Electron Transfer Reactions of Electronics Molecules Embedded in Cationic Lipid Thin Films

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We focus here the importance of cationic matrix lipid films for examination of the film electrochemistry of electronics molecules such as fullerene C_{70} and a double-decker lutetium(III) phthalocyanine, $[(C_6H_{13}S)_8Pc]_2Lu$, embedded in cast films of cationic lipids on electrodes in aqueous media. Chemical generation of fullerene or $[(C_6H_{13}S)_8Pc]_2Lu$ anions, using $Na_2S_2O_4$ as a reducing agent at lipid thin films, were investigated. Also, thermodynamics of the ion-pairing between the reduced double-decker phthalocyanine and a cationic lipid was investigated in aqueous KCl solution. All results obtained suggest that the charge of the lipid matrix and the hydrophobic microenvironment in the lipid films plays an important role in the generation of anions of fullerenes and $[(C_6H_{13}S)_8Pc]_2Lu$ in these film states in aqueous media. Film electrochemistry of a metal-metal bonded diruthenium complex $Ru_2(2,4,6-F_3ap)_4Cl$, where $2,4,6-F_3ap$ is 2-(2,4,6-trifluoroanilino)pyridinate anion, and their carbon monoxide (CO) binding ability were also investigated in the lipid matrix at an electrode. The diruthenium complex at the lipid modified electrode was able to bind CO molecules in the Ru_2^{4+}, Ru_2^{3+} and Ru_2^{2+} reduced forms. Here, we emphasize that the microenvironments of surfactant matrix films function as an interface for the electron transfer of electronics molecules on electrodes.
Key words: fullerene, double-decker phthalocyanine, diruthenium complex, bilayer membrane, electrochemistry

1. INTRODUCTION

One recent interest has focused on the construction and development of molecular-scale devices using redox active compounds that are easily tunable [1]. As electronics molecules, the intrinsic properties of fullerenes have been the subject of extensive investigations [2]. The chemistry of fullerene anions is among the most important in the study of fullerene chemistry [3]. However, the electron-transfer mechanisms of C_{60} and C_{70} on electrode surfaces are complicated and unstable in aqueous media [4,5]. We recently reported stable electrochemistry for C_{60} [6-8], C_{70} [8] and metallofullerenes [9] embedded in films of cationic lipids on electrodes in an aqueous system where strong binding of electrochemically reduced fullerenes to the matrix lipid cations was suggested to allow observation of stable electrochemistry of fullerenes. In this paper, we report the importance of the cationic lipid matrix for generation of reduced forms of fullerenes embedded in cast films of cationic lipids on substrates in aqueous media.

The same strategy was applied here to investigate the stable film electrochemistry of a highly reducible double-decker lutetium(III) phthalocyanine in aqueous media when embedded in a gel-like membrane matrix film of tetra-*n*-octylphosphonium bromide ($4C_8P^+Br^-$).

Studies of double-decker lutetium(III) phthalocyanines have had, as their main focus, a characterization of the compound's electrochromic properties [10]. In this regard, the film electrochemistry of these types of compounds as films on electrode surfaces has been the subject of an intense research focus [11]. We have reported that the reversible redox potentials of a gel-like cast film membrane containing a lutetium(III) phthalocyanine in $4C_8P^+Br^-$ matrix at an electrode are positively shifted by up to 0.51 V versus half-wave potentials for the same redox couples measured in dichloromethane [12]. This result is most likely due to the strong Coulomb-couple binding of the phthalocyanine reduction products in the film with the cationic sites of the matrix. Here, we utilize a thermodynamic approach to analyze the film electrochemistry of $[(C_6H_{13}S)_8Pc]_2Lu$ in a $4C_8P^+Br^-$ matrix film in aqueous media. The alkyl thio-substituted double-decker lutetium(III) phthalocyanine that was examined in this study is shown in Fig. 1a and is of interest both from chemical and physical points of view [13].

