take place when **a**$_1$ was used with dissolved ethylenediamine (the homogeneous analogue of **b**$_1$). Additional blank reactions were the treatment of 2-iodoethylbezene with **a**$_1$, which resulted in no reaction,[16] and the treatment of anisole and styrene with undoped silica sol–gel, to ensure that the acidity of the silica does not activate the alkylation reaction (which indeed it does not). Possible leaching was tested by refluxing **a**$_1$ or **b**$_2$ in benzene for 2 h, followed by extraction with water; the pH of the water was 7 in both cases which indicates that no leaching of the acid or base occured.

In conclusion, we have demonstrated a convenient approach for carrying out different reactions which require acids and bases in one pot. It is a general method, as the accumulated experience with doped sol–gel materials shows that *any* acid or base can be used, and this method leads the way to the simultaneous utilization of many other opposing reagents in various combinations.

Experimental Section

Preparation of the entrapped reagents: Nafion was entrapped in silica sol–gel at 13 % (by weight) following the procedure in ref. [9].

Sol–gel entrapment of the molibdic acid: Tetramethoxyorthosilicate (TMOS, 13 mmol), H_2O (0.33 mL, 18 mmol), HCl (0.09 mL; 0.04 M), and MeOH (2 mL, 49 mmol) were stirred at 40 °C for 6 h. To this solution was added a mixture of molibdic acid (0.06 g, 0.37 mmol), NH_4OH (0.1 mL, 25 %), and H_2O (2 mL). Gelation occurred within a few minutes. The resulting gel was dried at 180 °C for 16 h, then washed with water, sonicated twice in benzene for 20 min, and then dried again at 180 °C for 6 h, resulting in 0.84 g of the ceramic material. Preparation of the covalently entrapped bases was by the procedures in refs. [11, 12], at a 20 % molar loading.

Reaction pair I: **a**$_1$ (1.0 g) and **b**$_1$ (1.2 g) were suspended in dry benzene (5.0 mL). Pinacol (1.8 g, 1.5 mmol) was added and the mixture was then heated at reflux under N_2 for 30 min. Malononitrile (0.20 g, 3.0 mmol) was then added and the reflux continued for 7 h. Conversion of the pinacol was quantitative (100 %), out of which 83 % underwent alkylation/dehydration to $(CH_3)_3CC(CH_3){=}C(CN)_2$. A second run with the recovered catalysts resulted in a 76 % overall yield.

Reaction pair II, **b**$_2$/**a**$_1$ combination: **a**$_1$ (1.0 g), **b**$_2$ (0.9 g), 2-iodoethylbezene (0.35 g, 1.5 mmol), and anisole (0.16 g, 1.5 mmol) of were placed in dry benzene (5.0 mL) and the mixture heated at reflux under N_2. The reaction was stopped after 4 h at 32 % conversion yielding $4\text{-}MeOC_6H_4CH(CH_3)C_6H_5$ and $2\text{-}MeOC_6H_4CH(CH_3)C_6H_5$ in a 5:1 ratio.

The **b**$_1$/**a**$_2$ combination: under similar conditions to those above **a**$_2$ (0.84 g), **b**$_1$ (1.2 g), 2-iodoethylbenzene (0.35 g, 1.5mmol), anisole (0.16 g, 1.5 mmol), 4 h reflux) proceeded as well, although at a lower conversion of 21 % with a 3.5:1 product ratio. (It seems that the base **b**$_2$ is superior to **b**$_1$ because the latter may undergo some competitive N alkylation). All products in this report are known and were identified and characterized by standard techniques (NMR spectroscopy, gas chromatography (GC), and GC-mass spectrometry (GC-MS)).

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Photonic Transduction of a Three-State Electronic Memory and of Electrochemical Sensing of NADH by Using Surface Plasmon Resonance Spectroscopy**

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Signal-triggered switching of the functionalities of molecular,[1, 2] macromolecular,[3] or biomolecular systems[4, 5] has been suggested as a means to develop chemistry-based memory devices. Photonic,[6] electrochemical,[7] magnetic,[8] pH,[9] or thermal signals[10] can be used to switch molecular redox or optical functions. Phase transitions or random-coil/helix transformations of polymers are stimulated by temperature,[11] pH,[12] chemical,[13] electrical,[14] and photonic signals.[15] Similarly, enzyme transformations,[16] substrate–receptor complexes,[17] or double-stranded DNA interactions[18] are switched by photonic signals. The conversion of "ON"–"OFF" switchable chemical functionalities into memory devices requires, however, the integration of the chemical systems with surfaces such that the triggered functionality and the recorded information are transduced, without erasure of the encoded information. Advances in the field demonstrated the electronic transduction of photonically activated molecular redox functions on electrodes[19] or light-stimulated bioelectrocatalytic transformations on electrodes,[20] and also,

