

Articles

Synthesis and Electrochemical Studies of a Ferrocene Derivative for the Application to Metal Ion Sensor

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The combination of electrochemically active ferrocene and thioether-amine as a metal ion recognition site has formed an electrochemical sensor for metal ions. With an aim to apply the ferrocene derivative toward electrochemical sensing devices for heavy metal ions, electrochemical properties of 2-((bis(2-(ethylthio)ethyl)-amino)methyl)-*N*-ferrocenylmethyl aniline **A** were examined in the presence of Hg²⁺, Cd²⁺, Zn²⁺, and Mg²⁺. The cathodic oxidation potential shift of compound **A** was observed as $\Delta E_{pa} = 276$ mV in CH₃CN (0.1 M LiClO₄) with an equimolar Hg²⁺. The binding constant of compound **A** with Hg²⁺ was measured as $K_a = 8100$ M⁻¹ in CH₃CN *via* UV-vis absorbance spectroscopy. With the electrochemical and spectroscopic data, the binding event is speculated to occur at the tertiary amine proximal to the sulfide functional groups in compound **A** with the modest affinity.

Key Words : Ferrocene, Electrochemical sensor, Mercuric ion, Electrochemistry

Introduction

Despite the toxicity of heavy metal ions (*e.g.* mercury, cadmium etc) to human health and the environment, these metal salts are widely used in industrial processes.¹ Considerable efforts have been directed to control the heavy metal pollution by reducing the use of heavy metal species and developing selective recognition and sensing of heavy metal species. In supramolecular chemistry, many groups have developed efficient heavy metal ion receptors to remove them selectively using the concept of the host-guest complex formation.² In this sense, a variety of heavy metal ion sensors with the strong and selective recognition sites have been synthesized and their metal ion binding behaviors have been studied *via* spectroscopic methods.^{2b,3} Generally, sensors have two important parts which are a recognition site and a probe. As a recognition site for metal ions, heteroatoms (*e.g.* amine, thioether, and ether, etc) have been employed due to the substantial affinity toward cationic metal species. In

proximity to the recognition site, the probe is located, exhibiting physical property changes in color, fluorescence, or the redox potential shift upon the formation of complex between sensors and metal ions.⁴ Among various probes, to design the electrochemical heavy metal ion-sensor, redox active units have been incorporated. As the representative example of electrochemical sensors, shown in Figure 1, a range of ferrocene derivatives have been emerged as good metal ion sensors displaying remarkable potential shifts. Redox potential changes of ferrocene derivatives upon the addition of metal ions have been observed *via* cyclic voltammetry (CV), and the complexation mechanisms have been speculated based on the electrochemical studies.⁵

Recently, we have been interested in development of new ferrocene derivatives for the application to electrochemical metal ion sensor. As part of the program to investigate ferrocene based redox sensors, we reported the synthesis and electrochemical analysis of 2-(ethylthiomethyl)-*N*-ferrocenylmethyl aniline in the presence of metal ions.⁶ In this

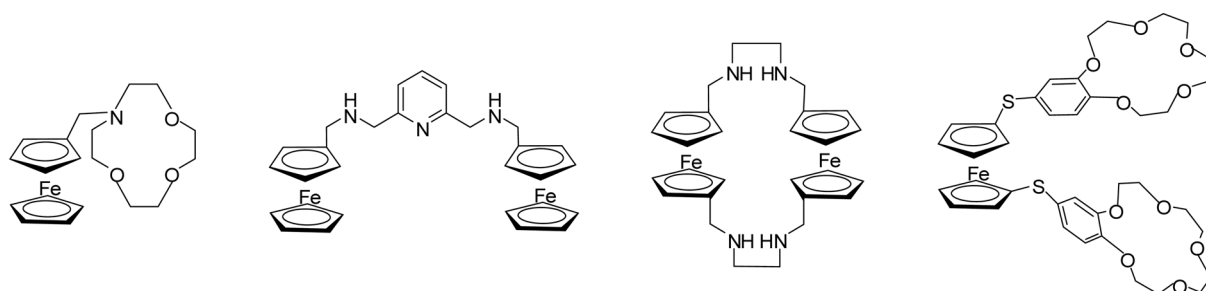


Figure 1. Ferrocene based electrochemical sensors.

