A β-amino-cyclodextrin monolayer-modified Au electrode: a command surface for the amperometric and microgravimetric transduction of optical signals recorded by a photoisomerizable bipyridinium–azobenzene diad

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A β-cyclodextrin monolayer assembled onto Au electrodes acts as an active interface for the electrochemical and microgravimetric transduction of optical signals recorded by a bipyridinium–azobenzene diad.

Molecular electronic and optoelectronic devices are the subject of recent extensive research efforts.[1,2] Electrical triggering of molecular functions and physical transduction of the activated chemical functionality provide the grounds for molecular electronic systems.[3,4] Photonic or optical triggering of molecular functions and transduction of the light-activated chemical functionality represent the basic features of molecular optoelectronics.[5,6] Photochemical activation of the formation or dissociation of donor–acceptor complexes in the presence of photoisomerizable electron acceptors[7] or light-induced molecular isomerization into a redox-active photoisomer state[5] allows the spectroscopic or electrical transduction of the recorded optical signals. To design molecular electronic or optoelectronic devices integration of the molecular assembly with a transducing element (surface) is essential. Functionalized monolayers assembled onto electrode surfaces were applied as active interfaces for sensing,[8] concentration of redox-active compounds[9] and discrimination of molecular redox activities at electrode surfaces.[10] Recently, the assembly of functionalized photoisomerizable monolayers onto electrode surfaces enabled the amperometric and piezoelectric transduction of optical signals recorded by the monolayer.[11–13] Here, we report on the use of a β-amino-cyclodextrin monolayer-modified Au electrode as a command surface for electrochemical transduction of optical signals, recorded by *N*-methyl-*N*′-[1-phenylazobenzyl]-4,4′-bipyridinium **1**.

N-Methyl-*N*′-[1-phenylazobenzyl]-4,4′-bipyridinium exhibits reversible photoisomerizable properties. Irradiation of *trans-N*-methyl-*N*′-[1-phenylazobenzyl]-4,4′-bipyridinium **1t**, λ = 355 nm, yields the *cis* isomer **1c**† and further irradiation of **1c**, λ > 375 nm, regenerates the **1t** state. The two photoisomers reveal different association features to **2**. The association constants of **1t** and **1c** to **2** were determined spectroscopically by following the absorbance changes at λ = 420 nm, and correspond to K_a = 1700 and 180 $\mathbf{m}^{-1}$, respectively.

A primary monolayer of thiopropionic acid-active ester was assembled onto the electrode followed by coupling β-amino-cyclodextrin[14] **2** to the functionalized surface (Scheme 1).[15] The **2**-functionalized monolayer electrode acts as a command interface for the amperometric or microgravimetric quartz crystal microbalance (QCM) transduction of optical signals recorded by the photoisomerizable diad **1**.‡ Fig. 1 shows the cyclic voltammograms of **1t** and **1c** in the presence of the **2**-modified electrode. A high amperometric response corresponding to the one-electron reduction of the bipyridinium redox-active unit is observed for **1t** while the redox wave for **1c** is substantially lower.§ The peak currents of the redox waves of **1t** and **1c** show a linear relation with the scan rates ($i \propto \nu$ for $\nu \leqslant 3$ V s^{-1}) implying that the redox waves originate from surface-confined redox-active species. Control experiments at a bare Au electrode reveal that **1t** and **1c** yield under the same conditions identical, very weak, redox waves. The enhanced electrical responses of the photoisomerizable diad in the presence of the **2**-monolayer-modified electrode are attributed to its concentration at the electrode interface by association to

