Electrochemical and Quartz-Crystal-Microbalance Transduction of Light-Controlled Supramolecular Interactions at Monolayer-Functionalized Electrodes

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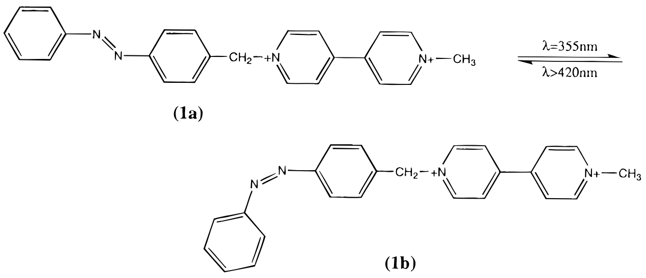
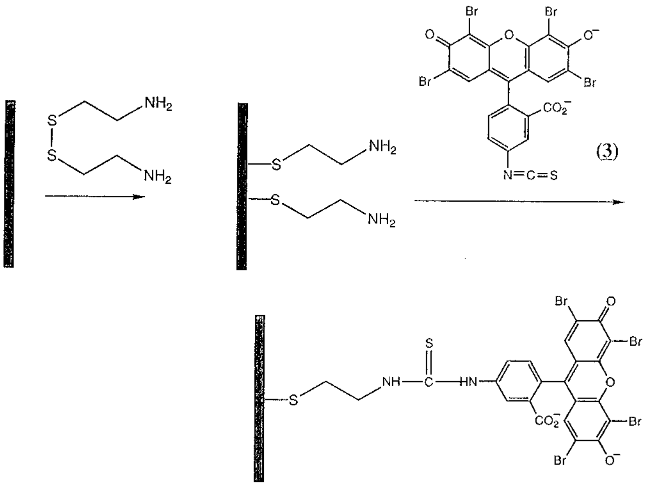
The control of interfacial electron transfer reactions at monolayer-modified electrodes attracted extensive research efforts[1−4] recently. Densely-packed monolayers assembled onto electrode surfaces perturb the electrochemical communication with redox-active compounds solubilized in the electrolyte,[1] where charged monolayers induce the electrostatic control of interfacial electron transfer with charged electroactive substrates.[2,3] The electron transfer rates within redox-active monolayers were shown to depend on the distance separating the electroactive group from the electrode.[4] Receptor-functionalized monolayer electrodes were used to control electron transfer at the electrode interface by complementary association of the substrate to the receptor monolayer.[5,6] For example, a β-cyclodextrin monolayer-modified electrode was applied to concentrate a ferrocene electroactive substrate at the electrode surface by its association to the receptor cavity.[6] The chemistry of donor−acceptor complexes formed between xanthene dyes and *N*,*N*′-dialkyl-4,4′-bipyridinium salts was characterized by us in the solid state and in solution.[7] The xanthene dyes−bipyridinium complexes are stabilized by charge transfer and $\pi-\pi$ interactions as well as electrostatic attraction and exhibit association constants in the range $K_a = 10^3-10^4\ M^{-1}$. By utilizing the photoisomerizable *N*-methyl-*N*′-[4-(phenylazo)benzyl]-4,4′-bipyridinium electron acceptor (**1**), photostimulated formation and dissociation of the donor−acceptor complex with the eosin dye (**2**) were demonstrated.[8] The *cis*-azobenzene−bipyridinium electron acceptor **1b** exhibits high affinity for **2**, while the *trans* isomer **1a** associates only weakly to eosin **2**. The increased affinity of **1b** to eosin was attributed to the high dipole moment (ca. 3.0 D) of the *cis*-azobenzene unit.[8] Here we wish to report on the photostimulated interactions of the azobenzene−bipyridinium electron acceptor **1** with an eosin monolayer-modified Au-electrode. The photoinduced formation and dissociation of the supramolecular complexes between **1** and the eosin monolayer are transduced as amperometric or quartz-crystal-microbalance, QCM, signals. The systems represent a means for the amperometric or QCM transduction of recorded optical signals.



(1a)

(1b)

Scheme 1. Assembly of an eosin monolayer on Au-surfaces



The eosin monolayer was assembled on a Au-electrode or a Au-electrode associated with a quartz crystal (9 MHz),[9] as outlined in Scheme 1. A primary cystamine monolayer[10] was assembled on the Au-electrode and was further modified with eosin isothiocyanate (**3**) to yield the eosin-modified monolayer. By following the frequency changes of the quartz crystal (Δf) upon the stepwise modification of the electrode, we estimate the surface density[11] of the eosin units on the Au surface to be 6.63×10^{-10} mole cm^{-2}.

