Synthesis and Electrochemistry of Diester-Anthraquinone as Lithium-Ion Selective Receptor

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Lithium ion is an important element for the treatment of manic depression and the lithium battery. Considering such applications, rapid and accurate methods for the determination of lithium ion and its separation in recycling are receiving intensive attention.[1,2] Because the high concentration of sodium ion exists in blood and sea water, an excellent selectivity of Li^+/Na^+ is required for the determination and separation of lithium ion in biological and environmental systems.

The cyclic and acyclic neutral carriers including crown ethers have been tested as ligands to form complexes with lithium ion, because the oxygen atom is a hard base and strongly binds to the lithium ion. The host molecules are an acyclic podand,[3] cyclic crown-ether,[4] calixarene, or bicyclic cryptand[5] which are designed to show cation binding properties even in the absence of the redox process, and an electroactive compounds[6-8] containing the proper geometrical orientation with respect to the cation binding center. Electrochemical reduction of the molecules leads to excess negative charge which in turn enhances the binding of the cation. Binding enhancement values between 10^2 and 10^6 have been reported.[3-8] Since the redox process is reversible, a switch is present which allows control between low and high cation binding states.[9] The anthraquinone moiety has proven to be the most versatile and useful redox-active group in chemical and biological systems.[3-4,8] Crown ether derivatives containing anthraquinone moiety were studied for cation binding-redox coupling.[10] A redox-switchable receptor is a compound capable of forming a complex with a given substrate in such a way that the thermodynamic stability of the complex is determined by the oxidation state of the receptor. These compounds must possess a redox-active subunit and a well-defined binding site.

The ester moiety as binding site in calixarene derivatives has shown the remarkable ionophoric properties toward alkali metals.[11] The calix[4]arenes with esters display selectivity for the sodium ion, on the other hand, the esters of calix[6]arene display selectivity for the cesium ion.[12] It was also reported that the esters of calix[4]quinone as redox-switchable calixarenes have been synthesized and studied for electrochemistry and ionic binding.[13-17]

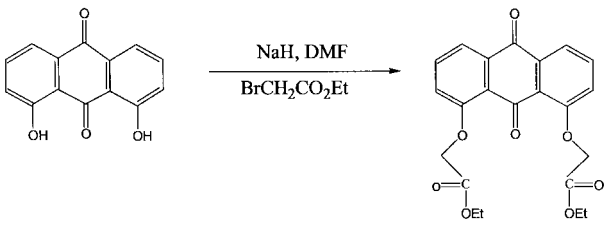
We designed a new redox-switchable receptor named diester-anthraquinone. In this paper we report the synthesis of diester-anthraquinone and the lithium ion binding of diester-anthraquinone in CH_2Cl_2.

Experimental Section

Synthesis of diester-anthraquinone. 1,8-dihydroxyanthraquinone (0.2 g, 0.83 mmol), sodium hydride (0.16 g, 6.7 mmol) and bromoethylacetate (1 mL, 9.1 mmol) in DMF (20 mL) was stirred and heated under reflux for 2 hrs. After cooling down to room temperature, the mixure was acidified with 2 M HCl solution and extracted with $CHCl_3$. The solvents were removed and the residue was treated with hexane to give 0.281 g (82%) as a product named diester-anthraquinone. Scheme 1 shows the synthetic process. ^{1}H NMR ($CDCl_3$) δ 7.93 (d, 2H, ArH, J = 0.63 Hz), 7.63 (t, 2H, ArH, J = 8.16), 7.23 (d, 2H, ArH, J = 8.31), 4.87 (s, 4H, $-OCH_2CO_2^-$), 4.27 (q, 4H, $-OCH_2-$, J = 7.14 Hz), 1.29 (t, 6H, $-CH_3$, J = 7.2 Hz).

Reagents. As a supporting electrolyte, tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was used as received from Fluka. 1,8-Dihydroxyanthraquinone was used as received from Aldrich. Anhydrous dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN), dimethyl formaldehyde (DMF) were used as received from Aldrich. All cations [$MClO_4$ (M=Li^+, Na^+, K^+), and $M(ClO_4)_2$ (M=Mg^{2+})] were used as received from Aldrich or Sigma. These were added at diester-anthraquinone solution with a microsyringe, after preparing 0.2 M cation solution in the solvents.

Instrument. The voltammetric measurements were accomplished with a potentiostat [Bioanalytical Systems (BAS 100B/W)]. A Ag/AgCl electrode supplied by BAS was used as a reference electrode. A platinum-wire electrode was used as an auxiliary electrode. A 3.0 mm diameter glassy carbon electrode was used as a working electrode, its surface was highly polished with alumina paste prior to each experment. All reported potentials were with respect to Ag/AgCl electrode at room temperature under argon atmosphere. Absorp-



Scheme 1

tion spectra were obtained with a Jasco V-530 spectrophotometer which an optical path length is 10 mm.

