1'-ferrocenyl diketone-derived *N*-tosylhydrazones. ^aReaction conditions: **1** (1.0 mmol), **4** (0.25 mmol), K₂CO₃ (6 equiv.), solvent (3 mL), 110 °C, 24 h. ^bIsolated yield.

2.2. The Application of **3k** as Chemosensor for Hg²⁺ ion

UV-Visible Absorption Studies

At the beginning, the UV-vis absorption studies were performed using the CH₃CN (10 μM) solution. The UV-vis spectra of **3k** (Figure 2a) showed the absorption of 225 nm, 254 nm and 300 nm were produced by π - π^* charge transfer (CT) transition of the phenyl group, the absorption of 310 nm was attributed to the -N=C-. To evaluate the selectivity of **3k**, we carried out the UV-vis absorption test of it in the presence of various metal salts Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Cd²⁺, Ag⁺, and Hg²⁺ ions. As shown in the Figure 2a, upon addition of Hg²⁺, the spectrum exhibited obvious changes. The absorption bands at 225 and 254 nm decreased, the absorption band at 310 nm also decreased with a 15 nm blue shift.

As the UV-vis titration shown (Figure 2b), the well defined isosbestic points at 230, 242, 259, 293 and 320 nm for **3k**-Hg²⁺

indicate the presence of a unique complexing equilibrium. The insert figure of Figure 2b is a Job's plot of **3k** with Hg²⁺ indicating the formation of 1:1 complexes. As the well known Benesi - Hilderbrand (BH) equation²⁷ (SFigure 1a, 1b) shows the binding constant (*K*) values was 1.2×10^5 M and the detection limit values could reach 9.56×10^{-7} M for **3k**-Hg²⁺.

Figure 2. (a) UV-vis absorption spectra of chemosensor **3k** observed upon addition of 1 equivalent of various metal ions in CH₃CN (10 μM); (b) UV-vis absorption titration spectra of chemosensor **3k** with Hg(ClO₄)₂ in CH₃CN (10 μM)

Electrochemical Studies

The electrochemical signal can be immediately read out, which is the essential advantage for ferrocene-based chemosensors in the recognition process. As containing the ferrocene/ferrocinium pair transformation, the chemosensors have been broadly studied as electrochemical sensors for metal cations.^[21] We investigated the cyclic voltammetry (Figure 3a) and differential pulse voltammetry (Figure 3b) of **3k** with various metal ions, in CH₃CN containing 0.1 M [(n-C₄H₉)₄NPF₆] as the supporting electrolyte. No obvious changes in CV and DPV of **3k** were observed upon addition of Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Fe²⁺, Co²⁺, Ni²⁺, Zn²⁺, Pb²⁺, Cd²⁺, Ag⁺ and Cu²⁺ ions. However, when the Hg²⁺ (0 - 1.0 equivalent) was added to the solution of **3k**, as the CV spectra shows (Figure 4a), the original reversible one-electron oxidation process at 0.67 V ($\Delta E_{1/2} = 63$ mV) gradually decreased, mean while a new reversible one-electron oxidation

process at 0.75 V ($\Delta E_{1/2} = 64$ mV) appeared. The DPV spectra of **3k** illustrated the similar results (Figure 4b).

Figure 3. Cyclic Voltammetry (a) and Differential Pulse Voltammetry (b) spectra of chemosensor **3k** observed upon addition of 1 equivalent of various metal ions in CH₃CN (100 μ M), containing 0.1 M [(n-C₄H₉)₄NPF₆] as supporting electrolyte and scanned at 0.1 V s⁻¹.

Figure 4. Cyclic Voltammetry (a) and Differential Pulse Voltammetry (b) titration spectra of chemosensor **3k** with Hg(ClO₄)₂ in CH₃CN (100 μ M), containing 0.1 M [(n-C₄H₉)₄NPF₆] as supporting electrolyte and scanned at 0.1 V s⁻¹.

