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Advanced Molecular Logic with Memory Function**

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The steadily growing demand for ever more powerful devices for information processing is expressed in Moore's law, which predicts the duplication of transistor density in an electronic circuit every 18–24 months. Current lithographic processes for microchip production have spatial resolution limits and thus, the quest for alternatives has created elevated interest in the so-called bottom-up approach, that is, the construction of functional (computing) devices from molecular building blocks. Because logic devices are a central component of information technology, the development of molecular systems for logic operations has received special attention. In 1993, de Silva and co-workers provided proof-of-principle that the universality of logic allows its implementation with bistable molecular systems and non-electrical input/output signals.[1] Since then, molecular logic has been extended in many directions, including functional integration, logic reconfiguration, reversible logic, resetting, all-photonic device operation, and signal communication. What started with basic logic gates like AND, OR, INH, and XOR has now reached high complexity, providing molecular mimics for adders–subtractors,[2] encoders–decoders,[3] and multiplexers–demultiplexers.[4]

These logic operations have in common that they are combinational in nature, meaning that the history of input application has no consequences for the device function. On the other hand, sequential logic is a function of past inputs, the thus-created current state of the system, and the actual inputs. Hence, sequential logic implies the existence of a memory function. This feature requires the introduction of feedback loops, which connect the output of a logic gate back to one of its inputs (Figure 1). In conventional electronics, sequential logic is applied in the design of memory elements such as flip-flops, latches, and registers. One of the first examples of still rarely reported molecular sequential logic is an OR gate with a feedback described by Raymo et al. They used a "cocktail" of two molecular switches, namely a photochromic spiropyran–merocyanine system and a 4,4′-pyridylpyridinium derivative, which is electroactive in its protonated state.[5] Proton transfer enabled switch-to-switch communication and the memorized bit was stable for roughly 11 hours. Recently, the van der Boom group has made progress in the demonstration of advanced molecular sequential logic, including the fundamental functionality of a molecular random-access memory (RAM) and reconfiguration between combinational and sequential logic.[6] The findings of their work will be discussed later in this Highlight.

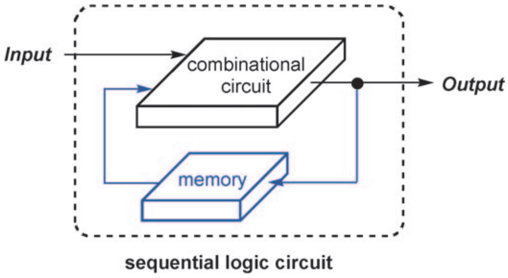

Figure 1. General representation of a sequential logic circuit.

A keypad lock, like that used for user identification at ATM terminals, can be implemented with sequential logic. In 2007, the Shanzer group presented the first molecular keypad lock, based on a pyrene–fluorescein dyad with a siderophore-type linker as a Fe^{3+} receptor.[7] The fluorescence response of the system relies on the balance between interchromophore energy transfer, pH-dependent fluorescein emission, and Fe^{3+}-induced fluorescence quenching. By clever exploitation of a pH-dependent kinetic effect on Fe^{3+} extraction by EDTA (ethylenediamine tetraacetate) as a competitive ligand, input sequences (EDTA and sodium acetate as inputs) can be differentiated through the corresponding fluorescein emission output. If the light excitation of the pyrene energy donor is defined as third input, a three-digit identification number is obtained. On the downside, the kinetic effect imposes certain temporal limitations for the unambiguous differentiation between input sequences.

An all-photonic version of a molecular keypad lock with reset function was presented by the groups of Gust and Andréasson.[8] The exclusive application of optical inputs and outputs enables remote operation and clean resetting without accumulation of chemical side products. To implement this feature a triad composed of fulgimide (FG) and dithienylethene (DTE) photochromes linked to a central fluorescent tetraarylporphyrin (P) was designed. Different wavelengths can be used as optical inputs to address the isomerization of

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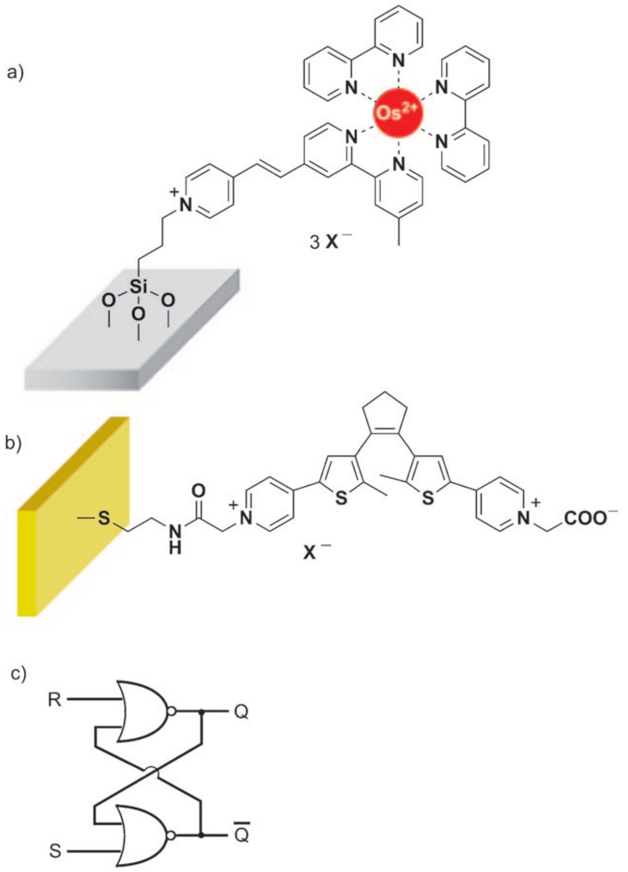
the photochromes. In essence, energy-transfer processes involving the porphyrin are switched by the state of the photochromes—open (o) or closed (c)—thereby leading to fluorescence modulation. It was found that the triad in its $\mathrm{FG_c}$–P–$\mathrm{DTE_o}$ configuration shows highest fluorescence of P. Starting with $\mathrm{FG_o}$–P–$\mathrm{DTE_o}$, this configuration is reached only upon sequential irradiation with UV light followed by red light. Broadband green light resets the system to its initial state. Noteworthy, keypad locks can be also described as priority AND (PAND) gates.