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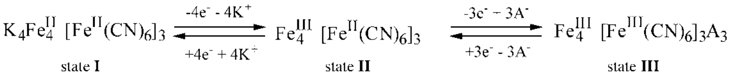
photonic[21] or mechanical[22] transduction of the electrochemically triggered redox functions of polymers. Here we report a chemical assembly that acts as a three-state switchable memory device. The electronic information of the three states is photonically transduced using surface plasmon resonance (SPR).[23] We also demonstrate that the redox-active film acts as an electrocatalyst for the oxidation of 1,4-dihydronicotinamide adenine dinucleotide (NADH). Surface plasmon resonance as well as amperometric measurements allow the quantitative analysis of NADH at the modified surface.

Prussian Blue (PB) is an inorganic, insoluble, three-dimensional polymer that exhibits three redox states [Eq. (1)].[24] PB-modified electrodes were previously investigated as electrocatalytic interfaces,[25] as electrochromic,[26] and photoresponsive[27] materials. Usually, electrochemical deposition of PB is performed on a graphite electrode. At neutral pH the cyclic voltammogram of the resulting material has two distinct redox waves.[28] Direct electrodeposition of PB onto a bare Au-electrode was performed under acidic conditions (pH 1.5), which leads to an unstable redox film with a single quasi-reversible redox wave in the cyclic voltammogram.[29] Primary functionalization of the Au-electrode with cysteic acid ($HS(CH_2)_2CO_2H$), followed by the electrodeposition of PB (10 cycles, 100 mV s^{-1}, between -0.2 V and 1.3 V vs. an Ag-quasi-reference electrode in the presence of 0.1M $K_3[Fe(CN)_6]$ and 0.1M $FeCl_3$, pH 7) yields, however, a stable film of PB. The film displays, at neutral conditions (0.1M KNO_3, pH 7), two redox waves, $E_1^{\circ} = 0.0$ V and $E_2^{\circ} = 0.72$ V (Figure 1 A; vs. Ag-quasi-reference electrode), which correspond to the transitions between the states designated II/I and III/II, respectively, in Equation (1). Thus, at a potential of $E = 0.3$ V the film exists in the PB configuration, state II. Switching the potential to $E = -0.2$ V transforms the film to state I, whereas the application of $E = +0.9$ V yields the fully oxidized state III.



$$\underset{\text{state I}}{K_4Fe_4^{II}\,[Fe^{II}(CN)_6]_3} \underset{+4e^- + 4K^+}{\overset{-4e^- - 4K^+}{\rightleftarrows}} \underset{\text{state II}}{Fe_4^{III}\,[Fe^{II}(CN)_6]_3} \underset{+3e^- - 3A^-}{\overset{-3e^- - 3A^-}{\rightleftarrows}} \underset{\text{state III}}{Fe_4^{III}\,[Fe^{III}(CN)_6]_3A_3} \qquad (1)$$

The SPR Kretschmann-type spectrometer "BIOSUPLAR-2" (light-emitted diode light source $\lambda = 670$ nm) and the Au-covered glass slides (20 × 20 mm) from "Analytical μ-Systems" (Germany) were used in this work. Figure 1 B shows the SPR spectra of the in situ electrochemically generated three redox-states of the film. Substantially different SPR spectra are observed for the three states, and as the thickness of the films is almost unaffected by the redox-state (see below) the different SPR curve may be attributed to changes in the refractive indexes of the polymers in the different redox states. The experimental SPR spectra of the PB film were fitted to the theoretical curves based on five-phase Fresnel calculations using the Neelder–Mid algorithm of minimization.[30] The computer fitting of the SPR spectra was performed primarily for the state II (curve b, Figure 1 B) using the known refractive index, $n_{re} = 1.45$, $\lambda = 670$ nm (n_{re} = real component of the refractive index).[29] The derived thickness of the inorganic film is about 80 nm. The complex refractive indexes of the film in state I ($n_{re} = 1.435$, $n_{im} = 0.020$; n_{im} = imaginary component of the refractive index) and state III ($n_{re} = 1.421$, $n_{im} = 0.044$), were calculated by assuming the same PB-film thickness in all three states. Coulometric analysis of the charge associated with the electrodeposition of the film indicates a thickness of approximately 80 nm taking into account the film density 2.6 g cm^{-3},[31] in good agreement with the value obtained from the SPR spectrum.