account, we present the synthesis and electrochemical studies of a functionalized ferrocene derivative, 2-((bis(2-(ethylthio)ethyl)amino)methyl)-*N*-ferrocenylmethyl aniline **A**, which is presumed to display remarkable redox potential changes upon metal ion binding. Since 2-((bis(2-(ethylthio)ethyl)amino)methyl)aniline **2**, part of compound **A** has been employed as a Hg^{2+} recognition site with high selectivity and strong binding ability, incorporation of compound **2** into the ferrocene derivative is expected to induce the unique electrochemical change in cyclic voltammograms (CV) upon the formation of Hg^{2+} complex. In addition, compound **A** possesses more binding units than previously synthesized 2-(ethylthiomethyl)-*N*-ferrocenylmethyl aniline. The electrochemical behaviors of 2-((bis(2-(ethylthio)ethyl)amino)methyl)-*N*-ferrocenylmethyl aniline **A** in the presence of a range of metal ions (Hg^{2+} , Cd^{2+} , Zn^{2+} , and Mg^{2+}) were observed, thus the selectivity of the ferrocene derivative toward Hg^{2+} was evaluated. The careful analysis of electrochemical results provides the reasonable conclusion regarding the actual binding site and the conformation of compound **A** upon the formation of the complex with metal ions. The quantitative binding constant of this ferrocene derivative with Hg^{2+} was calculated from the absorbance measurement by UV-Vis spectroscopy in CH_3CN at room temperature.

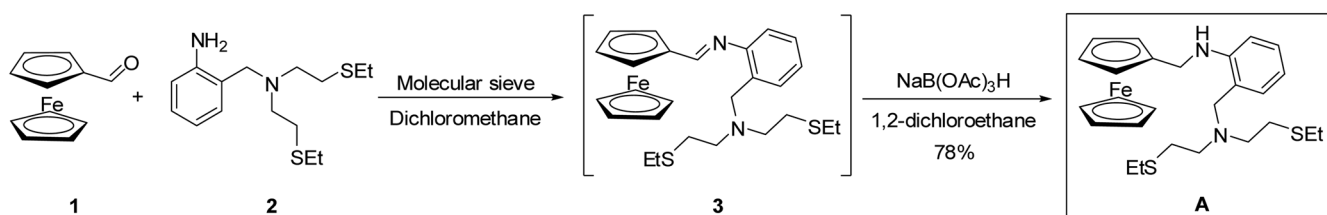
Results and Discussion

The synthesis of ferrocene derivative **A** began with the imine formation using ferrocene carboxaldehyde **1** and 2-((bis(2-(ethylthio)ethyl)amino)methyl)aniline **2**. The condensation was considered as a quantitative reaction. In the case of compound **3**, the decomposition of imine compounds was found during the column chromatography, thus the verification of imine formation was not performed. The collected compound from the imine formation reaction was filtered and used for the next reduction reaction without further purification. Therefore, subsequent reduction without isolation of imine compound **3** with $\text{NaB}(\text{OAc})_3\text{H}$ provided the desired product **A** in 78% yield.

Prior to the electrochemical studies of compound **A** with various metal ions, cyclic voltammograms of compound **A** were obtained using LiClO_4 as a supporting electrolyte in CH_3CN . In a range of 0.0 to 2.0 V, three oxidation peaks appear in the anodic scan to 2.0 V, and no reduction peaks appear in the reversed cathodic scan, which is shown in Figure 2a. At lower scan rates (20 mV/s and 50 mV/s), no reversible redox potential wave was observed. To assign the first oxidation peak at 0.55 V, the potential scan was

performed in a range of 0.0 to 0.8 V, showing that the quasi-reversible oxidation/reduction couple with a separation peak of cat. 120 mV. Based on these results, the first oxidation peak observed at 0.55 V corresponds to the oxidation of the ferrocene entity of compound **A**. When the potential scan was extended to 1.4 V to cover the second oxidation wave, only a reversible reduction potential wave corresponding to the ferrocene entity of compound **A** was observed. With the expanded redox potential range up to 2.0 V, no reversible cathodic wave was detected even at lower scan rates (20 mV/s and 50 mV/s). Interestingly, the anodic potential waves of the second oxidation at 1.19 V and third oxidation at 1.64 V do not couple with the reversible reduction.

