Molecular Devices

Electrochemical Addressing of the Optical Properties of a Monolayer on a Transparent Conducting Substrate**

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Thin-film chemistry and surface engineering, in particular the generation of new molecular electronic and photonic materials, are attracting considerable interest.[1] The development of a fundamental understanding of molecular interactions, orientation, and function is essential for the formation of device-quality organic mono- and multilayers.[2] Direct control of thin-film properties might lead to a wide range of applications in molecular-based optics and electronics. For instance, low-voltage redox-active molecules may be potentially useful for the design of new monolayers for charge-storage memory devices.[3,4] These molecular-based memories, bound to Si(100), withstand operation and device-processing temperatures.[4] However, many challenges need to be addressed before such systems will become readily available. It has been very difficult to predict and to switch reversibly the monolayer properties for a given molecular building block. Much effort has been devoted to the development of molecular switches in solution,[5–7] whereas such systems immobilized on substrate surfaces is a rapidly developing field.[3,4,8–11] Recently Di Bella and co-workers reported the first example of a redox switch self-assembled on an optically transparent Pt electrode.[9] The optical properties of the thiol-based monolayers can be controlled by chemical oxidation and reduction. Herein, we demonstrate electrochemical switching of the optical properties of a ruthenium-based monolayer, which is covalently attached to a transparent conducting substrate surface.

The molecular building block consists of a tris(bipyridyl)-ruthenium module for charge storage and a phenol unit for covalent surface attachment (Figure 1). Functional thin films are formed by covalent assembly of the previously reported ruthenium-based molecular building block at an organic interface (Figure 1).[12] The siloxane-based coupling layers (CL) were prepared on freshly cleaned float glass, Si(100), and glass-coated with indium tin oxide (ITO). Substrates were treated with a dry pentane solution of *p*-chloromethylphenyl-trichlorosilane (1:100, v/v) at room temperature for 30 min

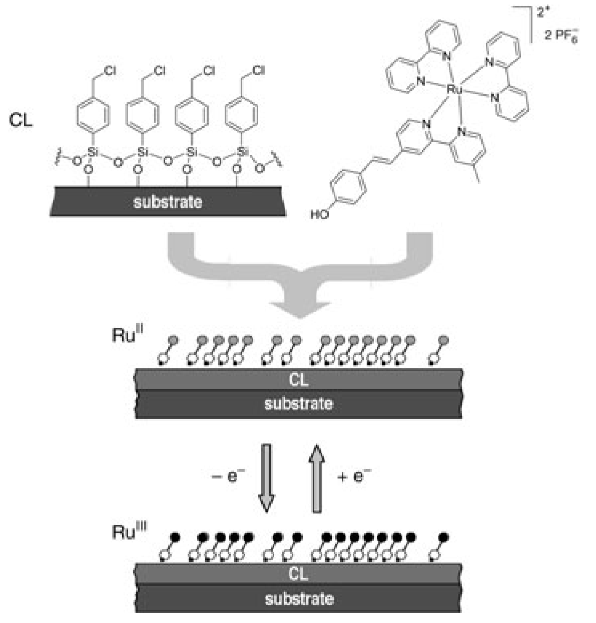

Figure 1. Formation of ruthenium-based monolayers on ITO-coated glass, glass, and silicon substrate surfaces functionalized with a chlorobenzyl-based coupling layer (CL). Electrochemical and spectroelectrochemical measurements were performed on glass coated with ITO on a single side. Monolayers were assembled only on the ITO side of the glass substrate by mechanical protection of the glass surface.

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[**] This research was supported by the Helen and Martin Kimmel Center for Molecular Design, the Yigal-Alon Fellowship program, MINERVA, the German BMBF, and the MJRG for Molecular Materials and Interface Design (M.E.v.d.B). A.D. thanks DST (India) for financial assistance. A.D.S. is the recipient of the Reva G. Stone Postdoctoral Fellowship. We thank M. Altman and H. Cohen (WIS) for the AFM and XPS measurements, respectively. M.E.v.d.B. is the incumbent of the Dewey David Stone and Harry Levine career development chair.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200461958

under N_2. The substrates were then thoroughly washed with copious amounts of dry pentane and dried at 115 °C for about 15 min. Subsequently, the colorless chlorobenzyl-functionalized substrates were immersed in a 2.0 mM toluene/CH_2Cl_2 (6:4, v/v) solution of the ruthenium complex, and heated for 48 h at 80 °C under N_2 by using glass pressure tubes. The resulting chromophore films were washed and sonicated (1 min) with copious amounts of CH_2Cl_2, acetone, and isopropyl alcohol, and dried under a gentle stream of N_2. Similar surface coupling reactions of benzyl halide interfaces with phenols or pyridine moieties to form ether linkages or pyridinium salts, respectively, have been reported.[13,14] The new monolayers strongly adhere to the glass and silicon substrates, are insoluble in common organic solvents, and cannot be removed by either the "Scotch-tape decohesion" test or by CO_2 snowjet cleaning.