The van der Boom group very recently presented a surface-immobilized $\mathrm{Os^{2+}}$ polypyridyl complex (Scheme 1a), which acts as logically active monolayer.[9] The redox-active metal center is conveniently addressed by oxidizing and reducing input reagents. The output is registered as a change in the absorption spectrum upon conversion of $\mathrm{Os^{2+}}$ to $\mathrm{Os^{3+}}$ and vice versa. Thus, various logic gates (e.g., AND, NAND, OR, NOR, XOR, INHIBIT) and circuits were generated with this extremely versatile platform. While these functions are of combinational logic nature, the same authors were now able to implement sequential logic devices with this platform.[6] One of them is an S–R latch, which integrates two cross-coupled NOR gates (Scheme 1c) and constitutes a fundamental element of static RAM devices.



Scheme 1. a) Structure of the surface-immobilized $\mathrm{Os^{2+}}$ polypyridyl complex (e.g. on glass). b) Gold electrode modified with a DTE photoelectroswitch. c) Electronic scheme of an S–R latch.

In the concrete system the 1 state ($Q = 1$) is defined as high absorption at 496 nm ($\mathrm{Os^{2+}}$ oxidation state), while the 0 state ($Q = 0$) corresponds to the $\mathrm{Os^{3+}}$ complex with a significantly lower absorption at this wavelength. The inputs are constituted by $\mathrm{Co^{2+}}$ and $\mathrm{Cr^{6+}}$ ($\mathrm{pH} < 1$) for the Set (S) and Reset (R), respectively. Whenever the Set input is high ($S = 1$), the system writes and memorizes the binary state 1 (Figure 2). On the other hand, when the Reset input is high ($R = 1$), the 1 state is erased and the 0 state is written and memorized. A low signal for S and R preserves the current state ($Q = 0$ or 1). The device has a bit retention time of at least 10 minutes, which could be further improved in the absence of water. Importantly, it has been shown that the switching can be repeated by alternating activation of S and R inputs in at least ten cycles without significant loss of performance. The conceptual flexibility of the system was further exploited for the realization of three-input sequential logic by invoking $\mathrm{Ir^{3+}}$ as an additional input. Intersections between combinational and sequential logic were shown by logic reconfiguration of the monolayer in dependence on the static or dynamic nature of the current state of the system.

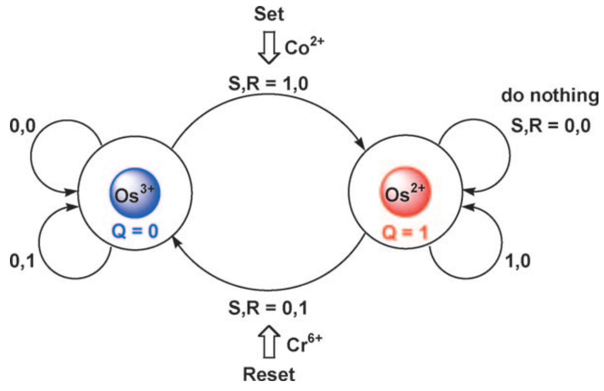


Figure 2. Illustration of the three different S,R input situations in combination with the two possible current states $Q = 0$ and 1 of the $\mathrm{Os^{2+}}$ polypyridyl device. Note that S,R = 1,1 is not allowed.

Noteworthy, Willner, Tian, and co-workers reported an electrochemically active DTE photochrome assembled on a gold electrode (Scheme 1b), which operates also as an S–R latch.[10] Their system relies on the electrocyclization of the open to the closed form of the DTE switch ($E = 0.35$ V; Reset input R) and, on the other hand, photochemical back-isomerization to the open form with 570 nm light (Set input S). The Q state is read as the fast scan cyclic voltammetric response of the switch, which differs for open and closed DTE.

Given the importance of sequential logic in conventional electronics, its proof-of-principle at the molecular level is an important conceptual advance toward molecular information processing. This includes examples like keypad locks,[7,8] S–R latches,[6,10] and the completely electrochemically driven set–reset logic machine based on a copper [2]rotaxane reported by Remacle et al.[11] However, for eventual future applications related to computing, the transfer of solution-phase demonstrations to interfaces is essential. Surface-confined systems, as herein discussed (Scheme 1 a and b), point in the right direction, but more challenges like the concatenation (communication) of several sequential logic layers lie ahead. Also, resetting should avoid the accumulation of chemical waste products, which is eventually a problem for long-term stable device operation. This issue could be addressed for example by all-photonic operation[8] or photoelectroswitches,[10] thereby eliminating chemical inputs.

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