Molecular Switches **Hot Paper**

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An Electrically Driven and Readable Molecular Monolayer Switch Based on a Solid Electrolyte

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Abstract: *The potential application of molecular switches as active elements in information storage has been demonstrated through numerous works. Importantly, such switching capabilities have also been reported for self-assembled monolayers (SAMs). SAMs of electroactive molecules have recently been exploited as electrochemical switches. Typically, the state of these switches could be read out through their optical and/or magnetic response. These output reading processes are difficult to integrate into devices, and furthermore, there is a need to use liquid environments for switching the redox-active molecular systems. In this work, both of these challenges were overcome by using an ionic gel as the electrolyte medium, which led to an unprecedented solid-state device based on a single molecular layer. Moreover, electrochemical impedance has been successfully exploited as the output of the system.*

Bistable molecules that can be externally switched between two or more states with different properties have been known for a long time, and their potential as active elements in information storage devices has been recognized.[1] To move towards device miniaturization, single molecules or monolayers of molecules have been employed as active components in switches. In such systems, the input and output signals can be of different nature, such as chemical, optical, magnetic, or electrical. However, electrical signals are particularly appealing as they can be more easily integrated with current technologies. Single electroactive molecules have been incorporated in three terminal junctions, where an electrical field generated by applying a voltage to a gate terminal was employed to modulate the molecular charge, and the current that passed through the molecule connecting two contacts was used as the readout mechanism.[2] Although scientifically extremely motivating, these devices are technologically very demanding and currently show poor fabrication yields and device reproducibility. The preparation of hybrid surfaces that consist of inorganic conducting supports functionalized with a chemically bonded self-assembled monolayer (SAM) offers a clear alternative platform for the preparation of molecular devices.[3]

The preparation of SAMs from solution by spontaneous surface self-organization of the molecules is an inexpensive as well as powerful and versatile method for the modification of surfaces at the molecular level. SAMs of electroactive molecules have been exploited as electrochemical switches in the last few years.[4] Typically, the state of these switches could be read out through their optical and/or magnetic response.[5] Despite the extremely encouraging results achieved thus far, two main bottlenecks have been clearly identified, which seriously hamper the progress in the field towards real applications: 1) The reading processes that are required to determine the output signals are difficult to integrate into devices, and 2) to switch between the different accessible redox states of the molecular systems, solutions containing an electrolyte are required to stabilize the charged states (i.e., ion pairing) and to ensure ionic conductivity in the electrochemical cell. Herein, we overcome both of these challenges by employing SAMs with an electroactive ferrocene (Fc) unit in a dual approach. First, electrochemical impedance spectroscopy (EIS) was used to measure the capacitance of the SAM to be employed as the output signal of the switch. Second, a solid-state device based on such a single molecular layer as the active component was prepared using a solid electrolyte medium. These results represent a step forward in the field, improving the perspectives of employing hybrid surfaces as molecular switches for their future integration in electronic applications.

SAMs of ferrocenyl alkylthiol derivatives on gold have been established as reference systems in electrochemical studies of surface-confined molecules.[6] For this reason, SAMs of 11-(ferrocenyl)undecanethiol ($FcC_{11}SH$) were employed as switchable redox units as ferrocene exhibits two accessible redox states (i.e., the neutral and oxidized redox states; Figure 1 a). The electrochemical cell shown in Figure 1 b was thus fabricated. Three coplanar gold electrodes (counter (CE), working (WE), and reference electrode (RE)) were thermally evaporated through a mask on a glass substrate, and a silicon mold or a Teflon ring were used to delimit a fixed area of the electrolyte in contact with the electrodes. The Au WE was modified with the ferrocene SAM by immersion in a 1 mM solution of $FcC_{11}SH$ in ethanol for 18 hours (Figure S1).