We also describe the electrochemical properties of diruthenium metal-metal bonded complexes in thin films which should be of interest, both from fundamental and practical viewpoints because supramolecular arrays

based on dimetal building blocks such as nanoscale molecular organometal wires are known [14,15]. Recently, we have reported the electrochemistry and spectroelectrochemistry in various nonaqueous media, and structural properties of a series of $Ru_2(L)_4Cl$ complexes where L = 2-CH_3ap, 2-Fap, 2,5-F_2ap, 2,6-F_2ap, 2,4,6-F_3ap or F_5ap and ap is the 2-anilinopyridinate anion [16,17]. We have also reported the film electrochemistry of $Ru_2(2$-CH_3ap$)_4Cl$ in aqueous media at an electrode containing various cationic matrices and demonstrated that the matrix films utilized provide suitable microenvironments for examining the film electrochemistry of the complex [18]. As a representative diruthenium complex, a Ru_2^{5+} derivative $Ru_2(2,4,6$-F_3ap$)_4Cl$, where 2,4,6-F_3ap is the 2-(2,4,6-trifluoroanilino)pyridinate anion (Fig. 1b), was selected for film characterization in the electrochemical and carbon monoxide binding studies described here.
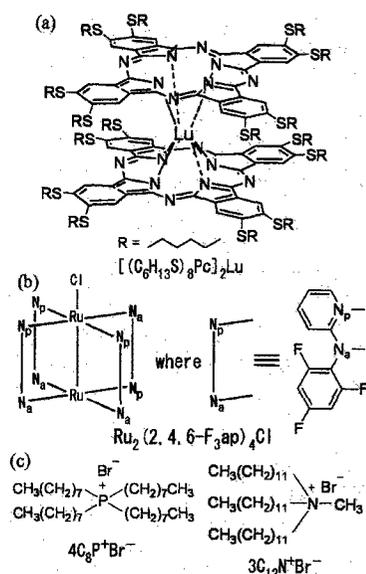
Figure 1. Chemical structures of (a) [($C_6H_{13}S)_8$Pc]$_2$Lu, (b) $Ru_2(2,4,6$-F_3ap$)_4Cl$ and (c) cationic matrix lipids employed in this study.

2. EXPERIMENTAL

2.1. Materials

C_{70} (99.5 %) was purchased from the Material and Electrochemical Research Co. Fig. 1 shows chemical structures of the double-decker lutetium(III) phthalocyanine, the diruthenium complex and matrix synthetic artificial lipids employed in this study. The synthesis of bis[octakis(hexythio)phthalocyaninato] lutetium(III) [13] ([($C_6H_{13}S)_8$Pc]$_2$Lu) and $Ru_2(2,4,6$-F_3ap$)_4Cl$ [18] have been described previously. Tri-*n*-dodecylmethylammonium bromide (3$C_{12}N^+Br^-$) was prepared previously [19]. Tetra-*n*-octyl phosphonium bromide (4$C_8P^+Br^-$, Aldrich) and potassium chloride (KCl, Wako Chemicals) were used as received.

2.2. Instrumentation

Cyclic voltammetry (CV) measurements were carried out an EG&G model 173 potentiostat or a BAS-100BW Electrochemical Analyzer, Bioanalytical Systems. A three-electrode system was used for CV measurements

of fullerene C_{70}, a double-decker lutetium(III) phthalocyanine [($C_6H_{13}S)_8$Pc]$_2$Lu or $Ru_2(2,4,6$-F_3ap$)_4Cl$ as a cast film on a homemade basal plane pyrolytic graphite (BPG) electrode with the matrix in a 0.5 M aqueous KCl solution under nitrogen (N_2) or carbon monoxide (CO) atmosphere. A saturated calomel electrode (SCE) and a Pt plate electrode were used as the reference and counter electrodes, respectively. Electrochemical measurements were carried out at 25 ± 0.5 °C.

Pyrolytic graphite (Union Carbon Co.) was sheathed in an epoxy resin (Torr Seal, Barian Co.) to expose a basal plane and connected to a glass tube. The electrode surface was polished with 1500 grit SiC emory paper, washed with deionized water, and then air-dried. To expose a fresh basal plane, the surface of the BPG electrode was peeled off with Scotch adhesive tape immediately before use.

