Electrochemistry and Anion Binding of Urea Functionalized Calix[4]monoquinone

Haesang Jeong, Eun Mi Choi, Sung Ok Kang, Kye Chun Nam,* and Seungwon Jeon*

Department of Chemistry and Institute of Basic Science, Chonnam National University, Kwangju 500-757, Korea
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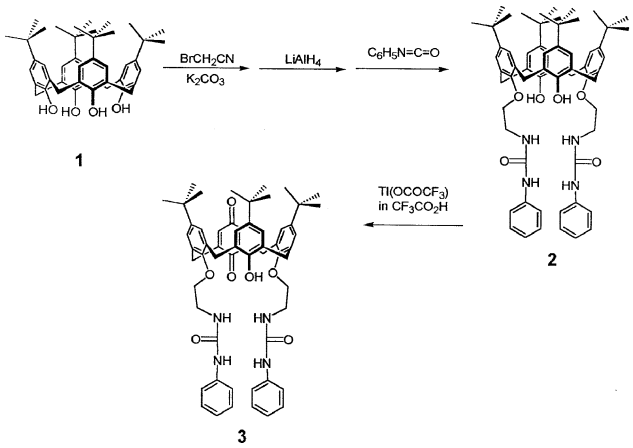
Calix[4]arenes have received much attention as an interesting class of cyclophanes possessing ionic and molecular binding properties.[1,2] Their potential as enzyme mimics has been suggested that appropriate functionalization of the phenolic units could extend this comparison to redox-switching enzyme.[3] It has been studied that various derivative (ester or ether groups) calixarenes and calixquinones were selectively host molecules for cations (alkali metal cations, alkylammonium ions)[4-7] as well as incorporated into polymeric membrane ion selective electrode.[8] Anions play ubiquitous roles in chemical and biochemical processes and some are crucial for environmental and medical concern.[9] Selective complexation of anions is more demanding than that of cations in the view of the higher free energies of solvation of anions and the pH dependence of anion complexation.[10] It was recently reported that derivative calix[4]arenes of electrochemically actived groups cobaltocenium or ferrocene unit together with an amide N–H group were used as selective molecules of anions ($H_2PO_4^-$, HSO_4^-, Cl^-).[11-13] It was also reported that a selective complexation of Cl^-, Br^- or I^- can be achieved by the neutral urea receptors derived from the lower rim of calix[4]arene,[14] and that three urea groups at the lower rim of calix[6]arene are well suited for complexation of tricarboxylate.[15] The urea moiety is a powerful hydrogen bond donor as recently shown in the complexation of dicarboxylate anion.[16] The quinone moieties of ester derivative calix[4]quinones were known to hydrogen bonding with proton of NH_4^+.[4-7,17]

We recently reported the synthesis and anion binding of urea functionalized calix[4]diquinone.[18] Here, we wish to report the electrochemical behavior of calix[4]monoquinone **3** and its novel binding property with anion HSO_4^-.



Scheme 1. Synthesis of urea functionalized calix[4]monoquinone.

Experimental Section

The urea derivative calix[4]arene **2** was obtained by the reaction of bisaminoethylcalix[4]arene and phenylisocyanate as shown in Scheme 1. Reaction of calix[4]arene **2** with TTFA (thallium trifluoroacetate) in trifluoroacetic acid produced a mixture of calix[4]monoquinone **3** and calix[4]-diquinone. The urea derivative of calix[4]monoquinone was isolated from column chromatography. The ^{1}H NMR spectrum of **3** shows two pairs of doublet at δ 4.32 and 4.21, δ 3.24 and 3.06 for the bridge methylene protons, two singlets at δ 6.74 and 6.45 and one doublet at δ 6.55 for the aromatic and quinone protons, and two singlets at δ 1.39 and 0.91 for the *t*-butyl protons indicating that **3** exists as a cone conformation.

