

Determination of Reorganization Energy from the Temperature Dependence of Electron Transfer Rate Constant for Hydroquinone-tethered Self-assembled Monolayers (SAMs)

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The temperature dependence on the electron transfer rate constant (k_{app}) for hydroquinone redox center in H₂Q(CH₂)_nSH-SAMs (n = 1, 4, 6, 8, 10, and 12) on gold electrode was investigated to obtain reorganization energy (λ) using Laviron's formalism and Arrhenius plot of $\ln [k_{app}/T^{1/2}]$ vs. T^{-1} based on the Marcus density-of-states model. All the symmetry factors measured for the SAMs were relatively close to unity and rarely varied to temperature change as expected. The electron tunneling constant (β) determined from the dependence of the k_{app} on the distance between the redox center and the electrode surface gives almost the same β values which are quite insensitive to temperature change. Good linear relationship of Arrhenius plot for all H₂Q(CH₂)_nSH-SAMs on gold electrode was obtained in the temperature range from 273 to 328 K. The slopes in Arrhenius plot deduced that λ of hydroquinone moiety is *ca.* 1.3-1.4 eV irrespectively of alkyl chain length of the electroactive SAM.

Key Words : Hydroquinone-tethered SAM, Reorganization energy, Temperature dependence, Rate constant, Heterogeneous electron transfer

Introduction

The phenomenon of long-range electron transfer (ET) has been a crucial research topic not only for the vectorial electron flow in the biological macrostructure such as redox proteins, metalloenzymes, and photosynthetic reaction centers but also for the development of biomolecular electronics and nanometer-scale electronic materials.^{1,2} As model structures to study the long-range ET, many electroactive SAMs³ recently have drawn much interests because they provide an ideal two-dimensional molecular arrangement of a specific redox molecule containing alkanethiol tether attached on an electrode surface. With their controlled thickness and chemical functionality, the electroactive SAMs have been extensively investigated for the effects of distance, interfacial structure, and chemical environment on the electron transfer rate between the redox-active molecule and an electrode surface.⁴ However, there have been only a few studies⁵⁻⁸ on the temperature dependence of heterogeneous ET for the electroactive SAMs since Murray⁹ *et al.* have reported cyclic voltammetry from 115 to 180 K in butyronitrile/ethyl chloride solvent for monolayer films of ferrocene-terminated SAM on gold electrode. With an exception of Forster and Faulkner's report⁵ for the temperature dependence on the ET dynamics using Os(II) bipyridyl complexes monolayer, all these studies have been directed on SAMs containing ferrocene to estimate the reorganization energy (λ) from the slope of an Arrhenius plot^{7,8} using a Marcus formalism^{10,11} with potential steps and cyclic voltammetry. λ is a parameter of great interest in ET chemistry because it controls rate constant of ET reaction

with the reaction free energy. λ is a measure of the free energy required to activate the motions of all the atoms of the initial state, including those in the solvent shell, from their equilibrium positions to those of the final state.¹⁰ One method to estimate λ in electrochemical redox reaction is to measure the temperature dependence of ET rate constant at different temperatures. Recently, we have reported the electrochemical characteristics such as distance-dependence of ET rate and kinetic parameters for H₂Q-terminated SAMs.¹² In this note, for the first time, we report the reorganization energy of H₂Q-terminated SAMs on gold. It is interesting to estimate the λ of H₂Q moiety because its ET mechanism is quite different from that of ferrocene in SAMs. For example, ferrocene as a typical outer-sphere redox couple undergoes simple one electron transfer reaction without structural change in nuclear configuration. However, H₂Q follows complex 2H⁺, 2e⁻ coupled redox reaction accompanying severe molecular structural changes.

Experimental Section

Materials and Reagents. Gold wire (99.999%, 0.5 mm diameter) for electrode was obtained from Johnson Matthey. Ethanol (J.T. Baker) and perchloric acid (70% in water, reagent grade from GFS Chemicals) were used as received. The 2-(*n*-mercaptoalkyl)hydroquinone derivatives used in this work were synthesized and purified by a previously reported methods.¹² Their structures were confirmed by ¹H NMR spectroscopy.

