DOI: 10.1002/anie.201207778

Redox Electronics

Transistor Functions Based on Electrochemical Rectification[**]

Yaqing Liu, Bernhard Wolfrum, Martin Hüske, Andreas Offenhäusser, Erkang Wang, and Dirk Mayer[*]

Electronic elements built from organic semiconductors, such as molecular transistors, have significant potential for technical innovations and mass use owing to their flexible mechanical properties, cost-effective processability, and tuneable optical properties.[1] Self-assembled monolayer field-effect transistors (SAMFET) are among the latest developments of novel microelectronic devices.[2] In SAMFETs, charge carriers laterally pass through a molecular layer (parallel to substrate) and exhibit transistor behavior, which can be modulated by an electrostatic gate. The charge transport properties of the SAMFETs are affected by the length of the channel.[3,4] Herein, we present a novel chip-based molecular transistor concept, which is based on charge-transfer processes across a monolayer of molecules perpendicular to the sample surface plane. To this end, redox active molecules are adsorbed to a collector electrode (CE) acting as electron-transfer mediators. A two-step charge transfer between solid interdigitated array electrodes (IDA), charge transfer mediator, and liquid-phase redox probe yields a unidirectional current response. An adsorbate-free generator electrode (GE) can be used to modulate the unidirectional currents, resulting in a transistor-like behavior. The electrochemical transistor-like system exhibits high current outputs at a low-voltage operation, high on/off switching current ratios, and is operated as a 24-bit code generator.

To realize the molecular transistor function, we use a four-electrode configuration: Two interdigitated electrode arrays work as collector and a generator electrode (for the preparation procedure, see the Supporting Information, Figure S1). A high-impedance reference electrode (RE; Ag/AgCl) provides the potential reference for the IDAs. A low-impedance platinum wire is used as the counter electrode. The CE is modified by a self-assembled monolayer of the redox mediator 11-undecanethiol ferrocene (UDT-Fc), surrounded by insulating molecules of hexadecanethiol (HDT; Figure 1). Upon sweeping the electrode potential in supporting electrolyte, the redox mediator can be reversibly oxidized and reduced (Supporting Information, Figures S3, S6).[5] The GE is designed to facilitate a direct redox reaction with solution-phase redox probes and is therefore ideally adsorbate-free (Figure 2; Supporting Information, Figure S2). When the functionalized CE is subjected to a stimulus of chemical inputs, the system carries out transistor-like functions due to electrochemical current rectification (ECR).[6] Briefly, a unidirectional current is generated by the electron transfer between solution-phase redox probes and surface-confined

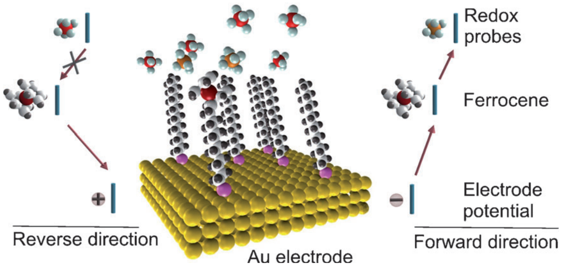

Figure 1. Mechanism of the cathodic ECR. Hexadecanethiol (HDT) and 11-undecanethiol–ferrocene (UDT-Fc) act as insulating layer and electron transfer mediator, respectively. The direct electron transfer between hexachloroiridate and the collector electrode is inhibited by the insulating HDT monolayer. Considering the relative redox potential of Fc (0.45 V) and hexachloroiridate(IV/III) (0.71 V), Fc as electron-transfer mediator receives an electron from the Au electrode and then transfers it to hexachloroiridate(IV) when the reduction potential of Fc is reached (right side). In the reverse scan, the electron transfer between hexachloroiridate(III) and Fc is thermodynamically unfavorable (left side). This directionally dependent electron transfer generates electrochemical current rectification with only cathodic current being observable.

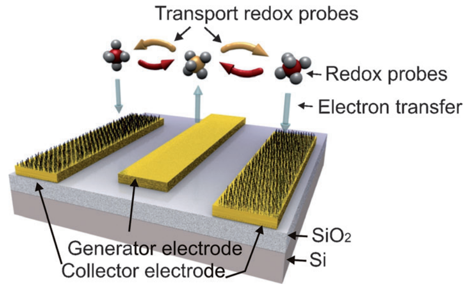

Figure 2. a) Illustration of a small number of extensions of the interdigitated electrode array with the bare gold generator electrode and the collector electrode modified by a mixed monolayer of UDT-Fc and HDT. The involved ion transport (yellow/red arrows) and electron transport processes (gray arrows) are shown (anodic transistor function).