To complete the assignment of the anodic waves in the oxidation of compound **A**, organic compound **2** which has similar structure with compound **A** other than the absence of ferrocene was subject to electrochemical studies in CH_3CN containing LiClO_4 as a supporting electrolyte (Figure 2b). At 1.08 V and 1.51 V, two oxidation peaks which are speculated as the successive formation of monocationic and dicationic radicals from compound **2** are detected with the irreversible redox feature. When the CV scan was reversed at 1.4 V after forming monocationic species, the reversible cathodic wave was not observed. Based on this result, monocationic and dicationic radicals formed from compound **2** have very short lifetime or undergo a following chemical reaction (EC) such as oxidation followed by hydrolysis to form aldehydes from the amine group. The electrochemical oxidation of amine-containing compounds to afford multispecies such as aldehydes or nitriles was reported in several articles.⁷ According to the Porter's electrochemical studies regarding the susceptibility of amines to the oxidation, tertiary amines tend to be oxidized easier than the primary amines due to the electronic effect of alkyl groups.^{7b} Therefore, the first oxidation at 1.08 V of compound **2** is considered as the oxidation of tertiary amine and the second oxidation at 1.51 V is assumed as the oxidation of primary amine. The possibility of sulfur oxidation can be ruled out based on the data regarding the oxidation potential of organic molecules reported by Miller, where the oxidation potential of sulfur in the sulfide compound is usually higher than that of nitrogen in the amine compounds.⁸ According to the electrochemical study of compound **2**, it could be concluded that the second (1.19 V) and third oxidation (1.64 V) of compound **A** in Figure 2a stem from the oxidation of nitrogens of compound **A**. As it was initially assigned, the first oxidation at 0.55 V is attributed to the redox couple of the ferrocene unit from compound **A**.



Scheme 1. Synthesis of compound **A**.

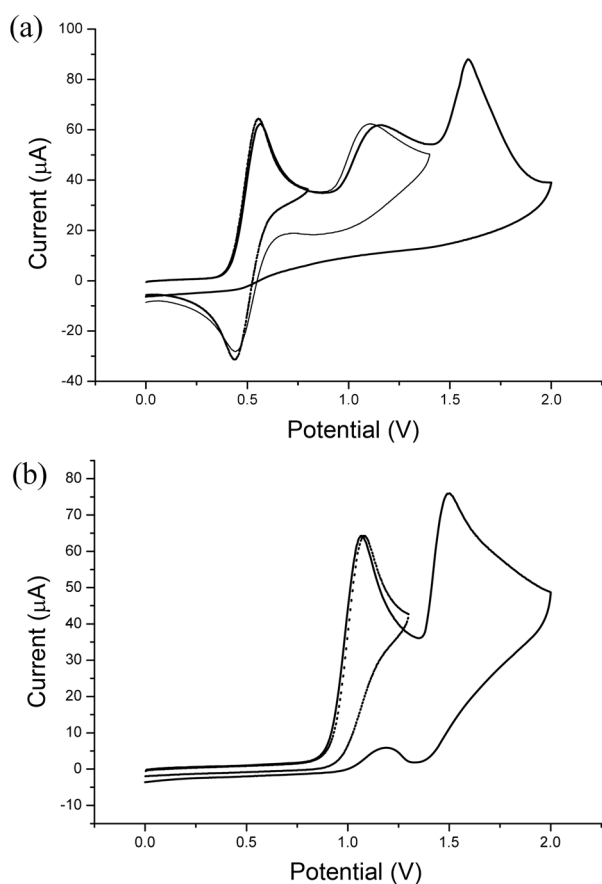


Figure 2. (a) Cyclic voltammograms of compound **A** obtained in 0.1 M LiClO₄ acetonitrile solution at a scan rate of 100 mV/s, (b) Cyclic voltammograms of compound **2** obtained in 0.1 M LiClO₄ solution at a scan rate of 100 mV/s.

