Beryllium ion sensing through the ion pair formation between the electrochemically reduced ferrocenyl naphthoquinone radicals and Be^{2+} ions

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Abstract. We explored the mechanistic aspects of ion pair formation between electrochemically reduced radicals ($\text{Fc-cnq-1a}^{\bullet-}/\text{Fc-cnq-1b}^{\bullet-}$) and dianions ($\text{Fc-cnq-1a}^{2-}/\text{Fc-cnq-1b}^{2-}$) of ferrocenyl naphthoquinones (**Fc-cnq-1a** and **Fc-cnq-1b**) and several metal ions by cyclic voltammetry (CV), square wave voltammetry (SWV) and spectroelectrochemistry, for the first time. The experiments demonstrated that $\text{Fc-cnq-1a}^{2-}/\text{Fc-cnq-1b}^{2-}$ were moderately affected with Na^+ , K^+ and Cs^+ by slightly shifting to the anodic side, but were strongly influenced with Li^+ ion. $\text{Fc-cnq-1a}^{\bullet-}/\text{Fc-cnq-1b}^{\bullet-}$ were not affected by alkali metal ions, indicating no ion pair formation between the radicals and these ions. $\text{Fc-cnq-1a}^{2-}/\text{Fc-cnq-1b}^{2-}$ was not evolved in the presence of Be^{2+} , Mg^{2+} and Ca^{2+} , but $\text{Fc-cnq-1a}^{\bullet-}/\text{Fc-cnq-1b}^{\bullet-}$ appeared with their cathodic waves, and participated with intermediates, $[(\text{Fc-cnq-1b})_2^{\bullet-}-\text{Be}^{2+}]$ and $[(\text{Fc-cnq-1a})^{\bullet-}-\text{Cl}]$. The most pronounced effect on the ion-pair formation of the $\text{Fc-cnq-1a}^{\bullet-}/\text{Fc-cnq-1b}^{\bullet-}$ was observed in Be^{2+} , indicating that **Fc-cnq-1a** or **Fc-cnq-1b** can selectively sense ultra-trace amount of Be^{2+} (LOD=3.6 ppb) among the other metal ions with SWV titration, for the first time, based on the strong ion pair formation reaction between the radicals and Be^{2+} .

Keywords. Beryllium; ion pair formation; naphthoquinone; metal sensor; spectro-electrochemistry.

1. Introduction

It is well-known that many quinones exhibit two successive one-electron reduction processes in a dry organic aprotic solvent. The first chemically reversible process at E_1 yields a monoanion radical (semiquinone) product and the second generally at least quasi-reversible process at a more negative potential, E_2 , produces dianion species at customary scan speeds.¹⁻⁵ The potentials of these reductions depend on the polarity of solvents, the nature of the supporting electrolyte and the presence of acidic additives, reflecting respectively non-specific solvation energies, ion-pairing and protonation.¹⁻⁵ Few studies have been devoted to exploring the ion-pair formation processes between the electrochemically reduced quinones and the cationic species, including some alkali metals and alkaline earth metal

cations in aprotic solvents.⁶⁻⁹ For these studies, some well-known electrochemical methods such as cyclic voltammetry (CV) and pulse-electrolysis stopped-flow were used to explore the mechanistic aspects of the electrochemical reduction of quinones in the presence of metal ions such as Na^+ , Mg^{+2} and Ba^{+2} . However, there is no comprehensive study in the literature to investigate the mechanism of the ion pair formation between electrochemically reduced quinones and alkali, alkaline earth metal and transition metals in a combined form. Moreover, as far as we know, spectroelectrochemistry has not been implemented to explain this mechanism.

In this study, firstly, we investigated the ion pair formation between the electrochemically reduced monoanion radicals/dianion products ($\text{Fc-cnq-1a}^{\bullet-}/\text{Fc-cnq-1b}^{\bullet-}$ and $\text{Fc-cnq-1a}^{2-}/\text{Fc-cnq-1b}^{2-}$) of ferrocenyl naphthoquinones (**Fc-cnq-1a** and **Fc-cnq-1b**) and

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Figure 1. Structures of the molecules **Fc-cnq-1a** and **Fc-cnq-1b**.

several metal ions (Li^+ , Na^+ , K^+ , Cs^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Ba^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} and Co^{2+}) by cyclic voltammetry, square wave voltammetry (SWV) and *in situ* spectroelectrochemistry in a thin layer cell. The reasons behind choosing the ferrocenyl naphthoquinone fused crown ether **Fc-cnq-1a** and model compound **Fc-cnq-1b** without crown ether unit in the molecular structure (Figure 1) are as follows: (1) the naphthoquinone skeletal structure provides electron transfer processes with tunable redox potential in the presence of metal ions along with thermal and chemical stability;^{4,10–14} (2) ferrocene unit in the molecular structure of **Fc-cnq-1a** and **Fc-cnq-1b** displays well-known one-electron reversible oxidation process which can serve as an internal electrochemical standard to evaluate ion pair formation; (3) the crown ether unit not only makes the compound **Fc-cnq-1a** highly soluble but also provides information about the ion pair formation mechanism only taking place between the reduced naphthoquinone products and metal ions, although it is capable of complex formation with proper metal ions; (4) the naphthoquinone fused crown ether **Fc-cnq-1a** as a triad molecule shows intramolecular charge-transfer (ICT) transition between the ferrocenyl donor and the naphthoquinonyl acceptor center [e_π (HOMO-Fc) $\rightarrow$ e_{π^*} (LUMO-cnq)] at near IR region, which renders monitoring spectral changes of the molecules during the electrolysis in thin layer cell, thereby understanding the ion pair formation reaction.

