$\nu_2$ transition is normally very weak and is rarely unequivocally observed. For most octahedral cobalt(II) complexes, a band around 8,000-10,000 $cm^{-1}$ is usually assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transition while a multiple structured band observed near 20,000 $cm^{-1}$ is assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$. The $^4A_{2g}$ transition appears as a very weak band around 12,000-14,000 $cm^{-1}$. The optical absorption spectrum of Co $(C_{15}H_{26}N_2)(NO_2)_2$ exhibit two bands at 9,615 $cm^{-1}$ and 18,330 $cm^{-1}$, and the electronic spectral assignments of Co $(C_{15}H_{26}N_2)(NO_2)_2$ are made tentatively as follow; 9,615 $cm^{-1}$ ($\nu_1$; $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$) and 18,330 $cm^{-1}$ ($\nu_3$; $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$). The optical absorption spectrum of $Ni(C_{15}H_{26}N_2)(NO_2)_2$ exhibits the characteristic spectral features of octahedral nickel(II) complexes. For octahedral nickel(II) complexes, three spin-allowed transitions are expected from the energy level diagram of $d^8$ ions[18] and three observed bands may thus be assigned; 9,852 $cm^{-1}$ ($\nu_1$; $^3A_{2g} \rightarrow {}^3T_{2g}$), 15,220 $cm^{-1}$ ($\nu_2$; $^3A_{2g} \rightarrow {}^3T_{1g}(F)$), 25,550 $cm^{-1}$ ($\nu_3$; $^3A_{2g} \rightarrow {}^3T_{1g}(P)$).

The infrared spectrum of $Ni(C_{15}H_{26}N_2)(NO_2)_2$ shows strong $NO_2$ stretching bands ($\nu_{a\ NO2}$ and $\nu_{s\ NO2}$) at 1307 $cm^{-1}$ and 1196 $cm^{-1}$, and a weak deformation band ($\delta_{NO2}$) at 872 $cm^{-1}$. These data are in good agreement with the crystallographically determined molecular structure in which the $NO_2^-$ groups[19] are almost symmetrically bidentated with nickel(II) center utilizing two oxygen donor atoms. The infrared spectra of $Co(C_{15}H_{26}N_2)(NO_2)_2$ shows strong stretching bands ($\nu_{a\ NO2}$ and $\nu_{s\ NO2}$) at 1273 $cm^{-1}$ and 1177 $cm^{-1}$, and a weak deformation band ($\delta_{NO2}$) at 857 $cm^{-1}$. The infrared spectral data of $Co(C_{15}H_{26}N_2)(NO_2)_2$ are also in agreement with the crystallographic results.

## Supplementary Data

Tables of (1) H-atom coordinates and isotropic thermal parameters, (2) anisotropic thermal parameters for non-hydrogen atoms, and (3) observed and calculated structure factors with estimated standard deviations are available from IHS.

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# Adsorbate Substitution and Electrochemical Behavior in Self-Assembled Monolayer of 2-Mercaptomethylhydroquinone ($MH_2Q$) on Gold

**Hyunsoo Kim and Hun-Gi Hong***

*Department of Chemistry, Sejong University, Seoul 143-747, Korea*
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Quinone/hydroquinone derivatives[1] take part in several biologically important oxidation-reduction processes. These redox-active molecules play key roles in electron/energy transfer occuring onto biological membrane which they are bound. This type of electron transfer in membrane systems can be mimicked by self-assembled monolayers[2] containing