Figure 2 A (panel 1) shows the sequence of multistep chronoamperometric transients applied in situ on the PB film, switching the electrode potential between the semi-oxidized state II, $E = 0.3$ V, and the reduced state I, $E = -0.2$ V. The electrochemical switching is transduced by following the changes in the reflected light intensities in the SPR spectra at a fixed angle of $\theta = 69.5°$, Figure 2 A (panel 2). The reversible change in the SPR signal is observed upon alteration of the potential applied to the electrode. Figure 2 B (panel 1) shows the

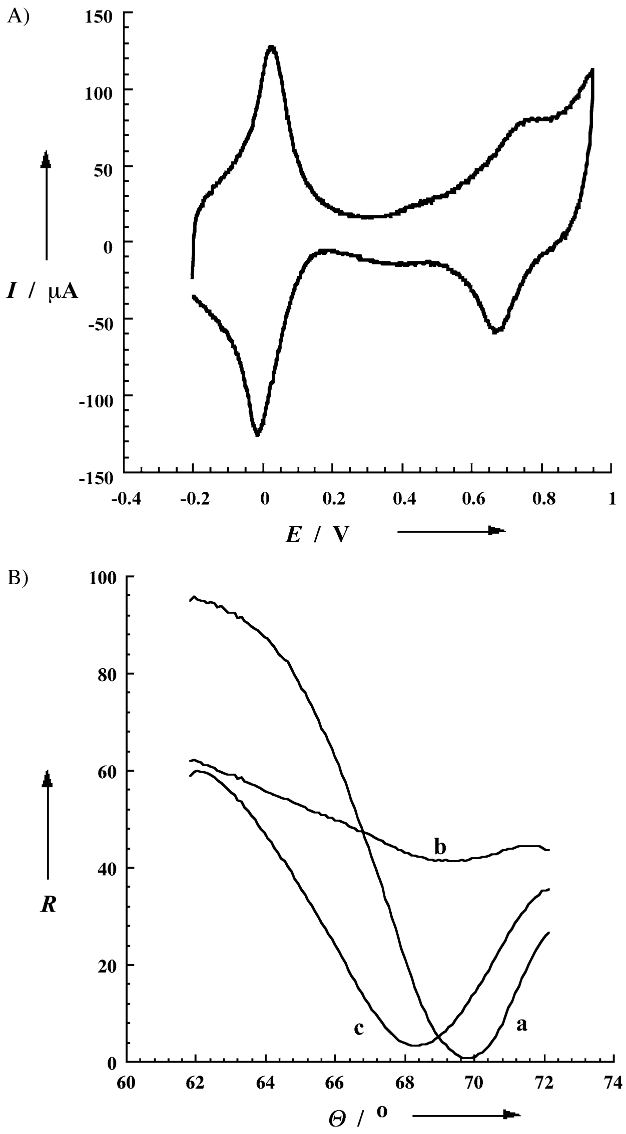


Figure 1. A) The cyclic voltammogram of the PB-functionalized Au-coated SPR slide recorded in 0.1M KNO_3, pH 7.0, potential scan rate 100 mV s^{-1}. B) SPR spectra measured for the PB-modified Au-surface in the presence of 0.1M KNO_3, pH 7.0, upon application of different potentials and the generation of the different redox states of the film: a) -0.2 V, state I, b) 0.3 V, state II, c) 0.9 V, state III.

