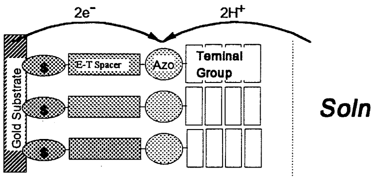
The Effect of Terminal Group on Electron-Transfer Kinetics of Azobenzene Self-Assembled Monolayers on Gold

Hua-Zhong Yu, Yong-Qiang Wang, Sheng-Min Cai, and Zhong-Fan Liu*
Center for Intelligent Materials Research (CIMR), College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

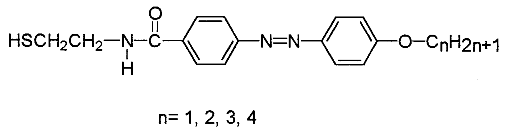
(Received July 3, 1996)

The apparent electron-transfer rates of a new class azobenzene self-assembled monolayers on gold decreased significantly with increasing chainlength of terminal groups. With terminal groups longer than three carbon atoms, no distinguish feature for faradic response was observed.

The electrochemical properties of azobenzene chromophore have attracted considerable interests due to its complex reaction mechanism that involves both ion-transport and structural conformational changes.[1-4] The azobenzene group was introduced into self-assembled monolayers (SAMs), and studied in aqueous medium for the first time by our group recently.[5] As well as the self-assembled monolayers have been widely used in the studies of electron-transfer at electrodes,[6] to study the distance dependence of electron-transfer rate, monolayers having an alkyl chain that separates the electrode surface and redox active groups are often used.[7-9] We present here the electrochemical studies of azobenzene redox center within novel fabricated self-assembled monolayers, which may shed lights in the effect of terminal group on the apparent electron-transfer kinetics (Scheme I).



Thiol-functionalized azobenzene molecules CnAzoC2 (n=1-4) (Scheme II) were prepared by following the similar method as described in Ref. 5.



Modified electrodes were prepared by the following procedure. A well-polished gold disk electrode (0.5 mm in diameter) was immersed in 1mM CnAzoC2/ethanol solutions for 24 h and then rinsed with ethanol. The obtained SAMs modified electrodes were rinsed with high-purified water, following nitrogen air-drying, and then used into electrochemical characterization. Cyclic voltammograms (Hokuto Denko HA-150 Potentiostat; HB-111 function generator; Riken Denshi F-35A X-Y recorder) were measured in deoxygenated aqueous 0.1 M $NaClO_4$, B-R buffer at 25 °C.

All these compounds spontaneously self-assemble into monolayer films on gold electrodes, allowing for the direct comparison of the electrochemical behavior of SAMs of these molecules. However, the electrochemical responses for SAMs of CnAzoC2 (n=1-4) on gold are remarkably different from n=1-3 to n=4, as shown in Figure 1A-1D, respectively. The SAMs of CnAzoC2 (n=1-3) exhibit qualitatively similar well-behaved electrochemical response, which are attributed to a 2e⁻, $2H^+$ reduction of azobenzene chromophores within the monolayer films.[3-5,10,11] However, we can found that: With increased chainlength of terminal group, the huge peak separation between reductive and oxidative waves becomes much larger, as well as the respective peak area.

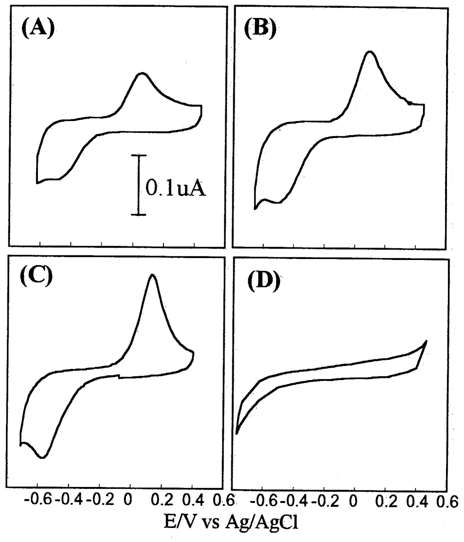


Figure 1. Cyclic voltammograms of CnAzoC2/Au SAMs in B-R buffer, pH 5.5, 0.1M $NaClO_4$, Scan rate: 0.05 V/s. A) C1AzoC2; B) C2AzoC2; C) C3AzoC2; D) C4AzoC2.

As discussed in forthcoming papers,[5] the large separation between reductive and oxidative waves of the azobenzene /hydrazobenzene redox couples suggests the sluggish electron-transfer kinetics, which can be attributed to the following factors: (1) The electron-transfer spacer between redox center and electrode surface; (2) The close-packing SAM structure restricts the structural conformational change of the azobenzene unit which is associated with both electron-transfer and protonation reactions. This restriction may also lead to a decrease of the standard rate constant. In the cases of CnAzoC2 SAMs, the effect of the distance seems to less predominate than the restriction to the conformational change.

For quantitative comparison, we calculated the surface reaction rate constants of these SAMs according to a procedure developed by Laviron.[11] The standard heterogeneous rate constant of electron transfer can be obtained in a straightforward manner from Eqn. 1 and 2 under totally irreversible conditions:

$$E_c = E^{0'} - \frac{RT}{\alpha nF}\ln\left(\frac{\alpha nFv}{RTk_{app}}\right) \qquad (1)$$

$$E_a = E^{0'} + \frac{RT}{(1-\alpha)nF}\ln\left(\frac{(1-\alpha)nFv}{RTk_{app}}\right) \qquad (2)$$

where the notation v means the potential scan rate and R, T and F have their usual meanings. For the respective slopes of the lines E_c~ln(v) and E_a~ln(v) are RT/(αnF) and RT/((1-α)nF), the values of αn and (1-α)n were thus obtained and substituted back in Eqn. 1 and 2 to solve for k_{app}.

