Molecular Logic

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An Electrochemically Transduced XOR Logic Gate at the Molecular Level**

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Organic molecules that can generate a detectable response to an external stimulus are of great scientific interest since they can be used in data-processing applications such as information storage, transformation, and communication.[1] Logic gates with Boolean functions including AND, OR, INHIBIT, XOR, XNOR, and NOR have been realized on the molecular level and are able to process information and perform arithmetic operations.[2–8] Although numerous molecular systems that perform different computing operations were developed, this research is still in a very early experimental and theoretical stage.[9,10] In order to achieve practical applications, the future of molecular logic elements is strongly related to the successful linkage of molecules onto a conductive or semiconductive support.[11–13] However, logic-gate functions performed by functionalized electrodes are relatively rare.[14–16] Recently, Katz and co-workers reported that various logic operations with electric readout could be realized by a carefully designed multicomponent biochemical system based on electrically wired enzymes.[16] Herein, we introduce a robust system that incorporates redox-active molecules bound to a gold surface in combination with solution-phase redox probes. This system is capable of mimicking XOR logic operations based on the function of an electrochemical current rectifier (ECR), which behaves like a diode.

The electron-transfer (ET) mechanism of ECRs is well-accepted, having been first reported by Murray and co-workers.[17] Briefly, the ET between an electrode and redox probes is controlled by the surface-confined electron-transfer mediators. If the redox potential of the redox probe is more negative than that of an electron-transfer mediator, a unidirectional current is produced by facilitating transfer of electrons from a redox probe to the electrode under the control of the applied potential. Although the transport of electrons in the reverse direction is prohibited for thermodynamic reasons, an anodic ECR is produced. Accordingly, a cathodic ECR is generated when the redox potential of the redox probe is positive compared to that of the electron-transfer mediator. To avoid short-circuiting the ET between mediators and the electrode surface, an insulating layer immobilized on the metal electrode is required to inhibit the direct ET between the electrode and redox probes.[18] In our experiments, the functionalized electrode was prepared by immersing a gold electrode into a mixture of 11-undecanethiol-1-ferrocene and hexandecanethiol (HDT). The compact monolayer of HDT molecules adsorbed to the gold surface acted as an insulator to inhibit direct ET. The ferrocenylthiol molecules embedded in a matrix of HDT molecules were used as charge-transfer mediators to control ET between the electrode and redox probes in solution. The functionalized electrode was operated either as an anodic or cathodic ECR, which permitted unidirectional current with opposite directions for different redox probes and realization of an XOR logic-gate function.

To perform the XOR operation, binary encoding of information contained in an electrical signal is required for data processing. Potassium ferrocyanide and potassium hexachloroiridate(IV) were selected as two inputs because both compounds act as ionic conductors in solution and exhibit fast and reversible ET on gold electrodes (Figure 1).[19]

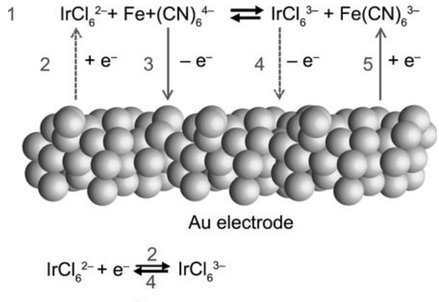

Figure 1. Electron-transfer processes between redox species and the bare electrode. Process 1: direct charge transfer between the two redox probes in solution. Processes 2–5: electron-transfer processes between redox probes and the gold electrode (see also Figure 2).

The equilibrium redox potentials of 0.23 V for ferrocyanide/ferricyanide (Figure 2a) and 0.71 V for iridate(IV/III) (Figure 2b), were calculated from the average peak-to-peak potential separation of the oxidation and reduction current responses. Both redox probes exhibited a pair of redox peaks with single ET behavior on the gold electrode. When both inputs were simultaneously present, the resulting reaction led to a coexistence of four different redox species [Eq. (1)]. Each

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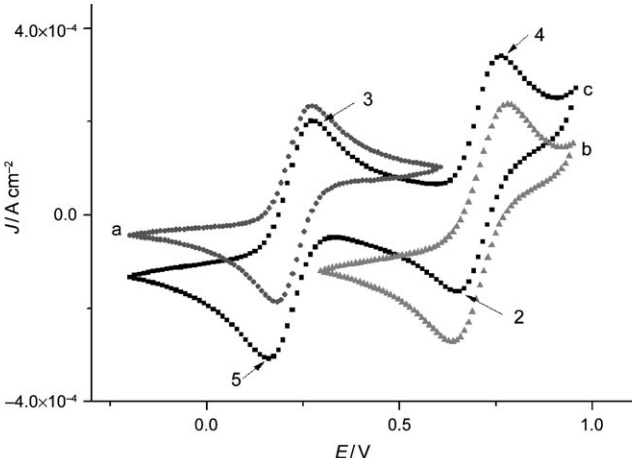

Figure 2. Cyclic voltammograms of a bare Au electrode in a) 1 mM ferrocyanide, b) 1 mM iridate(IV), and c) a mixture of 1 mM ferrocyanide and 1 mM iridate(IV) ions.