The voltammetric measurements were accomplished with a three electrode potentiostat [Bioanalytical Systems (BAS) 100B/W]. A platinum-wire electrode was used as an auxiliary electrode. A Ag/AgCl electrode supplied by BAS was used as a reference electrode. A 3.0 mm diameter glassy carbon was used as a working electrode, its surface was highly polished with alumina paste prior to each experiment. All reported potentials were with respect to a Ag/AgCl electrode at room temperature. Absorption spectra were obtained by a Jasco V-530 spectrophotometer equipped with an HMC-358 constant temperature cell holder. As a supporting electrolyte, tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was used as received from Fluka. Anhydrous acetonitrile (MeCN) was used as received from Aldrich. All anions [tetrabutylammonium salts Bu_4NX (X = Cl^-, Br^-, I^-, ClO_4^-, CH_3COO^-, H_2PO4^-, HSO_4^-)] were used as received from Aldrich or Fluka.

Results and Discussion

Redox chemistry of calix[4]monoquinone **3** was investigated in MeCN with Bu_4NPF_6 as a supporting electrolyte under an argon atmosphere. Initial cyclic voltammogram (CV) of calix[4]monoquinone is illustrated in Figure 1 (solid line), and CV of 2,6-*t*-butyl benzoquinone (BQ) is also exhibited in Figure 1 (dashed line). The reason for the comparison with calix[4]monoquinone **3** and BQ is that BQ is considered as very useful reference to elucidate electrochemical results for investigations of quinone compounds. Calix[4]monoquinone shows a reversible first wave ($E_{1/2}$ = -0.47 V) followed by a second wave at a much more negative potential with quasi-reversible ($E_{1/2}$ = -0.79 V). The first redox wave is symmetric, but the second wave is less symmetric. The peak current of the first reduction of calix[4]-

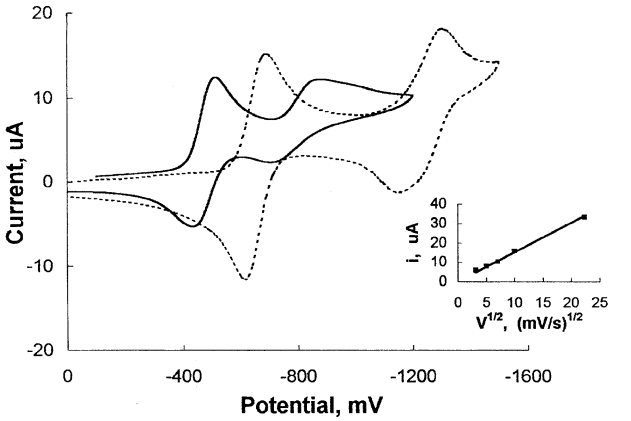


Figure 1. Cyclic voltammograms of 1.0 mM calix[4]monoquinone (solid line) and 1.0 mM 2,6-*t*-Bu-Benzoquinone (dashed line), the plot of the first reduction current of calix[4]monoquinone *vs*. square root of scan rate in MeCN (inset).

monoquinone is linearly increasing of the square root of scan rate in the range from 10 mV/s to 500 mV/s (see inset of Figure 1), indicating that calix[4]monoquinone follows only the diffusion controlled process in experimental conditions. It is well known that quinone compounds are initially reduced to semiquinone by one electron transfer, and then reduced to dianion at more negative potential.[4-7] On the basis of CV results, the reduction potential of calix[4]monouinone shifts to positive direction when compared with that of BQ.