Freshly prepared samples were characterized by a combination of semicontact atomic force microscopy (AFM), optical transmission (UV/Vis) spectrometry, X-ray photoelectron spectroscopy (XPS), electrochemistry, and spectroelectrochemistry.[14] The latter technique was used to vary and to read the optical properties of the system. XPS measurements of the Ru^{II}-based monolayer on ITO-coated glass revealed a Si/N ratio of about 1:2.1, which indicates that about 35 % of the CL molecules reacted. This is not uncommon.[15] The relatively small footprint of the CL molecules prohibits a quantitative reaction with the larger ruthenium complex. The film thickness derived from angle-resolved XPS is estimated to be 13 ± 2 Å. Semicontact AFM measurements on films grown on Si(100) substrates show an essentially smooth film surface with no evident grain boundaries. The root-mean-square surface roughness is about 0.1 nm for $1 \times 1\ \mu m^2$ scan areas (see the Supporting Information). Electrochemical measurements were performed to evaluate the redox activity of the monolayers. Figure 2 a shows the cyclic voltammograms of the monolayer on ITO-coated glass at different voltage scan rates (ν). The half-wave redox potential $E_{1/2}$ remains constant within $\nu = 100$–$1000\ mV\,s^{-1}$. The peak-to-peak separation (ΔE) is about 64 mV for $\nu = 500\ mV\,s^{-1}$. Figure 2 b shows the linear correlation of the peak current I_p versus ν. Apparently, a reversible redox process occurs involving a one-electron transfer. The ΔE value is expected to be about 60 mV for a Ru^{II}/Ru^{III} couple in solution.[16] The potential of the Ru^{II}/Ru^{III} couple $E_{1/2}$ is 0.95 V with respect to the ferrocene/ferrocenium standard.

After the initial conditioning scans, continuous cyclic voltammetry (CV) measurements show a repetitive redox behavior for at least 45 cycles. The magnitude of the ruthenium-centered oxidation current decreases slightly with the first six successive sweeps, possibly as a result of deactivation or reordering of the molecular components (Figure 3).

The UV/Vis optical absorbance measurements of the Ru^{II}-based films on glass and on ITO-coated glass substrates show a ligand-based π–π^* transition band at $\lambda_{max} = 314$ nm. The low-energy metal-to-ligand charge-transfer (MLCT) band appears at $\lambda = 462$ nm. Increasing the reaction time to 72 h does not affect the intensity of these absorbance bands. In situ spectroelectrochemistry performed in air showed a significant reversible change in the intensity of the absorbance band at $\lambda_{max} = 314$ nm upon alternation of the metal

