

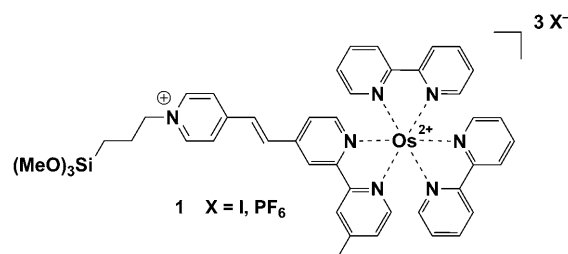
Sequential Logic Operations with Surface-Confined Polypyridyl Complexes Displaying Molecular Random Access Memory Features**

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The processing of molecular information is essential for organisms to respond to external/internal stimuli. For example, in vision, a single molecule of 11-*cis*-retinal is photoisomerized to all-*trans*-retinal, which starts a cascade of signal transduction pathways that eventually enables us to see.^[1] The fact that molecules can be implemented for processing information akin to electronic systems was recognized and demonstrated by the construction of a photo-ionic AND gate by de Silva et al.^[2] This opened up an exciting research area that led to a variety of molecular logic systems such as logic gates,^[3] half-adders and subtractors,^[4] multiplexers,^[5] and encoders.^[6] Bio-inspired systems have also attracted much attention.^[7]

The output of these combinatorial systems is exclusively a Boolean function of the current inputs.^[8] In contrast, the output of sequential systems is determined by the current state of the system, which is usually a function of the previous input and the present input.^[9] This situation thus requires that the molecular-based system must remember information about the previous input, and hence, functions as a basic memory element. Consequently, sequential logic systems are commonly used in the construction of memory devices, delay and storage elements, and finite-state machines.^[9] The demonstration of sequential logic operations with molecular-based systems is relatively rare,^[10] and includes circuits,^[11] molecular keypad locks,^[12,13] and finite-state machines.^[14] Furthermore, previous studies on molecular-based logic are almost exclusively based on solution-based chemistry.^[15]

Recently, we reported the proof-of-principle that 1-based monolayers (Scheme 1) can perform combinatorial logic operations. The system mimics the input and output characteristics of electronic circuitry when using chemical reagents



Scheme 1. The osmium polypyridyl complex used in this study.

as inputs and the formal oxidation state of the system as the output.^[16] Here, we demonstrate a fundamentally new concept towards reversible and reconfigurable sequential logic operations by addressing the memory function of the 1-based monolayers. Interestingly, not only were we able to generate sequential logic circuits with one, two, and even three chemical inputs, but we were also able to use this sequential logic approach to model the memory function of random access memory (RAM).^[17] Moreover, by keeping the starting state static or dynamic, delicate control is obtained regarding which kind of logic is performed—combinatorial or sequential logic. A dynamic starting state generates sequential circuits, whereas a static starting state produces combinatorial circuits.^[16]

For sequential operations with the 1-based monolayer, the presence or absence of an arbitrary chemical input is defined as a logical 1 or 0, respectively. The output or state is dependent on the formal oxidation state of the system, which is monitored by UV/Vis spectroscopy in the transmission mode. The logical outputs 1 and 0 are defined as Os²⁺ and Os³⁺, respectively (See the Supporting Information). For example, a one-input sequential system was designed with Cr⁶⁺ ions in an aqueous solution at pH < 1 as the input.^[18] The four possible combinations were demonstrated with the same monolayer (Table 1). Only when Cr⁶⁺ ions are present and the monolayer is in state 1 (Os²⁺) can the logic gate change to state 0 (Os³⁺; Table 1, see also Figure S1 in the Supporting Information). Since the current state is variable, the output

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Table 1: Characteristics table of the 1-based monolayer operated with one chemical input with different current states (Os²⁺/Os³⁺).

Entry	Input Cr ⁶⁺	Current state	Next state	Output
1	0	1	1	1
2	1	1	0	0
3	0	0	0	0
4	1	0	0	0

becomes dependent on the previous input of the logic gate. This situation corresponds to a sequential logic circuit (Figure 1).