In the second part of this study, based on the ion pair formation between the electrochemically reduced monoanion radical products (**Fc-cnq-1a** $^{\bullet-}$ /**Fc-cnq-1b** $^{\bullet-}$) and several metal ions, we demonstrate that the molecules **Fc-cnq-1a** and **Fc-cnq-1b** could serve as electrochemical Be^{2+} ion sensors among the studied metal ions. Beryllium (Be) is extremely harmful to health and is the most toxic element without radioactivity. However, it is widely used for defence materials, aerospace, nuclear energy and weapons, electronics and communications, and automobile manufacturing.¹⁵ Be

can lead to an immune system failure known as Be sensitization, and can cause documented illnesses of chronic Be disease (CBD) or berylliosis, an incurable and potentially fatal progressive lung ailment.^{16–20} International Agency for Research on Cancer (IARC)²¹ and the World Health Organization (WHO)²² have underlined the carcinogenic risks of Be and its compounds for humans. Despite the scarcity of Be in the earth's crust ($2.8\text{--}5.0\mu\text{g.g}^{-1}$), water supplies and atmosphere are contaminated by Be via discharges from anthropogenic sources.²² Hence, sensitively determination of Be is very important for environmental protection and human health. Be^{2+} ion in the different samples have been determined with varying analytical techniques, e.g., spectrophotometry,^{23–25} gravimetry,²⁶ chromatography,^{27–29} spectrofluorimetry,³⁰ gas chromatography,³¹ atomic absorption spectrometry (AAS),³² inductively coupled plasma mass spectrometry (ICP-MS),³³ and electrothermal atomic absorption spectrometry (ETAAS).³⁴ However, most of these methods are time-consuming, and relatively expensive. Therefore, electrochemical methods can be preferred because of cheap, sensitive and practical methods to determine ultra-trace amount of Be^{2+} .¹⁵

In the present work, a simple and sensitive electrochemical method was developed for the determination of Be^{2+} using SWV through the ion pair formation between the electrochemically reduced monoanion radical products (**Fc-cnq-1a** $^{\bullet-}$ /**Fc-cnq-1b** $^{\bullet-}$) and Be^{2+} . In the past studies, although trace amount of Be^{2+} was determined by using adsorptive stripping voltammetry and adsorption voltammetry based on the polymeric-electrosensor,^{15,35–37} the ion-pair formation process is facilitated for the first time to determine ultra-trace amount of Be^{2+} in our study.

2. Experimental

2.1 Chemicals

Fc-cnq-1a¹⁰ and **Fc-cnq-1b**⁵ studied herein were previously synthesized by our research group. All reagents were used as purchased from a commercial supplier (Sigma Aldrich) without further purification unless otherwise indicated. Tetra-*n*-butylammonium perchlorate used as supporting electrolyte (*n*- Bu_4NClO_4 , Fluka Chemical Co.) was recrystallized from ethyl alcohol and dried in a vacuum oven at 40°C for at least 1 week prior to use. Analytical grade Be^{2+} solution was prepared from its chloride salt and Li^+ , Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Ni^{2+} , Cu^{2+} , Co^{2+} and Zn^{2+} solutions were prepared from their perchlorate salts.

Figure 2. CVs of **Fc-cnq-1a** (A) and **Fc-cnq-1b** (B) in DMF solution containing 0.2 M *n*-Bu₄NClO₄ at different scan rates (0.025 V s⁻¹–0.500 V s⁻¹). Inset a: SWVs of **Fc-cnq-1a** and **Fc-cnq-1b**. For SWV Pulse PH/PW: 0.025 V for 0.01 s; Step Height: 2.00 mV; Scan rate: 0.100. Inset b: Plot of $v^{1/2}$ vs first reduction cathodic peak current. Working electrode: glassy carbon disk electrode (3.0 mm diameter). The concentrations of **Fc-cnq-1a** and **Fc-cnq-1b** = 5.0×10^{-3} M.

2.2 Measurements

Cyclic (CV) and Square Wave Voltammetry (SWV) were carried out by a Princeton Applied Research model 2263 potentiostat controlled by an external PC. A three-electrode system [BAS model (Bioanalytical System Inc.) solid cell stand] was used for CV and SWV measurements in DMF, and it consisted of glassy carbon (3.0 mm diameter) disc electrodes as the working electrode, a platinum wire counter electrode, and an Ag/AgNO₃ (non-aqueous) reference electrode. The reference electrode separated from the bulk solutions containing **Fc-cnq-1a** and **Fc-cnq-1b** were deoxygenated by a stream of high purity argon for 35 min before running the experiment, and the solution was protected from air by a blanket of argon during the experiment. The sample and solvent were placed into the electrolysis cell under argon. *In situ* UV–vis, spectroelectrochemical experiments were performed with a home-built thin-layer cell that utilized a light transparent platinum gauze working electrode.³⁸ Potentials were applied and monitored with a Princeton Applied Research model 2263 potentiostat. Time-resolved UV–vis spectra were recorded on an Agilent model 8453 diode array spectrophotometer.