¹H NMR Titration Studies

In order to understand the binding mechanism, ¹H NMR experiments were carried out by stepwise addition of Hg²⁺ in CD₃CN solution of the free chemosensor **3k** at room temperature. As illustrated in Figure 5, significant shifts in the ¹H NMR spectrum were observed upon addition of Hg²⁺. When 0.5 - 1.0 equivalent Hg(ClO₄)₂ was added to the solution of **3k**, the ferrocenyl proton (Hc) slightly downfield shift ($\Delta Hc = 0.1$ ppm), the tertiary carbon proton (Ha) highfield shift: $\Delta Ha = 0.3$ ppm, the methyl proton (Hb) does not shift, the benzimidazolyl proton (Hd) downfield shift: $\Delta Hd = 0.2$ ppm. In addition, the number of all proton peaks decreased along with the addition of Hg(ClO₄)₂. Depending on these changes of the ¹H NMR spectrum and the formation of 1:1 complexes, we proposed the plausible binding mode (Figure 5).

Figure 5. The ¹H NMR titration spectra of chemosensor **3k** upon addition of Hg²⁺ in CD₃CN and the plausible binding mode.

3. Conclusions

In summary, we have developed a simple and efficient method for the synthesis of ferrocene-based thioether ligands through metal-free C-S bond-forming between thiols and ferrocenyl ketone tosylhydrazones. This method had good functional group tolerance, mild conditions and available starting materials, giving the corresponding ferrocenyl-based ligands in moderate to good yields. Moreover, the compound **3k** as a novel chemosensor has shown excellent recognition towards Hg^{2+} ions *via* optical and electrochemical signals.

4. Experimental Section

General experimental methods.

All NMR experiments were carried out on a 500 MHz spectrometer using CDCl_3 or $\text{DMSO}-d_6$ as the solvent with tetramethylsilane as the internal standard. HRMS data were obtained on BrukerMALDI-TOF/TOF instrument. The melting points were determined on an X-4 binocular microscope melting point apparatus and are uncorrected. CH_3CN , dioxane, toluene, DMF, THF and DCE were dried according to literature techniques.

General Procedure for Metal-Free Reaction.

Thiol **1a** (72.3 mg, 0.5 mmol), tosylhydrazone **2a** (99.1 mg, 0.25 mmol), K_2CO_3 (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 ambient temperature, and diluted with 20 mL of CH_2Cl_2 . The organic phase was washed with saturated brine, dried with MgSO_4 and filtered. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel.

(4-chlorophenyl)(1-ferrocenylethyl)sulfane (**3a**).

Yellow solid, 75.8 mg (85% yield); mp 91–93 °C; Rf (petroleum ether/ethyl acetate 100:1) = 0.43. ^1H NMR (500 MHz, CDCl_3) δ 7.27–7.18 (m, 4H), 4.13 (s, 5H), 4.12–4.10 (m, 2H), 4.10–4.05 (m, 2H), 4.02–3.98 (m, 1H), 1.61 (d, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 134.8, 133.5, 133.5, 128.8, 90.5, 68.7, 68.0, 67.8, 67.7, 66.0, 44.0, 21.1. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{18}\text{H}_{17}\text{ClFeS}$: 356.0089; Found: 356.0084.

(4-fluorophenyl)(1-ferrocenylethyl)sulfane (**3b**).

Yellow oil, 68.9 mg (81% yield); Rf (petroleum ether/ethyl acetate 100:1) = 0.42. ^1H NMR (500 MHz, CDCl_3) δ 7.29 (m, 2H), 6.94 (m, 2H), 4.13 (s, 5H), 4.11–4.05 (m, 3H), 4.02 (q, J = 6.9 Hz, 1H), 3.99–3.93 (m, 1H), 1.59 (d, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 163.6, 161.7, 136.5, 136.4, 129.8, 129.7, 115.8, 115.6, 90.7, 68.7, 68.0, 67.7, 67.6, 65.9, 44.5, 21.0. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{18}\text{H}_{17}\text{FeFS}$: 340.0384; Found: 340.0380.

(4-bromophenyl)(1-ferrocenylethyl)sulfane (**3c**).

Yellow solid, 80.2 mg (80% yield); mp 83–85 °C; Rf (petroleum ether/ethyl acetate 100:1) = 0.43. ^1H NMR (500 MHz, CDCl_3) δ 7.37 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 4.13 (s, 5H), 4.13–4.11 (m, 2H), 4.11–4.07 (m, 2H), 4.03–3.98 (m, 1H), 1.61 (d, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 134.9, 134.2, 131.7, 121.5, 90.5, 68.7, 68.0, 67.8, 67.7, 66.1, 43.9, 21.1. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{18}\text{H}_{17}\text{BrFeS}$: 399.9584; Found: 399.9583.

