

## Electron Transfer Reactions of Methylene Blue at Self-Assembled Monolayer Modified Electrodes

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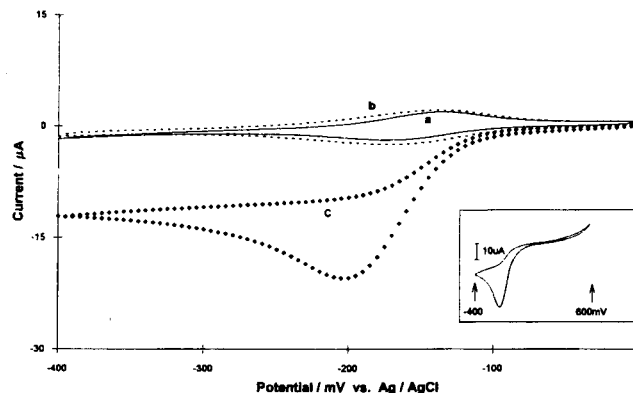
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The uni-directional electron flow between electrodes and redox active materials, in which the presence of intermediate spacer materials prohibits the direct electrical contact between the two, has been of interest since this phenomenon could be utilized in a wide range of examples.<sup>1-5</sup> Murray *et al.*<sup>1</sup> have reported that rectified electron transfer reactions can be applied for the preparation of charge trapping devices, when redox active species are electroactive polymers prepared on judiciously chosen polymer modified electrodes. It was also shown that the direction of electron transfer between the electrode and the redox species in solutions can be controlled by using monolayer modified electrodes generated through either Langmuir-Blodgett<sup>3</sup> or self-assembly methods.<sup>4,5</sup> For instance, Kunitake *et al.*<sup>4</sup> showed that a rectified transmembrane electron transfer from  $\beta$ -NADH to the electrode *via* a  $\pi$ -conjugated electroactive compound with the *o*-quinoidal moiety embedded in an octadecanethiol monolayer. These works have been a concern as rectified electron transfer reactions play an important role in a number of biological systems.<sup>6</sup>

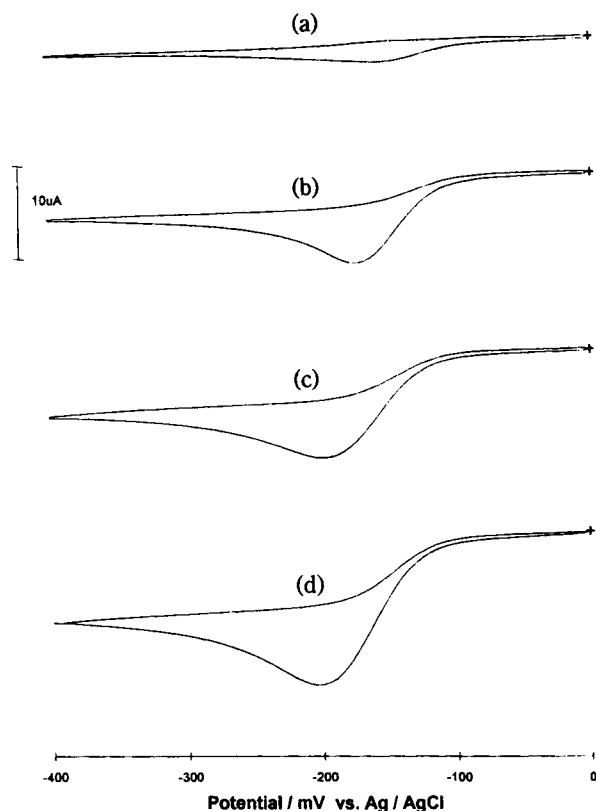
In this communication, we address that electron transfer reactions between 11-mercaptopundecanoic acid ( $\text{HSC}_{10}\text{H}_{20}\text{COOH}$ ) modified Au electrodes and  $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$  redox species in phosphate buffer solutions (pH=7.7). Methylene blue (MB) was embedded in self-assembled monolayers (SAMs) and its electrochemical behaviors in  $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$  solutions were investigated by voltammetry. We chose this system since it is well known that MB can easily penetrate into organic monolayers, but does not directly contact with underlying electrodes,<sup>7</sup> and  $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$  in a solution is electrochemically inactive on SAM modified electrodes. It should be also mentioned that, since MB is well known as a specific intercalation probe with DNA,<sup>8</sup> the elucidation of electrochemical behaviors of MB at electrode-SAM-solution interfaces might provide the possibility of construction of DNA modified electrodes.<sup>9</sup>