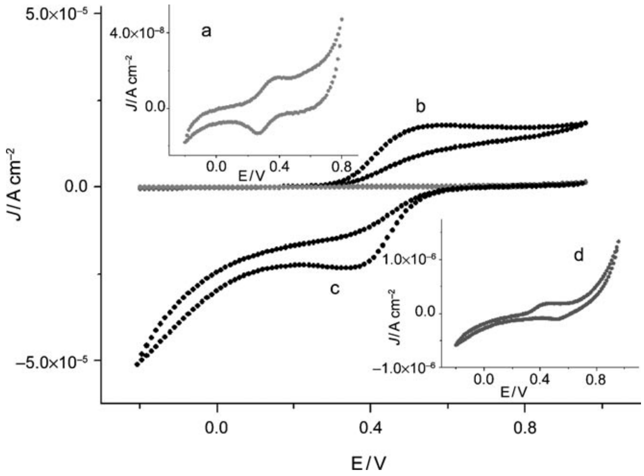

Figure 3. Cyclic voltammograms of the functionalized electrode in a) PBS, b) 0.5 mM iridate(IV), c) 0.5 mM ferrocyanide, and d) a mixture of 0.5 mM ferrocyanide and 0.5 mM iridate(IV) ions. Curves (a) and (d) are also shown as base lines of curves (b) and (c).

$$Fe(CN)_6^{-4} + IrCl_6^{-2} \rightleftharpoons Fe(CN)_6^{-3} + IrCl_6^{-3} \qquad (1)$$

of these species was able to exchange electrons with the bare gold electrode. Consequently, two pairs of redox peaks, which were ascribed to the electron transfer of ferrocyanide/ferricyanide and iridate (IV/III) ions, appeared in the electrochemical responses on the Au electrode (Figure 2c). Compared to the independent responses of each pair of redox probes (Figure 2a,b), no obvious shifts were observed in the redox potentials of the mixture, thus indicating that the ET between redox probes and the Au electrode was not influenced by the chemical interaction between the redox probes. Figure 1 shows the ET processes between redox species and the bare gold electrode. The direct charge transfer between ferrocyanide and iridate(IV) ions (process 1), reduced the quantity of iridate(IV) ions in the bulk solution. However, the generated iridate(III) ions were subsequently reoxidized to iridate(IV) ions by the electrode at anodic potential (process 4). This reoxidization increased the quantity of iridate(IV) ions at the electrode surface. The enriched iridate(IV) ions were reduced to iridate(III) ions at cathodic potentials (process 2) before it could diffuse into the bulk of the solution.

As soon as the electrode was modified with ferrocenylthiol ions, the charge-transfer mediator, the current responses of the ferrocyanide and iridate(IV) ions inputs changed significantly. The equilibrium potential of the surface-confined ferrocenylthiol ions in the supporting electrolyte that contained no redox probes was found to be 0.34 V (Figure 3a, inset), which is located in between the redox potentials of the two inputs. This value is of importance for the successful realization of the XOR logic gate function. The observed redox current for the charge transfer between ferrocenylthiol ions and the electrode was low because of the small number of redox-active molecules on the surface. After adding iridate(IV) ions (0.5 mM) as the only input, the current response obtained during the cathodic potential sweep strongly exceeded that of the modified electrode in a solution of free iridate(IV) ions (Figure 3b). However, consistent with the features of an ECR, no anodic current response was observed during the reverse potential sweep. It is clear that the rectified behavior originated from the consecutive charge transfer between the electrode, surface-confined molecules, and the redox probes in solution. Figure 4 shows the electron-transfer sequence. The ET between redox probes in solution and the electrode was inhibited by the HDT monolayer but mediated by the surface-confined ferrocenylthiol. During the negative potential sweep, the gold electrode acted as an electron donor as soon as the reduction potential of the ferrocenylthiol was reached and electrons were transferred from the electrode to the ferrocenylthiol ions. Afterwards, the electrons were forwarded immediately to the iridate(IV) ions, thus leading