Subsequent to the electrochemical studies of metal free compound **A**, the binding of compound **A** to Hg²⁺ was investigated *via* CV in CH₃CN, assuming that the binding of compound **A** to Hg²⁺ ions may lead to a potential shift through the electrostatic interaction between the redox center and the metal ion. As the amounts of Hg²⁺ were increased from 0.1 eq to 1.0 eq with respect to the compound **A**, the shape of the potential wave was changed with the concomitant negative shift of the potential wave in a range of 0.0 to 2.0 V (Figure 3). As the amount of added Hg²⁺ ions increased up to an equimolar to compound **A**, the first and third anodic waves progressively underwent the cathodic shift with no visible decrease in the current density. However, a progressive decrease in the current density of second oxidation peak was observed, together with the cathodic peak shift, which resulted in the clear disappearance of second oxidation peak upon the addition of an equimolar amount of mercuric ions.

Assuming that the oxidation of tertiary amine of compound **A** corresponds to the second anodic wave in Figure 2a, the diminished current density of the second anodic wave in the presence of an equimolar Hg²⁺ ion clearly indicates the significant interaction of Hg²⁺ ion and the tertiary amine in compound **A**. Presumably, tertiary amine close to thio-

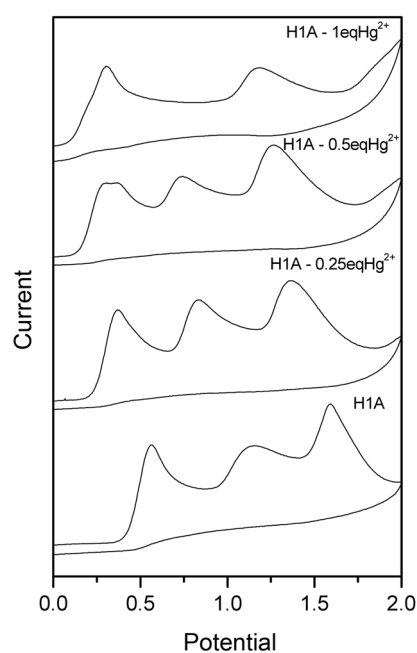


Figure 3. Cyclic voltammograms obtained from compound **A** with 0, 0.25, 0.5, 1.0 eq of Hg²⁺ added in 0.1 M LiClO₄ acetonitrile solution at a scan rate of 100 mV/s.

ethers, expected to be a strong Hg²⁺ binding unit due to the affinity of sulfur to Hg²⁺, might be better able to bind Hg²⁺ ion compared to secondary amine in compound **A**. The ferrocene entity and the secondary amine of compound **A** are relatively remote from the Hg²⁺ binding site, rendering the weak interaction. Observed cathodic shift of the anodic waves of compound **A** in the presence of Hg²⁺ is attributed that the electron density proximal to the ferrocene group increases when the tertiary amine is coordinated to Hg²⁺. Similar cathodic shift was observed with ferrocene-based thiocalix[4]arene compound upon Eu³⁺ binding, which was reported by Guo and co-workers.⁹

The electrochemical responses of compound **A** toward Cd²⁺, Zn²⁺, and Mg²⁺ were also investigated in CH₃CN containing LiClO₄ electrolytes, showing negative shifts of anodic potential waves and the reduced current density of second oxidation peak upon complexation depending on metal ions (Figure 4). The interaction of compound **A** with Hg²⁺ and Zn²⁺ shows the most significant change in terms of the shape of potential waves and the degree of cathodic shifts. The binding of Hg²⁺ and Zn²⁺ to the tertiary amine of compound **A** strongly induces the tertiary amine, the metal ion binding unit, to be closer to the ferrocenyl group, which results in the most cathodic shift of the first anodic potential waves along with the third anodic wave. The potential waves of compound **A** in the presence of Cd²⁺, Mg²⁺ exhibit modest shifts and changes of potential waves, compared to Hg²⁺ and Zn²⁺.

