Photoswitching of a Vectorial Electron Transfer Reaction at a Diarylethene Modified Electrode

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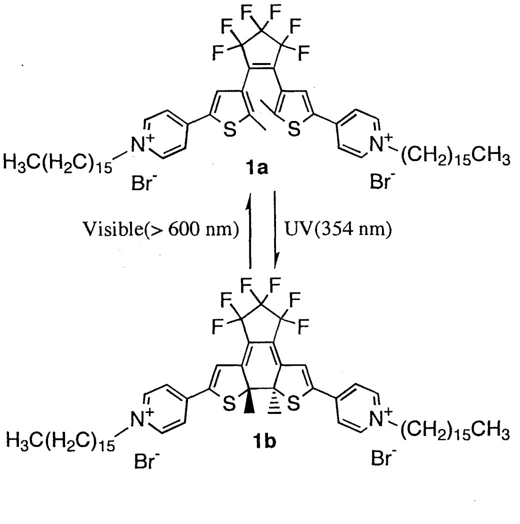
We describe here the construction of a diarylethene modified electrode system in which the photoswitchable vectorial electron-transfer from the electroactive diarylethene on the electrode to hexacyanoferrate(III) in solution is possible.

The construction of stimuli-responsive electron-transfer electrode devices is of interest and of a progressing research project. Willner and coworkers described the photoswitchable electrochemical communication between the electrode and cytochrome *c*[1] at a self-assembled monolayer of a photoisomerizable spiropyran as well as the light-controlled biocatalyst for amperometric transduction of recorded optical signals at a spiropyran-containing glucose oxidase monolayer electrode.[2] We have shown that the tuning of lipid bilayer fluidity between crystal-to-liquid crystal phases regulates the vectorial electron transfer from a flavin embedded in the Langmuir-Blodgett film of a synthetic lipid on a gold electrode to hexacyanoferrate(III) in solution[3] as well as the regulated catalytic electron transfer reaction of glucose oxidase immobilized on a lipid cast film on an electrode.[4]

We describe here, for the first time, photoswitching of the vectorial electron transfer through a photochromic compound bearing a redox group immobilized on an electrode to electroactive species in solution. A diarylethene compound with light-controlled redox active function was chosen for the purpose. 1,2-Diarylethenes with heterocyclic rings are photochromic compounds with high photofatigue resistance and have a potential for the application to optical memory media.[5-6] The light-controlled redox tuning of diarylethenes dissolved in organic solvents were described by Lehn and coworkers.[7-8] We have recently developed an electrode modified with a diarylethene compound (**1**) and a synthetic lipid which possesses light-triggered optical (scheme 1) and electrochemical switching function.[9]

Scheme 1.



The preparation procedure of a diarylethene-modified electrode is as follows. A gold disk electrode (Bioanalytical Systems, diameter 1.6 mm) was polished well with an alumina slurry (Beuhler) of 0.3 and subsequently 0.05 μm, and sonicated in pure water, 0.5 mol dm^{-3} HNO$_3$ and then pure water to remove the alumina particles. The electrode thus prepared was immersed in 1.0 mmol dm^{-3} n-octadecanethiol in acetonitrile for 4 min and then rinsed with acetonitrile. A five microliter portion of

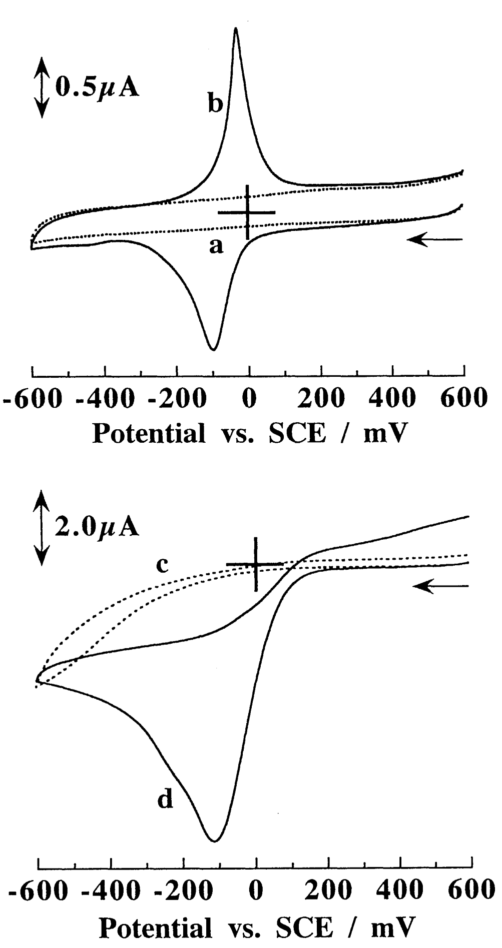


Figure 1. Cyclic voltammograms for a **1** cast film on a self-assembled monolayer of n-octadecanethiol on a gold electrode at 100 mVs^{-1} in the absence (a , b) and presence (c , d) of 2.0 mM K$_3$[Fe(CN)$_6$] in 0.1 M KCl at 25 °C. Solid lines : after UV light irtradiation (1 min). Dotted lines : after visible light irradiation (60 min).

chloroform solution of **1** (1.0 mmol dm^{-3}) was placed on the modified electrode surface, followed by the solvent evaporation. Cyclic voltammograms using an electrochemical analyzer (BAS-100B, Bioanalytical Systems) were measured in deoxygenated aqueous KCl (0.1 mol dm^{-3}) solution at 25 °C upon alternating irradiation of UV and visible light.[10]

Photoswitching of the electron transfer of **1** on the electrode is shown in Figure 1 (traces a and b). UV light irradiation gives a well-defined surface wave-like cyclic voltammogram[11] with the formal potential of - 65 mV vs. SCE that is attributable to the redox couple of the closed form of **1** (scheme 1). Visible light irradiation on the modified electrode, on the contrary, results in no redox current in the measured potential range. This behavior resembles the reported result.[9]

Mediated electron transfer to hexacyanoferrate(III) *via* **1** on the electrode was examined. The result is shown in Figure 1 (traces c and d). The direct electron transfer of $[Fe(CN)_6]^{3-/4-}$ with the underlying electrode is inhibited in this system. It is evident by the comparison between traces b and d in Figure 1 that after UV light irradiation, the presence of hexacyanoferrate(III) induces catalytic waves due to the reduction of hexacyanoferrate(III) mediated by surface-confined **1b**.[12] No such mediation current was observed after visible light irradiation. Alternating irradiation of UV and visible light revealed that on-off light-controllable vectorial electron transfer was possible, though repeated UV irradiation caused gradual decrease in the mediation current which might be due to the instability of the reduced form of **1b**.

In conclusion, we demonstrated, for the first time, a light-controlled vectorial electron-transfer reaction at the diarylethene modified electrode. Intense effort is currently under way in our laboratory to develop diarylethene-based light-controlled vectorial electron-transfer systems with high photo-fatigue resistance.

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10 The light source was a 500 W Xenon lamp (Ushio UI-501C). UV- and visible light irradiation were conducted by passing the light through a visible absorbing filter (Toshiba R- 60) or a UV-absorbing filter (Toshiba UV-D33S), respectively.
11 The surface coverage of **1b** calculated fron the CV peak area was 7×10^{-12} mol / cm^2.
12 The electron transfer from the reduced form of **1b** to $[Fe(CN)_6]^{3-}$ is downhill by 145 mV.