(3-chlorophenyl)(1-ferrocenylethyl)sulfane (**3d**).

Yellow oil, 75.0 mg (84% yield); Rf (petroleum ether/ethyl acetate 100:1) = 0.42. ^1H NMR (500 MHz, CDCl_3) δ 7.33 (s, 1H), 7.24–7.14 (m, 3H), 4.24–4.13 (m, 7H), 4.13–4.11 (m, 1H), 4.10 (m, 1H), 4.03 (m, 1H), 1.63 (d, J = 6.9 Hz, 3H). ^{13}C NMR

(126 MHz, CDCl_3) δ 137.4, 134.3, 132.2, 130.7, 129.7, 127.2, 90.3, 68.7, 67.9, 67.8, 67.7, 66.1, 43.6, 21.3. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{18}\text{H}_{17}\text{ClFeS}$: 356.0089; Found: 356.0087.

(2-chlorophenyl)(1-ferrocenylethyl)sulfane (**3e**).

Yellow solid, 73.1 mg (82% yield); mp 77–79 °C; Rf (petroleum ether/ethyl acetate 100:1) = 0.42. ^1H NMR (500 MHz, CDCl_3) δ 7.38 (m, 2H), 7.19–7.11 (m, 2H), 4.26 (q, J = 6.9 Hz, 1H), 4.24–4.21 (m, 1H), 4.17 (s, 5H), 4.14–4.10 (m, 1H), 4.08 (m, 1H), 4.04–3.99 (m, 1H), 1.64 (d, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 136.8, 134.7, 134.0, 129.8, 128.2, 126.9, 90.3, 68.7, 67.9, 67.8, 67.7, 66.2, 42.4, 21.2. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{18}\text{H}_{17}\text{ClFeS}$: 356.0089; Found: 356.0083.

(1-ferrocenylethyl)(4-methylphenyl)sulfane (**3f**).

Yellow oil, 70.6 mg (84% yield); Rf (petroleum ether/ethyl acetate 100:1) = 0.41. ^1H NMR (500 MHz, CDCl_3) δ 7.24 (d, J = 8.1 Hz, 2H), 7.06 (d, J = 8.1 Hz, 2H), 4.13 (m, 6H), 4.10 (m, 1H), 4.08–4.02 (m, 2H), 4.02–3.99 (m, 1H), 2.31 (s, 3H), 1.59 (d, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 137.4, 133.8, 131.4, 129.5, 91.0, 68.7, 68.0, 67.6, 67.5, 66.0, 44.0, 21.2, 21.2. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{19}\text{H}_{20}\text{FeS}$: 336.0635; Found: 336.0629.

(1-ferrocenylethyl)(4-nitrophenyl)sulfane (**3g**).

Orange solid, 32.1 mg (35% yield); mp 79–81 °C; Rf (petroleum ether/ethyl acetate 100:1) = 0.14. ^1H NMR (500 MHz, CDCl_3) δ 8.12 (d, J = 8.9 Hz, 2H), 7.39 (d, J = 8.9 Hz, 2H), 4.39 (q, J = 6.8 Hz, 1H), 4.27–4.19 (m, 6H), 4.18 (m, 1H), 4.16 (m, 1H), 4.13 (m, 1H), 1.74 (d, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 146.7, 145.6, 129.2, 123.9, 89.6, 68.9, 68.2, 68.1, 67.8, 66.5, 42.3, 21.3. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{18}\text{H}_{17}\text{FeN}_2\text{OS}$: 367.0329; Found: 367.0325.

(1-ferrocenylethyl)(4-methoxyphenyl)sulfane (**3h**).

Yellow oil, 64.3 mg (73% yield); Rf (petroleum ether/ethyl acetate 100:1) = 0.16. ^1H NMR (500 MHz, CDCl_3) δ 7.26 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 4.12 (s, 5H), 4.09 (m, 2H), 4.07 (m, 1H), 3.96 (m, 2H), 3.77 (s, 3H), 1.57 (d, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.6, 136.5, 125.2, 114.1, 91.0, 68.6, 68.1, 67.6, 67.5, 65.9, 55.3, 44.6, 20.9. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{19}\text{H}_{20}\text{FeOS}$: 352.0584; Found: 352.0579.