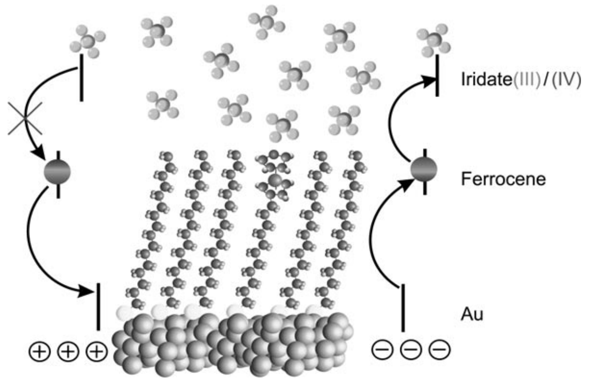

Figure 4. Electron-transfer mechanism of the cathodic electrochemical current rectification. HDT and ferrocenylthiol act as the insulating layer and electron transfer mediator, respectively. Considering the relative redox potentials of ferrocenythiol (0.34 V) and iridate(IV/III) ions (0.71 V), ferrocene receives an electron from the Au electrode and then transfers it to iridate(IV) ions when the reduction potential of ferrocene is reached (right-hand side). In the reverse scan, the electron transfer between iridate(III) ions and ferrocene is thermodynamically unfavorable (left-hand side). Only cathodic current is allowed to flow across the modified electrode.

to an enhanced cathodic current since the formal redox potential of iridate(IV/III), 0.71 V, was more positive than that of the ferrocenylthiol ions. On the reverse sweep, however, the charge transfer between the oxidized ferrocenylthiol and the iridate(III) ions was thermodynamically unfavorable and led to the absence of anodic current. In this case, the modified electrode can be referred to as a cathodic ECR and functioned similar to a diode, which allows an electric current in one direction (forward-biased conditions) and blocks the current in the opposite direction (reverse-biased conditions). Based on the same mechanism, rectified current was also realized when ferrocyanide ions (0.5 mᴍ) were added. Contrary to the current responses of iridate on the modified electrode, no obvious cathodic current was observed, but a strong anodic current response occurred (Figure 3c), which is consistent with previous reports.[20] In this case, the ferro/ferricyanide equilibrium redox potential (0.23 V) is more negative than that of the surface-confined ferrocenylthiol (0.34 V). The oxidation of ferrocyanide ions by the oxidized ferrocenylthiol was thermodynamically favorable, however, the reduction of ferricyanide ions was thermodynamically forbidden, which resulted in the observed anodic ECR. In summary, the modified electrode can work as a cathodic ECR and an anodic ECR for iridate and ferrocyanide ions, respectively.

When both inputs were applied simultaneously, the current response on the modified electrode was clearly changed and a pair of redox peaks were observed (Figure 3d). The current response was about one order of magnitude higher than that of the ferrocenylthiol-modified electrode in PBS (Figure 3a), and was more than one order of magnitude lower than the current response of the modified electrode in solutions containing only one kind of redox probe (Figure 3b,c). The modified current response can be ascribed to the interplay of different interfacial and solution-based charge-transfer processes (Figure 5). As mentioned above, four kinds of redox species exist in the mixture as the reaction shown in Equation (1) spontaneously occurs in solution. In this example, and based on the electron transfer mechanism of ECR discussed above, ferricyanide and iridate(III) ions did not exchange electrons with the modified electrode, thus decreasing the current response of the redox species to a certain degree. On the other hand, the oxidation of residual ferrocyanide ions and the reduction of residual iridate(IV) ions occurred because of the anodic ECR and cathodic ECR functions, respectively. It is noteworthy that both the reduction of iridate(IV) ions and the oxidation of ferrocyanide occurred at potentials near the redox potential of surface-confined ferrocenylthiol, since the charge transfer of the redox probes followed the charge transfer between electrode and redox mediator. The peak potentials of the anodic and cathodic ECR were 0.51 V and 0.37 V, respectively (Figure 3b,c). The small difference of only 0.14 V between these potentials led to a strong reduction of the current responses; this reduction arose from the compensation of oxidative and reductive currents. The surface-tethered redox mediator was of fundamental importance for the independent, unidirectional current responses of each kind of redox probe, and also the low current response of the mixture compared to the current responses of redox probes on the bare gold electrode (Figure 2).

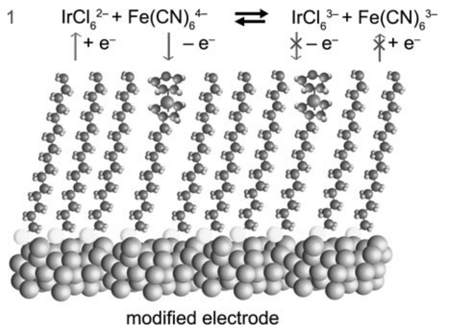

Figure 5. Electron transfer processes between redox species and the modified electrode. Process 1: direct charge transfer between the two redox probes in solution.