3. Results and Discussion

3.1 Mechanistic aspects of ion pair formation

The mechanistic aspects of the ion pair formation between the electrochemically reduced products of naphthoquinones **Fc-cnq-1a** and **Fc-cnq-1b** and several metal ions (Li⁺, Na⁺, K⁺, Cs⁺, Be²⁺, Mg²⁺, Ca²⁺, Ba²⁺, Ni²⁺, Zn²⁺, Cu²⁺ and Co²⁺ in DMF were comparatively investigated in detail by voltammetric titration technique. In this part of the study, first, the routine

electrochemical behavior of **Fc-cnq-1a** and **Fc-cnq-1b** was investigated by CV in the presence of 0.2 M tetra-*n*-butylammonium perchlorate (*n*-Bu₄NClO₄) as a supporting electrolyte in DMF. Figure 2 shows the CVs of **Fc-cnq-1a** (A) and **Fc-cnq-1b** (B) in the scan rates between 0.025 and 0.500 V.s⁻¹, where SWVs of **Fc-cnq-1a** and **Fc-cnq-1b** and the plot of I_c vs. square root of scan rate ($v^{1/2}$) for the first reduction process are represented as insets a and b, respectively. It can be seen that **Fc-cnq-1a** exhibits chemically reversible one-electron reduction process to form semiquinone radical product, monoanion **Fc-cnq-1a**^{•-} at $E_{1/2}^{(1)} = -1.22$ V [ΔE_p (the anodic to cathodic peak-to-peak separation) = 0.095 V, I_{pa}/I_{pc} (the anodic-cathodic peak ratio) = 0.98]. Following one-electron reduction is observed at more negative potential as a quasi-reversible process at $E_{1/2}^{(2)} = -1.78$ V [$\Delta E_p = 0.110$ V, $I_{pa}/I_{pc} = 0.50$] to form the doubly reduced product, dianion **Fc-cnq-1a**²⁻ at a scan rate of 0.050 V s⁻¹ (magenta line in Figure 2A). **Fc-cnq-1a** also displays chemically reversible one-electron oxidation process corresponding to the ferrocenium/ferrocene (**Fc**⁺-**cnq-1a**/**Fc-cnq-1a**) couple at $E_{1/2}^{(Fc)} = 0.102$ V ($\Delta E_p = 0.096$ V, $I_{pa}/I_{pc} = 1.0$). The reaction mechanism corresponding to the reduction and the oxidation processes is represented in Scheme 1.

The processes are similar to typical CVs of benzoquinone, naphthoquinone, and ferrocene derivatives in aprotic organic solvents without water and acidic ingredients.^{4,5,39–41} On the other hand, the electrochemistry of **Fc-cnq-1b** is similar to that of **Fc-cnq-1a** under the same conditions (Figure 2B). Compared to the CVs of **Fc-cnq-1a** (blue line) and **Fc-cnq-1b** (red line) in Figure 3, the first reduction potential of

Scheme 1. The representative mechanism of the electrochemical processes for **Fc-cnq-1a**, and the ion pair formation between the dianion **Fc-cnq-1a**^{2−} and alkali metal ions (Li⁺, Na⁺, K⁺ and Cs⁺) in DMF.

Figure 3. CVs of **Fc-cnq-1a** (blue line) and **Fc-cnq-1b** (red line) in DMF containing 0.2 M *n*-Bu₄NClO₄ at scan rate of 0.100 V s^{−1}, the concentration of **Fc-cnq-1a** and **Fc-cnq-1b** = 5.0 × 10^{−3} M. Working electrode: glassy carbon disk electrode (3.0 mm diameter).

Fc-cnq-1a shifted to the cathodic region because of more electron-donating oxygen atoms in case of **Fc-cnq-1a**.

The loss of the current observed for the second reduction processes of **Fc-cnq-1a** and **Fc-cnq-1b** compared to the first reduction processes is probably due to a complexation reaction between the doubly reduced product (**Fc-cnq-1a**^{2−} or **Fc-cnq-1b**^{2−}) and neutral state of the molecules or an adsorption of the reduced species on the electrode surface, which was previously reported for several quinones in aprotic media.¹ The differences between the half-wave potentials of the first oxidation and the first reduction processes (¹Δ*E*_p) of **Fc-cnq-1a** and **Fc-cnq-1b**, related to the energy of the CT between the ferrocenyl donor and naphthoquinonyl acceptor centers [*e*_π (HOMO-Fc) → *e*_{π*} (LUMO-cnq)], were found to be 1.32 V and 1.26 V, respectively. The differences between the half-wave potentials of the first and the