(1-ferrocenylethyl)(3-methoxyphenyl)sulfane (**3i**).

Yellow oil, 65.2 mg (74% yield); Rf (petroleum ether/ethyl acetate 100:1) = 0.15. ^1H NMR (500 MHz, CDCl_3) δ 7.18 (m, 1H), 6.95 (d, J = 7.7 Hz, 1H), 6.86 (s, 1H), 6.77 (m, 1H), 4.15 (m, 7H), 4.11 (m, 1H), 4.09 (m, 1H), 4.06 (m, 1H), 3.75 (s, 3H), 1.63 (d, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.5, 136.5, 129.5, 125.1, 117.9, 113.2, 90.8, 68.7, 68.0, 67.8, 67.6, 66.2, 55.3, 43.5, 21.3. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{19}\text{H}_{20}\text{FeOS}$: 352.0584; Found: 352.0579.

(1-ferrocenylethyl)(2-methoxyphenyl)sulfane (**3j**).

Yellow oil, 58.1 mg (66% yield); Rf (petroleum ether/ethyl acetate 100:1) = 0.15. ^1H NMR (500 MHz, CDCl_3) δ 7.31 (m, 1H), 7.23 (m, 1H), 6.88–6.82 (m, 2H), 4.28–4.17 (m, 2H), 4.14 (s, 5H), 4.09 (m, 1H), 4.05 (m, 1H), 4.01–3.95 (m, 1H), 3.84 (s, 3H), 1.60 (d, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 158.9, 134.4, 128.8, 123.4, 120.7, 110.7, 91.0, 68.6, 67.9, 67.5, 67.5, 66.0, 55.9, 55.8, 41.4, 21.2. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{19}\text{H}_{20}\text{FeOS}$: 352.0584; Found: 352.0579.

Benzimidazolyl(1-ferrocenylethyl)sulfane (**3k**).

Light red solid, 40.7 mg (45% yield); mp 192–193 °C; Rf (petroleum ether/ethyl acetate 10:1) = 0.33. ^1H NMR (500 MHz, CDCl_3) δ 11.23 (s, 1H), 7.28 (d, J = 6.2 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 7.00 (t, J = 7.7 Hz, 1H), 6.63 (q, J = 7.1 Hz, 1H), 4.55 (s, 1H), 4.29 (s, 6H), 4.24 (s, 1H), 4.16

(s, 1H), 1.87 (d, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.3, 130.9, 130.7, 122.9, 122.4, 111.4, 110.1, 86.5, 77.4, 76.9, 69.4, 69.0, 67.5, 66.9, 51.9, 17.1. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{19}\text{H}_{18}\text{FeN}_2\text{S}$: 362.0540; Found: 362.0574

Benzyl(1-ferrocenylethyl)sulfane (3l).

Yellow oil, 21.9 mg (26% yield); Rf (petroleum ether/ethyl acetate 100:1) = 0.26. ^1H NMR (500 MHz, CDCl_3) δ 7.37 – 7.26 (m, 4H), 7.23 (m, 1H), 4.18 (m, 2H), 4.13 (m, 7H), 3.76 – 3.56 (m, 3H), 1.64 (d, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 138.6, 128.9, 128.5, 126.9, 91.6, 68.7, 67.9, 67.7, 67.5, 66.0, 38.7, 35.6, 21.4. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{19}\text{H}_{20}\text{FeS}$: 336.0635; Found: 336.0630.

(4-chlorophenyl)(1-ferrocenylpropyl)sulfane (3m).

Yellow oil, 64.9 mg (70% yield); Rf (petroleum ether/ethyl acetate 100:1) = 0.46. ^1H NMR (500 MHz, CDCl_3) δ 7.26 – 7.14 (m, 4H), 4.12 (s, 5H), 4.09 – 4.04 (m, 2H), 4.04 – 3.92 (m, 2H), 3.80 (m, 1H), 2.06 (m, 1H), 1.67 (m, 1H), 1.11 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 135.1, 133.5, 133.3, 128.7, 90.8, 68.8, 67.7, 67.6, 67.4, 67.0, 51.8, 27.8, 12.4. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{19}\text{H}_{19}\text{ClFeS}$: 370.0245; Found: 370.0240.