Vis–near-IR absorption spectral measurements (JASCO V-570 UV–vis–near-IR spectrophotometer with a JASCO ISN-470 integrating sphere) for the modified quartz substrate were examined in Milli-Q water (Millipore Corp. > 18MΩcm) or D_2O for C_{70} and [($C_6H_{13}S)_8$Pc]$_2$Lu in the absence or the presence of $Na_2S_2O_4$ as a reducing agent at 25 ± 1 °C under argon atmosphere. The wavelength scan rate was 200 nm min^{-1}. The modified quartz substrate was vertically inserted into a quartz cuvette with a light path length of 10.0 mm. The cuvette was filled with Milli-Q water or D_2O and then deoxygenated using argon gas. Five hundred micrograms of $Na_2S_2O_4$ was placed in a disposable syringe and then dissolved in argon-degassed water within the syringe, after which the aqueous $Na_2S_2O_4$ solution was injected into the cuvette.

2.3. Preparation of cast films

Typical procedures for preparation of the modified BPG electrodes are as follows: A 30 μL potion of electronics molecules (C_{70}, [($C_6H_{13}S)_8$Pc]$_2$Lu or $Ru_2(2,4,6$-F_3ap$)_4Cl$)/matrix (4$C_8P^+Br^-$ or 3$C_{12}N^+Br^-$) in chloroform or toluene ([electronics molecule] = 0.25 mM and [matrix] = 4.75 mM, molar ratio = 1/19) was placed on a BPG electrode surface (geometric area, 0.36 cm^2) and then air-dried. The modified electrodes were immersed in a 0.5 M aqueous KCl solution after which electrochemical measurements were carried out.

3. RESULTS AND DISCUSSION

3.1 Chemical reduction of fullerene C_{70} embedded in cast films of a cationic lipid

We recently reported the electrochemical and chemical reduction of fullerenes C_{60} and C_{70} embedded in cast films of cationic lipids in aqueous media [8]. Here we introduce chemical reduction of fullerene C_{70} that is embedded in thin films of a cationic matrix lipid (3$C_{12}N^+Br^-$) on quartz substrates. A characteristic band around 1370 nm for $C_{70}{}^{\bullet-}$, generated by chemical [20] or electrochemical [21] reduction, is observed in homogeneous organic solutions. Because H_2O has absorption bands near 1400 nm, the detection of $C_{70}{}^{\bullet-}$ is difficult in H_2O. Hence, D_2O was used instead of H_2O. Like the film of C_{60} [8], a cast film of single component (C_{70}) did not exhibit the $C_{70}{}^{\bullet-}$ peak in the presence of $Na_2S_2O_4$. Visible-near IR absorption spectra of a cast

film of $C_{70}/3C_{12}N^+Br^-$ on a quartz substrate in argon-saturated D_2O are shown in Fig. 2. By adding $Na_2S_2O_4$, the film turned dark red, and the absorbance at 1376 and 790 nm increased to reach maximum intensity in ca. 20 min. The band at 1376 nm is assigned to the $a_2 \rightarrow e_1$ allowed electronic transition [21]. We emphasize the importance of the strong ion-pairing formation between the fullerene anions and the matrix-lipid cations that are formed in the hydrophobic microenvironments in the films on the quartz substrate.
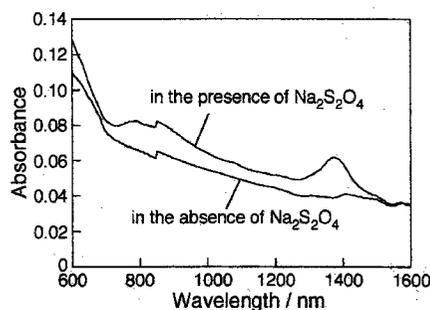
Figure 2. Visible–near IR absorption spectra for a cast film of $C_{70}/3C_{12}N^+Br^-$ (molar ratio, 1:19) on a quartz plate in D_2O in the absence and the presence of $Na_2S_2O_4$ under Ar.