Figure 4. CVs of **Fc-cnq-1a** (a) and **Fc-cnq-1b** (b) in the presence of 2.0 equiv. alkali metal (Li^+ , Na^+ , K^+ and Cs^+) perchlorates in DMF solution containing 0.2 M $n\text{-Bu}_4\text{NClO}_4$ at scan rate of 0.100 V s^{-1} , the concentration of **Fc-cnq-1a** and **Fc-cnq-1b** = $5.0 \times 10^{-3} \text{ M}$. Working electrode: glassy carbon disk electrode (3.0 mm diameter).

second reduction processes ($^2\Delta E_p$) for **Fc-cnq-1a** and **Fc-cnq-1b** were calculated as 0.56 and 0.72 V, respectively. The $^1\Delta E_p$ and $^2\Delta E_p$ values of **Fc-cnq-1a** and **Fc-cnq-1b** showed a good agreement with those of the ferrocenyl naphthoquinones bearing different substituents in the same experimental conditions.^{4,5}

For the ferrocene molecule, under our experimental conditions, $E_{1/2}$ of Fc^+/Fc was calculated as $E_{1/2} = 0.069 \text{ V}$ ($\Delta E_p = 0.085 \text{ V}$) at the scan rate of 0.100 V s^{-1} , which can be used as a criterion for electrochemical reversibility.^{5,42–44} The redox processes of **Fc-cnq-1a** and **Fc-cnq-1b** were examined as a function of potential scan rate in order to ascertain the mode of mass transport. The cathodic and anodic currents for the oxidation and reduction couples in DMF increased in direct proportion to the square root of scan rates between 0.025 and 0.500 V s^{-1} . Thus, this implied that the redox reactions in the solution were controlled by diffusion^{5,42–44} (insets b in Figure 2). Second, the ion pair formation between electrochemically reduced products (**Fc-cnq-1a** $^{\bullet-}/\text{Fc-cnq-1b}^{\bullet-}$ and **Fc-cnq-1a** $^{2-}/\text{Fc-cnq-1b}^{2-}$) and several metal ions (Li^+ , Na^+ , K^+ , Cs^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Ba^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} and Co^{2+}) were investigated in detail by voltammetric titration technique using CV at scan rate of 0.100 V s^{-1} in the presence of 0.2 M tetra-*n*-butyl-ammonium perchlorate ($n\text{-Bu}_4\text{NClO}_4$) as a supporting electrolyte in DMF. The CVs obtained from voltammetric titrations of **Fc-cnq-1a** and **Fc-cnq-1b** with alkali metal (Li^+ , Na^+ , K^+ , and Cs^+) perchlorates in DMF are separately represented in Figures 1S–4S. To be able to compare better, the CVs of **Fc-cnq-1a** and **Fc-cnq-1b** in the presence of 2.0 equiv. alkali metal perchlorates are combined in Figure 4. As seen from Figure 4, **Fc-cnq-1a** and **Fc-cnq-1b** displayed

almost similar electrochemical behavior in the presence of 2.0 equiv. alkali metal (Li^+ , Na^+ , K^+ and Cs^+) ions.

The model compound **Fc-cnq-1b** in the absence of alkali metal ions exhibited the cathodic peak potentials at -1.96 V corresponding to the dianionic species **Fc-cnq-1b** $^{2-}$ while **Fc-cnq-1b** in the presence of 2.0 equiv. Li^+ , Na^+ , K^+ and Cs^+ ions, displayed the cathodic peak potentials at -1.79 V , -1.91 V , -1.95 V and -1.95 V , respectively for the same dianionic species. The differences of the cathodic peak potentials between **Fc-cnq-1b** in the absence and presence of Li^+ , Na^+ , K^+ and Cs^+ ions were calculated as 0.17 V, 0.05 V, 0.01 V and 0.01 V, respectively. As seen from this comparison, the peak potentials corresponding to the dianionic species **Fc-cnq-1b** $^{2-}$ in the presence of 2.0 equiv. alkali metal ions shifted to anodic region relative to that of **Fc-cnq-1b** in the absence of alkali metal ions, probably due to the ion pair formation reaction between the dianionic species with negatively charged oxygen atoms and metal cations⁶ (Figure 4b). The most pronounced shift was observed in the case of Li^+ ion as a result of having the highest charge density (98 C mm^{-3}) within alkali metal ions.⁴⁵ Here, we compared with the anodic shift potentials of **Fc-cnq-1b** $^{2-}$ and in the presence of 2.0 equiv. alkali metal ions. The semiquinone radical **Fc-cnq-1b** $^{\bullet-}$ product was almost not affected by alkali metal ions, indicating no ion pairing formation between **Fc-cnq-1b** $^{\bullet-}$ and alkali metal ions. As expected, almost no potential shift was also observed for the oxidized product **Fc** $^+$ -**cnq-1b**. The compound **Fc-cnq-1a** in the absence of alkali metal ions exhibited the cathodic peak potentials at -1.92 V corresponding to the dianionic species **Fc-cnq-1a** $^{2-}$ while **Fc-cnq-1a**

Figure 5. CVs of **Fc-cnq-1a** (a) and **Fc-cnq-1b** (b) in the presence of 2.0 equiv. alkaline earth metal (Be^{2+} , Mg^{2+} , Ca^{2+} , and Ba^{2+}) salts in DMF solution containing 0.2 M $n\text{-Bu}_4\text{NClO}_4$ at scan rate of 0.100 V s^{-1} , the concentration of **Fc-cnq-1a** and **Fc-cnq-1b** = $5.0 \times 10^{-3} \text{ M}$. Working electrode: glassy carbon disk electrode (3.0 mm diameter).