---

[*] Prof. B. Wolfrum, M. Hüske, Prof. A. Offenhäusser, Dr. D. Mayer
Peter Grünberg Institute, PGI-8, Research Center Jülich (Germany)
JARA-Fundamentals of Future Information Technology
E-mail: dirk.mayer@fz-juelich.de
Dr. Y. Liu, Prof. E. Wang
State Key Lab of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences
Changchun, 130022 (China)

[**] We kindly acknowledge Marko Banzet for the fabrication of the IDE chips. We are grateful to Clara Chow for supporting comments. Y.L. and E.W. also appreciate the National Natural Science Foundation of China for financial support (Nos. 21105095 and 21190040).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201207778.

electron-transfer mediator (Figure 1). A direct electron transfer between solution-phase redox probes and collector electrode is inhibited by the insulating HDT monolayer.

In a first set of experiments, we used the redox couple hexachloroiridate(IV/III) as the redox probe. The redox potential of hexachloroiridate (0.71 V) is more anodic than that of surface-confined ferrocene (0.45 V; Supporting Information, Figure S3 a).[7] Therefore, electrons are transferred from the CE via the mediator to the redox probe if the electrode potential is more cathodic than 0.45 V. However, if hexachloroiridate(III) is added to the electrolyte solution, then no electrons can be transferred from ferrocene to the redox probe since hexachloroiridate(III) cannot be further reduced (Figure 3 a, $E_G = 0.3$ V). The adsorbate free GE can be utilized to oxidize and thereby activate hexachloroiridate. Consequently, hexachloroiridate(III) transfers electrons to the GE and a large fraction of the produced activated redox probes subsequently diffuse to the CE. There, the oxidized redox probe can be reduced back by the surface-tethered ferrocene depending on the potential of the collector electrode. When the potential of the collector electrode is scanned from positive to negative potentials, electrons are transferred from the electrode via the mediator to the activated redox probe hexachloroiridate(IV) as soon as the redox potential of the redox mediator is reached. The reverse process, however, is thermodynamically hindered. The unidirectional output current increases with decreasing potential of the collector electrode until the current becomes diffusion-limited. The current output at the collector electrode strongly depends on the potential applied to the generator electrode. With a positive shift of the gate voltage (0.3 V to 0.85 V), more hexachloroiridate(IV) is generated, which enhances the output signals of the collector electrode acting as the drain (Supporting Information, Figure S3 c). Thus, the current measured at the collector electrode can be modulated independently by tuning the amount of activated redox probes by the generator electrode (I_C–E_G characteristics) or by varying the number of active redox mediators at the collector electrode by their electrode potential (I_C–E_C characteristics; Supporting Information, Figure S5). Furthermore, the gate electrode reactivates redox probes that have been deactivated at the collector electrode and thereby enhances the detectable current output by a redox cycling process.[8]

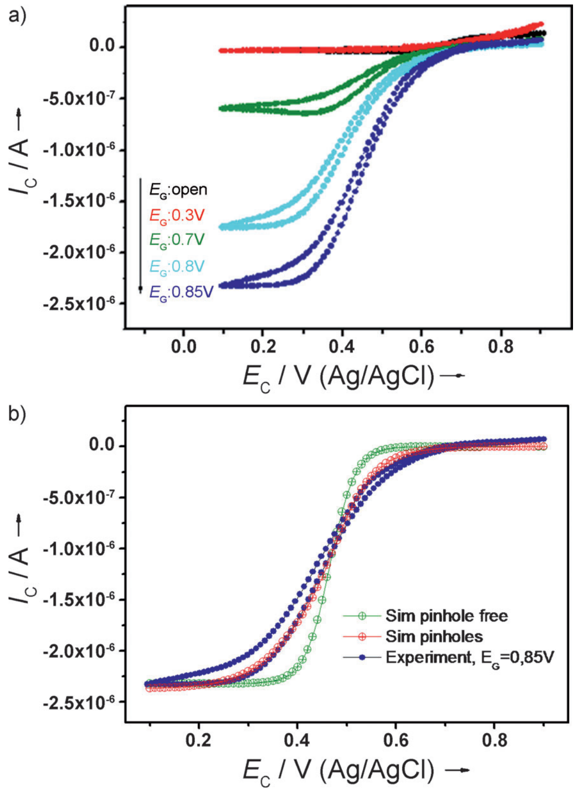

Figure 3. Characterization of cathodic transistor function. a) Collector current (I_C) versus collector electrode potential (E_C) characteristics of hexachloroiridate (0.5 mM) at the Fc modified collector electrode in 0.1 M perchloric acid. The current response was modulated by varying the generator electrode potentials (E_G). b) Experimental I_C–E_C characteristic and corresponding simulations for dense and pinhole containing monolayers. The "Sim pinhole" curve was normalized to limiting current.