Electrode and Monolayer Preparation. The gold bead electrodes were prepared by annealing the tip of a gold wire

in a gas-oxygen flame. This bead electrode was immersed for 10 min in a hot "pirhana" solution (3 : 1 mixture of concentrated H_2SO_4 and 30% H_2O_2). After copious rinsing with deionized water, the Au electrode was electrochemically cleaned by potential cycling in 0.5 M H_2SO_4 in the potential range of -0.30 V and 1.5 V vs. SCE until typical cyclic voltammogram of clean gold was obtained. Roughness factor for these Au electrodes was measured to be in the 1.1-1.2 range and actual areas were obtained from the slope of the linear plot of cathodic current versus (scan rate)^{1/2} for the reversible reduction of $\text{Ru}(\text{NH}_3)_6^{3+}$. To do this, we have utilized a diffusion coefficient of $7.5 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$ (at 25 °C in 0.1 M NaCl) as previously reported.¹³

After rinsing with deionized water, ethanol, and drying with nitrogen gas blowing, the gold electrode was immersed for 1 day in the ethanol solution containing 1 mM $\text{H}_2\text{Q}(\text{CH}_2)_n\text{SH}$ ($n = 1, 4, 6, 8, 10, \text{ and } 12$). The electrode was rinsed with copious amount of fresh ethanol and deionized water prior to use in electrochemical experiments.

Measurements. Electrochemical measurements were carried out in a dual jacketed-electrochemical cell (BAS) with home-made Au bead electrode as a working electrode, platinum counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. Voltammetric experiments were performed with the use of a BAS 100B/W Potentiostat and a software package. A low temperature thermostat (Lauda Co., RE104) was used for temperature control of dual jacketed-electrochemical cell. Electrochemical measurements were performed in aqueous 0.1 M HClO_4 solutions. The electrolyte solutions were prepared with deionized water purified to a resistivity of 18 $\text{M}\Omega/\text{cm}$ with a UHQ II system (Elga) and deaerated by purging with nitrogen gas.

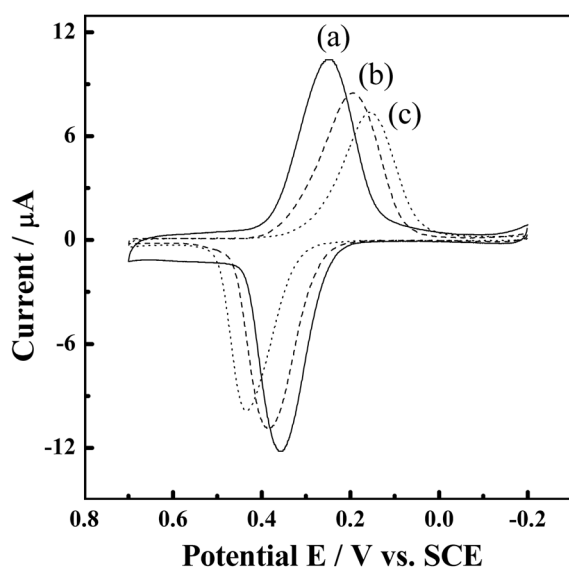


Figure 1. Cyclic voltammograms of three different gold bead electrodes coated with 4-mercaptobutylhydroquinone in contact with a 0.1 M HClO_4 solution at (a) 328 K; (b) 298 K; (c) 273 K. All scan rates were 100 mV s^{-1} .

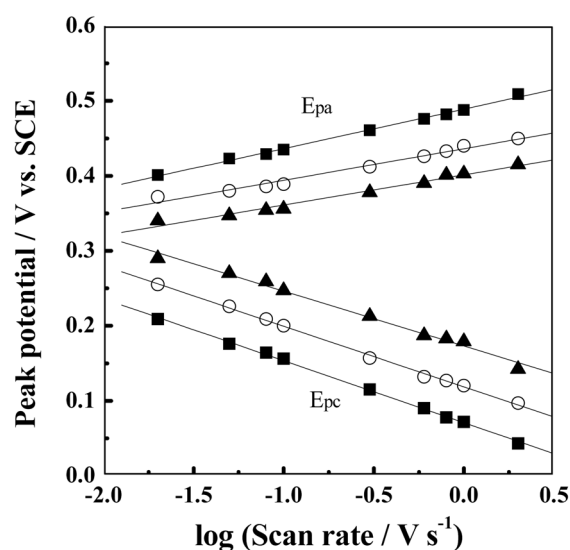


Figure 2. Plot of Redox peak potentials (E_{pa} and E_{pc}) vs. $\log(\text{scan rate}/\text{V s}^{-1})$ for the 6-mercaptohexylhydroquinone SAM on gold in aqueous 0.1 M HClO_4 at (■) 328 K; (○) 298 K; (▲) 273 K.