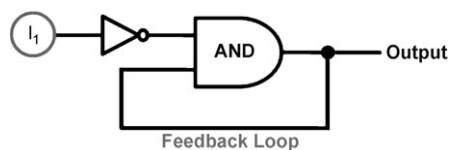


Figure 1. Sequential logic circuit based on the optical output of a monolayer based on **1** at $\lambda = 496$ nm with four combinations of one input (Table 1).

This one-input sequential logic system was expanded towards a 1-bit RAM cell, which is the elementary unit from which static RAM memory is constructed. This unit is comprised of a memory function represented by a Set/Reset (SR) latch. Note that additional logic elements are required to activate/select the latch.^[9] The SR latch is a two-input finite-state machine that reflects the input/output behavior of two cross-coupled NOR gates (Figure 2a)^[9] that have two internal states ($\text{Os}^{2+}/\text{Os}^{3+}$) and two inputs: Set (Co^{2+}) and Reset (Cr^{6+}), respectively. The output Q of the SR latch is the absorption intensity of the metal-to-ligand charge-transfer

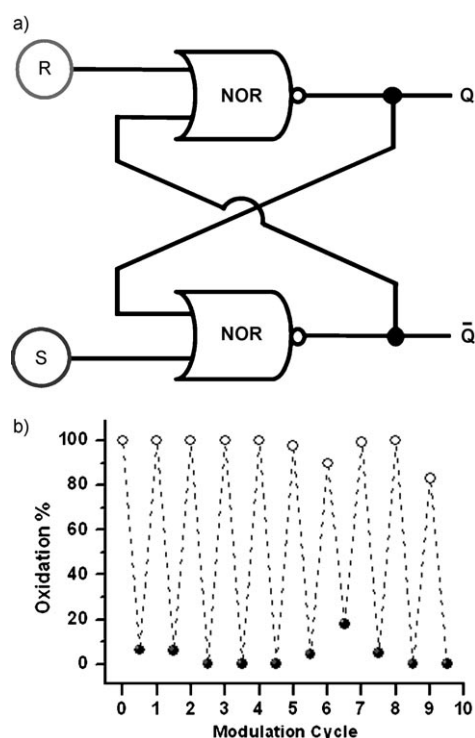


Figure 2. a) SR latch generated with the **1**-based monolayer with Cr^{6+} (Reset input) and Co^{2+} ions (Set input). The output (Q) corresponds to the optical output at $\lambda = 496$ nm (Table 2). b) Modulation of the internal states of the monolayer ($\text{Os}^{2+}/\text{Os}^{3+}$) by applying the Set input (1 mM aqueous solution of Cr^{6+} at pH < 1 (○)) or the Reset input (1 mM solution of Co^{2+} (●) in acetonitrile) as a function of the number of cycles.

(MLCT) band at $\lambda = 496$ nm of the **1**-based monolayer.^[19] The operation of the SR latch is as follows: the system writes and preserves state 1 (Os^{2+}) when the Set input is pulsed high (input = 1), whereas the system writes and preserves state 0 (Os^{3+}) if the Reset input is pulsed high (input = 1), with the subsequent erase of state 1 (see Figure 2b, Figure S2 in the Supporting Information, and Table 2).^[20] Additionally, the

Table 2: Characteristics table of the **1**-based monolayer operating as an SR latch with two chemical inputs: Set: Co^{2+} and Reset: Cr^{6+} .

Entry	Inputs		Current state	Next state	Output Q
	S	R			
1	0	0	1	1	1
2	0	1	1	0	0
3	0	0	0	0	0
4	0	1	0	0	0
5	1	0	0	1	1
6	1	0	1	1	1

state of the SR latch is stored when both S and R are low (input = 0). Indeed, without any inputs the monolayer maintains its current state (see Figure S3 in the Supporting Information). The retention time of these states are 10 minutes, without significant signal loss (< 10 %), as observed by UV/Vis spectroscopy. However, these retention times can be significantly improved in the absence of water.^[21]