The electrochemical properties of the SAMs were first investigated using an ionic liquid (IL) as the electrolyte. Figure 1 c shows the cyclic voltammogram (CV) of the Fc-SAM obtained when using 1-ethyl-3-methylimidazoliumbis-(trifluoromethylsulfonyl) imide (EMIM-TFSI) as the electrolyte and employing the electrochemical cell described above. A redox peak was observed at $E^{1/2} = 0.23$ V (vs. Au at a scan rate of 200 $mV\,s^{-1}$), which corresponds to the Fc/Fc^{+} pair. The almost insignificant voltage difference observed between the cathodic and anodic peak ($\Delta E = 22$ mV at 200 $mV\,s^{-1}$) is

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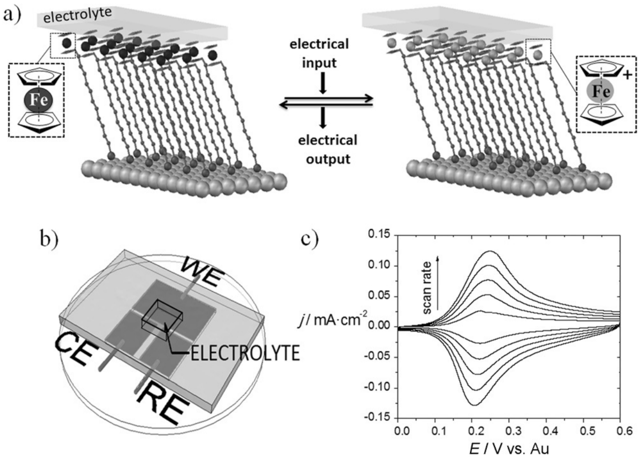

Figure 1. a) Molecular switch based on a ferrocene SAM on gold. b) Home-made electrochemical cell with three coplanar gold electrodes. c) Cyclic voltammograms of the Fc-SAM at different scan rates (100, 200, 300, 400, and 500 $\mathrm{mV\,s^{-1}}$) using a modified gold working electrode and gold reference and counter electrodes and the ionic liquid EMIM-TFSI.

characteristic of surface-confined molecules, which was further confirmed by the linear dependence of the current density of the redox peak (J_{p}) on the scan rate in the range of 50–500 $\mathrm{mV\,s^{-1}}$ (Figure S2).[7] A surface coverage of $3.7\times10^{-10}\,\mathrm{mol\,cm^{-2}}$ was estimated, which is slightly lower than the reported theoretical value (4.5×10^{-10}).[8] The observed smaller number of electroactive sites within the SAM could be explained by the large size of the TFSI$^-$ anion, which controls the ion pairing. As reported, if the anion cannot fully compensate the positive charges of all Fc$^+$ ions, some of the Fc units will appear to be non-electroactive.[9]

Electrochemical impedance spectroscopy (EIS) is a powerful method to characterize the electrical properties of interfaces.[10–12] Here, EIS was exploited to measure the capacitance of the different redox states of the switchable SAM. In an ideal situation, the gold metal surface would act as one of the capacitor plates, and the physisorbed ions at the SAM/electrolyte interface would act as the other capacitor plate.[13]

EIS measurements were performed at two different applied DC biases, before ($V_0 = +10$ mV) and after ($V_1 = +450$ mV) the redox peak, which define the states 0 and 1 of the switch (see the Supporting Information for experimental details). The Bode magnitude plot (impedance modulus ($|Z|$) vs. frequency) is shown in Figure 2a. At low frequencies, the graphs for the two states are two parallel straight lines with slopes of approximately -0.9. This behavior is characteristic of capacitor-like systems, and the deviation from a slope of -1 can be explained by capacitance dispersion owing to the adsorption of ions on the electrodes and the roughness of the electrode surface.[14] Accordingly, in the Bode phase plot (φ vs. f), the phase angle slightly deviates from 90° at low frequency, which would be expected for an ideal ionic insulator (Supporting Information, Figure S3a).[12a] Remarkably, a significant decrease in $|Z|$ of one order of magnitude was observed between state 0 and state 1 at low frequencies, indicating that the impedance can be used as a readout of the molecular switch. For comparison, the same experiments were performed with undecanethiol SAMs, but no impedance differences were observed when different DC biases were applied to the functionalized WE in this frequency region (Figure S4). This result indicates that the changes observed in $|Z|$ for the Fc-SAMs do not arise from the simple polarization of the electrode/electrolyte interface by the applied voltage; instead, the redox state of the electroactive species plays a crucial role.