Results and Discussion

Figure 1 shows typical cyclic voltammograms recorded from three different gold electrodes coated with $\text{H}_2\text{Q}(\text{CH}_2)_4\text{SH}$ -SAM and measured in the 0.1 M HClO_4 solution at three different temperatures at a scan rate of 100 mV s^{-1} . In each voltammogram, a pair of redox peaks was observed to be symmetrical around its formal potential and due to the oxidation and reduction of hydroquinone which follows a $2e^-$, 2H^+ transfer reaction mechanism. The surface density of hydroquinone estimated from the integration of the redox peak areas was in the range of $(3.8\text{-}4.7) \times 10^{-10} \text{ mole}\cdot\text{cm}^{-2}$, which is close to a full monolayer coverage. When the temperature is increased, the peak-to-peak separation (ΔE_p) in voltammogram is decreased. The peak splittings observed are 282 mV at 273 K, 191 mV at 298 K, and 110 mV at 328 K, respectively. This change in the peak splitting demonstrates that the electron-transfer rate increases as temperature rises as expected. The temperature dependence of ΔE_p is generally observed for all the other hydroquinone-terminated SAMs with different alkyl chain length.

In order to investigate the temperature dependence on the ET rate constant for hydroquinone redox center in $\text{H}_2\text{Q}(\text{CH}_2)_n\text{SH}$ -SAMs, we have measured a change in peak splitting as a function of $\log(\text{scan rate})$ using well-known Laviron's formalism.¹⁴ Figure 2 presents typical changes in ΔE_p depending on $\log(\text{scan rate})$ for $\text{H}_2\text{Q}(\text{CH}_2)_6\text{SH}$ -SAMs on gold at three different temperatures. According to Laviron's formalism, the apparent ET rate constant (k_{app}) and symmetry factors (αn or $(1-\alpha)n$) can be determined in a straightforward manner from the equation 1 and 2, *i.e.*

$$E_{pc} = E_c^{\circ'} - (RT/\alpha nF) \ln[\alpha nF v_c / RTk_{app}] \quad (1)$$

$$E_{pa} = E_a^{\circ'} - (RT/(1-\alpha)nF) \ln[(1-\alpha)nF v_a / RTk_{app}] \quad (2)$$

Table 1. Symmetry factors of H₂Q(CH₂)_nSH-SAMs (*n* = 1, 4, 6, 8, 10, and 12) on Au electrode in aqueous 0.1 M HClO₄ at six different temperatures. The values of αn and $(1-\alpha)n$ are symmetry factors due to reduction and oxidation of hydroquinone group, respectively

| Temp. | 273 K | | 288 K | | 298 K | | 308 K | | 318 K | | 328 K | |
|--------------|-------------------------|------------|-------------------------|------------|-------------------------|------------|-------------------------|------------|-------------------------|------------|-------------------------|------------|
| | (1- α) <i>n</i> | αn | (1- α) <i>n</i> | αn | (1- α) <i>n</i> | αn | (1- α) <i>n</i> | αn | (1- α) <i>n</i> | αn | (1- α) <i>n</i> | αn |
| <i>n</i> = 1 | 0.97 | 0.96 | 1.09 | 1.07 | 0.89 | 1.01 | 0.88 | 1.02 | 0.99 | 1.01 | 0.92 | 0.98 |
| 4 | 1.16 | 0.71 | 1.12 | 0.70 | 1.20 | 0.77 | 1.06 | 0.74 | 1.12 | 0.72 | 1.22 | 0.78 |
| 6 | 1.06 | 0.69 | 1.13 | 0.75 | 1.14 | 0.86 | 1.12 | 0.79 | 1.23 | 0.76 | 1.20 | 0.72 |
| 8 | 1.08 | 0.65 | 0.98 | 0.93 | 1.03 | 0.67 | 1.04 | 0.83 | 1.06 | 0.76 | 0.99 | 0.79 |
| 10 | 1.01 | 0.65 | 1.13 | 0.67 | 0.94 | 0.69 | 0.98 | 0.81 | 1.02 | 0.88 | 1.10 | 0.77 |
| 12 | 0.88 | 0.64 | 0.93 | 0.69 | 1.00 | 0.69 | 0.88 | 0.78 | 0.94 | 0.75 | 1.04 | 0.75 |