(4-chlorophenyl)(1-ferrocenylbutyl)sulfane (3n).

Yellow oil, 68.3 mg (71% yield); Rf (petroleum ether/ethyl acetate 100:1) = 0.47. ^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.04 (m, 4H), 4.11 (s, 5H), 4.07 (m, 2H), 3.97 (m, 2H), 3.88 (m, 1H), 2.08 – 1.91 (m, 1H), 1.73 – 1.59 (m, 2H), 1.54 (m, 1H), 0.96 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 135.2, 133.5, 133.2, 128.7, 91.1, 68.8, 67.7, 67.6, 67.4, 66.8, 49.6, 36.8, 20.6, 14.0. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{20}\text{H}_{21}\text{ClFeS}$: 384.0402; Found: 384.0397.

(4-chlorophenyl)(2-methyl-1-ferrocenylpropyl)sulfane (3o).

Yellow solid, 75.0 mg (78% yield); mp 72–74 °C; Rf (petroleum ether/ethyl acetate 100:1) = 0.47. ^1H NMR (500 MHz, CDCl_3) δ 7.39 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 4.24 – 4.11 (m, 8H), 4.09 (m, 1H), 4.06 (m, 1H), 2.05 – 1.89 (m, 1H), 0.84 (d, J = 8.0 Hz, 3H), 0.83 (d, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 135.5, 133.1, 132.6, 129.1, 87.2, 69.2, 69.0, 68.1, 67.5, 66.9, 56.3, 32.3, 20.3, 18.1. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{20}\text{H}_{21}\text{ClFeS}$: 384.0402; Found: 384.0398.

(4-chlorophenyl)(2,2-dimethyl-1-ferrocenylpropyl)sulfane (3p).

Yellow solid, 61.8 mg (62% yield); mp 90–92 °C; Rf (petroleum ether/ethyl acetate 100:1) = 0.48. ^1H NMR (500 MHz, CDCl_3) δ 7.41 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H), 4.25 – 4.17 (m, 1H), 4.17 – 4.10 (m, 2H), 4.10 – 3.90 (m, 6H), 3.83 (s, 1H), 0.88 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 138.7, 130.9, 129.3, 129.1, 90.7, 70.5, 69.0, 68.4, 67.8, 65.8, 61.1, 37.9, 28.2. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{21}\text{H}_{23}\text{ClFeS}$: 398.0558; Found: 398.0554.

(4-chlorophenyl)(1-ferrocenylbenzyl)sulfane (3q).

Yellow oil, 84.8 mg (81% yield); Rf (petroleum ether/ethyl acetate 100:1) = 0.30. ^1H NMR (500 MHz, CDCl_3) δ 7.35 (m, 2H), 7.26 (m, 2H), 7.20 (m, 1H), 7.16 – 7.04 (m, 4H), 5.08 (s, 1H), 4.19 – 4.09 (m, 3H), 4.07 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 141.6, 134.1, 134.0, 133.3, 128.7, 128.4, 128.2, 127.3, 89.1, 69.0, 68.5, 68.3, 67.8, 67.6, 54.7. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{23}\text{H}_{19}\text{ClFeS}$: 418.0245; Found: 418.0240.

1,1'-bis(1-(4-chlorophenylthio)ethyl)ferrocene (5a).

Yellow solid, 84.3 mg (64% yield); mp 46–48 °C; Rf (petroleum ether/ethyl acetate 30:1) = 0.52. ^1H NMR (500 MHz, CDCl_3) δ 7.61 – 6.85 (m, 8H), 4.08 (m, 8H), 3.99 (m, 2H), 1.58 (d, J = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 134.9, 134.8, 133.6, 133.3, 128.8, 91.0, 90.9, 68.9, 68.8, 68.7, 68.6, 66.8, 66.5, 43.9,

43.8, 21.3, 21.2. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{26}\text{H}_{24}\text{Cl}_2\text{FeS}_2$: 526.0046; Found: 526.0042.

1,1'-bis(1-(4-fluorophenylthio)ethyl)ferrocene (5b).