At higher frequencies ($f > 10$ kHz), the frequency-independent impedance (Figure 2a) and a phase angle close to zero (Figure S3a,c) indicate that the system behaves as a resistor, that is, the total impedance is dominated by the solution resistance.[13] This is due to the fact that at high frequencies, the capacitor behaves as a short-circuit element as the charging time is too short, allowing the AC current to pass.

The EIS results can also be presented in the form of the real or imaginary part of the interfacial complex capacitance as a function of frequency. The real part of the capacitance per unit area (C_{re}) was calculated by the following equation:[15]

$$C_{\mathrm{re}}(f) = \frac{1}{2\pi f}\frac{Z_{\mathrm{im}}}{\left[Z_{\mathrm{re}}^2 + Z_{\mathrm{im}}^2\right]}\frac{1}{A} \tag{1}$$

where A is the area of the working electrode, Z_{re} and Z_{im} are the real and imaginary parts of the complex impedance, respectively, and f is the frequency.

The dependence of the C_{re} value on the frequency for the Fc-SAMs at both applied DC bias voltages is shown in Figure 2b. At high frequencies, the measured capacitance corresponds to the bulk capacitance, whereas at low frequencies, a plateau was reached, reflecting the interfacial capacitance.[15c] The C_{re} value measured at 1 Hz is significantly different for state 0 ($V = 10$ mV) and state 1 ($V = 450$ mV). Such large on/off ratios in the capacitance measured for the two states ($\Delta C_{\mathrm{re}} = 44\,\mu\mathrm{F\,cm^{-2}}$) make it possible to use this parameter to follow the switching. We attribute this difference in capacitance mainly to the charges accumulated at the

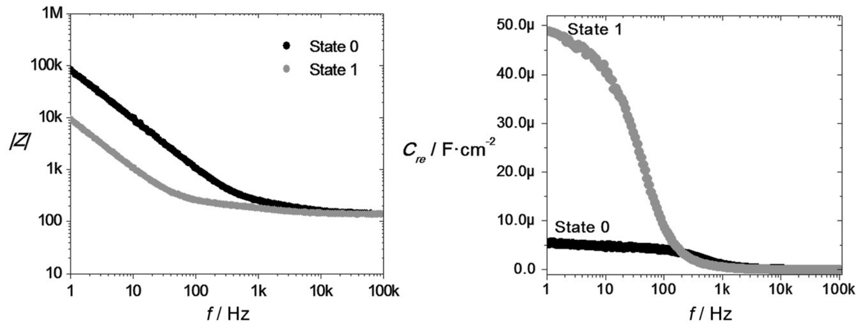

Figure 2. a) Bode magnitude plot (($|Z|$) vs. f). b) The real part of the complex capacitance as a function of frequency (C_{re} vs. f) for Fc-SAM on Au using EMIM-TFSI as the electrolyte. Black line: state 0 at +10 mV, gray line: state 1 at +450 mV.

electrode interface, which are influenced by the redox state of the Fc molecules, although a certain contribution from structural changes in the SAM cannot be ruled out completely.[16] Overall, it was demonstrated that the investigated surface-confined electrochemical switch can be electrically driven as well as read.

A second important challenge in the field is the lack of solid-state devices with such electrochemically switchable SAMs. To overcome this issue, an ionic gel (IG) was employed as the electrolyte medium. Generally, IGs are prepared by entrapping an IL in a polymer matrix.[17] IGs have already been exploited in several electronic devices, such as in inorganic electrochemical transistors,[18] as photo-actuated microvalves,[19] and as high-capacitance gate dielectrics.[20] However, to the best of our knowledge, this is the first time that a solid electrolyte has been employed to electrochemically control a molecular redox switch grafted onto a surface.

The IG based on poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) and EMIM-TFSI (1:4) was prepared as described in the literature (Figure S5 and S7).[20a,b] The IG acetone solution was drop-casted onto the modified gold electrodes, with the active area limited by the silicon mold, in a chamber with an inert and low-humidity atmosphere. After solvent evaporation and solidification of the gel mixture, the sample was removed from the glove box and analyzed in air. Figure 3a shows a photograph of the solid-state device based on the IG film.