3.2 Thermodynamics of film electrochemistry for double-decker lutetium phthalocyanine

We used a thermodynamic approach to analyze the film electrochemistry of $[(C_6H_{13}S)_8Pc]_2Lu$ in a $4C_8P^+Br^-$ matrix film in aqueous media. The $[(C_6H_{13}S)_8Pc]_2Lu/4C_8P^+Br^-$ modified electrodes show a single oxidation and up to five reductions although when dissolved in organic solvents the same $[(C_6H_{13}S)_8Pc]_2Lu$ undergoes a single oxidation and up to four reductions [22]. The half-wave potentials for reductions in the film are located at $E_{1/2} = 0.26, -0.58, -0.88, -1.19,$ and -1.41 V while the single oxidation is seen at $E_{1/2} = 0.88$ V vs. SCE. The half-wave potentials of the $[(C_6H_{13}S)_8Pc]_2Lu/4C_8P^+Br^-$ modified electrodes are all more positive by 0.21 to 0.49 V than the measured $E_{1/2}$ values in CH_2Cl_2 [22]. The cationic sites in the matrix lead to a larger stabilization of the electroreduced forms of the compound in the film.

A cast film of $[(C_6H_{13}S)_8Pc]_2Lu$ displays only one redox couple at $E_{1/2} = 0.88$ V when examined in the absence of a matrix at an electrode surface. No reductions at all can be observed under our experimental conditions and this result is similar to behavior reported by Simon and coworkers for $[(C_nH_{2n+1}OCH_2)_8Pc]_2Lu$ in an LB film of the compound [23]. This behavior contrasts significantly with what is observed in the present study for $[(C_6H_{13}S)_8Pc]_2Lu$ where up to five well-defined reductions are seen in a cationic matrix film.

A thermodynamic analysis of the electrochemical data was carried out at different concentrations of supporting electrolyte (KCl) in order to explain any ion-pairing effects [22]. In fact, there is a linear relationship between the half-wave potentials for each of the redox reactions of the $[(C_6H_{13}S)_8Pc]_2Lu/4C_8P^+Br^-$ modified electrode and the ln[Cl⁻] which was varied from 1.0 M to 0.005 M using KCl. The linear relationship observed in the plot provides evidence that the

thermodynamic analysis is appropriate. Thus, the binding of the reduced form of $[(C_6H_{13}S)_8Pc]_2Lu$ to the cationic site of $4C_8P^+Br^-$ as a matrix in the film is responsible for the positive shift of the formal potentials.

To better understand ion-paring interactions between reduced forms of $[(C_6H_{13}S)_8Pc]_2Lu$ and cationic sites of the matrix, we examined the chemically reduced complex using $Na_2S_2O_4$ as a reducing agent in aqueous solutions [22]. Characteristic Q bands of neutral $[(C_6H_{13}S)_8Pc]_2Lu$ of the film, either in the presence of $4C_8P^+Br^-$ or in the absence of a matrix are red-shifted with respect that in CH_2Cl_2, and this is due to a strong aggregation of the phthalocyanines in the films. The band at 954 nm is associated with the radical character of the phthalocyanine macrocycle [24], and the band, along with the phthalocyanine Q bands, both decreased in intensity upon reduction. This is seen, for example, where there was a disappearance of Q and radical bands and the appearance of four new bands at 592, 658, 740, and 835 nm within 10 min of adding $Na_2S_2O_4$ to a cuvette containing the phthalocyanine in the cast film with $4C_8P^+Br^-$. In contrast, cast films of $[(C_6H_{13}S)_8Pc]_2Lu$ in the absence of a matrix show no significant spectral changes in pure water even 30 min after adding $Na_2S_2O_4$ to the cuvette. These results indicate that the cationic site of the matrix film plays the role of a counter cation for the chemically reduced lutetium(III) phthalocyanines.

3.3 Electrochemistry and CO binding properties of films containing a diruthenium complex

Here we investigated film electrochemistry of $Ru_2(2,4,6-F_3ap)_4Cl$, whose ligands contain electron-withdrawing groups (F), in aqueous media when embedded in a cationic $4C_8P^+Br^-$ matrix film on an electrode. When under N_2 atmosphere, $Ru_2(2,4,6-F_3ap)_4Cl$ undergoes three single-electron metal-centered processes (Fig. 3a). An oxidation in the film (Ru_2^{5+}/Ru_2^{6+}) occurs at $E_{1/2} = 0.53$ V while the first reversible reduction (Ru_2^{5+}/Ru_2^{4+}) is located at $E_{1/2} = -0.37$ V. The Ru_2^{4+}/Ru_2^{3+} process is irreversible at the modified electrode and located at $E_{pc} = -1.57$ V for a scan rate of 0.1 V/s.