SAM was prepared by dipping the Au electrode (Valpey Fisher Co., geometrical area=0.71 cm<sup>2</sup>) for 3 hours into an ethanol solution of 10.0 mM 11-mercaptopundecanoic acid, the synthesis of which was largely based on a procedure by Everett *et al.*<sup>10</sup> SAM modified electrodes were thoroughly washed with a copious amount of 50 mM phosphate buffer and immediately immersed into aq. buffer solutions of 0.1 mM MB (pH=7.7). MB was introduced into the SAM by applying the potential at +0.40 V for 30 min. We found slightly faster MB incorporation under potential application than at open circuit and applied +0.4 V to attain MB saturation quickly. A Pt flag and Ag/AgCl were used as a counter and a reference electrode, respectively.

Figure 1 demonstrates cyclic voltammograms when the MB-embedded SAM electrode is potential switched in buffer solutions containing (a) no redox active species, (b) 1.0 mM  $[\text{Fe}(\text{CN})_6]^{4-}$ , and (c) 1.0 mM  $[\text{Fe}(\text{CN})_6]^{3-}$ . Figure 1a shows the reversible cyclic voltammogram of the MB-embedded SAM when cycled in a buffer solution of pH 7.7 at 50 mV/s. Although electrochemical responses due to incorporation of MB are relatively small, the prolonged exposure of the SAM electrode to MB or the variation of the applied potential during MB-embedding process leads to an identical result, indicating that the small electroactivity does not result from insufficient incorporation of MB into the SAM electrode. The amount of entrapped MB, calculated from the charge during anodic scan, was  $2.0 \times 10^{-11}$  mol/cm<sup>2</sup>. While the electrode, when cycled in 1.0 mM  $[\text{Fe}(\text{CN})_6]^{4-}$ , behaves as in a solution containing no electroactive species (Figure 1b), it experiences *ca.* 10 times enhancement of the cathodic peak current and shows no anodic current of MB in 1.0 mM  $[\text{Fe}(\text{CN})_6]^{3-}$  (Figure 1c). This suggests that leucomethylene blue (LMB), generated at the SAM-solution interface by MB reduction, is rapidly converted to MB through the electron transfer to  $[\text{Fe}(\text{CN})_6]^{3-}$  (electron transfer from electrode  $\rightarrow$  MB  $\rightarrow$   $[\text{Fe}(\text{CN})_6]^{3-}$ ) and the reverse process is prohibited due to depletion of LMB, making the electrode possess the rectified electron transfer property. It should be noted that no  $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$  redox process is seen at *ca.* 0.25 V as in the inset, indicating that Au- $\text{SC}_{10}\text{H}_{20}\text{COO}^-$  monolayers completely block the electron transfer between Au and negatively charged redox active species.



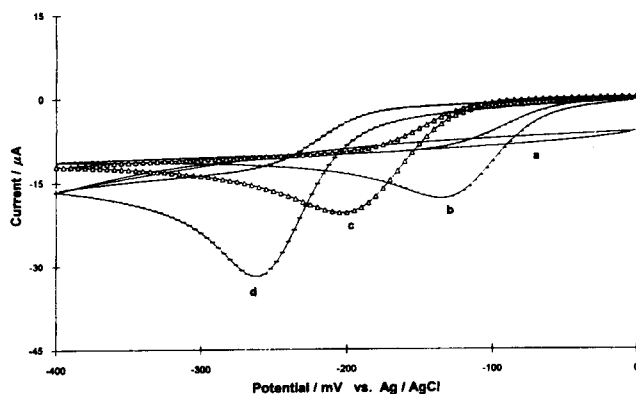
**Figure 1.** Cyclic voltammograms of the MB-embedded SAM at 50 mV/s in buffer solutions (pH=7.7) containing (a) no redox couple, (b) 1.0 mM  $[\text{Fe}(\text{CN})_6]^{4-}$ , and (c) 1.0 mM  $[\text{Fe}(\text{CN})_6]^{3-}$ . Inset shows a cyclic voltammogram of (c) in a wide potential window.



**Figure 2.** Cyclic voltammograms of the MB-embedded SAM at 50 mV/s in buffer solutions (pH=7.7) containing (a) 0.1 mM, (b) 0.5 mM, (c) 0.75 mM, and (d) 1.0 mM  $[\text{Fe}(\text{CN})_6]^{3-}$ .