Results and Discussion

Diester-anthraquinone is synthesized and employed as the selective receptor for lithium ion. The electrochemical properties of diester-anthraquinone are investigated in CH_2Cl_2 using cyclic voltammetry with Bu_4NPF_6 as a supporting electrolyte under an argon atmosphere. Cyclic voltammograms of diester-anthraquinone in the absence and presence of excess cations (Li^+ and Na^+) are illustrated in Figure 1. Diester-anthraquinone shows the reversible first wave (E_1= -1022 mV) followed by the second wave (E_2=-1247 mV) at more negative potential with quasi-reversible behavior. The first reduction potential of the synthesized diester-anthraquinone is more negative than that of 1,8-dihydroxyanthraquinone (E_1=-890 mV) and slightly more positive than that of anthraquinone (E_1=-1040 mV). It was well known that the reduction waves corresponded to the respective formation of a radical anion and dianion, respectively. The first reduction potential of diester-anthraquinone is expected to shift to a more positive value than the original potential when stoichiometric equivalents of cation guests are added to the electrochemical solutions of diester-anthraquinone. The positive shift of the first reduction wave for diester-anthraquinone was observed in the presence of Li^+ or Na^+, but the positive perturbation of the reduction potential was not observed in the presence of K^+ or Mg^{2+}. Potential shift values of the first redution potential of diester-anthraquinone in the presence of excess cations are summarized in Table 1. The excess addition of Li^+ to the electrochemical solution of diester-anthraquinone caused positive shift by 539 mV in the first reduction potential, but the excess addition of Na^+ caused only 260 mV shift. This large positive shift suggests a strong stabilization of diester-anthraquinone with Li^+ in lithium ion solution. Also because the shift of the first redution potential for unsubstituted anthraquinone in the presence Li^+ was not observed, this result indicates that Li^+ is bound to the ester moieties and quinone moiety. Finally, the

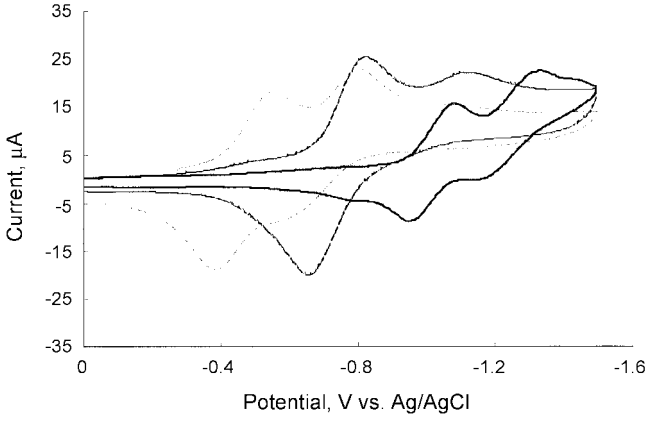


Figure 1. Cyclic voltammograms of diester-anthraquinone in the absence and presence of excess cations under an argon atmosphere. (a) Free (—). (b) Li^+ (·····). (c) Na^+ (–––).

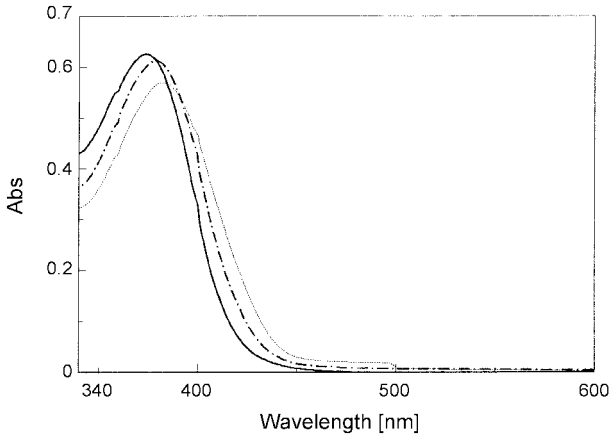


Figure 2. UV-vis spectra of diester-anthraquinone in the absence and presence of excess cations under an argon atmosphere. (a) Free or K^+ (—). (b) Li^+ (·····). (c) Na^+ (–––).

Table 1. Electrochemical and spectroscopic properties of diester-anthraquinone in the absence and presence of cations

	E (mV)	ΔE (mV)	λ_{max} (nm)	$\Delta\lambda$ (nm)
Free	-1091	–	374	–
Li^+	-552	539	382	8
Na^+	-831	260	378	4
K^+	-1082	9	374	0

effect of Li^+ binding to diester-anthraquinone may be stronger than other cations employed, and the reason is ascribed to the effect of ion size.

The result of spectroscopic experiment shows one of many evidences to binding property. Absorption spectrum of diester-anthraquinone in CH_2Cl_2 are illustrated in Figure 2. The λ_{max} of diester-anthraquinone shifts progressively to a longer wavelength with increasing concentration of Li^+ ion, and finally has a constant value with excess Li^+ ion. The Soret band of diester-anthraquinone shows red shift compared with that of diester-anthraquinone in the presence of excess cations (Li^+ or Na^+) and they are also summarized in Table 1. The shift of 8 nm for Li^+ and 4 nm for Na^+ is observed. This suggests that Li^+ binding to diester-anthraquinone is the strongest than other cations.

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