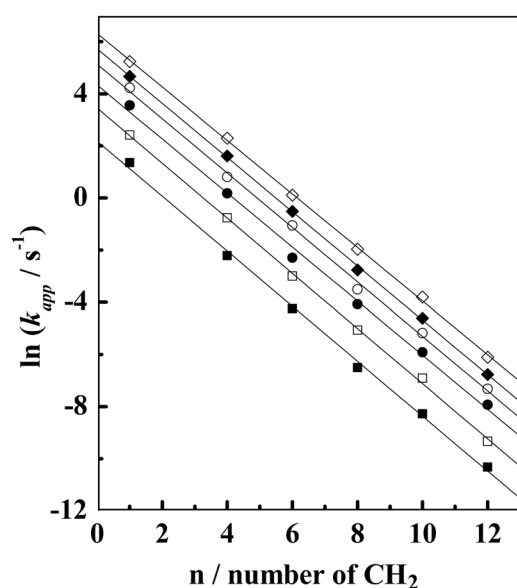
where the peak potential separation is larger than 200 mV/*n*. v_c and v_a are the critical scan rates obtained by extrapolating the linear portion of the plot of peak potential (E_p) vs. $\ln(v)$ to the formal cathodic and anodic potentials, *i.e.* E_c^o and E_a^o . The slope of the linear portion in the plot of E_p vs. $\ln(v)$ curve is $RT/\alpha nF$ for the cathodic branch and $RT/(1-\alpha)nF$ for the anodic branch, respectively. The values of αn and $(1-\alpha)n$ were obtained from the values of each slope and substituted back into the equation 1 and 2 to solve for k_{app} . The values of k_{app} obtained in this way were averaged and denoted as k_{app} . Using the two equations, we have obtained kinetic parameter values for H₂Q(CH₂)_nSH (*n* = 1, 4, 6, 8, 10, and 12)-SAMs on gold electrode at six different temperatures and those values were summarized in Table 1. All the symmetry factor values listed in Table 1 are relatively close to unity. This observation indicates that the symmetry factor rarely varies to temperature change, which is consistent with the classical Butler-Volmer formulation of electrode kinetics.¹⁵ Nagy and co-workers¹⁶ have shown that the transfer coefficient is temperature independent in the electron transfer of ferrous-ferric redox system over the

temperature range from 25 to 275 °C. Therefore, this work shows that the temperature independence of the symmetry factor can be also observed for the electroactive SAMs immobilized on gold electrode. The sum of αn and $(1-\alpha)n$ values obtained in each condition of temperature and alkyl chain number (*n*) is very close to 2, *i.e.* the total number of transferred electrons in the redox reaction of hydroquinone/quinone.

We have already reported the distance dependence of k_{app} for the H₂Q(CH₂)_nSH-SAMs with different alkyl chain length on gold at room temperature only.^{12b} In order to see the temperature dependence of k_{app} in this work, we have extended the electrochemical kinetic measurement for the same SAMs over the temperatures range 273-328 K. Figure 3 shows the plot of the logarithmic heterogeneous ET rate constant with respect to the number (*n*) of methylene group of alkyl chain spacer at each temperature. The simplified equation 3 derived from the Marcus theory¹⁰ gives the electron tunneling constant (β) from the dependence of the k_{app} on the distance (*d*) between the redox center and the electrode surface.

$$k_{app}(d_2) = k_{app}(d_1) \exp[-\beta(d_2 - d_1)] \quad (3)$$

In the equation 3, β is the slope of the plot of $\ln(k_{app})$ vs. *d*. Here, the distance *d* can be simply displaced with the number of CH₂ group in alkyl chain length(*n*). The slopes of the plot shown in Figure 3 give almost the same β value, which are ranging from 1.0 to 1.1 per CH₂ unit within alkyl chain spacer (shown in Table 2). This observation indicates that the β value, as a measure of the activation energy barrier at electron-transfer elementary step, is quite insensitive to temperature change. The physical meaning of the temperature independence of β value can be understood from that the structure of the monolayer does not change systemati-