The logarithmic rate constants decrease significantly with increased chainlength of terminal group, as shown in Figure 2. For the alkyl chain spacer between redox center and electrode for these SAMs is identical (see Scheme I and II), such a decrease of k_{app} might be understood from structural point of view.

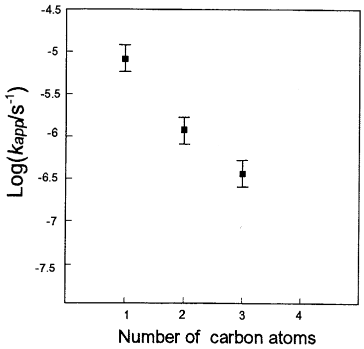


Figure 2. Dependence of log k_{app} on the number of carbon atoms involved in the terminal group of CnAzoC2 SAMs.

On the basis of above considerations, we calculated the surface concentrations of azobenzene moieties for CnAzoC2 (n=1-3) in respective monolayer.[12] They were calculated by area integration of reduction/oxidation peak of corresponding cyclic voltammogram assuming a two electron, two-proton reaction mechanism.[3-5] The order of Γ_{C3} (5.0) > Γ_{C2} (4.2) > Γ_{C1} (3.8×10^{-10} mol/cm^2) indicates that the packing density of monolayers becomes much higher with the increasing of carbon atoms in the terminal group. This was also supported by the double layer capacitance data and the increasing barrier effects of these SAMs on heterogeneous electron transfer of $Fe(CN)_6^{3-/4-}$ in solution to the electrode.

In contrast to the electrochemical reactivity of CnAzoC2 (n=1-3) SAMs, the cyclic voltammogram of C4AzoC2 SAMs did not show any discernible electrochemical waves (Figure 1D). Actually, we have also studied the monolayers derived from azobenzene molecules with much longer terminal groups, such as C5AzoC2, C6AzoC2 and C8AzoC3 etc. The same phenomenon was observed for all of these systems. The smallest double layer capacitance and the greatest barrier effect on heterogeneous electron transfer of the CnAzoC2 (n=1-4) monolayers suggest that the C4AzoC2 SAM has the most tightly packed structure. The surface concentration of C4AzoC2 SAM should be larger than that of C3AzoC2 SAM, and is nearly comparable to alkanethiols adsorbed on Au, which is believed to form the most closely packed and highly ordered monolayers on gold. As a result, the incorporation of charge-compensating ions (H$^+$) into the azobenzene moieties of the SAM would be prohibited,[13,14] which is responsible for the electrochemical inaccessibility of azobenzene groups in C4AzoC2 SAM. Self-assembled monolayers of CnAzoC2 (n=1-3) are more loosely packed with more free volume and disorder than C4AzoC2 SAM on gold, predominantly because of the nature of assembling prope0rties affected by the molecular structure with different terminal groups. This is reflected by that: the less carbon atoms in the terminal group, the lower surface concentration of CnAzoC2 SAM.

In summary, CnAzoC2(n=1-4) molecules self-assemble onto gold surface to form monolayers with different packing-densities, which relates to the structural change and protonation reactions of the azobenzene red-oxidation, and contribute to the unique effect of terminal group on the apparent electron-transfer kinetics. Furthermore, the work clearly shows the potential the azobenzene SAMs as a model system, combining with molecular designing method in investigating the electron-transfer and ion-transportation within highly organized molecular assemblies.

References and Notes

1 S. Wawzonek and J.D. Fredrikson, *J. Am. Chem. Soc.*, 77, 3985(1955).
2 E. Laviron, *J. Electroanal. Chem.*, **42**, 415(1973).
3 E. Laviron and Y Mugnier, *J. Electroanal. Chem.*, **111**, 337(1980).
4 Z.F. Liu, K. Hashimoto, and A. Fujishima, *J. Electroanal. Chem.*, **324**, 259(1992).
5 H.Z. Yu, Y.Q. Wang, J.Z. Cheng, J.W. Zhao, S.M. Cai, H. Inokuchi, A. Fujishima, and Z.F. Liu, *Langmuir*, **12,** 2843 (1996).
6 A. Ulman, An Introduction to Organic Thin Films, From Langmuir-Blodgett to Self-Assembly, Boston, Academic Press. CA. (1991).
7 C.E.D. Chidsey, *Science*, **251**, 919(1991).
8 H.O. Finklea and D.D. Hanshew, *J. Am. Chem. Soc.*, **114**, 3173(1992).
9 R.J. Forster, and L.R. Fualkner, *J. Am. Chem. Soc.*, **116**, 5455(1994), .
10 Z.F. Liu, B.H. Loo, K. Hashimoto, and A. Fujishima, *J. Electroanal. Chem.*, **297**, 133(1991).
11 E. Laviron, *J. Electroanal. Chem.*, **101**, 19(1979).
12 In the calculation of surface concentration, a roughness factor as 2.1 was taken into account to determine the real area of the electrodes.
13 B.R. Herr and C.A. Mirkin, *J. Am. Chem. Soc.*, **116,** 1157(1994).
14 W.B. Caldwell, D.J. Campbell, K.M. Chen, B.R. Herr, C.A. Mirkin, A. Malik, M.K. Durbin, P. Dutta, and K.G. Huang, *J. Am. Chem. Soc.*, **117,** 6071(1995).