Next, to measure the quantitative oxidation potential change of compound **A**, the first oxidation peak potential of compound **A** corresponding to the Fc/Fc⁺ redox couple in the presence of 1 eq of Hg²⁺, Cd²⁺, Zn²⁺, and Mg²⁺ were compared to those of the metal free compound **A** ($\Delta E_{pa} = E_{pa}(\text{Fc}/$

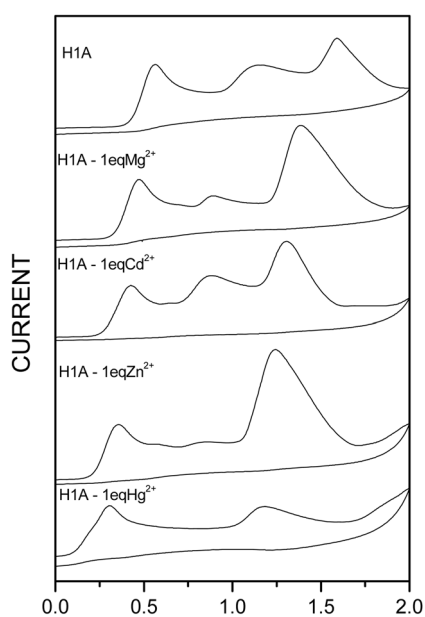


Figure 4. Cyclic voltammograms of compound **A** with 1 eq Hg^{2+} , Zn^{2+} , Cd^{2+} , and Mg^{2+} at 100 mV/s scan rate.

Fc^+ of the metal free compound **A**) – E_{pa} (Fc/Fc^+ of compound **A** with 1 eq of metal ions)). The maximum electrochemical shift of 276 mV (ΔE_{pa}) was observed when an equimolar amount of Hg^{2+} was added into the compound **A** in CH_3CN including LiClO_4 as a supporting electrolyte, followed by Zn^{2+} (202 mV), Cd^{2+} (135 mV), and Mg^{2+} (107 mV), shown in Table 1. To evaluate the effect of Li^+ ions from the electrolyte, cyclic voltammograms in the solution containing $n\text{Bu}_4\text{NClO}_4$ (TBAP), metal ion free electrolyte, as an electrolyte instead of LiClO_4 were obtained. As expected, upon the addition of 1 eq of Hg^{2+} into the compound **A** solution containing TBAP electrolyte, the potential wave of compound **A** was shifted remarkably ($\Delta E_{\text{pa}} = 397$ mV) far more than in the LiClO_4 electrolyte solution. However, the shape of cyclic voltammograms obtained from TBAP solution is similar to cyclic voltammograms obtained from LiClO_4 solution.

In an effort to obtain quantitative binding data of compound **A** toward metal ions, host-guest binding event was monitored and also evaluated by UV-Vis spectroscopic method in CH_3CN . It is frequent to apply the quantitative value of the redox potential shift between the two discrete potential waves of metal free and metal bound compounds to calculate the reaction coupling efficiency which indicates the electronic environment change of the receptor in the presence of metal ions.^{5b,10} With the previously reported 2-(ethylthiomethyl)-*N*-ferrocenylmethyl aniline in hand, anodically shifted redox potential wave corresponding to the metal bound ferrocene complex appeared. Accordingly, the reaction coupling efficiency was obtained using the oxidation potential difference between the metal free ferrocene derivative and the metal bound ferrocene derivative. However, with compound **A**, the redox potential waves of metal free compound **A** were gradually shifted cathodically with

Table 1. Cathodic potential shift (ΔE_{pa} , mV) of the first oxidation potential (Fc/Fc^+ redox couple) of compound **A**

Metal ion	Hg^{2+}	Hg^{2+}	Zn^{2+}	Cd^{2+}	Mg^{2+}
Electrolyte	LiClO_4	TBAP	LiClO_4	LiClO_4	LiClO_4
Potential shift ΔE_{pa} (mV) ^a	276	397	202	135	107

^aPotential shift values were observed upon the addition of 1.0 eq of metal ions to the solution of compound **A** in CH_3CN .