**Figure 3.** Dependence of $\ln(k_{app}/s^{-1})$ on temperature at (■) 273 K, (□) 288 K, (●) 298 K, (○) 308 K, (◆) 318 K, and (◇) 328 K for H₂Q(CH₂)_nSH-SAMs (*n* = 1, 4, 6, 8, 10, and 12) on Au electrode in aqueous 0.1 M HClO₄.**Table 2.** Values of electron tunneling constant (β) and intercept $\ln k_{app}$ (*n* = 0) obtained from the plots in Figure 3

| T (K) | β | $\ln k_{app}$ (<i>n</i> = 0) |
|-------|-----------|-------------------------------|
| 273 | 1.1 ± 0.1 | 2.1 ± 0.2 |
| 288 | 1.1 ± 0.1 | 3.4 ± 0.2 |
| 298 | 1.0 ± 0.1 | 4.3 ± 0.2 |
| 308 | 1.0 ± 0.1 | 5.1 ± 0.2 |
| 318 | 1.0 ± 0.1 | 5.8 ± 0.2 |
| 328 | 1.0 ± 0.1 | 6.3 ± 0.2 |

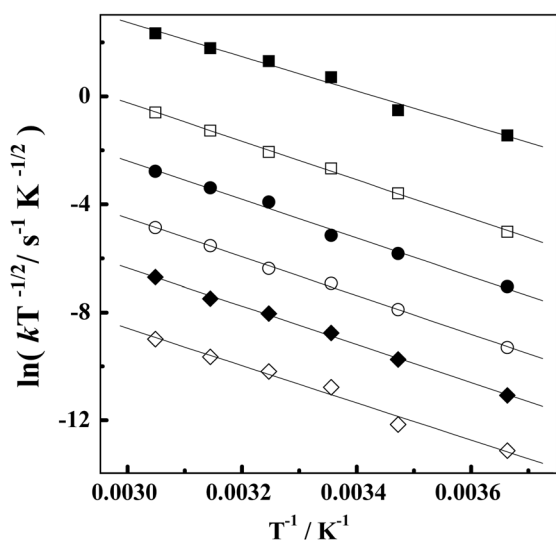


Figure 4. Arrhenius plot: $\ln k_{app} T^{-1/2}$ vs. T^{-1} for $H_2Q(CH_2)_nSH$ -SAMs (where, $n =$ (■) 1, (□) 4, (●) 6, (○) 8, (◆) 10, and (◇) 12) on Au electrode in aqueous 0.1 M $HClO_4$. Data were taken from Fig. 3.

Table 3. Slopes in the Arrhenius plot (Figure 4) and reorganization energy (λ) obtained for $H_2Q(CH_2)_nSH$ -SAMs ($n = 1, 4, 6, 8, 10,$ and 12) on Au electrode in aqueous 0.1 M $HClO_4$

| n | $-d \ln[kT^{-1/2}]/d T^{-1}/s^{-1}K^{1/2}$ | λ / eV |
|-----|--|----------------|
| 1 | $(6.4 \pm 0.1) \times 10^3$ | 1.3 ± 0.1 |
| 4 | $(7.2 \pm 0.2) \times 10^3$ | 1.4 ± 0.1 |
| 6 | $(7.2 \pm 0.2) \times 10^3$ | 1.4 ± 0.1 |
| 8 | $(7.2 \pm 0.2) \times 10^3$ | 1.4 ± 0.1 |
| 10 | $(7.1 \pm 0.2) \times 10^3$ | 1.4 ± 0.1 |
| 12 | $(6.9 \pm 0.2) \times 10^3$ | 1.4 ± 0.1 |

cally with temperature in the electron transfer process. The intercepts of the plot in Figure 3 present the heterogeneous rate constant of H_2Q at the electrode surface, which is extrapolated value for $n = 0$ (shown in Table 2). These k_{app} values are quite small compared to that (*ca.* $6 \times 10^8 s^{-1}$) of ferrocene as the outer-sphere redox couple.⁷ However, the k_{app} values roughly increase in double as the temperature increases by 10 K beyond the temperature of 288 K. This fact seems to be general in view of Arrhenius' classical reaction kinetics. On the other hand, it is interesting to note whether this characteristics is maintained in view of reorganization energy (λ). Each $\ln k_{app}$ value monotonously increases for each $H_2Q(CH_2)_nSH$ -SAM as the temperature increases. To see the temperature dependence of the electron transfer reaction clearly, we made another plot of $\ln[k_{app}/T^{1/2}]$ vs. T^{-1} . This is known as Arrhenius plot,⁷ which is derived from Chidsey's formulation¹⁷ based on the Marcus density-of-states model^{10,11} for electron transfer rate. Assuming that reorganization energy (λ) is temperature-independent, λ can be determined from the slope of an Arrhenius plot producing an activation energy that should be equal to exactly one-fourth of the reorganization energy¹⁰:

