VIP Boolean Logic

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Redox-Active Monolayers as a Versatile Platform for Integrating Boolean Logic Gates**

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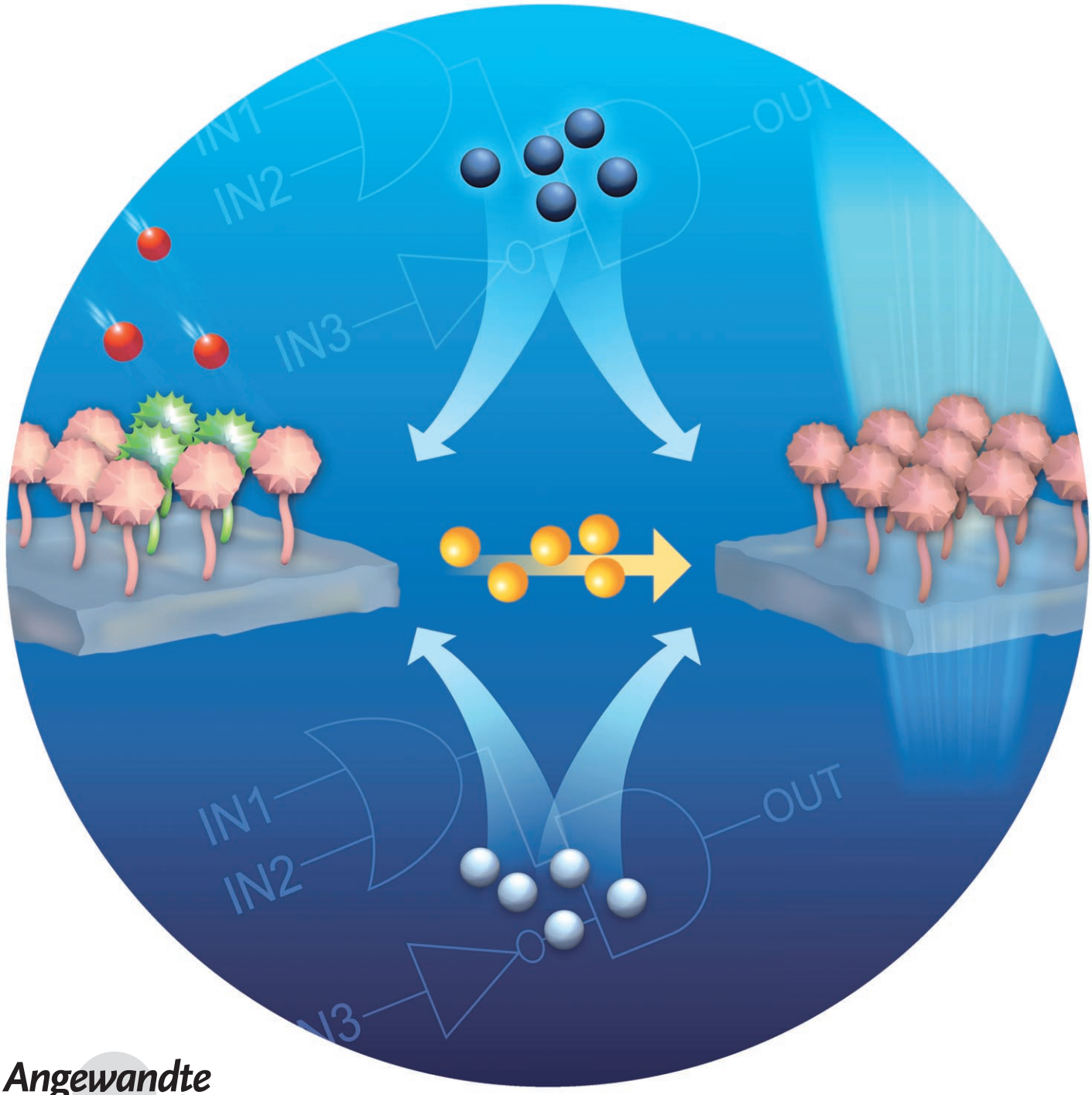
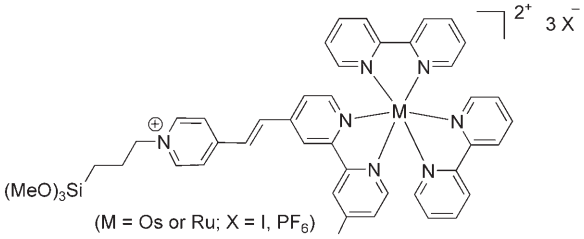


Molecular-based processes can be described using Boolean logic,[1,2] with the prospect of solving complex problems.[3] During the last decade, many new approaches towards designing advanced molecular logic gates emerged, ranging from host–guest interactions, coordination chemistry, and self-assembled systems to bioinspired networks.[4] Molecular-based mono- and multilayer assemblies, covalently attached to various substrates, have been shown to undergo selective chemical and optically induced transformations without system degradation.[5] Logic gates based on such functional molecular interfaces are relatively rare.[6] However, the design of practical applicable molecular-based logic gates attached to solid surfaces is not straightforward, since many material issues related to stability, reversibility, and processability have to be addressed. It is desirable that the gate operation is rapid and involves reliable, nondestructive readout. However, a series of gates could be offered that can be wired to generate sophisticated networks of logic circuits.