Figure 1(A) (curve a) shows the cyclic voltammogram of the *trans* isomer (**1a**), in the presence of the eosin-modified monolayer electrode. Figure 1(A) (curve b) shows the cyclic voltammogram of the *cis* isomer (**1b**) in the presence of the eosin-modified electrode. Figure 1(A) (curve c) shows the cyclic voltammogram of **1a** in the presence of a bare, unmodified, Au-electrode. An identical voltammetric wave was observed for **1b** in the presence of the unmodified electrode. These results indicate that the amperometric responses of **1a** and **1b**, corresponding to the one-electron reduction of the bipyridinium units, are enhanced as compared to those of the systems that include the bare electrodes.[12] These results suggest that the eosin monolayer concentrates **1a** or **1b** at the electrode interface due to the formation of a donor−acceptor complex between the xanthene dye and the bipyridinium units. Concentration of the electron acceptor at the electrode surface increases the voltammetric response as compared to that of the

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[11] To correlate the frequency change, Δf, with the mass change, Δm, on the crystal, the Sauerbrey equation $\Delta f = (-2.3 \times 10^{-6}) f_o^2 (\Delta m/A)$ was applied.

[12] The cyclic voltammograms of **1a** and **1b** (4.1×10^{-6} M) at cysteic acid-, cystamine-, or mercaptoethanol-modified Au-electrodes were similar and resemble the cyclic voltammograms of **1a** or **1b** at a bare electrode. These results suggest that electrostatic or hydrophobic interactions cannot account for the different association features of **1a** or **1b** to the eosin monolayer. The eosin monolayer-modified electrode reveals, however, the concentration effect on *N*,*N*′-dimethyl-4,4′-bipyridinium (methyl viologen) as compared to a bare Au-electrode. This indicates that association of **1a** or **1b** to the eosin monolayer electrode results from a specific interaction between the xanthene dye and the bipyridinium units.

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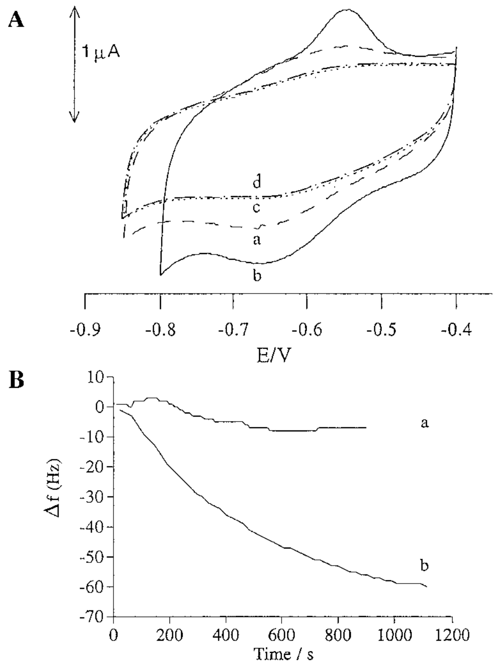

Figure 1. (A) Cyclic voltammograms of (a) **1a** (4.1×10^{-6} M) and (b) **1b** (4.1×10^{-6} M) at an eosin-modified Au-electrode and (c) **1a** (4.1×10^{-6} M) and (d) **1b** (4.1×10^{-6} M) at a bare non-modified Au-electrode. All experiments were recorded in 1 mM aqueous KCl solution at a scan rate of 50 mV s^{-1}. A gold wire working electrode ($A \approx 0.2$ cm^2) and SCE reference electrode were used. (B) Frequency changes of the eosin-modified quartz crystal in the presence of (a) **1a** (1.82×10^{-5} M) and (b) **1b** (1.82×10^{-5} M). Data recorded by the injection of 100 μL of a concentrated **1a** or **1b** solution into the QCM cell that includes 1 mL of water.

unmodified electrodes. The amperometric response of the *cis*-azobenzene−bipyridinium electron acceptor (**1b**) is substantially higher than that of the *trans* isomer (**1a**). The higher amperometric response of the eosin-monolayer electrode in the presence of **1b** is attributed to the higher association constant of *cis*−azobenzene-bipyridinium (**1b**) to eosin.[8] The higher association constant of **1b** to the monolayer components increases its concentration at the electrode interface as compared to that of **1a**. The amperometric responses of the eosin-modified electrode can be reversibly cycled by photochemical isomerization of **1**. In the presence of **1b**, generated by a Nd-Yag pulse irradiation ($\lambda = 355$ nm) of the **1a** in the electrolyte solution, a high amperometric response is observed. Irradiation of the **1b** solution ($\lambda > 420$ nm (150 W Xe lamp)) gives **1a** and results in a low amperometric response of the electrode. Further isomerization of the **1a**-electrolyte solution ($\lambda = 355$ nm) restores **1b** and the high amperometric response of the eosin-monolayer electrode. Figure 2(A) shows the cyclic amperometric responses of the modified electrode upon reversible isomerization of the electron acceptor between states **1a** and **1b**.