The results presented above show that an XOR logic-gate operation, which has previously proven difficult to implement on a molecular level, can be performed at the functionalized electrode.[1,5] To perform the logic operation, the input defined as "1" corresponded to the addition of 0.5 mᴍ ferrocyanide or iridate(IV) ions, while the absence of the respective species was considered as input "0". In addition, the output signal "1" was defined as the current produced by the functionalized electrode when the absolute value of the current was higher than a threshold value 0.4 μA, and "0" when the current was lower than 0.02 μA, resulting in a magnitude difference of 20 times between the output signals "0" and "1". Similar to the approach used in electronics, our case had an undefined output signal (here, the current range from 0.02 to 0.4 μA). The threshold values are defined with respect to the standard deviation of the output signals and the concentration of the input signals. As can be seen in Figure 3, a strong current signal within the potential range from 0.42 V to 0.50 V was present (output: "1") when either ferrocyanide or iridate(IV) ions were added (input: "1,0" or "0,1"). A pronounced current signal was absent (output: "0") when neither or both of the inputs were added (input: "0,0" or "1,1"). Figure 6a shows the current responses (absolute values) of the modified electrode with respect to different input signals at a potential of 0.48 V. By summarizing input and output signals in a truth table, it becomes obvious that an XOR logic gate function was realized for the investigated system of coupled redox species (Table 1). It is worth noting that an XOR logic gate can also be operated as a comparator, which distinguishes whether the input signals have the same value or not.[2] Additionally, the modified electrode can be used to successively perform XOR logic gate functions (Figure 6b) without renewing the system (electrode and solution) after finishing the first operation of the XOR logic gate function. The total level of the output signal encodes additional information of the signal application history (see the Supporting Information). This property will allow application of several input cycles, thus underlining the reproducibility of the system and is a prerequisite for many electronic applications.

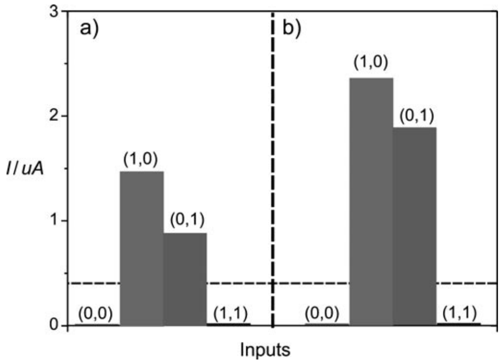

Figure 6. Current responses (output signals) of the modified electrode corresponding to various input signals at the potential of 0.48 V. Here, the current was shown as absolute value independently on the current direction. a) XOR logic gate function during the first operation. b) XOR logic function after subsequent inputs.

Table 1: Truth table corresponding to XOR logic-gate operation of the modified electrode.

Potential	Input 1	Input 2	Output
0.42–0.50 V	0	0	0
	1	0	1
	0	1	1
	1	1	0

In conclusion, an XOR logic gate function with electric readout was successfully realized by immobilizing robust, redox-active thiol molecules on a surface and applying two different redox probes as input signals. The functionalized electrode acted as an ECR with opposite signs when each of the two inputs were applied separately. When integrating the resulting cathodic and anodic current rectifier, the XOR logic gate showed a high switching ratio between output signals “1” and “0”. Furthermore, the modified electrode can successively conduct XOR logic gate functions without resetting the system. The results obtained confirmed that XOR logic gates can be realized on the molecular level, if redox species and the corresponding redox potentials are carefully considered. The strategy to link different surface-bound and unbound redox centers to electrified interfaces can be further expanded to the development of other molecular logic gates with electrical readout, which might pave the way for the integration of logic and sensing operations for advanced sensor performance. The opportunity to use different sensory inputs that are processed by a logic gate will improve the reliability of senor responses by suppressing cross-sensitivity and linking the signal of several (bio)markers together. Furthermore, it can be envisioned that this XOR logic gate can be operated as switch triggered by redox probe inputs.

Experimental Section

A gold bead electrode with 0.11 cm^2 area was used as working electrode. To generate a clean electrode surface, the gold electrode was first annealed with hydrogen flame and then cooled to room temperature in an argon atmosphere. The functionalized electrode was prepared by immersing the gold electrode into a 1 mM mixture of 1:50 11-undecanethiol-1-ferrocene/hexandecanethiol (HDT) overnight. Purified water (Milli-Q system, Millipore Co.) was used for the preparation of all electrolyte solutions and for rinsing all glassware and electrodes.

Cyclic voltammograms were recorded in a classical three-electrode configuration. Platinum foil and a saturated calomel electrode (SCE) worked as counter- and reference electrode, respectively. A sodium phosphate buffer solution (0.01 M, pH 5.6) was used as supporting electrolyte. The solutions were deoxygenated by purging them with argon. The measurements were performed under an argon atmosphere. The cyclic voltammograms were recorded by an Autolab Electrochemical System (Eco Chemie, Netherlands).

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