redox-active species which act as a channel or gate site in membrane. Majda[3] recently reported formation of mixed monolayer assemblies consisting of octadecanethiol and ubiquinone on electrode surface in which ubiquinone is a gate molecule in electron transfer. Hubbard and co-authors[4] have extensively investigated on the structure, orientation, and electrochemical behavior of various quinone derivatives adsorbed on well-defined metal surfaces. In recent years, the *in situ* FT-IR[5] and quartz crystal microgravimetric methods[6] have been used to probe potential-dependent orientation and structure of 2,5-dihydroxythiophenol (DHT) derivatives monolayer attached on electrode in electrolyte solution. Especially, Soriaga and co-workers[7] studied for substrate-mediated adsorbate-adsorbate interaction within an adsorbed layer of DHT molecule on Au and Pt electrode and they reported the effects of submonolayer coverage and coadsorbed iodine on the interaction between adsorbate and substituent using thin-layer electrochemical techniques. It is important to investigate how the electroactive surface-bound species behaves when another surface-active reagent is introduced. The adsobate substitution always takes place on solid surface exposed to the solution containing other species and it provides means of fabrication of stable mixed monolayer, which has many applications for sensoring material. In view of these aspects, it is necessary to estimate factors determining surface substitution of adsorbate for preparation of coadsorbed monolayer on electrode surface.

In this paper, we have constructed a self-assembled monolayer of a 2-mercaptomethylhydroquinone ($MH_2Q$) as an adsorbate on smooth gold electrode and reported pH defendence of redox peak potential and adsorbate displacement reaction between $MH_2Q$ and n-alkyl or benzylmercaptan(as a substituent). These adsorbates have been chosen because they have surface-active thiol group. In addition, $MH_2Q$ shows reversible electrochemical activity in adsorbed state. Thus, it is easy to monitor the surface coverage of adsorbate which remains on the surface in coadsorbed surface states.

## Experimental

The electrochemical measurements were carried out in one-compartment cell with Au thin film (purchased from EMF Corp., Ithaca, N.Y.) or disk electrode (BAS, West Lafayette, IN) as working electrode, platinum counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. Voltammetric experiments were performed with the use of a EG&G/PAR 273A Potentiostat coupled to a HP 7475A x-y plottor. The electrolyte solutions were prepared with deionized water purified to a resistivity of 18 MΩ/cm with UHQ II system (Elga) and deaerated by purging with nitrogen. The pH of electrolyte solution was adjusted with adding of 0.1 M NaOH to 0.1 M $HClO_4$ solution. Propanethiol, hexanethiol, decanethiol, benzylmercaptan, toluhydroquinone and all other chemicals were used as received. $MH_2Q$ was synthesized according to published procedures.[5a]

The Au electrode was cleaned by sonication in chloroform followed by immersion for 10 s in a hot "piranha" solution (3 : 1 mixture of concentrated $H_2SO_4$ and 30% $H_2O_2$) prior to use. Gold disk electrode (geometric area, 0.02 $cm^2$) was polished to a mirror finish with aqueous slurries of 1.0, 0.3, and 0.05 μm alumina before adsorption of $MH_2Q$. After rinsing with deionized water and drying with nitrogen gas blowing, gold electrode was immersed in 10 mM ethanol solution of $MH_2Q$ for 1 h. The electrode was then rinsed with fresh ethanol and deionized water and then used for voltammetric studies.

## Results and Discussion

Figure 1 shows typical cyclic voltammograms for 2-mercaptomethylhydroquinone ($MH_2Q$) chemisorbed with maximum coverage at smooth polycrystalline gold electrode in 0.1 M $HClO_4$ solution. These cyclic current-potential curves present well-developed surface wave characteristics in which peak current is linearly proportional to scan rate and peak potential separation ($\Delta E_p$) is *ca.* 5-10 mV independent of hired scan rates in the range of 50 to 500 mV/s. With the anodic/cathodic peak current ratio of unity, these facts indicate that the electron transfer of $MH_2Q$ molecule is highly reversible in its adsorption state, unlike hydroquinone which is known as slow redox couple in solution phase. The Faradaic charge under the cathodic or anodic peak for chemisorbed $MH_2Q$ in this study generally yields surface coverage of $5.9(\pm 0.4)\times 10^{-10}$ mole·cm $^{2}$. This value almost corresponds to a coverage of full monolayer of $MH_2Q$ when compared to coverage ($5.7\times 10^{-10}$ mole·$cm^{-2}$) of 2,5-dihydroxythiophenol adsorbed on gold previously reported.[4] This implies that $MH_2Q$ molecule is vertically chemisorbed through the SH group and that self-assembled monolayer of $MH_2Q$ is structurally close-packed on gold surface.[7b]