in the presence of 2.0 equiv. Li^+ , Na^+ , K^+ and Cs^+ ions, displayed the cathodic peak potentials at -1.87 V , -1.75 V , -1.85 V and -1.81 V , respectively for the same dianionic species. The differences of the cathodic peak potentials between **Fc-cnq-1a** in the absence and presence of Li^+ , Na^+ , K^+ and Cs^+ ions were calculated as 0.05 V , 0.17 V , 0.07 V and 0.11 V , respectively. It could be interpreted from the similarity of the CV responses of **Fc-cnq-1a** and **Fc-cnq-1b** toward alkali metal ions in the solution of DMF that alkali metal ion binding processes for **Fc-cnq-1a** also proceed *via* the ion pairing formation as observed for **Fc-cnq-1b**. However, the peak potentials corresponding to the dianionic species **Fc-cnq-1a** $^{2-}$ in the presence of Li^+ ion was slightly shifted to anodic site compared to that of **Fc-cnq-1b** $^{2-}$, which indicated that there was a weak ion pairing formation between Li^+ ion and the doubly reduced species **Fc-cnq-1a** $^{2-}$, probably due to the complexation between the crown ether unit in the sensor and Li^+ ion with small atomic radius (73 pm).⁴⁵ The representative mechanism of the electrochemical processes for **Fc-cnq-1a**, and the ion pair formation between the dianion **Fc-cnq-1a** $^{2-}$ and alkali metal ions (Li^+ , Na^+ , K^+ and Cs^+) in DMF are given in Scheme 1.

The CVs obtained from voltammetric titrations of **Fc-cnq-1a** and **Fc-cnq-1b** with alkaline earth metal (Be^{2+} , Mg^{2+} , Ca^{2+} and Ba^{2+}) perchlorates in DMF were represented in (Figure 5S–7S). Figure 5 shows the combined CVs of **Fc-cnq-1a** and **Fc-cnq-1b** in the presence of 2.0 equiv. alkaline earth metal perchlorates. As seen from Figure 5, **Fc-cnq-1a** and **Fc-cnq-1b** displayed almost similar electrochemical behavior in the presence of 2.0 equiv. alkaline earth metal (Be^{2+} , Mg^{2+} , Ca^{2+} and Ba^{2+}) ions, which strongly supports the pair formation between the reduced species of **Fc-cnq-1a** and

alkaline earth metal ions as observed in the presence of alkali metal ions. The CVs of **Fc-cnq-1a** and **Fc-cnq-1b** in the presence of 2.0 equiv. Ba^{2+} ions (purple short dash-dot line in Figure 5) are similar to the CVs of these molecules in the presence of alkali metal ions. However, we did not observe the corresponding dianionic wave, indicating the formation of unstable dianionic species **Fc-cnq-1a** $^{2-}$ or **Fc-cnq-1b** $^{2-}$. Although there are some similarities between voltammetric changes of the studied metal cations (Be^{2+} , Mg^{2+} and Ca^{2+}), among them, especially, Be^{2+} ion has the strongest effect on the electrochemical reduction processes, probably due to its highest reactivity for the ion pairing interaction.

The voltammetric changes observed for **Fc-cnq-1a** and **Fc-cnq-1b** with an increasing amount of Be^{2+} ion (0–2.0 equiv.) are exhibited in Figure 6. The illustrative electrochemical mechanism corresponding to the ion pair formation reaction between Be^{2+} ion and the electrochemically reduced species of **Fc-cnq-1a** is depicted in Scheme 2.

This mechanism can also be applied for **Fc-cnq-1b** in the same approach. In Figure 6 and Scheme 2, the cathodic and anodic waves in the absence of Be^{2+} ion were designated by Ic and Ia for the first reduction process, IIc and IIa for the second reduction process, and IIIc and IIIa for the oxidation process (blue solid line in Figure 6), respectively.

The CVs of **Fc-cnq-1a** and **Fc-cnq-1b** in the presence of 2.0 equiv. Be^{2+} ion are exhibited as a red solid line in Figures 5 and 6. As seen from Figure 6, a significant change in CVs of **Fc-cnq-1a** and **Fc-cnq-1b** was observed when they were titrated with an increasing amount of Be^{2+} ion in DMF. Most importantly, the dianionic waves (IIc and IIa) for the second reduction processes of **Fc-cnq-1a** and **Fc-cnq-1b** almost

Figure 6. CVs of **Fc-cnq-1a** (a) and **Fc-cnq-1b** (b) for increasing amount of Be^{2+} ion (0–2.0 equiv.) in DMF solution containing 0.2 M $n\text{-Bu}_4\text{NClO}_4$ at scan rate of 0.100 V s^{-1} , the concentration of **Fc-cnq-1a** and **Fc-cnq-1b** = $5.0 \times 10^{-3} \text{ M}$. Working electrode: glassy carbon disk electrode (3.0 mm diameter). Inset in Figure 6 (a) shows the CV of **Fc-cnq-1a** for 2.0 equiv. Be^{2+} ion (red solid line) and the CV of **Fc-cnq-1a** for 2.0 equiv. Be^{2+} ion during anodic scan in the range of -0.400 V to 0.700 V (blue dash line).