An upper limit of the redox cycling response can be calculated by an analytical model for the diffusion-controlled current of IDA, derived by Aoki et al.[9] The calculated limiting current of $I^{\text{lim}} = -5.4\ \mu\text{A}$ for $E_G = 0.85$ V clearly exceeds the experimental values. This is expected, as the model is based on Nernstian boundary conditions that do not account for kinetic limitations at the electrodes. Therefore, we performed a numerical simulation including the two-step electron-transfer kinetics described by two coupled Butler–Volmer equations (see Figure 3 b and the Supporting Information). The simulation provides a good estimation of the limiting current. The shallow slope of the current increase can be explained by taking into account pinholes in the insulating layer of the cathode (see also the Supporting Information).[7]

For the above described operation of the interdigitated electrode array, we observe a cathodic current response. Therefore, the device can be considered as operating in a cathodic transistor-like mode. If a redox probe with a redox potential more cathodic than that of the mediator is used, a reversed anodic transistor function can be realized. For this purpose we used the redox couple ferro-/ferricyanide, which has a redox potential (0.23 V; Supporting Information, Figure S3 b) that is distinctively lower than that of ferrocene (0.45 V). Again, the collector current can be modulated separately by both collector and generator potential similar to the cathodic system but with opposite sign (Figure 4 a; Supporting Information, Figure S5 a).

Remarkably, the presented conceptual device is based on an open electrochemical setup where the number of charge carriers is not fixed by the fabrication process. This contrasts with conventional transistor devices, where the doping level or the chemical structure of the molecules determines the amount of free charge carriers. Here, the number of charge carriers depends on the concentration of added redox probes and can be changed during operation of the system. Figure 4 b shows the boost of the current signal of the collector electrode at increasing concentrations of solution-phase redox probe.[6,10] The open configuration and the dependence of

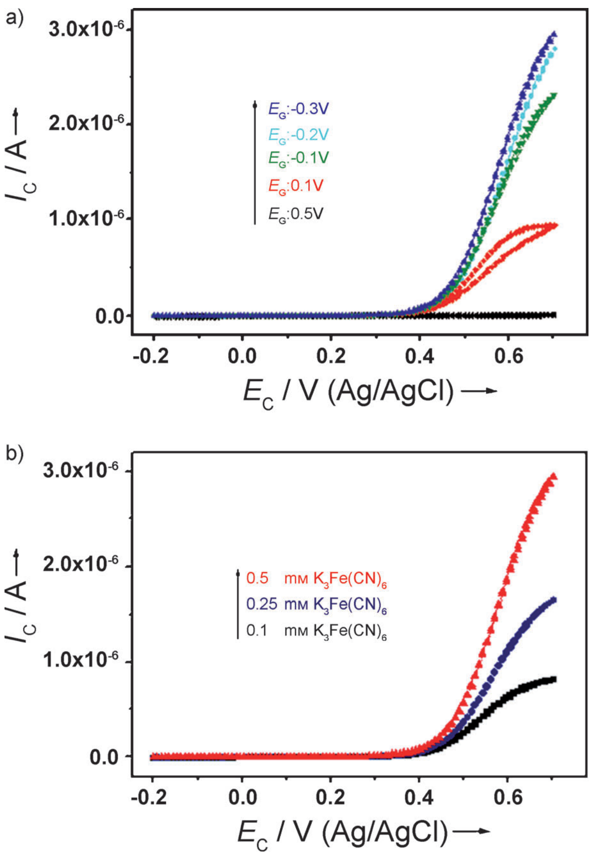

Figure 4. Characterization of anodic transistor function. a) Collector current (I_C) versus collector electrode potential (E_C) characteristics of ferro-/ferricyanide (0.5 mm) at the Fc-modified collector electrode in phosphate-buffered solution (PBS, pH 5.6). The current response was modulated by varying the generator electrode potentials (E_G). b) I_C–E_C characteristics of ferro-/ferricyanide at the Fc-modified collector electrode at different redox probe concentrations. The generator electrode potential was set to −0.2 V.