$$\lambda = -4.03 d \ln[k_{app}/T^{1/2}]/d [T^{-1}] \quad (4)$$

where $d \ln[k_{app}/T^{1/2}]/d [T^{-1}]$ is simply the slope in the plot of $\ln [k_{app}/T^{1/2}]$ vs. T^{-1} . The term of $T^{1/2}$ in a $\ln[k_{app}/T^{1/2}]$ is originated from the $T^{-1/2}$ dependence of the prefactor in the electron transfer rate expression. Figure 4 shows good linear relationship of Arrhenius plot for all $H_2Q(CH_2)_nSH$ -SAMs on gold for the temperature range from 273 to 328 K in this work. The slope for each of these lines and the corresponding values of λ calculated from equation 4 are given in Table 3. The deduced reorganization energy of H_2Q moiety presents values of $\lambda = 1.3$ -1.4 eV irrespectively of alkyl chain length of the electroactive SAM. The λ estimation, to the best of our knowledge, is the first for the confined hydroquinone redox center on the electrode surface. Smalley⁷ *et al.* also reported that the λ value determined from large overpotential chronoamperometric experiments does not largely vary for n -mercaptoalkyl ferrocenecarboxamide SAMs on gold when $n \geq 6$ and that their reorganization energies are around 0.9 eV in 1.0 M $HClO_4$. This value is similar to the value of 0.87 eV, which Creager and Weber⁸ reported for a ferrocene-terminated SAM. The larger λ value of H_2Q than that of ferrocene might be due to the molecular structural change of the redox center in SAM. The λ is a parameter describing the energetics of nuclear motion in the redox molecule and the solvent shell surrounding the molecule as the redox system adopts a nuclear configuration from which electron transfer take place.¹⁸ The reorganization energy consists of an inner-sphere (λ_{is}) and an outer-sphere (λ_{os}) components. λ_{is} is the energy associated with the equilibrium internal structure of the redox molecule as a function of the oxidation state, while λ_{os} is the energy change associated with the equilibrium solvation sphere surrounding the redox molecule. For outer-sphere redox couples such as ferrocene, λ_{is} is negligibly small because there is no severe molecular geometric change in their redox processes.^{5,19} Therefore, λ value of ferrocene is mainly dominated by solvent reorganization component (λ_{os}). Marcus²⁰ showed that the magnitude of contribution to the λ from the solvent reorganization could be simply estimated by equation 5,

$$\lambda_{os} = [Ne^2/8\pi\epsilon_0](r^{-1} - R^{-1})(\epsilon_{op}^{-1} - \epsilon_s^{-1}) \quad (5)$$

where e is the electronic charge, ϵ_0 is the permittivity of free space, r is the radius of redox molecule, R is the distance from the redox center to its image charge in the metal electrode, and ϵ_{op} and ϵ_s are the optical and static dielectric constants of the solvent. We have used literature values²¹ of $\epsilon_{op} = 1.78$ and $\epsilon_s = 87.9$ for water at 273 K, and $r = 3.5 \text{ \AA}$ and $R = 14$ -26 \AA for mercaptoalkylhydroquinone derivatives. From the equation 5, we have calculated the λ_{os} of 0.85-0.98 eV for H_2Q -SAMs at 273 K. This value does not nearly vary with temperature unless the λ_{op} and λ_s values are temperature independent as the equation 5 implies. The difference between the λ values shown in Table 3 and the λ_{os} for H_2Q -SAMs is *ca.* 0.4 eV. At this moment we cannot discourse that this amount of energy should be equivalent to the λ_{is} value of H_2Q molecule without knowing exactly the nuclear

configurational change. However, H₂Q undergoes substantially large molecular structural changes in nuclear configuration during its proton-coupled redox process: *e.g.* dissociation of two O-H bonds and losing of resonance characteristic of a benzene ring. This configurational change might be responsible for the λ_{is} value of H₂Q moiety in the electroactive SAMs on gold.

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