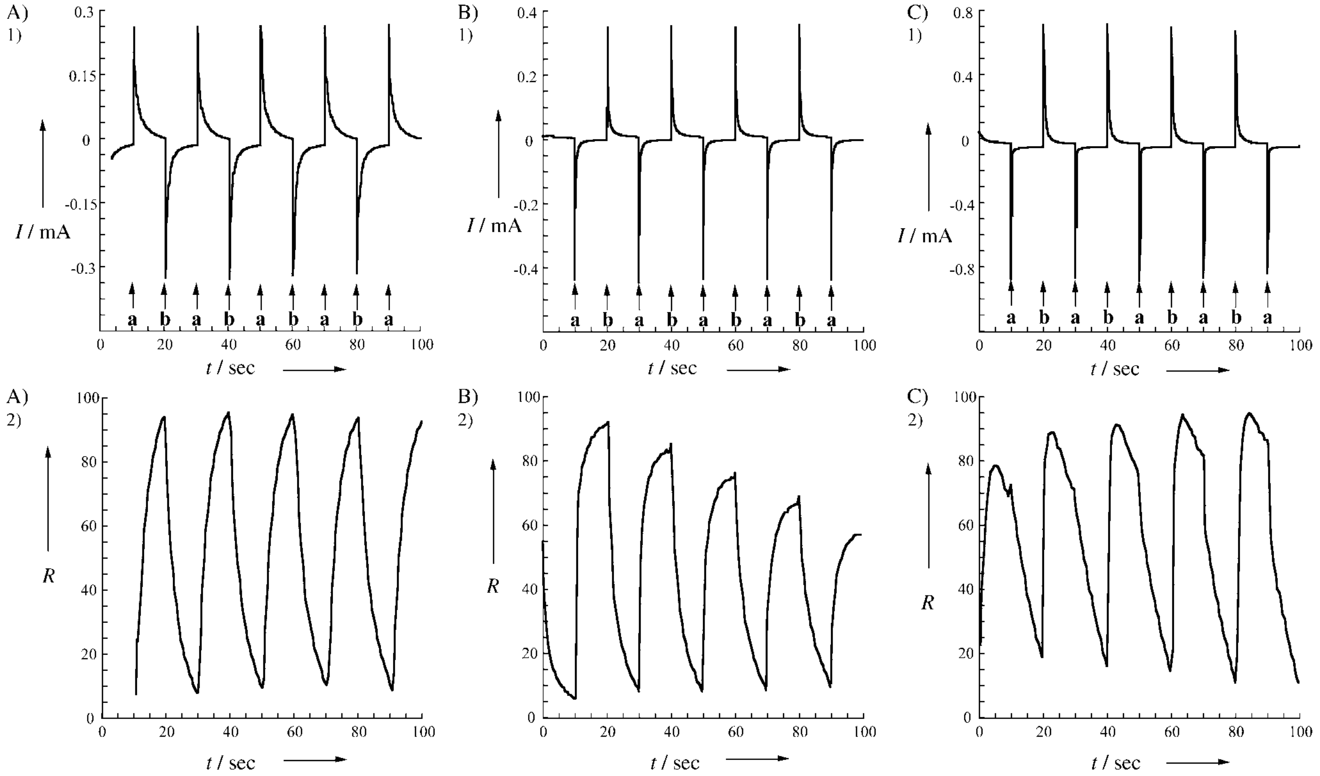


Figure 2. Multipotential step chronoamperometric transients corresponding to the transformations between A) 1) state II and state I, B) 1) state III and state II, and C) 1) state III and state I of the film. The arrows (labeled a and b) show the time of the application of the oxidative and reductive steps. Panels 2) show the time-dependent reflectance changes measured at a fixed angle of incidence at A) 2) $\theta = 69.5^\circ$, B) 2) $\theta = 68^\circ$, C) 2) $\theta = 69.5^\circ$ upon the multipotential step experiment. The measurements were performed in 0.1 M KNO_3, pH 7.0.

sequence of multistep chronoamperometric transients applied in situ on the PB film, switching the electrode potential between the semi-oxidized state II, $E = 0.3$ V, and the fully oxidized state III, $E = 0.9$ V. The signal intensity decreases with the number of cycles implying a partial degradation of the system (Figure 2B, panel 2). The degradation of the system is attributed to the partial oxidation of the base cysteic monolayer and desorption of the redox-active film from the interface. In fact, reduction of the potential-step time interval from 10 s to 1.5 s leads to ten indistinguishable switchable cycles of reflected light intensity. Thus, although the reflected light intensities reveal smaller amplitude because of incomplete oxidation or reduction within the 1.5 s pulse duration, the system reveals higher stability since the film is not desorbed from the electrode. Finally, the system can be electrochemically switched between the two extreme redox-states of the fully reduced state I, $E = -0.2$ V, and the fully oxidized state III, $E = 0.9$ V, Figure 2C.