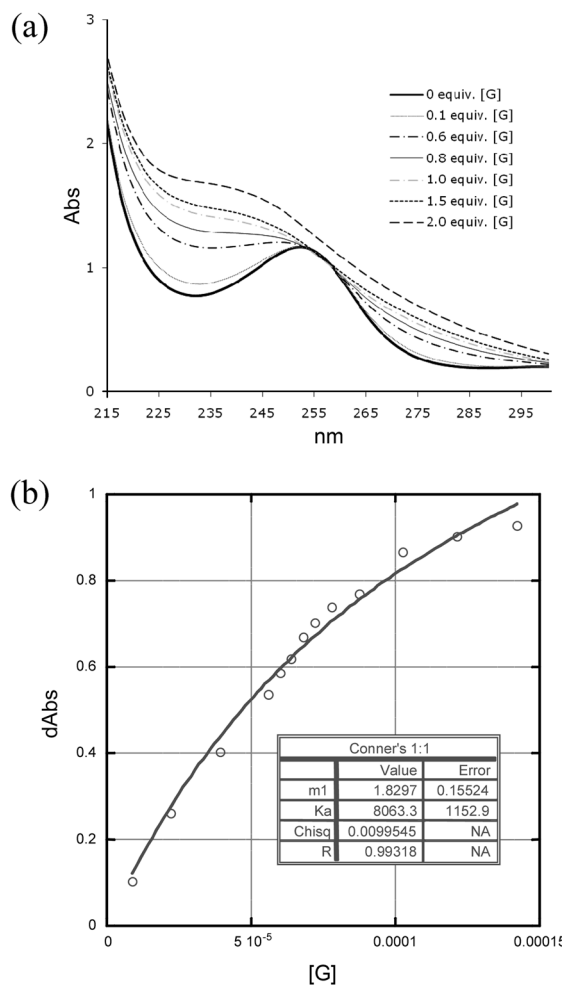


Figure 5. (a) UV-vis absorbance changes of compound **A** upon the addition of Hg^{2+} , (b) observed and calculated 1:1 binding profile associated with UV-vis absorbance changes.

no new potential wave stemming from the metal bound compound **A**. Therefore, UV-vis absorbance spectroscopy is employed for the determination of the binding constant of compound **A**. Reliable absorbance titration data were obtained only with Hg^{2+} . As shown in Figure 5, the absorbance band at 230 nm slowly increases upon the successive addition of Hg^{2+} ions. Using Connors's 1:1 equation,¹¹ the binding constant of compound **A** (6.64×10^{-5} M) with Hg^{2+} in CH_3CN was calculated as $K_a = 8100 \text{ M}^{-1}$. As expected from the electrochemical data of compound **A** with Hg^{2+} , the moderate binding affinity of compound **A** toward Hg^{2+} is confirmed by the relatively small binding constant from the

spectroscopic method.

$$\frac{\Delta A}{L} = \frac{[H]_t K_a \Delta \varepsilon [G]_t}{1 + K_a [G]_t} \quad (1)$$

L = cell length

$[H]_t$ = total concentration of the host

$[G]_t$ = total concentration of the guest

$\Delta \varepsilon = \varepsilon_H - \varepsilon_G$ (H: Host, G: Guest)

Conclusions

In summary, we have synthesized ferrocene derivative **A** which is subject to the electrochemical studies and UV-vis absorbance spectroscopy in the presence of various metal ions. Among the metal ions, the maximum electrochemical shift of compound **A** was shown in the presence of Hg^{2+} . Both electrochemical data and spectroscopic data verify the modest binding affinity of compound **A** with Hg^{2+} . Hence, the electrochemical data in the present account provide the valuable information to identify the binding mode, which will be used for the further synthetic modification of ferrocene derivatives to improve the sensing ability. In addition to the electrochemical study, by applying spectroscopic analysis, the binding constant of compound **A** with Hg^{2+} was obtained.