As shown in Figure 3b, the CV electrochemical characteristics of the Fc-SAM could be successfully determined by using co-planar electrodes coated with the transparent, flexible, and solid IG. Remarkably, the CV could also be measured by employing a thin film of an IG that was prepared first on a glass slide and then transferred with tweezers and laminated on top of the three gold coplanar electrodes, with the WE modified with the ferrocene SAM. The cyclic voltammogram thus obtained showed very similar features as the ones shown in Figure 3b (see also Figure S7).

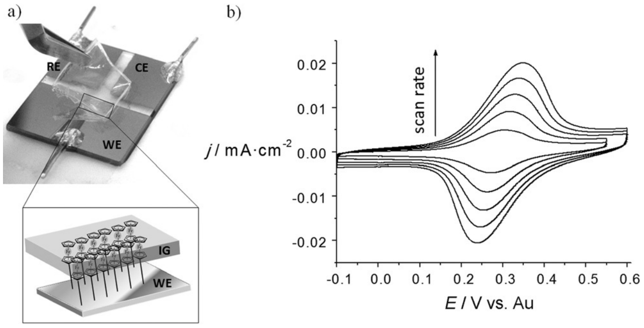

Figure 3. a) The three coplanar gold working (WE), counter (CE), and reference (RE) electrodes with the IG electrolyte (top). Scheme of the area between the WE modified with Fc-SAM and the solid electrolyte (bottom). b) Cyclic voltammograms of the Au/Fc-SAM/solid IG device at different scan rates (100, 200, 300, 400, and 500 mV s^{-1}).

When the CV obtained with the solid electrolyte is compared to the one obtained with the IL, there are few differences in the electrochemical characteristics commonly used for evaluating the response of surface-grafted molecules. In the case of the IG, a larger peak-to-peak voltage difference (ΔE) was observed, which also depended more strongly on the scan rate. This is indicative of a slower electron-transfer process, which is expected to occur because of the lower ion mobility in the solid IG film. Furthermore, a lower current density was observed for the IG despite the fact that the density of the ferrocene molecules grafted onto the gold electrode should be very similar to that of the SAMs studied with the IL. In other words, the number of redox-active ferrocene species electrochemically visualized is considerably lower when the IG is used. This can be explained in terms of the less homogenous and intimate contact between the IG and the SAM as well as the less effective charge compensation of the ferrocinium molecules with the TFSI$^-$ ion, which is again probably due to the more limited ion diffusion at the solid-state interface. This observation can be quantified by the integration of the CV redox peaks; it was found that the number of molecules that participate in the electrochemical process is reduced to 30–50 % on going from the IL to the IG device.

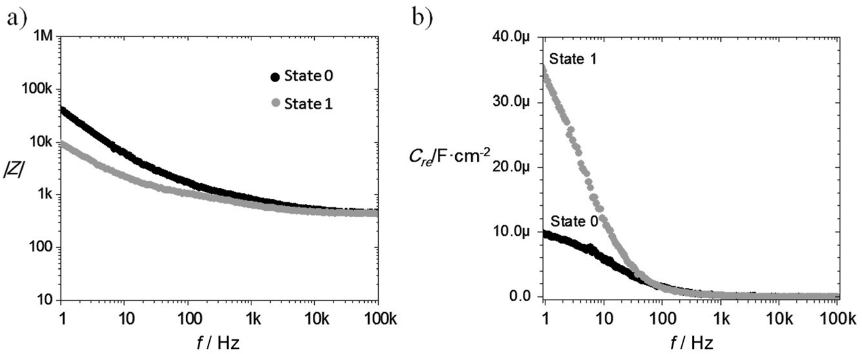

Figure 4. a) Bode magnitude plot ((|Z|) vs. f). b) Real part of the capacitance as a function of frequency for the electrochemical device, with the solid IG as the electrolyte. State 0 (black) and state 1 (gray) correspond to DC applied biases of 10 mV and 600 mV, respectively.