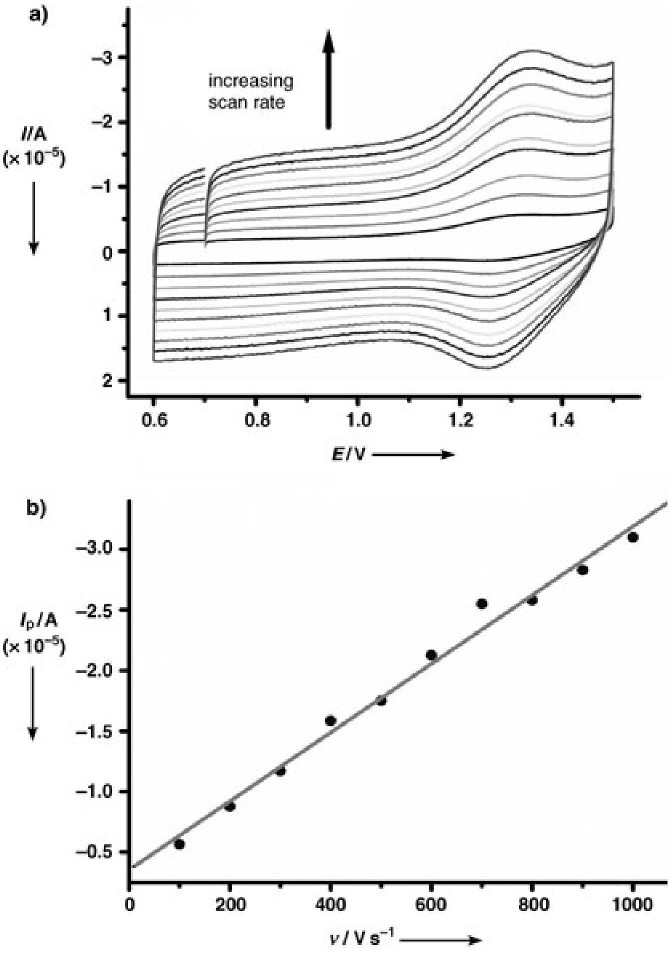

Figure 2. a) Representative cyclic voltammetric responses at different scan rates of the ruthenium-based monolayer on ITO-coated glass, which operates as the working electrode. Pt wires were used as reference and counter electrodes. The electrochemical (EC) experiments were carried out at room temperature in dry acetonitrile containing 20 mM nBu_4NPF_6 with a CHI660A potentiostat. The voltage scan rate was varied from 100 to 1000 $mV\,s^{-1}$ with steps of 100 $mV\,s^{-1}$. b) Linear correlation ($R^2 = 0.988$) of the peak current I_p versus the scan rate ν.

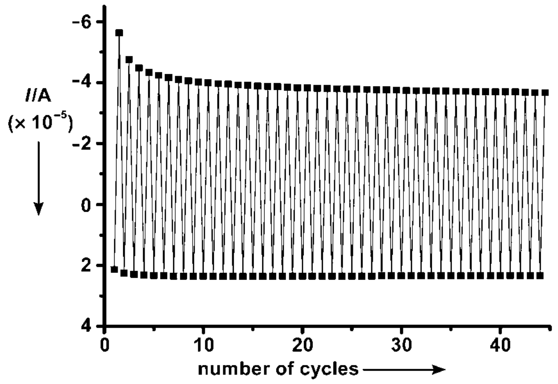

Figure 3. Representative EC redox switching as a function of redox cycles. The CV experiments were conducted at a sweep rate of 1000 $mV\,s^{-1}$. The lines are drawn as a guide to the eye.

oxidation state, Ru^{II}/Ru^{III} (Figure 4). Nine repetitions of the phenomenon are shown in the inset of Figure 4; they demonstrate the possibility of optical readout of the charge storage. The MLCT band is too weak for accurate monitoring by transmission UV/Vis spectrometry.

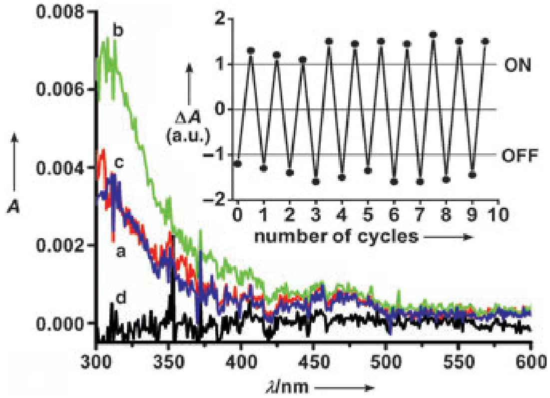

Figure 4. Absorption spectra for the optical switching of the ruthenium-based monolayer on ITO at $\lambda = 314$ nm for 10 min: a) Ru^{II}, b) Ru^{III}, c) Ru^{II}, d) baseline. The inset shows the EC on/off switching of the intensity change of the absorbance band at $\lambda = 314$ nm (ΔA, a.u.) versus the number of Ru^{II}/Ru^{III} cycles. The lines are drawn as a guide to the eye. EC oxidation was carried out by bulk electrolysis at 1.4 V, while reduction was performed at −0.1 V (20 min each). UV/Vis spectra were recorded in situ on a Cary 100 spectrophotometer after each oxidation state change.

In summary, the formation and characterization of a ruthenium-based monolayer on hydrophilic substrates, including ITO-coated glass, is described. Electrochemical variation of the metal oxidation state of the covalently surface-bound molecular building blocks triggers a reversible change in the optical properties of the ligand module. This read/write process can be carried out conveniently in air and monitored with a standard UV/Vis spectrophotometer. The low-voltage operation and the stability of the monolayer may make it a suitable candidate for nonvolatile memory devices. Extension of the scope of the work presented herein to mono- and multilayers of other metal-based chromophores, as well as to modulation of luminescence intensity and nonlinear optical responses, is in progress.

Received: September 12, 2004
Revised: January 27, 2005

Keywords: molecular devices · monolayers · ruthenium · switches · thin films

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