The enhancement of cathodic currents in  $[\text{Fe}(\text{CN})_6]^{3-}$  was further investigated in solutions of various  $[\text{Fe}(\text{CN})_6]^{3-}$  concentrations. Figure 2 shows voltammograms when the MB-embedded SAM electrode was cycled at 50 mV/s in buffer solutions (pH=7.7) of (a) 0.1 mM, (b) 0.5 mM, (c) 0.75 mM, and (d) 1.0 mM  $[\text{Fe}(\text{CN})_6]^{3-}$ . The catalytic effect of  $[\text{Fe}(\text{CN})_6]^{3-}$  on MB reduction seems to be linearly dependent on the  $[\text{Fe}(\text{CN})_6]^{3-}$  concentration since the cathodic peak currents increase 1.3, 5.7, 7.6, and 11.1 times, compared with the peak current in a  $[\text{Fe}(\text{CN})_6]^{3-}$  free-solution. This fact suggests that the rate of regeneration of LMB involves the diffusional problem of  $[\text{Fe}(\text{CN})_6]^{3-}$  to the SAM-solution interface and the reaction cannot be considered as a pseudo-first order process within the experimental concentration ranges.<sup>11</sup>

The effects of solution pH on the rectified electron transfer were also examined since it was addressed that the reduction of MB involves 2 electrons and 1 proton,<sup>12</sup> resulting in that the formal potential of MB is dependent on the solution pHs. We first obtained cyclic voltammograms on the MB-free SAM in 0.1 mM MB buffer solutions of various pHs. The voltammograms were reversible in between pH 5.6 and 9.0 and showed *ca.* -32 mV/pH shifts as expected for reversible systems ( $E^0 = -130, -195, -240$  mV in 5.6, 7.7, 9.0 pH solutions, respectively). These formal potentials on the SAM are close to the values on bare ( $E^0 = -200$  mV in pH 7.7). In a highly acidic solution, however, the formal potential shifted with a slope of *ca.* -110 mV/pH ( $E^0 = 90$  mV in pH=3.6). This is quite larger than the expected value for



**Figure 3.** Cyclic voltammograms of the MB-embedded SAM at 50 mV/s in 1.0 mM  $[\text{Fe}(\text{CN})_6]^{3-}$  buffer solutions of pH (a) 3.6, (b) 5.6, (c) 7.7, and (d) 9.0.

2 electrons and 1 proton processes, indicative of a different reaction pathway in a low pH solution.

Figure 3 shows cyclic voltammograms of the MB-embedded SAM electrode in 1.0 mM  $[\text{Fe}(\text{CN})_6]^{3-}$  buffer of (a) 3.6, (b) 5.6, (c) 7.7, and (d) 9.0 pHs. Since the formal potential of a  $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$  redox couple is invariant and that of LMB/MB decreased with solution pH, a faster electron transfer from LMB to  $[\text{Fe}(\text{CN})_6]^{3-}$ , which leads to the increase of cathodic currents of MB, can be expected in a basic solution. This trend was shown in Figure 3b through 3d. It should be noted that no electron transfer is likely to occur in a highly acidic solution (Figure 3a), supporting the previous speculation (a different reaction pathway in a low pH solution) since the formal potential of LMB/MB is still lower than that of  $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$  in a solution of pH 3.6.

We believe that the concept explained above can be utilized for the preparation of pH dependent one-directional electron flow electrodes. We are currently investigating the electrochemical behaviors of MB in highly acidic media and will extend the whole concepts to other modified electrodes such as conducting polymers and cation terminated SAMs to examine the possible use of the electrodes as a charge trapping device or the possibility of the DNA modified electrode preparation.

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## Inhibition of Photochemical Processes by a Hydroxyl Group in the Photochemistry of a $\beta,\gamma$ -Unsaturated *o*-Hydroxyphenyl 1,2-Dimethylcyclopent-2-enyl ketone