Figure 2 shows cyclic voltammetric curves for chemisorbed $MH_2Q$ obtained in the electrolyte solutions of different pH value. It is remarkable to note that the geometric shape of each cyclic voltammogram was maintained to have the same i-E features at different pH solutions. The observed surface formal potential of $MH_2Q$ is 0.37 V *vs.* SCE in 0.1

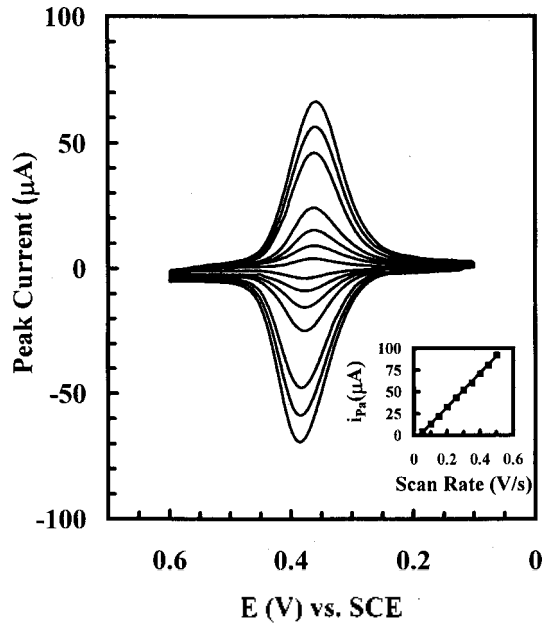


**Figure 1.** Cyclic voltammograms of 2-mercaptomethylhydroquinone ($MH_2Q$) modified Au electrode in 0.1 M $HClO_4$. Inset is the plot of anodic peak current *vs.* scan rate (mV/s).

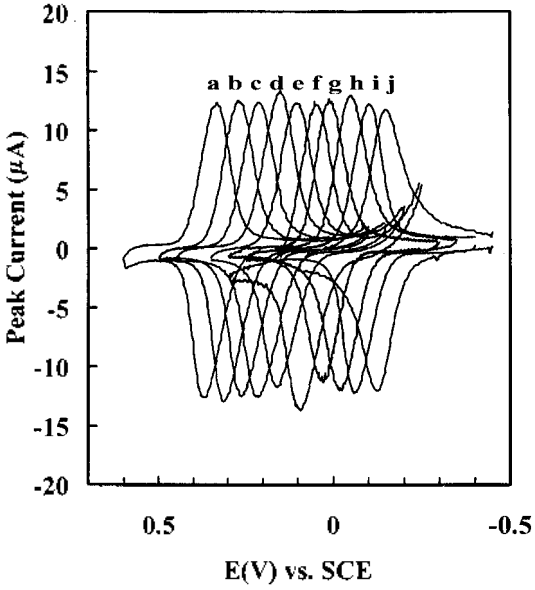


**Figure 2.** Cyclic voltammograms of gold electrode modified with $MH_2Q$ molecule in the electrolyte solutions of different pH. Voltammetric curves of (a) to (j) were respectively obtained in the solution pH of 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0. All scan rates were 100 mV/s.