When anions are added to the MeCN solution of calix[4]-monoquinone, the first reduction potential will be expected to shift more negatively than original potential.[11-13] Cyclic voltammograms of calix[4]monoquinone in the presence of Cl^-, $H_2PO_4^-$ and HSO_4^- are shown in Figure 2. In the Figure 2a and 2b, the first reduction peak of calix[4]monoquinone with one equivalent Cl^- and $H_2PO_4^-$ exhibits slightly negative value than original peak potential. However in the Figure 2c, cyclic voltammograms of calix[4]-monoquinone in the presence of HSO_4^- are shown a new prewave and the reduction peak at the more negative potential. A prewave seems to be appeared due to the protonation of reduced calix[4]monoquinone by free HSO_4^- or HSO_4^- bound to calix[4]monoquinone. Cathodic shifts of the first reduction potential of calix[4]monoquinone in the presence of one equivalent anions are summarized in Table 1. The addition of HSO_4^- causes a 64 mV cathodic shift in the first redox couple. This large cathodic shift suggests a strong stabilization of calix[4]monoquinone in the presence of HSO_4^-. This result indicates that HSO_4^- coordinates to the amide moieties of calix[4]monoquinone and also binds to quinone moiety by hydrogen bonding. Moreover the binding of HSO_4^- to calix[4]monoquinone proposes that a prewave appears due to the intramolecular protonation of reduced calix[4]monoquinone by HSO_4^- bound to calix[4]monoquinone rather than by free HSO_4^-. With the increasing concentrations of HSO_4^- the redox wave becomes irreversible. The hydrogen atom in HSO_4^- is formed hydrogen bonding at the oxygen moiety (=O) of quinone.[4-7,19] When calix[4]monoquinone is reduced electrochemically, the oxygen moiety of reduced

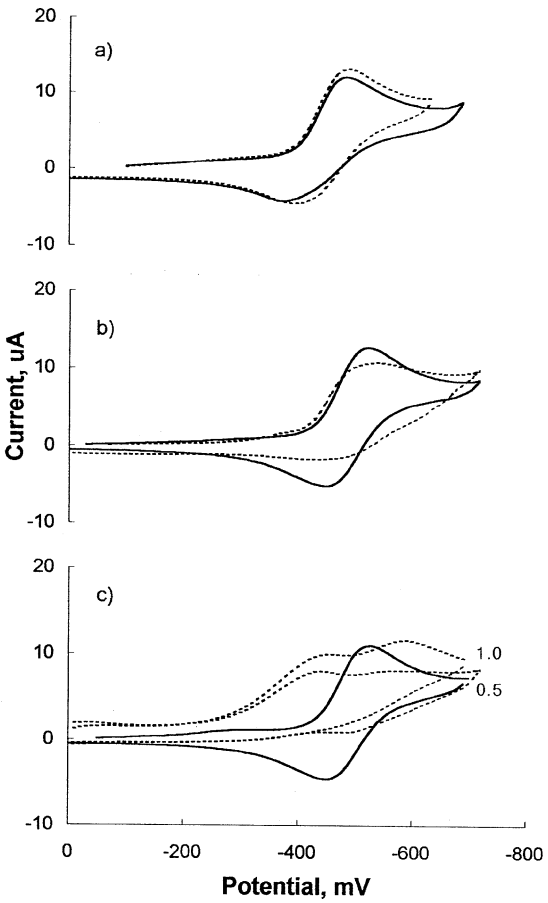


Figure 2. Cyclic voltammograms of 1.0 mM calix[4]monoquinone in the absence (solid line) and presence (dashed line) of anions a) 1.0 eq Cl^-, b) 1.0 eq $H_2PO_4^-$, c) 0.5, and 1.0 eq HSO_4^-.

Table 1. Cathodic shift of the first reduction potential of 1.0 mM calix[4]monoquinone in the presence of one equivalent anions

Anions	ΔE_{pc1} (mV)
ClO_4^-	~0
I^-	~0
Br^-	~0
CH_3COO^-	~0
Cl^-	5
$H_2PO_4^-$	19
HSO_4^-	64

quinone is protonated by the proton of HSO_4^- (pK_a = 1.9 in H_2O)[20] binded to calix[4]monoquinone. Unlike HSO_4^-, the oxygen moiety of reduced quinone isn't easily protonated by the proton $H_2PO_4^-$ (pK_a = 7.8 in H_2O). As a result, the effect of HSO_4^- binding to calix[4]monoquinone may be stronger than other anions employed, because of the powerful intramolecular hydrogen bonding between calix[4]monoquinone and bound HSO_4^-.