1t

λ>375 nm ⇅ λ = 355 nm

1c
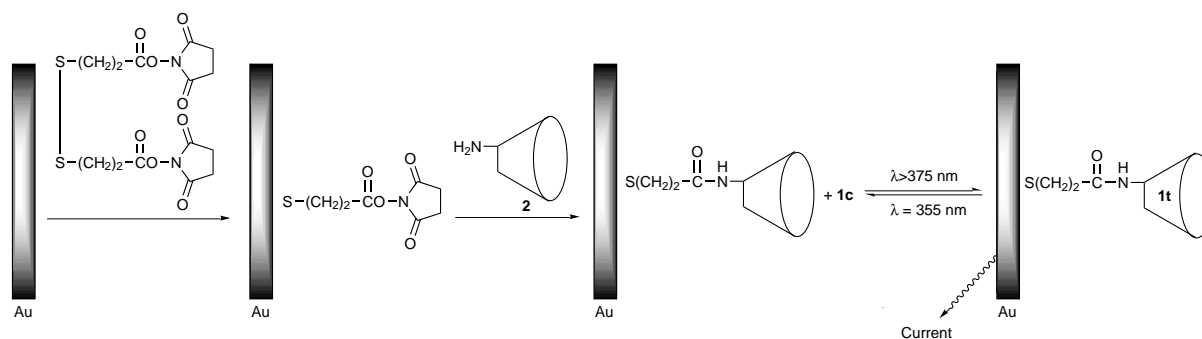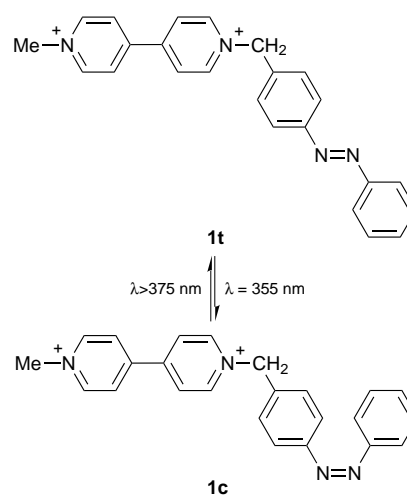
Scheme 1 Assembly of the **2** monolayer onto Au surfaces

the cyclodextrin cavity. The photoisomer **1t** exhibits high affinity for **2** and yields a high amperometric response. The photoisomer **1c** exhibits a low association constant to the receptor sites and results in a low redox signal. Coulometric analysis of the redox waves of **1t** and **1c** implies surface coverages of the functionalized cyclodextrin by **1t** and **1c** that correspond to 2.7×10^{-11} and 1.5×10^{-11} mol cm^{-2}, respectively. These values are consistent with the surface coverages evaluated by the microgravimetric experiments. By reversible photoisomerization of the diad between the states **1t** and **1c**, cyclic high and low amperometric signals are transduced from the system (inset, Fig. 1).

Microgravimetric analysis of the association of **1t** to the **2** interface and the dissociation of **1c** from the functionalized monolayer using a quartz crystal microbalance provides a further means for the electronic transduction of the recorded optical signals.[16] The Au electrodes associated with a quartz crystal (9 MHz) were modified by the **2** monolayer as described in Scheme 1. Fig. 2 shows the crystal frequency changes upon its interaction with **1c** and **1t** [curves (*a*) and (*b*), respectively]. A high frequency change of $\Delta f = -11 \pm 1$ Hz is observed for **1t**, while a substantially lower frequency change, $\Delta f = -5 \pm 0.5$, is detected for **1c**. These results clearly demonstrate that **1t**
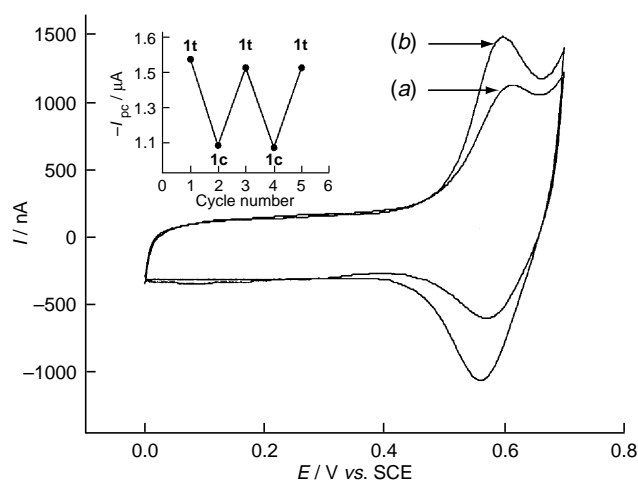
associates to the **2** receptor interface while **1c** reveals a substantially lower affinity for the monolayer electrode. From the frequency changes observed upon interaction of photoisomers **1t** and **1c** with the **2**-monolayer electrode, and by the application of the Sauerbrey equation [eqn. (1), where Δf is the crystal frequency change upon changing the crystal mass by Δm, and A is the surface area], the surface densities of **1t** and **1c** on the monolayer electrode are estimated to be 2.8×10^{-11} and 1.3×10^{-11} mol cm^{-2}, respectively.¶ By cyclic photoisomerization of the diad between the states **1t** and **1c**, reversible high- and low-frequency changes of the modified quartz crystal are observed [Fig. 2 (inset)].