Yellow oil, 64.3 mg (52% yield); Rf (petroleum ether/ethyl acetate 30:1) = 0.53. ^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.26 (m, 4H), 7.01 – 6.88 (m, 4H), 4.08 (m, 5H), 4.06 – 4.03 (m, 1H), 4.01 (m, 2H), 3.98 – 3.90 (m, 2H), 1.56 (d, J = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 163.7, 161.7, 136.6, 136.5, 136.4, 129.6, 115.9, 115.7, 91.1, 68.9, 68.8, 68.7, 68.6, 68.5, 66.6, 66.4, 44.4, 21.1. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{26}\text{H}_{24}\text{F}_2\text{FeS}_2$: 494.0637; Found: 494.0632.

1,1'-bis(1-(4-bromophenylthio)ethyl)ferrocene (5c).

Yellow oil, 83.2 mg (54% yield); Rf (petroleum ether/ethyl acetate 30:1) = 0.51. ^1H NMR (500 MHz, CDCl_3) δ 7.37 (m, 4H), 7.17 (m, 4H), 4.21 – 4.04 (m, 8H), 4.02 (m, 1H), 3.98 (m, 1H), 1.59 (d, J = 6.8 Hz, 3H), 1.58 (d, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 135.0, 134.9, 134.1, 134.0, 131.8, 121.7, 121.7, 91.0, 90.9, 68.9, 68.8, 68.8, 68.7, 68.6, 68.6, 66.8, 66.6, 43.8, 43.7, 21.3, 21.2. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{26}\text{H}_{24}\text{Br}_2\text{FeS}_2$: 615.9015; Found: 615.9011.

1,1'-bis(1-(3-chlorophenylthio)ethyl)ferrocene (5d).

Yellow oil, 89.6 mg (68% yield); Rf (petroleum ether/ethyl acetate 30:1) = 0.51. ^1H NMR (500 MHz, CDCl_3) δ 7.36 – 7.30 (m, 2H), 7.22 – 7.15 (m, 6H), 4.19 – 4.10 (m, 8H), 4.06 (m, 1H), 4.02 (m, 1H), 1.61 (d, J = 6.8 Hz, 3H), 1.60 (d, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 137.3, 137.2, 134.3, 134.3, 132.3, 132.3, 130.8, 130.7, 129.7, 129.7, 127.3, 127.3, 90.8, 90.7, 69.0, 68.8, 68.7, 68.7, 68.6, 66.9, 66.7, 43.5, 43.4, 21.4, 21.4. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{26}\text{H}_{24}\text{Cl}_2\text{FeS}_2$: 526.0046; Found: 526.0041.

1,1'-bis(1-(2-chlorophenylthio)ethyl)ferrocene (5e).

Yellow solid, 79.1 mg (60% yield); mp 79–81 °C; Rf (petroleum ether/ethyl acetate 30:1) = 0.49. ^1H NMR (500 MHz, CDCl_3) δ 7.44 – 7.34 (m, 4H), 7.16 (m, 4H), 4.33 – 4.26 (m, 2H), 4.26 – 4.20 (m, 2H), 4.20 – 4.14 (m, 2H), 4.12 (m, 2H), 4.05 (m, 2H), 1.63 (d, J = 6.9 Hz, 3H), 1.61 (d, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 136.9, 136.8, 134.6, 134.5, 134.1, 133.9, 129.9, 128.3, 128.3, 127.0, 90.8, 90.7, 68.9, 68.8, 68.7, 68.7, 68.7, 68.6, 67.0, 66.8, 42.2, 42.1, 21.3. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{26}\text{H}_{24}\text{Cl}_2\text{FeS}_2$: 526.0046; Found: 526.0043.

1,1'-bis(1-(4-methylphenylthio)ethyl)ferrocene (5f).

Yellow oil, 70.5 mg (58% yield); Rf (petroleum ether/ethyl acetate 30:1) = 0.50. ^1H NMR (500 MHz, CDCl_3) δ 7.23 (d, J = 8.1 Hz, 4H), 7.07 (d, J = 8.1 Hz, 4H), 4.14 – 4.11 (m, 1H), 4.11 – 4.04 (m, 7H), 4.02 (m, 1H), 4.01 – 3.98 (m, 1H), 2.32 (s, 6H), 1.58 (d, J = 6.8 Hz, 3H), 1.56 (d, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 137.5, 137.5, 133.9, 133.8, 131.3, 131.3, 129.5, 91.3, 91.3, 68.9, 68.8, 68.7, 68.6, 68.5, 68.4, 66.7, 66.5, 43.9, 43.9, 21.3, 21.2. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{28}\text{H}_{30}\text{FeS}_2$: 486.1138; Found: 486.1133.