Interestingly, EIS measurements were also used to follow the switching process in this solid-state device. In this case, state 0 and state 1 were written using a DC voltage of 10 mV and 600 mV vs. Au, respectively (see the corresponding cyclic voltammogram in Figure S8). The dependence of the impedance modulus, |Z|, on the frequency of the solid-state device is depicted in Figure 4a. As before, there is a clear diminution of the impedance value on going from state 0 to state 1, although this time, the variation is smaller. Furthermore, a noticeable difference is that in the case of the IL-based device, the on/off ratio of the |Z| values between the two states is maintained constant in the range 1–100 Hz, whereas in the IG device, the plots corresponding to the two states start to converge in the region of 10–100 Hz. This could again be caused by the lower mobility of the ions in the gel preventing the formation of a compensated double layer at lower frequencies.

The C_{re} value was calculated as explained above for the IL-based switch (Figure 4b). The C_{re} values at 1 Hz in state 0 for the IL and IG devices are very similar, namely 5.3 $\mu F\,cm^{-2}$ and 9.25 $\mu F\,cm^{-2}$, respectively. Although the on/off ratio is lower for the IG-based device than for the IL device, the ΔC_{re} value is still outstanding, 25 $\mu F\,cm^{-2}$ at 1 Hz.

To explore the stability of the switch, it was subjected to 100 switching cycles, and the C_{re} values measured at 1 Hz were plotted as a function of the cycle number for both electrolyte media, namely IL (Figure 5a) and IG (Figure 5b).

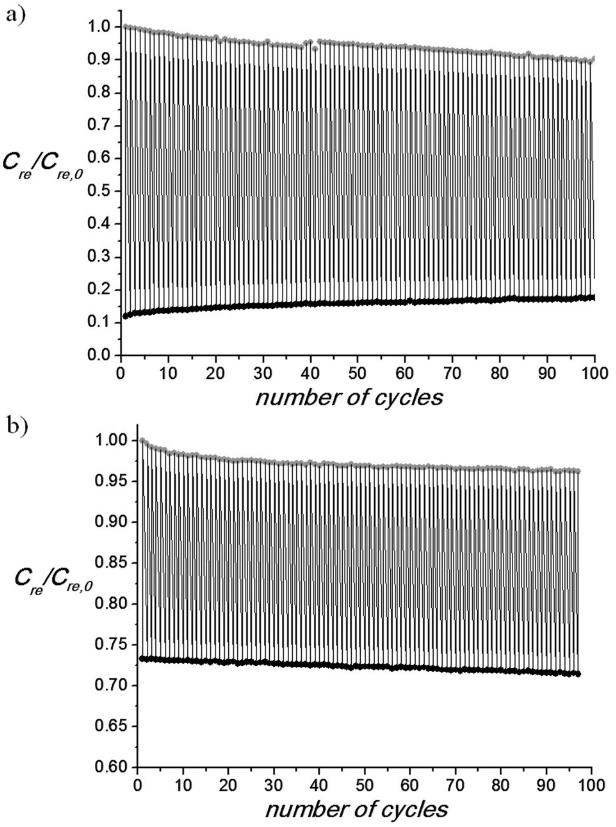

Figure 5. $C_{re}/C_{re,0}$ (at 1 Hz) switching over 100 cycles by alternating the applied bias with a) the IL and b) the IG as the electrolyte for state 0 (black) and state 1 (gray).

There was a small decrease in the on/off ratio under the IL conditions, which we attribute to ion permeation, which can additionally cause some molecular desorption. Remarkably, despite the lower on/off ratio, the stability of the switchable system, that is, the switching fatigue, was improved by the use of the solid electrolyte. This finding demonstrates the feasibility of using the C_{re} value as the output of the switch even when using a solid-state electrochemical device.

In summary, we have demonstrated that it is possible to write and read an electrochemical switch that is based on a self-assembled monolayer of an electroactive molecule by using an electrical input to control the switch as well as an electrical output to monitor it. This has been achieved not only in liquid environments but also in a solid-state device based on an ion gel electrolyte. The method employed here is inexpensive and simple and could also be extended to other redox-active molecules. These results represent a proof-of-concept study of a feasible approach for the integration of molecular-monolayer-based electrochemical switches.

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