disappeared, clearly indicating the unstable doubly reduced products **Fc-cnq-1a** $^{2-}$ and **Fc-cnq-1b** $^{2-}$ in the presence of Be^{2+} ion. As shown in Figure 6a and Scheme 2, the cathodic wave potential of **Fc-cnq-1a** $^{\bullet-}$ (Ic), displayed at -1.31 V in the absence of Be^{2+} ion, anodically shifted to -1.25 V in the presence of Be^{2+} ion as a result of the ion pair formation between the monoanionic species **Fc-cnq-1a** $^{\bullet-}$ (the wave Ic) and Be^{2+} ion to produce the product $[(\text{Fc-cnq-1b})_2^{\bullet-} - \text{Be}^{2+}]$ (the wave Ic'). The anodic wave of **Fc-cnq-1a** $^{\bullet-}$ (Ia) for the first re-oxidation process gradually diminished depending on the increasing amount of Be^{2+} , which reappeared as new anodic waves (Ia') at -0.191 V and (Ia) at 0.051 V corresponding to the products $[(\text{Fc-cnq-1a})^{\bullet-} - \text{Cl}]$ and **Fc-cnq-1a**, respectively.

Following **Fc-cnq-1a** irreversibly oxidized to the ferrocenium species **Fc** $^+$ -**cnq-1a** at $E_{\text{pa}}^{(\text{Fc})} = 0.224 \text{ V}$ as result of decreasing cathodic wave (IIIc) and appearing new corresponding cathodic wave at -0.453 V , indicated as asterisk, which also clearly observed during scanning in the range of -0.4 V to 0.7 V (inset in Figure 6 (a), blue dash line). Similar electrochemical behavior as depicted in Scheme 2 was also observed for **Fc-cnq-1b** under identical conditions. The maximum anodic shift for the first reduction processes of **Fc-cnq-1a** and **Fc-cnq-1b** (the waves Ic') was observed for Be^{2+} ion within studied alkali and alkaline earth metals verifying that Be^{2+} ion has the highest reactivity for the ion pairing interaction for the electrochemically reduced products of **Fc-cnq-1a** and **Fc-cnq-1b**. The CVs obtained from voltammetric titrations of **Fc-cnq-1b** with varying transition metal (Ni^{+2} , Co^{+2} , Zn^{+2} and Cu^{+2}) perchlorates in DMF were separately represented (Figure 8S,

Supplementary Information) in DMF at the scan rate of 0.100 V.s^{-1} containing 0.2 M TBAP supporting electrolyte. As seen from Figure 8S (Supplementary Information), no visible change was observed on the current or the formal potentials of redox processes corresponding to **Fc-cnq-1b**.

3.2 In situ spectroelectrochemical experiment

In this study, **Fc-cnq-1a** as a naphthoquinone derivative was studied for the first time by *in situ* spectroelectrochemical experiments in a thin-layer cell^{4,5,38,42,46} in order to verify the ion-pair formation reaction between Be^{2+} ion and the electrochemically reduced species of **Fc-cnq-1a** that was observed during the voltammetric titration studies above. The experiment was performed for **Fc-cnq-1a** in the absence and presence of Be^{2+} ion to compare UV-vis spectra of the reduced products **Fc-cnq-1b** $^{\bullet-}$ and the ion pairing complex $[(\text{Fc-cnq-1a})_2^{\bullet-} - \text{Be}^{2+}]$. Time-resolved UV-vis spectral changes of **Fc-cnq-1a** during the first oxidation at $E_{\text{app}} = 0.700 \text{ V}$ and the first reduction at $E_{\text{app}} = -1.75 \text{ V}$ in DMF solution containing 0.2 M $n\text{-Bu}_4\text{NClO}_4$ are presented in Figure 7.

The spectra of the oxidized and the reduced products presented characteristic view for ferrocenium **Fc** $^+$ -**cnq-1a** and semiquinone radical anion **Fc-cnq-1a** $^{\bullet-}$ which were well-consistent with previously described ferrocene-benzoquinone/naphthoquinone systems.^{4,5}

When we recorded the time-resolved UV-vis spectral changes of **Fc-cnq-1a** in the presence of excess amount of Be^{2+} in DMF solution during the first reduction process at $E_{\text{app}} = -1.75 \text{ V}$, noticeable changes in

Figure 8. Time-resolved UV-vis spectral changes of **Fc-cnq-1a** in the presence of Be^{2+} ion during the first reduction at $E_{\text{app}} = -1.75$ V in DMF solution containing 0.2 M $n\text{-Bu}_4\text{NClO}_4$.

the intensity for the spectrum of the reduced product $[(\text{Fc-cnq-1a})_2^{\bullet-} - \text{Be}^{2+}]$ (red solid line) in the presence of Be^{2+} ion were observed, compared to the spectrum of the reduced form (orange solid line) **Fc-cnq-1a** $^{\bullet-}$ in the absence of Be^{2+} ion (Figure 8). Additionally, the original spectrum of **Fc-cnq-1a** (green solid line) could not be recovered upon re-oxidation operation ($E_{\text{app}} = -0.400$ V) during the spectroelectrochemical timescale. These results clearly confirmed that the semiquinone radical anion **Fc-cnq-1a** $^{\bullet-}$ and Be^{2+} ion resulted in the ion pair formation $[(\text{Fc-cnq-1a})_2^{\bullet-} - \text{Be}^{2+}]$ which did not remain chemically stable throughout the experiment. By this way, the ion pair formation reaction between Be^{2+} ion and the electrochemically reduced species was for the first time observed by *in situ* spectroelectrochemical experiments.