1,1'-bis(1-(4-methoxyphenylthio)ethyl)ferrocene (5g).

Yellow oil, 51.8 mg (40% yield); Rf (petroleum ether/ethyl acetate 30:1) = 0.20. ^1H NMR (500 MHz, CDCl_3) δ 7.25 (d, J = 7.8 Hz, 4H), 6.79 (d, J = 7.8 Hz, 4H), 4.06 (m, 6H), 4.00 – 3.91 (m, 4H), 3.79 (s, 6H), 1.55 (d, J = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.7, 136.6, 136.6, 125.1, 114.2, 91.3, 91.3, 69.0, 68.7, 68.7, 68.5, 68.4, 68.3, 66.5, 66.3, 55.3, 44.5, 44.5, 21.1, 21.0. HRMS (ESI-TOF) m/z : $[\text{M}]^+\text{calcd}$ for $\text{C}_{28}\text{H}_{30}\text{FeO}_2\text{S}_2$: 518.1037; Found: 518.1037.

1,1'-bis(1-(3-methoxyphenylthio)ethyl)ferrocene (5h).

Yellow oil, 55.7 mg (43% yield); Rf (petroleum ether/ethyl acetate 30:1) = 0.18. ^1H NMR (500 MHz, CDCl_3) δ 7.18 (m, 2H),

6.95 (d, $J = 7.9$ Hz, 2H), 6.86 (s, 2H), 6.83 – 6.72 (m, 2H), 4.20 – 4.09 (m, 8H), 4.09 – 4.06 (m, 1H), 4.04 (m, 1H), 3.75 (s, 6H), 1.62 (d, $J = 6.9$ Hz, 3H), 1.60 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.6, 136.4, 136.3, 129.5, 125.2, 125.1, 118.0, 117.9, 113.3, 113.3, 91.2, 91.1, 68.9, 68.9, 68.7, 68.7, 68.6, 68.5, 66.9, 66.7, 55.3, 43.4, 43.3, 21.4. HRMS (ESI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{28}\text{H}_{30}\text{FeO}_2\text{S}_2$: 518.1037; Found: 518.1033.

1,1'-bis(1-(2-methoxyphenylthio)ethyl)ferrocene (5i).

Yellow oil, 44.1 mg (34% yield); R_f (petroleum ether/ethyl acetate 30:1) = 0.19. ^1H NMR (500 MHz, CDCl_3) δ 7.31 (m, 2H), 7.27 – 7.23 (m, 2H), 6.86 (m, 4H), 4.33 – 4.22 (m, 3H), 4.18 (m, 2H), 4.13 – 4.07 (m, 3H), 3.99 (m, 2H), 3.85 (s, 6H), 1.58 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.1, 134.6, 134.6, 128.9, 123.4, 120.8, 110.8, 91.4, 91.3, 68.8, 68.6, 68.5, 68.4, 66.7, 66.5, 65.6, 55.8, 41.3, 41.2, 21.3. HRMS (ESI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{28}\text{H}_{30}\text{FeO}_2\text{S}_2$: 518.1037; Found: 518.1034.

1,1'-bis(1-(3-chlorophenylthio)propyl)ferrocene (5j).

Yellow oil, 80.6 mg (58% yield); R_f (petroleum ether/ethyl acetate 30:1) = 0.53. ^1H NMR (500 MHz, CDCl_3) δ 7.29 (m, 2H), 7.19 – 7.13 (m, 6H), 4.13 – 4.07 (m, 4H), 4.04 – 3.99 (m, 4H), 3.95 – 3.89 (m, 2H), 2.05 – 1.93 (m, 2H), 1.73 – 1.67 (m, 2H), 1.07 (t, $J = 7.3$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 137.3, 137.2, 134.2, 134.2, 132.5, 132.5, 131.0, 130.9, 129.7, 129.6, 127.2, 90.9, 90.9, 69.0, 68.8, 68.8, 68.5, 68.5, 68.4, 68.3, 68.0, 67.9, 51.1, 28.3, 12.2. HRMS (ESI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{28}\text{H}_{28}\text{Cl}_2\text{FeS}_2$: 554.0359; Found: 554.0354.