the output signal on external stimuli make this setup interesting for sensor applications. The readout response is furthermore affected if several input signals are mixed together to realize logic gates.[11]

As the current of the collector electrode can be controlled by changing the generator electrode potential with large on–off current modulation, the IDA system can be operated as a switch. Therefore, the collector electrode is set to a potential at which the respective electrochemical rectifier shows a pronounced forward current (reading potential). For an anodic ECR, the reading potential should be higher than the redox potential of the charge transfer mediator. Figure 5 shows the chronoamperometric responses recorded by an IDA in ferricyanide solution. The collector electrode potential was fixed to 0.7 V and the generator electrode is pulsed between 0.5 V and −0.2 V. The resulting current of the collector electrode is measured over time. The potentials of the voltage pulses are selected such that the potential of the generator electrode turns from a non-activation to an activation regime. During activation, a strong increase of the collector electrode current is observed without changing its potential. After stepping E_G back to 0.5 V, the activation of ferrocyanide interrupts and the current at the collector drops down to the background level.

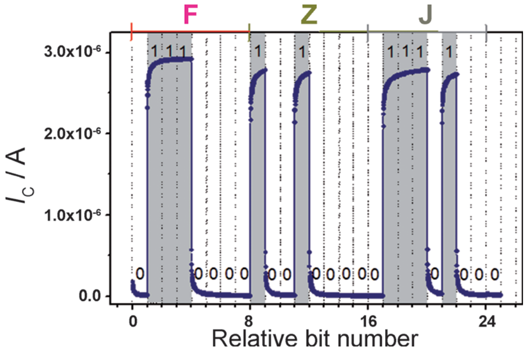

Figure 5. Output of a 24-bit code generator that encodes "FZJ". The encoding was performed in 0.5 mm ferricyanide containing PBS. The collector electrode serves as signal output and the generator electrode as the independent switching electrode.

The system switches between off and on states in a few seconds (95% maximum on current within 2 s). The switching speed is comparable with ion-modulated organic transistors, which could be used in applications that do not require high-speed switching.[12] The ratio of on versus off currents is higher than 400 for the particular redox probe concentration and IDA layout used in this experiment; however, this value can be boosted by changing the arrangement of collector and generator electrodes into a cavity arrangement.[13] A shorter distance between the collector and generator electrodes would reduce the time required to establish a stable limiting current and enhance the switching speed. The relation between redox current and electrode separation has been investigated by scanning electrochemical microscopy.[14]

The switching capability of the interdigitated electrode array can be used to encode information (Figure 5). We defined a string of 0 and 1, which can be converted to the ASCII characters for FZJ (for Forschungszentrum Jülich; see the Supporting Information) and performed the corresponding switching sequence. 80% of the limiting current was defined as threshold to indicate the 0 or 1 state when the output current is lower or higher than this threshold value, respectively. The total length of the string is 24 bits. Stepping the potential of the generator electrode from 0.5 V to −0.2 V leads to a pronounced switching of the output signal from 0 to 1 and vice versa, which is independent of the number of consecutive bits of the same type and the corresponding effective pulse length.

In summary, we have demonstrated that metal electrode arrays modified by redox molecules can perform transistor-like functions with opposite current directions depending on the specific redox input. A unidirectional current recorded at a chemically modified collector electrode can be tuned by the potential applied to an independent generator electrode, which allows switching of the output current and information encoding. The open configuration facilitates the manipulation of the electrochemical characteristics by external stimuli. However, a few engineering challenges remain. Although it is unlikely that this setup will be able to compete with siliconbased transistors in terms of switching speed, it is possible to improve the response time by reducing the distance between generator and collector electrode.

Merging the concept of redox-based transistor functions with chemical logic gates provides a platform to directly link the emerging field of chemical computing with common strategies of information processing. Moreover, if chemical processes involving recognition reactions are integrated into the system, devices can be envisioned that internally process obtained sensoric information.

Received: September 26, 2012
Revised: December 4, 2012

Keywords: electrochemical current rectifier · electrochemical transistor · molecular electronics · redox chemistry · self-assembly

---

[1] a) A. Kamal, W. Yu, G. Fatemeh, R. Petra, P. W. M. Blom, *Adv. Mater.* **2009**, *21*, 4109 – 4114; b) B. Crone, A. Dodabalapur, Y. Y. Lin, R. W. Filas, Z. Bao, A. LaDuca, R. Sarpeshkar, H. E. Katz, W. Li, *Nature* **2000**, *403*, 521 – 523; c) H. Sirringhaus, N. Tessler, R. H. Friend, *Science* **1998**, *280*, 1741 – 1744.