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The  $\beta,\gamma$ -UKs undergo virtually all types of photochemical processes known for isolated ketones or alkenes as well as two unique processes. The two particular processes result from the presence of an alkenyl group at the  $\beta,\gamma$ -position from a carbonyl chromophore in a single molecule: the [1,3] acyl shift (1,3-AS) and [1,2] acyl shift (1,2-AS) or oxa-di- $\pi$ -methane (ODPM) rearrangement. Direct irradiation usually leads to a new rearranged  $\beta,\gamma$ -UK, which is the result of a 1,3-AS reaction. In contrast, triplet sensitized irradiation usually gives rise to a cyclopropyl ketone, the result of a 1,2-AS or ODPM rearrangement. With regard to the spin multiplicity and configuration of the state from which a reaction occurs, the  $n,\pi^*$  excited singlet state is believed to give the 1,3-AS product in most cases, whereas the 1,2-AS product comes from a  $\pi-\pi^*$  triplet excited state.<sup>2a</sup> It should be noted, however, that the observations about the photorearrangement mentioned above are only generalities and that the specific mechanism for any single ketone may deviate substantially from this simple, approximate description. Quite naturally, a fairly thorough study has been conducted on the substituent effect in  $\beta,\gamma$ -UKs to elucidate the exact nature of the mechanistic behavior of this interesting chromophore.<sup>2</sup> But the effect of a hydroxyl group positioned at the  $\alpha$ -position to the carbonyl, that is believed to play a very crucial role in the polymer photochemistry of UV stabilizers, has not been studied. In the chemistry of light stabilizers such as *o*-hydroxybenzophenone and *o*-hydroxyphenylbenzotriazole, the light absorbing group capable of forming an intramolecular hydrogen bonding would funnel away the light energy absorbed by the chromophore.<sup>3a,b,4</sup> Then one would say that the photochemical outcome of the introduction of a molecular geometry capable of forming a six-membered ring intramolecular hydrogen bonding would be the inactivation of the otherwise photoreactive group. Thus we have chosen two compounds, *o*-hydroxyphenyl 1,2-dimethylcyclopent-2-enyl ketone **1**, and *o*-methoxyphenyl 1,2-dimethylcyclopent-2-enyl ketone **2** to study the effect of intramolecular hydrogen bonding on the photochemistry of  $\beta,\gamma$ -UKs. By comparing the photochemistry of **1** and its non-hydrogen bonding analog **2**, we hoped to clarify the effect of

$\alpha$ -hydroxyl group on the photochemistry of  $\beta,\gamma$ -UKs.

The compounds **1** and **2** were chosen for this study because photorearrangement of this carbon skeleton, as a  $\beta,\gamma$ -unsaturated ketone, had well been established.<sup>5</sup> Thus the comparison of the rearrangemental behavior could be made relatively easily with many other previously studied compounds.<sup>5</sup> The other advantages of selecting this  $\beta,\gamma$ -UK carbon framework, except the ease of syntheses, was that 1,3-AS from the starting ketone **2**, if at all occurred, could readily be detected by NMR. Unlike the starting ketone, the products resulted from 1,3-AS of **1** and **2** would have no vinylic proton. This would help determine the structure of the 1,3-AS product easier. For synthesis, the method of Schaffner and coworkers<sup>5a</sup> was adopted with several modification. Starting from ethyl 2-oxocyclopentanecarboxylate (**3**), the ester was methylated with  $\text{CH}_3\text{I}/t\text{-BuOK}$  (**4**) and then converted to a hydroxy ester with a concomitant introduction of the second methyl group by Grignard reaction with  $\text{CH}_3\text{MgI}$  (**5**). Dehydration was followed to complete the formation of  $\beta,\gamma$ -alkene functionality (**6**). The ester group was then replaced to *ortho*-methoxy- or *ortho*-hydroxyphenyl ketone by sequential reactions of LAH reduction (**7**), oxidation by PDC (**8**), Grignard reaction (**9**), and the second oxidation with PDC. For demethylation at the last step, we have tried a few methods, but  $\text{BBr}_3$  worked best as far as the yield and the neatness of the reaction were concerned. Thus the hydroxyphenyl  $\beta,\gamma$ -UK **1** was synthesized from ethyl 2-oxocyclopentanecarboxylate in 18% overall yield. The structures of all intermediary products along the synthetic schemes were positively identified by NMR and IR.<sup>6</sup> The synthetic scheme is depicted in Scheme 1.

For direct irradiation of *o*-methoxyphenyl 1,2-dimethylcyclopent-2-enyl ketone **2**, the cyclohexane solutions of 0.01 M of **2** were put into Pyrex tubes and photolyzed in the Rayonet Photochemical Reactor using 16 RUL-350 lamps. Progress of the photolysis was followed and analyzed by GC using 30 m HP-1 column and octadecane as an internal standard. Photostationary state was reached in 1.5 h under our reaction condition, which composed of 63% of the starting ketone **2**, 8% of the 1,3-AS product **10**, 5% of an al-