M $HClO_4$. However, the redox peak potential of pendant hydroquinone moiety in $MH_2Q$ shifts toward negative potential direction as pH of the electrolyte solution increases. Figure 3 shows that the pH-sensitive gold electrode modified with $MH_2Q$ monolayer exhibits a near-Nernstian response with a slope of 54 mV/ pH in the wide range from 1 to 10 of pH. This remarkable pH dependence of $E_{1/2}$ shift is definitely due to the fact that the adsorbed $MH_2Q$ in self-assembled monolayer undergoes reversible two-electron, two-proton electrochemical oxidation-reduction reaction to adsorbed quinone molecule (Q(ads))( eq 1).[4]

$$MH_2Q(ads) \rightleftarrows Q(ads) + 2H^+ + 2e^- \quad (1)$$

The surface coverage of $MH_2Q$ monolayer on gold is typically decreased by only one tenth of its original value ($5.9\times10^{-10}$ mole·cm$^{-2}$) even after extensive potential cycling for 4 h in 0.1 M $HClO_4$ solution. This demonstrates that the irreversible chemisorption of $MH_2Q$ is thermodynamically quite stable in acidic condition. However, the adsorbed $MH_2Q$ molecule is easily displaced by other adsorbate molecule like alkylthiol or benzylthiol on gold surface. Figure 4 shows time-courses of surface displacement behavior in which the coverage of $MH_2Q$ is quickly decreased with immersion into solution containing mercaptan molecules. In this experiment, gold disk electrodes pretreated with a full monolayer of $MH_2Q$ were exposed to 5 mM ethanol solu- tion of electroinactive organomercaptans. During the substitution of adsorbed thiol, surface coverage of $MH_2Q$ remained on Au surface was monitored by cyclic voltammetry at regular interval. This surface displacement reaction (eq. 2) on gold may be written

$$H_2Q\text{-}CH_2S\text{-}Au(ads) + RSH(solution) \rightleftarrows RS\text{-}Au(ads) + H_2Q\text{-}CH_2SH(solution) \quad (2)$$

where the $H_2Q$-$CH_2SH$ represents $MH_2Q$ molecule.

Among organomercaptans used in this study, decanethiol was shown to be the most effective substituent in comparison with short chain-length alkylthiols. In case of decanethiol, the coverage of $MH_2Q$ was dramatically decreased to *ca.* 3% of full monolayer coverage within 5 min and was converted to zero value after 20 min of immersion. This fact indicates that the equilibrium of the RSH-$MH_2Q$ displacement reaction (eq 2) lies far to the right. The equilibrium position is further supported by experiment in which a gold electrode was first treated with a full monolayer of decanethiol and later exposed to 5 mM ethanol solution of $MH_2Q$. No electrochemical response resulting from the adsorption of $MH_2Q$ was measured in this experiment. This observation implies that $MH_2Q$ in solution is unable to displace the initially chemisorbed decanethiol. The driving force for surface substitution of chemisorbed $MH_2Q$ might be ascribed to the hydrophobic interaction between alkylchain of adsorbate thiol and readiness in packing of

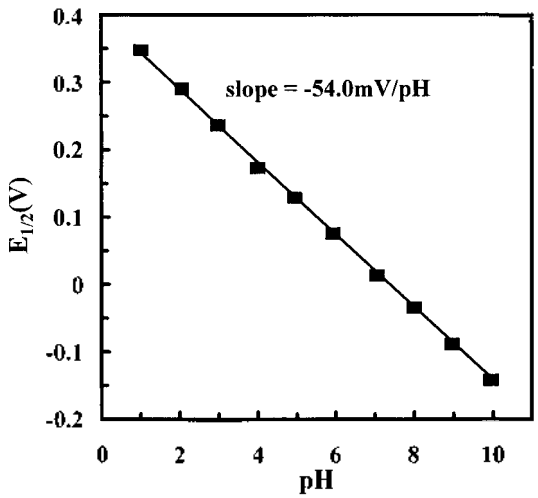


**Figure 3.** Plot of redox peak potential ($E_{1/2}$) of $MH_2Q$ adsorbed on Au electrode *vs.* Electrolyte solution pH. Data in Figure 2 were used in this plot.