[2] a) S. G. J. Mathijssen, E. C. P. Smits, P. A. van Hal, H. J. Wondergem, S. A. Ponomarenko, A. Moser, R. Resel, P. A. Bobbert, M. Kemerink, R. A. J. Janssen, D. M. de Leeuw, *Nat. Nanotechnol.* **2009**, *4*, 674 – 680; b) E. C. P. Smits, S. G. J. Mathijssen, P. A. van Hal, S. Setayesh, T. C. T. Geuns, K. Mutsaers, E. Cantatore, H. J. Wondergem, O. Werzer, R. Resel, M. Kemerink, S. Kirchmeyer, A. M. Muzafarov, S. A. Ponomarenko, B. de Boer, P. W. M. Blom, D. M. de Leeuw, *Nature* **2008**, *455*, 956 – 959.

[3] M. Mottaghi, P. Lang, F. Rodriguez, A. Rumyantseva, A. Yassar, G. Horowitz, S. Lenfant, D. Tondelier, D. Vuillaume, *Adv. Funct. Mater.* **2007**, *17*, 597 – 604.

[4] a) X. Guo, M. Myers, S. Xiao, M. Lefenfeld, R. Steiner, G. S. Tulevski, J. Tang, J. Baumert, F. Leibfarth, J. T. Yardley, M. L. Steigerwald, P. Kim, C. Nuckolls, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 11452 – 11456; b) G. S. Tulevski, Q. Miao, M. Fukuto, R. Abram, B. Ocko, R. Pindak, M. L. Steigerwald, C. R. Kagan, C. Nuckolls, *J. Am. Chem. Soc.* **2004**, *126*, 15048 – 15050.

[5] C. E. D. Chidsey, *Science* **1991**, *251*, 919 – 922.

[6] a) H. D. Abruna, P. Denisevich, M. Umana, T. J. Meyer, R. W. Murray, *J. Am. Chem. Soc.* **1981**, *103*, 1 – 5; b) Y. Liu, A. Offenhäusser, D. Mayer, *Bioelectrochemistry* **2010**, *77*, 89 – 93; c) Y. Qin, L. Xu, J. Ren, Y. Liu, E. Wang, *Chem. Commun.* **2011**, *47*, 8232 – 8234.

[7] B. Liu, A. J. Bard, M. V. Mirkin, S. E. Creager, *J. Am. Chem. Soc.* **2004**, *126*, 1485 – 1492.

[8] a) D. G. Sanderson, L. B. Anderson, *Anal. Chem.* **1985**, *57*, 2388 – 2393; b) O. Niwa, M. Morita, H. Tabei, *Anal. Chem.* **1990**, *62*, 447 – 452; c) O. Niwa, *Electroanalysis* **1995**, *7*, 606 – 613; d) F. R. F. Fan, A. J. Bard, *Science* **1995**, *267*, 871 – 874.

[9] K. Aoki, M. Morita, O. Niwa, H. Tabei, *J. Electroanal. Chem.* **1988**, *256*, 269 – 282.

[10] K. S. Alleman, K. Weber, S. E. Creager, *J. Phys. Chem.* **1996**, *100*, 17050 – 17058.

[11] Y. Liu, A. Offenhäusser, D. Mayer, *Angew. Chem.* **2010**, *122*, 2649 – 2652; *Angew. Chem. Int. Ed.* **2010**, *49*, 2595 – 2598.

[12] N. J. Kaihovirta, C.-J. Wikman, T. Mäkelä, C.-E. Wilén, R. Österbacka, *Adv. Mater.* **2009**, *21*, 2520 – 2523.

[13] B. Wolfrum, M. Zevenbergen, S. Lemay, *Anal. Chem.* **2008**, *80*, 972 – 977.

[14] a) C. Wei, A. J. Bard, M. V. Mirkin, *J. Phys. Chem.* **1995**, *99*, 16033 – 16042; b) G. Wittstock, M. Burchardt, S. E. Pust, Y. Shen, C. Zhao, *Angew. Chem.* **2007**, *119*, 1604 – 1640; *Angew. Chem. Int. Ed.* **2007**, *46*, 1584 – 1617; c) D. Zigah, C. Herrier, L. Scheres, M. Giesbers, B. Fabre, P. Hapiot, H. Zuilhof, *Angew. Chem.* **2010**, *122*, 3225 – 3228; *Angew. Chem. Int. Ed.* **2010**, *49*, 3157 – 3160.