We show herein a series of Boolean operations using previously reported redox-active monolayers of osmium and ruthenium complexes (Scheme 1) on glass substrates.[7–9] High



Scheme 1. Osmium and ruthenium complexes used in this study.

stability, selective reactivity, and reversible redox-chemistry, coupled with significant optical changes, make these monolayers versatile logic gates. The operations are based on chemical input signals, coupled with an optical and a chemical output. The logic operations are dependent on the metal oxidation state of the polypyridyl complexes. Furthermore, we demonstrate gate-to-gate communication by using the chemical output of one logic gate as input for another monolayer-based logic gate that is placed in the same chemical environment.

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The Boolean operations are based on electron transfer between the immobilized metal complexes and various reagents in solution. This setup provides a large set of possible inputs and allows the formation of a series of logic gates and circuits with one or two monolayers that have only two distinct operation states (i.e., M^{2+}/M^{3+}). To perform the operations, we must define the combination of one, two, or three reagents (i.e., Ce^{4+}, Cr^{6+}, H_2O, Fe^{3+}, Fe^{2+}, NO^+, Ag^+, Co^{2+}, and DCM) as input = 1, whereas the absence of these compounds is considered as input = 0. The changes in the formal metal oxidation state of the surface-bound metal complexes can be detected by standard UV/Vis spectroscopy in the transmission mode (Figure 1).

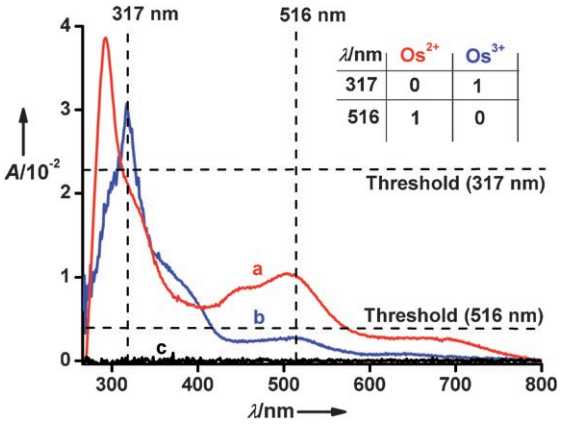

Figure 1. Representative absorption spectra of Os^{2+}/Os^{3+}-based monolayers. a) Os^{2+}, red line, b) Os^{3+}, blue line, c) baseline, black line. The absorption intensities at $\lambda = 317$ and 516 nm were used as output (0 or 1). Inset: Truth table for the Boolean logic of a function of the wavelength and metal oxidation state. The optical absorption spectra of the Ru-based monolayer is somewhat similar to the isostructural Os-based monolayer (although the Ru^{2+} system lacks a broad ^{3}MLCT band; see the Supporting Information).

In the following series of experiments, the characteristic metal-to-ligand charge-transfer (MLCT) band at $\lambda = 516$ nm and the ligand-to-metal charge-transfer (LMCT) band at $\lambda =$ 317 nm of the Os^{2+}/Os^{3+}-based monolayers were used as the output signals. The intensities of these bands are directly related to the formal metal oxidation state and exhibit good ON/OFF ratios. The absorption intensities of these two bands change simultaneously in opposite directions, allowing one to define two different logic gates for the same input or to combine two outputs into one system. Output = 1 when the absorption at $\lambda = 516$ nm or at $\lambda = 317$ nm is higher than the threshold values of 4.0×10^{-3} and 2.3×10^{-2}, respectively. For example, oxidizing the Os^{2+}-based monolayer with Ag^+ in dichloromethane (DCM) as input = 1,1 results in two different optical outputs: 0 = disappearance of the band at $\lambda =$ 516 nm and 1 = concurrent formation of the band at $\lambda =$ 317 nm (Figure 1). A combination of Ag^+ in MeCN, acetone, or THF results in optical changes lower than the above-mentioned threshold values.[10] Apparently, the monolayer meets the criteria for both AND ($\lambda = 516$ nm) and NAND ($\lambda = 317$ nm) gates, depending on the wavelength of the

output signal (Figure 2). Subsequently, the resulting Os^{3+}-based monolayer can be used as molecular OR ($\lambda = 516$ nm) and NOR ($\lambda = 317$ nm) logic gates, since cobaltocene and H_2O as inputs (i.e., 1,0; 0,1; or 1,1) reduce the immobilized metal complexes and regenerate the original absorption spectrum. Other logic gates and combinations thereof are possible, including XOR, XNOR, INHIBIT, and an implication (IMP) gate (Figures 2 and 3). Note that according to De Morgan's law, each of these pairs of logic gates with an output at the two different wavelengths with the same chemical inputs are equivalent because the initial polarity of the system is arbitrarily assigned to begin with. The reversible redox chemistry allows the systems to be reset. Each experiment was repeated at least seven times. For example, the Os^{2+}-based monolayer was oxidized and reduced with Ag^+ and water over 30 cycles without noticeable system degradation (see the Supporting Information).