Experimental Section

Anhydrous solvents were transferred by an oven dried syringe. Flasks were flame-dried and cooled under a stream of nitrogen. Dichloromethane and 1,2-dichloroethane were distilled from calcium hydride. THF was distilled from benzophenone ketyl. Acetonitrile was purchased from Fluka and distilled from calcium hydride. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded with a Varian Mercury plus (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, part per million (ppm) downfield from trimethylsilane. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian Mercury plus (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, part per million (ppm) relative to the center of the triplet at 77.00 ppm for deuteriochloroform. Elemental analysis was carried out at the Inter-University Center Natural Science Facilities, Seoul National University. Electrochemical data were recorded on a potentiostat/galvanostat (PARC (Princeton Applied Research), model 263) with Electrochemistry Power Suite Module and Cyclic voltammetry software. The three-electrode cell consisting of Pt disc (the working electrode), Ag wire (the pseudo reference electrode), and Pt wire (the auxiliary electrode) was employed. Compound **A** (0.01 M) were dissolved in CH_3CN solution containing 0.1 M LiClO_4 or $n\text{Bu}_4\text{NClO}_4$ (TBAP). The resulting solutions were subject to cyclic voltammetry experiments at a scan rate of 100 mV/s. UV-vis spectra were conducted on Varian (model Carry 300). The host solution

containing compound **A** was titrated by adding known quantities of a concentrated solution of $\text{Hg}(\text{ClO}_4)_2$. The data was fit to a 1:1 binding profile according to the method of Connors using the change of absorbance at 230 nm in UV-vis spectra.

Synthesis of Compound A. 2-((bis(2-(ethylthio)ethyl)-amino)methyl)aniline **2** (608 mg, 2 mmol) was dissolved in the dichloromethane solution (5 mL) of ferrocene carboxaldehyde **1** (475 mg, 2.4 mmol) and molecular sieve. The mixture was refluxed for 18 hrs under the nitrogen atmosphere. After being cooled to room temperature, the solution was filtered through Celite and the filtered solution was evaporated. This mixture was dissolved in 1,2-dichloroethane (8 mL), and subsequently $\text{NaB}(\text{OAc})_3\text{H}$ (509 mg, 2.4 mmol) was added. The reaction mixture was allowed to stir overnight at room temperature. The solution was diluted with CH_2Cl_2 (2×10 mL), extracted with saturated NaHCO_3 (15 mL), and washed with water (2×10 mL). The organic layer dried over MgSO_4 and the solvent was evaporated. The purification was conducted *via* flash column chromatography (25:1, hexanes:ethyl acetate) to provide **A** (774 mg, 1.6 mmol) as a yellow oil in 78% yield. TLC $R_f = 0.68$ (3:1 hexanes:ethyl acetate). ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.16$ (t, $J = 8$ Hz, 1H), 6.95 (d, $J = 7.2$ Hz, 1H), 6.65 (d, $J = 8$ Hz, 1H), 6.59 (t, $J = 7.6$ Hz, 1H), 6.14 (br, 1H), 4.25 (s, 2H), 4.16 (s, 5H), 4.09 (s, 2H), 4.04 (s, 2H), 3.60 (s, 2H), 2.63 (dd, $J = 6.8, 5.6$ Hz, 4H), 2.50 (dd, $J = 7.2, 5.6$ Hz, 4H), 2.40 (q, $J = 7.4$ Hz, 4H), 1.17 (t, $J = 5.4$ Hz, 6H) ppm. ^{13}C NMR (CDCl_3 , 100Hz) $\delta = 15.18, 26.24, 29.31, 43.39, 53.70, 58.79, 67.97, 68.77, 68.80, 86.31, 110.18, 116.18, 121.90, 128.78, 130.32, 148.18$. FABMS Calcd for $\text{C}_{26}\text{H}_{36}\text{FeN}_2\text{S}_2$, 496.1669; Found, 496.1660.

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