Figure 3 illustrates electronic absorption spectra of calix-[4]monoquinone and BQ in MeCN. Soret band (λ_{max} = 347 nm) of calix[4]monoquinone shows red shift compared with that of BQ (λ_{max} = 316 nm) or calix[4]diquinone (λ_{max} = 327 nm). The λ_{max} of calix[4]monoquinone shifts to short wave-

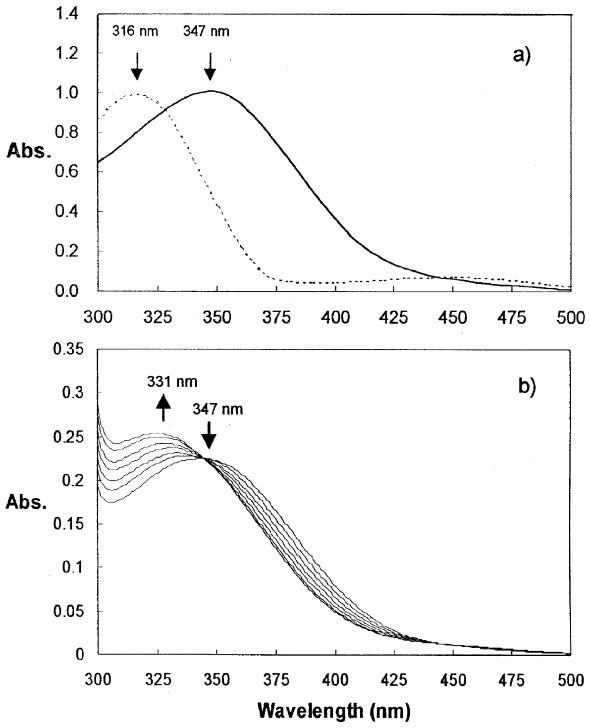


Figure 3. UV-vis spectra of a) 1.0 mM calix[4]monoquinone (solid line) and 2.0 mM 2,6-*t*-Bu-Benzoquinone (dashed line), b) 0.2 mM calix[4]monoquinone in the presence of $H_2PO_4^-$ (0.5, 1.0, 2.0, 4.0, 10, 20 eq) in MeCN.

Table 2. λ_{max} of 0.2 mM calix[4]monoquinone in the presence of excess anions

Anions	λ_{max} (nm)	$\Delta\lambda_{max}$ (nm)
Free	347	–
ClO_4^-	347	0
I^-	347	0
HSO_4^-	340	7
Br^-	340	7
Cl^-	337	10
$H_2PO_4^-$	331	16
CH_3COO^-	330	17

length with the increasing concentrations of $H_2PO_4^-$ (Figure 3b), and the extend of blue shift depends on the basicity of anions (Table 2). There are seen isosbestic points (344 nm and 444 nm) which demonstrate the absence of any long-lived intermediates. The result suggests that calix[4]monoquinone exhibits hydrogen bonding intramolecularly between the oxygen moiety of quinone and hydroxyl group in the absence of anions. The addition of anions to the quinone solutions breaks the hydrogen bonding, occurs acid-base interaction between hydroxyl group of quinone and anion employed.

In conclusion, urea functionalized calix[4]monoquinone is more easily reduced than BQ due to the cyclic structure of calix[4]monoquinone. Calix[4]monoquinone exhibits itself hydrogen bonding between the oxygen moiety of quinone and hydroxyl group. The acid-base interaction between hydroxyl group of quinone and anion added into the solution of quinone breaks the hydrogen bonding, and shifts the absorption band to short wavelength. The extend of blue shift depends on the basicity of anions ($CH_3COO^- > H_2PO_4^-$ > etc.). Meanwhile the binding effect to the amide moieties of calix[4]monoquinone may be stronger for HSO_4^- than for other anions employed, because of the intramolecularly powerful hydrogen bonding between quinone and HSO_4^- bound to the calix[4]monoquinone.

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