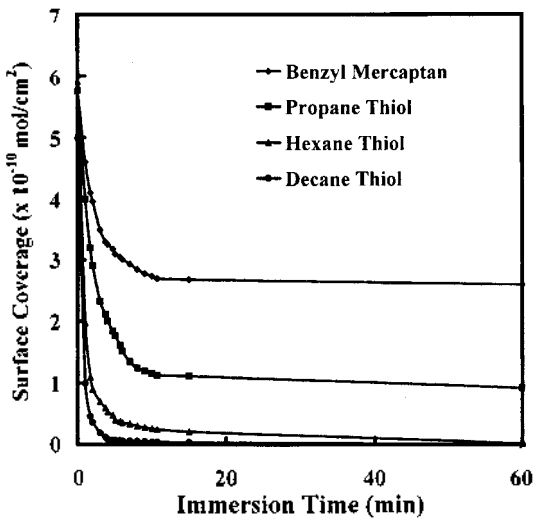


**Figure 4.** Plot of surface coverage ($\times10^{-10}$ mole·cm$^{-2}$) of $MH_2Q$ *vs.* Immersion time (min) of $MH_2Q$-modified Au electrode into the ethanol solution (5 mM) of organomercaptans.

alkylthiol. As known, the van der Waals interaction between alkylchain becomes larger as alkyl chain-length of organomercaptan increases. Therefore, the longer alkylthiol as adsorbate makes desorption more $MH_2Q$ molecules on electrode surface. However, unlike alkylthiols, benzylthiol made displacement only one half of a total amount of the adsorbed $MH_2Q$ even in longer immersion time. This demonstrates that there is no preference in chemisorption of benzylthiol and $MH_2Q$ on gold surface. In fact, $MH_2Q$ molecule has the same chemical structure and size as benzylthiol except two hydroxy groups on benzene ring and their nonpreferential chemisorption is a result from the structural similarity between adsorbate and substituent molecules. However, as shown in Figure 4, the fact that long alkylthiol readily displaces $MH_2Q$ from Au surface states that alkylthiol is preferentially or selectively chemisorbed into $MH_2Q$ layer. In this substitution, the adsorbate and the substituent are not only structurally dissimilar to each other but also different in size. The theoretical calculation[4d] of molecular cross-sectional area ($\sigma$) determined from van der Waals radii by Pauling[8] gives insight on size effect of substituent molecule. According to literature,[4d] the $\sigma$ value (22.5 $Å^2$/molecule) of alkylthiol is only one half of that of benzylthiol (47.4 $Å^2$/molecule). Therefore, it seems to be much easier for alkylthiol to be displaced on gold surface than benzylthiol over the SH functional group of $MH_2Q$. It is nontrivial question whether the two different components in the surface mixture are present homogeneously or heterogeneously. Although this question cannot be answered unambiguously at this moment, hiring of redox-active substituent and adsorbate molecules can provide indications of the heterogeneity of the mixed adsorbed layer from the comparison in the apparent cross sectional areas of substituent and adsorbate.

In conclusion, it is important to take into account the chemical/geometrical structure of substituent molecule in surface-adsorbate displacement reaction which is analogous to ligand exchange on metal substrate. Especially, when the substituent molecule has the same functional group as adsorbate, structural similarities in those molecules play a key role on preferential and nonpreferential coadsorptions of surface ligands on substrate.

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# Synthesis and Properties of Branched Polycarbonates

**Sang-Pil Kim, Bong Hee Lee*, Sang Hern Kim**, Hee-Gweon Woo***, and Whan-Gi Kim†**

*Sam Yang Group Research Center,*
**Department of Chemical Engineering, Chungbuk National University,*
***Department of Chemical Technology, Taejeon National University of Technology,*
****Department of Chemistry, Chonnam National University,*
*†Department of Applied Chemistry, College of Natural Science, Kon-Kuk University*
*Received August 13, 1998*

Polycarbonates are one of the major thermoplastic engineering polymers and well known not only their excellent mechanical and electrical properties but also optical and self-extinguish characteristics.[1-4] Most polycarbonates are manufactured by an interfacial polymerization process which offers advantage to modify chemical structure and process. The linear polycarbonate has been severely restricted their use in the production of large hollow bodies by conventional

†To whom correspondence should be addressed.