3.3 Electrochemical sensing Be^{2+} ion

These results clearly indicate that **Fc-cnq-1a** or **Fc-cnq-1b** can selectively sense Be^{2+} ion among several metal ions studied here by voltammetric titration technique using SWV, through the strong ion pair formation reaction between the electrochemically reduced monoanion radicals and Be^{2+} ions. In the first part of this study, as shown in Figure 6 recorded by CV, the anodic current of **Fc-cnq-1a** $^{\bullet-}$ and **Fc-cnq-1b** $^{\bullet-}$ for the first reduction process gradually decreased depending on the increasing amount of Be^{2+} , Mg^{2+} and Ca^{2+} .

It can be seen from Figure 9 that the first anodic peak corresponding to the radical **Fc-cnq-1a** $^{\bullet-}$ gradually decreases depending on the increasing amount of Be^{2+} , where the plot of ΔI_a vs $[\text{Be}^{2+}]$ ion for the

Figure 9. SWV changes of **Fc-cnq-1a** (5.0×10^{-3} M) titrated with Be^{2+} ion ($0-2.5 \times 10^{-3}$ M) at 0.100 V s^{-1} scan rate in DMF/TBAP. Inset: the plot of ΔI_a vs $[\text{Be}^{2+}]$ for SWV, Pulse PH/PW: 0.025 V for 0.01 s; Step Height: 2.00 mV; Scan rate: 0.100 V s^{-1} .

current is inserted in Figure 9. Linear range of the sensor **Fc-cnq-1a** for determining Be^{2+} ion via SWV technique was found in the range of $1.1 \times 10^{-6} \text{ M} - 8.8 \times 10^{-4} \text{ M}$. The linear regression equation for Be^{2+} is $y = -49876x + 44.0$ with $R^2 = 0.986$. The limit of detection ($\text{LOD} = 3 \alpha / \text{slope}$)⁴⁷⁻⁵⁰ was calculated to be $3.9 \times 10^{-7} \text{ M}$ (3.6 ppb) which is below the critical Be^{2+} level in water (4 ppb) as reported by World Health Organization (WHO). In the present case, α (0.00634) is the standard deviation for 10 parallel determinations of ligand solution.

On the other hand, **Fc-cnq-1a** was titrated with Mg^{2+} and Ca^{2+} under the same experimental conditions. As seen from Figures 10a and b, the first anodic peaks of **Fc-cnq-1a** $^{\bullet-}$ gradually decreased depending on increasing amounts of Mg^{2+} and Ca^{2+} , respectively, where the plots of ΔI_a vs $[\text{Mg}^{2+}]$ and $[\text{Ca}^{2+}]$ ions for the anodic waves are inserted in Figures 10a and b. Linear ranges of the sensor **Fc-cnq-1a** for sensing Mg^{2+} and Ca^{2+} ions via SWV technique were found in the range of $4.1 \times 10^{-5} \text{ M} - 1.9 \times 10^{-3} \text{ M}$, and $2.1 \times 10^{-5} \text{ M} - 4.2 \times 10^{-4} \text{ M}$, respectively. The sensitivity sequence of **Fc-cnq-1a** is as follows: $\text{Be}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ in view of the linear ranges, indicating that **Fc-cnq-1a** can be exploited for selective electrochemical recognition of Be^{2+} , Mg^{2+} and Ca^{2+} ions as well as more sensitive performance for ultra-trace amount of Be^{2+} among the other metal ions. The titration experiments of **Fc-cnq-1b** in the presence of Be^{2+} , Ca^{2+} and Mg^{2+} were also performed by the SWV, which showed similar electrochemical responses with what was observed for **Fc-cnq-1a** (Figure 9S, Supplementary Information). The linear range of **Fc-cnq-1b** for determining Be^{2+} ion via SWV technique

Figure 10. SWV changes of **Fc-cnq-1a** (5.0×10^{-3} M) titrated with Mg^{2+} and Ca^{2+} ($0-2.0 \times 10^{-3}$ M) ions at 0.100 V.s^{-1} scan rate in DMF/TBAP. Inset a: the plot of $\Delta I/a$ vs. $[\text{Mg}^{2+}]$ for SWV. Inset b: the plot of I/a vs. $[\text{Ca}^{2+}]$ for SWV. Pulse PH/PW: 0.025 V for 0.01 s; Step Height: 2.00 mV; Scan rate: 0.100 V s^{-1} .