The aforementioned examples demonstrate that the **1**-based monolayer is capable of performing sequential logic operations with one and two inputs, respectively. In the following set of experiments, combinatorial and sequential logic is performed with the same system. A distinct metal oxidation state before each entry of inputs results in combinatorial logic, whereas a dynamic state generates a sequential system. In addition, a third input is introduced in the form of Ir^{3+} ions to mimic the characteristics of circuits rather than gates. For example, the starting state (1; Os^{2+}) of the combinatorial system is preserved in the absence of inputs or when Co^{2+} is present (Table 3, Output A). However, the metal center becomes oxidized by Ir^{3+} , Cr^{6+} , or both, as evident by the bleaching of the MLCT band at $\lambda = 496$ nm (see Figure S4 in the Supporting Information). Since the

Table 3: Truth table for the combinatorial logic operations of the **1**-based monolayer operating with three chemical inputs.

Entry	Chemical inputs			Output A ^[a]	Output B ^[b]
	Cr^{6+}	Co^{2+}	Ir^{3+}		
1	0	0	0	1	0
2	0	0	1	0	0
3	0	1	0	1	1
4	0	1	1	1	1
5	1	0	0	0	0
6	1	0	1	0	0
7	1	1	0	1	1
8	1	1	1	1	1

[a] The monolayer is in state 1 (Os^{2+}). [b] The monolayer is in state 0 (Os^{3+}).

starting state is always formatted to state 1, the eight outputs are independent of the starting state. Therefore, it mimics the operation characteristics of the combinatorial circuit presented in Figure 3a. Alternatively, a YES gate is generated

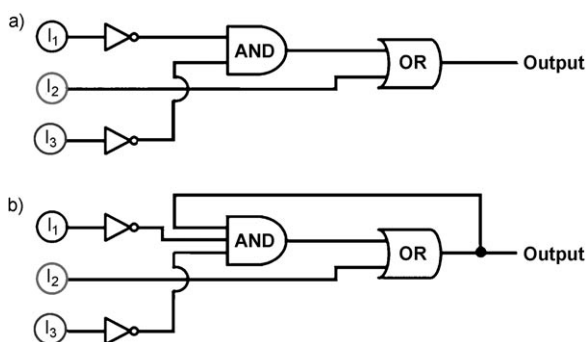


Figure 3. Logic circuits of the monolayer based on **1** operating with three chemical inputs (Table 3): $I_1 = \text{Cr}^{6+}$, $I_2 = \text{Co}^{2+}$, and $I_3 = \text{Ir}^{3+}$. a) Combinatorial circuit generated with a static current state ($1, \text{Os}^{2+}$). b) Sequential circuit generated with a dynamic current state.

with respect to input B (Co^{2+}) when the monolayer is formatted to state 0 (Os^{3+}) before each entry (Table 3, Output B). The use of combinatorial logic with opposite states results here in distinctly different systems: a circuit and gate. Importantly, analysis of Table 3 also reveals the sequential logic elements, since the system's output from the input string 000 is dependent on the current state. This fact demonstrates that the set-up can easily be reconfigured since opposite starting states generate different logic devices. Indeed, performing the same experiment with a dynamic starting state (0 or 1) results in the sequential circuit presented in Figure 3b, which produces the same output as a combination of the outputs of the individual combinatorial circuit and the YES gate. Although this is fundamentally one sequential circuit, it consists of two individually addressable combinatorial scenarios (Table 3).

In conclusion, the **1**-based monolayer is a unique solid-state platform for generating sequential logic systems. We have shown here that several sequential logic systems are obtained when the number of inputs is gradually increased from one to three. Remarkably, we were able to use those sequential logic circuits to display RAM functionality by demonstration of an SR latch. Moreover, although the three-input sequential circuit is basically one unit, one can address two combinatorial sequences in isolation. Furthermore, the same input combinations with a dynamic or static starting state (0 or 1) allows one to select sequential or combinatorial logic. This ability demonstrates the versatility and novelty of this approach towards sequential logic circuits. Nevertheless, the inputs still have to be applied as solutions of chemical reagents. Future research will be directed towards electronically addressable systems.^[22] Furthermore, the sequential circuits generated could, in principle, be modified or extended by using different (concatenated) monolayers or by changing the nature/number of inputs.

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