The SPR transduction of the redox states of the polymer film enables the use of the modified surface as a sensing interface for the in situ electrochemical/SPR detection of NADH. The PB film in state II, $E = 0.3$ V, acts as an electrocatalyst for the oxidation of NADH. In the presence of NADH the PB-functionalized electrode, state II, is reduced to state I. The application of a constant potential, $E = 0.3$ V, on the electrode allows the reoxidation of the film and the regeneration of state II. Assuming that the electrocatalytic oxidation of NADH is fast, compared to the oxidation of state I to II, the film, subjected to the oxidizing potential of 0.3 V, will exist as a steady-state ratio of states I/II that is controlled by the concentration of NADH. That is, at high NADH concentrations the film will exist mainly in state I, whereas at low concentrations of NADH, the film is mostly in state II. Figure 3A shows the SPR spectra of the PB-modified electrode subjected to the potential of 0.3 V in the presence of variable concentrations of NADH. As the concentration of NADH is higher, the SPR spectrum of the film is shifted and enriched with the state I of the film. Figure 3B, curve a, shows the derived calibration curve corresponding to the changes in the reflected light intensity at variable NADH concentrations measured at $\theta = 68.5^\circ$. For comparison, the in situ amperometric responses of the system, I_{cat}, as a result of the electrocatalyzed oxidation of NADH, are plotted in Figure 3B, curve b. It is evident that NADH can be analyzed in the concentration range of 5×10^{-4} M to 1×10^{-2} M. At NADH concentrations higher than 1×10^{-2} M the electrocatalytic current in the system reaches a constant value of approximately 0.9 mA and the SPR spectrum reaches a constant shape. Under these conditions, the film operates at its highest turnover in respect to the catalytic oxidation of NADH. Note, however, that the SPR spectrum of the film at high concentrations of NADH, curve h, where the film consists of state I, differs substantially from the characteristic SPR spectrum of state I, Figure 3A, curve a. This difference is attributed to the effect of applied potential on the electrode on the resulting SPR spectrum. While state I shown in curve a is formed at a

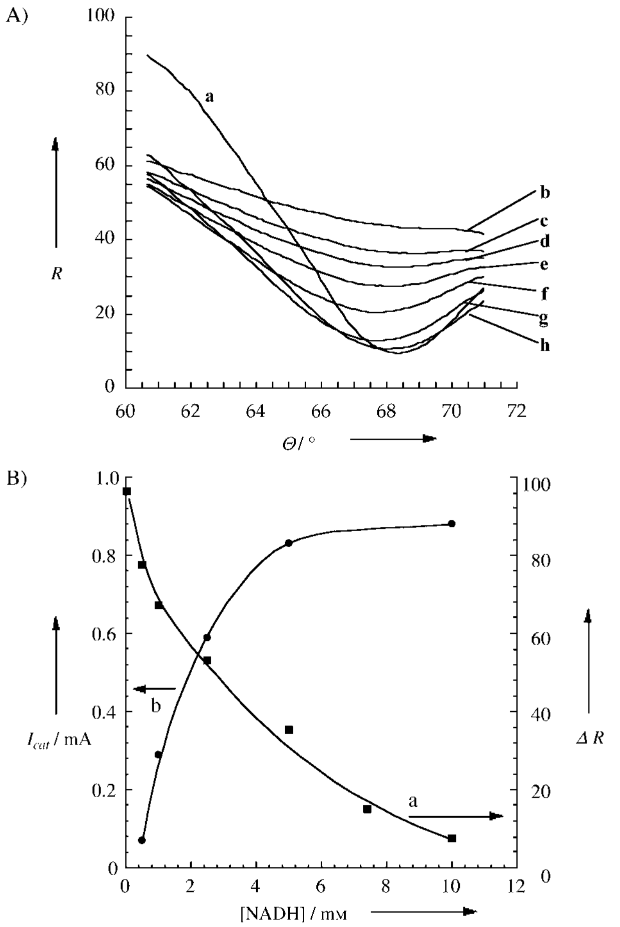


Figure 3. A) SPR spectra of the PB-modified Au-surface measured: a) At an applied potential −0.2 V in the absence of NADH. b–h) At an applied potential 0.3 V and in the presence of variable concentrations of NADH: b) 0 mM, c) 0.5 mM, d) 1.0 mM, e) 2.5 mM, f) 5.0 mM, g) 7.5 mM, h) 10.0 mM. The experiment was performed using 0.1M KNO_3 as a background electrolyte. B) Calibration plots corresponding to the analysis of NADH by: a) The SPR response. b) The electrocatalytic current measured in situ upon application of 0.3 V to the PB film in the presence of variable concentrations of NADH. The SPR response is defined as the difference of PB-film reflectance measured at $\theta = 68.5°$ in the presence of variable NADH concentrations and in the absence of NADH. All the data were recorded in 0.1M KNO_3, pH 7.0.

potential of −0.2 V, the film in state I shown in curve h is generated under an applied potential of +0.3 V (in the presence of NADH).

In conclusion, the present study has integrated a three-state redox-active film with an Au surface to yield a three-state switchable optoelectronic system, where the electrical information stored in the redox states is optically transduced by SPR. In contrast to an electrochemical read-out signal of the redox states that erases the information, the SPR signal does not affect the redox state. In principle, the study implies that complex multistep redox transformations may be used to generate multiswitching optoelectronic systems. Furthermore, the SPR transduction of the electrocatalyzed oxidation of NADH reveals a novel means to develop optoelectronic sensors and to follow electrocatalytic transformations.

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