Figure 11. SWV changes of **Fc-cnq-1b** (5.0×10^{-3} M) titrated with Be^{2+} ion ($0-2.5 \times 10^{-3}$ M) at 0.100 V.s^{-1} scan rate in DMF/TBAP. Inset: the plot of $\Delta E^{(1)}$ vs $[\text{Be}^{2+}]$ for SWV Pulse PH/PW: 0.025 V for 0.01 s; Step Height: 2.00 mV; Scan rate: 0.100 V s^{-1} .

was found in the range of $1.1 \times 10^{-6} \text{ M} - 1.7 \times 10^{-3} \text{ M}$ and LOD was calculated to be $4.7 \times 10^{-7} \text{ M}$ (4.5 ppb). The linear ranges of **Fc-cnq-1b** for sensing Mg^{2+} and Ca^{2+} ions were found in the range of $2.5 \times 10^{-5} \text{ M} - 1.4 \times 10^{-3} \text{ M}$ and $1.3 \times 10^{-6} \text{ M} - 6.3 \times 10^{-4} \text{ M}$, respectively. The sensitivity sequence for these ions in case of **Fc-cnq-1b** is similar to that was observed for **Fc-cnq-1a**. Unlike the first anodic peak of **Fc-cnq-1a** $^{\bullet-}$, that of **Fc-cnq-1b** $^{\bullet-}$ gradually shifted to anodic site depending on the increasing amount of Be^{2+} , which was not observed for Mg^{2+} and Ca^{2+} (Figure 11). Inset in Figure 11 shows the plot of $\Delta E^{(1)}$ vs $[\text{Be}^{2+}]$ ion for the anodic waves. The linear range of the sensor **Fc-cnq-1b** for determining Be^{2+} ion based on the first anodic wave was found in the range of $5.6 \times 10^{-6} \text{ M} - 1.7 \times 10^{-3} \text{ M}$, which is close to the range calculated with the plot of ΔI vs $[\text{Be}^{2+}]$ ion.

4. Conclusions

In summary, the mechanistic aspects of the ion pair formation between the electrochemically reduced monoanion radical and dianion products of ferrocenyl naphthoquinones (**Fc-cnq-1a** and **Fc-cnq-1b**) and several metal ions were for the first time studied in detail for a large number of metal ions using CV, SWV and *in situ* spectroelectrochemistry. The experiments indicated that alkali metal (Li^+ , Na^+ , K^+ and Cs^+) and Ba^{2+} metal ions have an impact on the dianions **Fc-cnq-1a** $^{2-}$ /**Fc-cnq-1b** $^{2-}$ to a certain extent but no effect on the semiquinone radicals **Fc-cnq-1a** $^{\bullet-}$ /**Fc-cnq-1b** $^{\bullet-}$ which are distinctly influenced by Be^{2+} , Mg^{2+} and Ca^{2+} in DMF due to the strong ion pair formation between the electrochemically reduced monoanion radicals and these ions. On the other hand, the most pronounced effect on the ion-pair formation was observed for Be^{2+} among studied metal ions, which could be facilitated to selectively sense Be^{2+} ion by SWV titration technique for the first time based on the strong ion pair formation reaction between the radicals and Be^{2+} . The experiments demonstrated that the sensitivity sequence of the radicals is as follows: $\text{Be}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$, indicating that **Fc-cnq-1a** and **Fc-cnq-1b** can be exploited for electrochemical recognition of Be^{2+} , Mg^{2+} and Ca^{2+} ions as well as more sensitive performance for ultra-trace amount of Be^{2+} among the other metal ions. LOD of **Fc-cnq-1a** for Be^{2+} ($3.9 \times 10^{-7} \text{ M}$ (3.6 ppb)) is lower than that of **Fc-cnq-1b** ($4.7 \times 10^{-7} \text{ M}$ (4.5 ppb)), and below the critical Be^{2+} level in water (4.0 ppb) as reported by World Health Organization (WHO). The new sensors **Fc-cnq-1a** and **Fc-cnq-1b** with these LOD values have a moderate analytical performance for Be^{2+} ion determination compared to the previous sensors based

on electrochemical methods (Table S1, Supplementary Information).

Supplementary Information (SI)

The CVs obtained from voltammetric titrations of **Fc-cnq-1a** and **Fc-cnq-1b** with alkali metal (Li^+ , Na^+ , K^+ , and Cs^+) perchlorates in DMF were separately represented in (Figure 1S–4S). The CVs obtained from voltammetric titrations of **Fc-cnq-1a** and **Fc-cnq-1b** with alkaline earth metal (Mg^{2+} , Ca^{2+} and Ba^{2+}) perchlorates (0–2.0 equiv.) in DMF were represented in Figure 5S–7S. The CVs obtained from voltammetric titrations of **Fc-cnq-1b** with varying transition metal (Ni^{+2} , Co^{+2} , Zn^{+2} and Cu^{+2}) perchlorates in DMF were separately represented (Figure 8S) in DMF at the scan rate of 0.100 V.s^{-1} containing 0.2 M TBAP supporting electrolyte. The titration experiments of **Fc-cnq-1b** in the presence of Be^{+2} , Ca^{+2} and Mg^{+2} were performed by the SWV (Figure 9S).

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