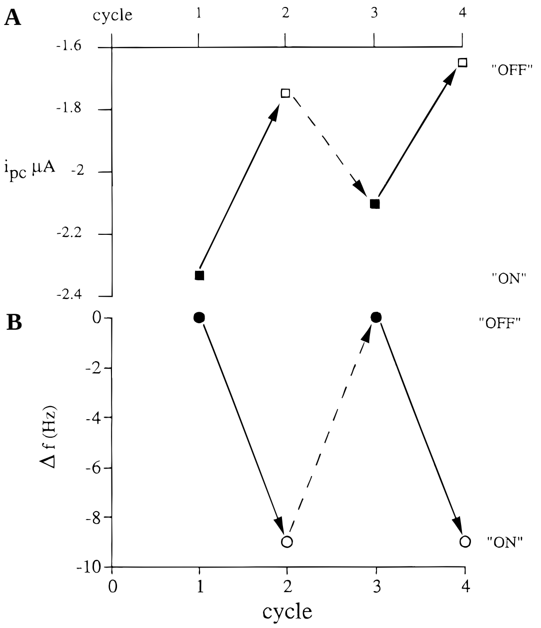

Figure 2. (A) Cyclic amperometric responses of the eosin-monolayer Au-electrode upon photoisomerization of the guest substrate: in the presence of (□) **1a** and (■) with **1b**. Data extracted from the cathodic peak currents of the cyclic voltammograms with [**1a**] and [**1b**] = 1×10^{-5} M. **1a** or **1b** was photogenerated in the electrolyte solution in the absence of the monolayer electrode. (B) Reversible frequency changes of the eosin-modified QCM upon photoisomerization of the guest substrate: in the presence of (●) **1a** (5×10^{-6} M) and 1 mM KCl and (○) **1b** (5×10^{-6} M) and 1 mM KCl. Data were recorded in a QCM cell equipped with a flow system. **1a** or **1b** was produced photochemically in an external reservoir and pumped into the cell for each of the measurements. Between any two measurements, the QCM electrode was washed with a 1 mM KCl solution.

The different association properties of **1a** and **1b** to the eosin-modified monolayer are clearly evident from the QCM experiments shown in Figure 1(B). The frequency change of the quartz crystal in the presence of **1a** is minute (curve a), implying very little association of **1a** to the monolayer. The frequency change of the crystal in the presence of **1b** is high, implying a substantial mass change as a result of its association to the monolayer. From the frequency change (Δf) we estimate the surface density[11] of **1b** in the monolayer array to be 6.64×10^{-10} mole cm^{-2}. Photochemical isomerization of **1a** ($\lambda = 355$ nm) in the presence of the eosin-monolayer-modified quartz crystal results in the observed frequency decrease. Nonetheless, upon cyclic photoisomerization of the electron acceptor between states **1a** and **1b**, the crystal frequency could not be switched between the two values.[13] Note, however, that the QCM experiment is performed at zero ionic strength in contrast to the electrochemical experiments where the electrolyte concentration is [KCl] = 1×10^{-3} M. As the association constant of the donor−acceptor complex is strongly dependent on the ionic strength, we attribute the lack of switchable frequency changes in the QCM experiment to the tight association of **1b** to the monolayer. Indeed, when the QCM experiment was performed at the identical conditions employed in the electrochemical experiments, [KCl] = 1×10^{-3} M, reversible piezoelectric transduction of the formation or dissociation of the supramolecular complexes between **1** and the monolayer-modified crystal was detected (Figure 2(B)). In the presence of **1a**, a minute frequency change is detected, implying that **1a** is almost not associated with the eosin monolayer. Photoisomerization ($\lambda = 355$ nm) of **1a** to **1b** yields a frequency decrease indicating the association of **1b** to the monolayer. Note, however, that the frequency change at this ionic strength is only $\Delta f = 9$ Hz (corresponding to a surface density of 9.65×10^{-11} mole cm^{-2}). Thus, the association of **1b** to the eosin monolayer is perturbed upon increasing the ionic strength of the medium.

In conclusion, we demonstrated that an eosin-monolayer-modified electrode or quartz crystal provides active interfaces for the amperometric or QCM transduction of light-stimulated formation or dissociation of supramolecular complexes formed at the functionalized surfaces. The assemblies represent novel optoelectronic systems for the physical transduction of recorded optical signals.

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[13] Interaction of the bare QCM crystal with **1a** or **1b** (1.82×10^{-5} M) did not yield any noticeable frequency changes ($\Delta f = \pm 2$ Hz), indicating that no adsorption of **1a** or **1b** to the bare crystal occurs.