1,1'-bis(1-(3-chlorophenylthio)butyl)ferrocene (5k).

Yellow oil, 90.5 mg (62% yield); R_f (petroleum ether/ethyl acetate 30:1) = 0.54. ^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.25 (m, 2H), 7.21 – 7.13 (m, 6H), 4.13 – 4.04 (m, 4H), 4.03 – 3.94 (m, 6H), 1.99 – 1.87 (m, 2H), 1.74 – 1.65 (m, 2H), 1.60 (m, 2H), 1.51 (m, 2H), 0.93 (t, $J = 7.3$, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 137.2, 137.2, 134.2, 132.6, 132.6, 131.0, 131.0, 129.6, 127.2, 91.3, 68.7, 68.7, 68.5, 68.5, 68.4, 68.3, 67.8, 67.7, 49.0, 37.3, 37.3, 20.5, 20.5, 13.4. HRMS (ESI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{30}\text{H}_{32}\text{Cl}_2\text{FeS}_2$: 582.0672; Found: 582.0667.

1,1'-bis(1-(3-chlorophenylthio)-2-methylpropyl)ferrocene (5l).

Yellow oil, 93.4 mg (64% yield); R_f (petroleum ether/ethyl acetate 30:1) = 0.55. ^1H NMR (500 MHz, CDCl_3) δ 7.51 (m, 1H), 7.43 (m, 1H), 7.40 – 7.34 (m, 1H), 7.31 (m, 1H), 7.27 – 7.17 (m, 4H), 4.24 (m, 1H), 4.18 (m, 1H), 4.17 – 4.10 (m, 8H), 2.03 – 1.91 (m, 2H), 0.85 – 0.77 (m, 12H). ^{13}C NMR (126 MHz, CDCl_3) δ 139.2, 134.7, 134.6, 130.7, 130.6, 130.0, 129.1, 129.0, 126.5, 126.5, 87.5, 87.4, 70.5, 70.5, 69.3, 69.1, 68.9, 68.7, 68.5, 68.0, 55.4, 55.3, 32.6, 32.3, 20.3, 18.0, 17.8. HRMS (ESI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{30}\text{H}_{32}\text{Cl}_2\text{FeS}_2$: 582.0672; Found: 582.0673.

1,1'-bis(1-(3-chlorophenylthio)benzyl)ferrocene (5m).

Yellow oil, 83.1 mg (51% yield); R_f (petroleum ether/ethyl acetate 30:1) = 0.45. ^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.20 (m, 11H), 7.19 – 7.16 (m, 2H), 7.09 (m, 2H), 7.06 – 7.00 (m, 3H), 4.98 (s, 1H), 4.97 (s, 1H), 4.14 – 4.09 (m, 1H), 4.06 (m, 4H), 4.02 – 3.99 (m, 2H), 3.97 (d, $J = 1.3$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 141.5, 141.2, 137.6, 137.4, 134.1, 132.0, 131.8, 130.3, 130.2, 129.6, 128.5, 128.3, 127.5, 127.4, 127.2, 127.2, 89.5, 89.4, 69.6, 69.3, 69.2, 69.2, 69.1, 68.9, 68.9, 68.7, 54.0, 53.9. HRMS (ESI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{36}\text{H}_{28}\text{Cl}_2\text{FeS}_2$: 650.0359; Found: 650.0355.

Absorption Studies

The solutions were prepared with 1 mM concentration of various metal ions (salts of perchlorate) in double-distilled water. The solutions of **3k** (1 mM) were prepared in CH_3CN . In selectivity experiments, the solution of **3k** was diluted to 10 μM CH_3CN .

Each time $3 \times 10 \mu\text{M}$ solution of **3k** were taken into a quartz cuvette, and the ion solutions 30 μL were added into using a micropipette. In selectivity experiments, the concentration of the ion solutions was kept at 1 mM.

Electrochemical Studies

CV and DPV techniques were carried out using a three-electrode configuration consisting of glassy carbon electrode as working electrode, platinum as the supporting electrode and an Ag/AgCl electrode as a reference electrode. The concentration of the sample solutions was 100 μM in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (7:3, v/v) containing 0.1 M $[(\text{n-C}_4\text{H}_9)_4\text{NPF}_6]$ as supporting electrolyte and the scan rate was 0.1 V s^{-1} .

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