$$\Delta f = (-2.3 \times 10^{-6}) f_0^2 (\Delta m / A) \qquad (1)$$

$$\text{—}\beta\text{-CD} \; + \; \begin{matrix} \textbf{1t} \\ \text{or} \\ \textbf{1c} \end{matrix} \; \rightleftharpoons \; \text{—}\beta\text{-CD} \bullet \bullet \bullet \begin{matrix} \textbf{1t} \\ \text{or} \\ \textbf{1c} \end{matrix} \qquad (2)$$

In conclusion, we have demonstrated that the β-amino-cyclodextrin-modified Au electrodes or piezoelectric crystals provide active interfaces for electronic transduction of optical signals recorded by the photoisomerizable electroactive bipyridinium–azobenzene diad **1**.

Footnotes

† A photostationary state corresponding to 92% of **1c** is formed.
‡ Microgravimetric QCM analysis of the modified monolayer indicates a surface coverage of $(4.7 \pm 0.1) \times 10^{-10}$ mol cm^{-2} of β-amino-CD.
§ As the **1c** state represents a photostationary state where *ca*. 8% of **1t** is present (*ca*. 90 nA) of the total current response of **1c** (1.12 μA) is attributed to residual **1t** in the system.
¶ By following the frequency changes of the β-amino-CD modified crystal at different bulk concentrations of **1t** and **1c**, the association constants of the two photoisomers to the monolayer receptor sites, [eqn. (2)] were estimated to be $K_a(\textbf{1t}) = 7000$ m^{-1} and $K_a(\textbf{1c}) = 3000$ m^{-1}.

Fig. 1 Cyclic voltammograms of (*a*) [**1c**] = 1×10^{-6} **m** and (*b*) [**1t**] = 1×10^{-6} **m** in 0.01 **m** phosphate buffer, pH = 10.8, scan rate 100 mV s^{-1}, $T = 25$ °C. Inset: Cyclic cathodic responses of the **2**-monolayer electrode measured at 0.6 V upon reversible photoisomerization of the diad between **1t** and **1c**, respectively.
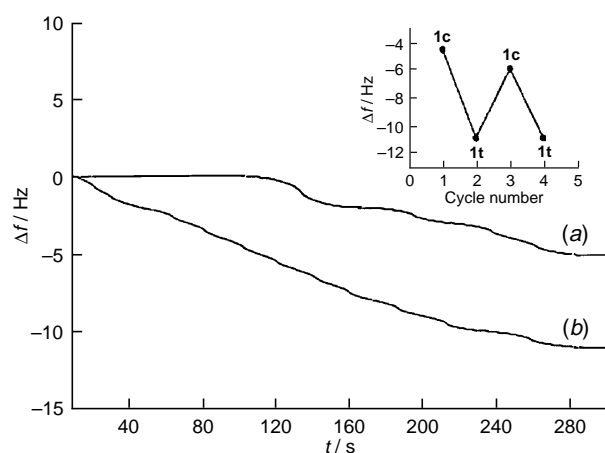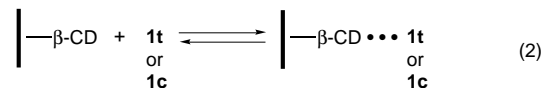

Fig. 2 Frequency changes of the **2**-modified quartz crystal upon interaction with: (*a*) [**1c**] = 3×10^{-6} **m**; (*b*) [**1t**] = 3×10^{-6} **m**. Inset: cyclic frequency changes of the crystal upon reversible photoisomerization of the diad between state **1c** and **1t**, respectively. Frequencies are measured after 300 s of interaction of the crystal with the respective isomer. Experiments were performed in an aqueous environment.

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