The cathodic and anodic peak currents for the Ru_2^{5+}/Ru_2^{6+} and Ru_2^{5+}/Ru_2^{4+} processes of $Ru_2(2,4,6-F_3ap)_4Cl/4C_8P^+Br^-$ on the electrode increase in proportion to the square root of scan rate between 0.05 and 0.5 V/s indicating that the electrochemistry in the film is controlled by diffusion over the range of potential scan rates utilized [25a]. However, at scan rates below 0.03 V/s, the peak currents were directly proportional to the scan rate, consistent with thin-layer electrochemical behavior [25b]. The amount of complex reacted, calculated from the peak areas in the CV at a scan rate of 0.005 V/s of the $Ru_2(2,4,6-F_3ap)_4Cl/4C_8P^+Br^-$ modified electrodes, was 4.56×10^{-9} molcm⁻², indicating that about 61% of the complex in the film of $4C_8P^+Br^-$ is electrochemically active.

Under a CO atmosphere, $E_{1/2}$ value for an oxidation of the complex (Ru_2^{5+}/Ru_2^{6+}) is the same as that under N_2 (0.53 V), consistent with a lack of CO binding to the neutral and Ru_2^{6+} oxidation state. Three reductions are

seen in the same $Ru_2(2,4,6-F_3ap)_4Cl/4C_8P^+Br^-$ modified electrodes under a CO atmosphere (Fig. 3b). The second and third reductions of the complex under CO are assigned to the Ru_2^{4+}/Ru_2^{3+} ($E_{1/2} = -0.52$ V) and Ru_2^{3+}/Ru_2^{2+} ($E_{1/2} = -1.42$ V) redox couples. The Ru_2^{4+} species under CO are proposed to axially coordinate a single molecule while both Ru_2^{3+} and Ru_2^{2+} adducts are proposed to contain two CO axial ligands. The CO binding features of the complex $Ru_2(2,4,6-F_3ap)_4Cl$ at the $4C_8P^+Br^-$ modified electrode are consistent with the electrochemical behavior of the same complex in nonaqueous media, as homogeneous solutions under CO [26]. The results under N_2 and CO indicate that the $4C_8P^+Br^-$ matrix film acts as a suitable electrode modifier for examination of film electrochemistry and CO binding properties of the diruthenium complex without any inactivation. Aggregation of the complexes in the film might be inhibited to some extent by the addition of surfactant type matrices during preparation of the films. This is why unambiguous film electrochemistry and CO binding features were obtained in the matrix films.
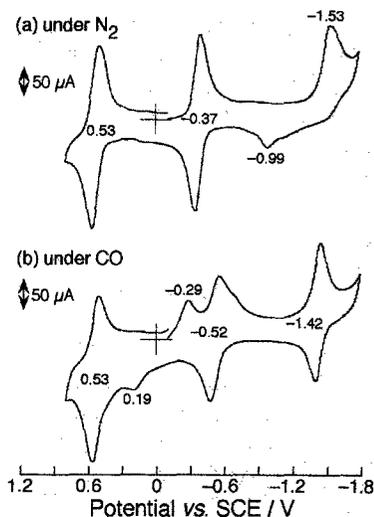
Figure 3. Cyclic voltammograms for a cast film of $Ru_2(2,4,6-F_3ap)_4Cl/4C_8P^+Br^-$ (molar ratio, 1:19) on a BPG electrode in a 0.5 M aqueous KCl solution at 25 °C (a) under N_2 and (b) under CO. Scan rate 0.1 V/s.

4. CONCLUSION

In this research, cationic matrix films are proven as suitable microenvironments for film electrochemistry and gas sensing of electronics materials such as fullerenes, double-decker lutetium(III) phthalocyanines, and metal-metal bonded diruthenium complexes in aqueous media. We have highlighted the importance of the cationic charge of the lipids and hydrophobic microenvironments formed in the films for the stable electrochemistry of the electronics materials. We emphasize here that the microenvironments of surfactant matrix films function as an interface for the electron transfer of electronics molecules on electrodes. This should be a great advantage for the construction of molecular devices consisting of fullerenes, π-conjugated materials (phthalocyanines and porphyrins) or organic-inorganic hybrid materials in many applications.

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