The Os^{2+}-based monolayer output at $\lambda = 317$ nm is equivalent to the output of an INHIBIT system when NO^+ in an organic solvent (MeCN or CH_2Cl_2) and H_2O were used as inputs (Table 1, Figure 3). However, it would be physically impossible in our system to utilize any of the NOT, AND, and OR gates of such a circuit in isolation. There is no means of independently addressing either "gate" in this physical system, as they are fundamentally one unit (an Os^{2+} polypyridyl monolayer). An INHIBIT circuit expresses non-communicative behavior; one input can disable the entire system. The absorption spectra do not change (output = 0) in the absence of NO^+ (input = 0), and in the presence of H_2O (input = 1), whereas NO^+ (input = 1) in dry organic solvents (input = 0) generates a band at 317 nm (output = 1). Combining both NO^+ (input = 1) and H_2O (input = 1) does not change the optical properties of the Os^{2+}-based monolayer (output = 0) because of the reactivity of these inputs with each other. As expected, the output at $\lambda = 516$ nm demonstrates that the wavelength dependence of the monolayer can be used to operate an IMP gate with the same inputs (Table 1, Figure 3).[11]

Table 1: Truth table and absorption data for the Boolean logic functions for the Os^{2+}-based monolayer operating with two inputs.

Input[a]		Output (A [$\times 10^{-4}$])	
IN1	IN2	$\lambda = 317$ nm	$\lambda = 516$ nm
0	0	0 (197 ± 10)	1 (106 ± 05)
0	1	0 (223 ± 09)	1 (93 ± 08)
1	0	1 (327 ± 11)	0 (30 ± 02)
1	1	0 (201 ± 09)	1 (102 ± 06)

[a] IN1 = NO^+ in MeCN or CH_2Cl_2, IN2 = H_2O.

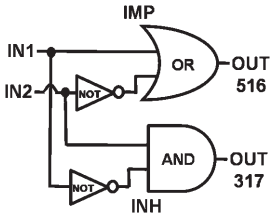

Figure 3. The output at $\lambda = 317$ nm equals the output of an INHIBIT (INH) gate whereas the output at $\lambda = 516$ nm equals the output of an implication (IMP) gate.

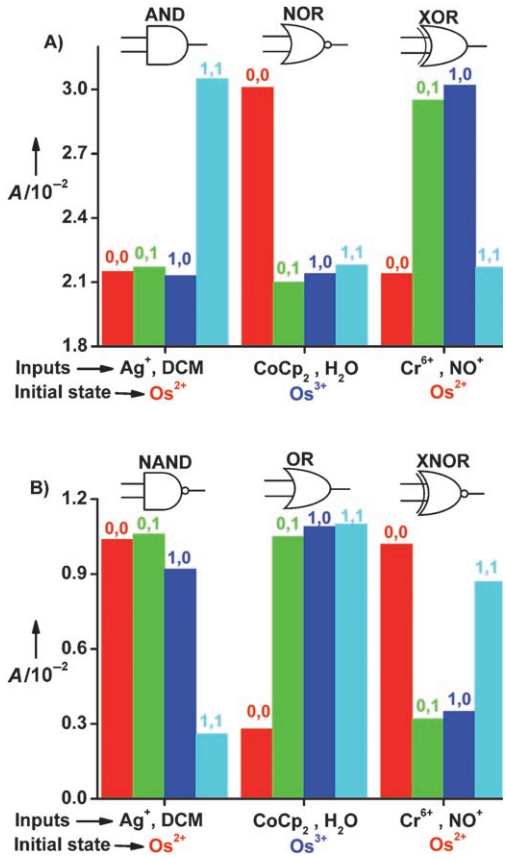

Figure 2. Optical responses (i.e., output signals) and their respective logic gates at $\lambda = 317$ nm (A) and 516 nm (B) for Os^{2+}/Os^{3+}-based monolayers upon applying combinations of two chemical inputs. Os^{2+}-based monolayers were used to demonstrate AND, NAND, XOR, and XNOR gates, whereas Os^{3+}-based monolayers were used to generate the OR and NOR gates. Concentrations of the inputs was 100 ppm; reaction time 1 min at room temperature. Truth table S1 in the Supporting Information lists the optical output values of the combination of two chemical inputs.

The aforementioned examples demonstrate that the monolayers are versatile logic gates based on two chemical inputs. In the following set of experiments, three chemical inputs are used to address the optical outputs of the Os^{2+}-based monolayer at $\lambda = 516$ nm (Table 2). In the following representative examples, eight combinations of two sets of three input signals were used to generate the equivalent output of the circuits shown below in Figure 4.

We recently demonstrated that the reaction of the Os^{2+}-based monolayer with ppm levels of Fe^{3+} in MeCN results in oxidation of the surface-bound metal centers with concomitant formation of Fe^{2+}.[9] Subsequently, the generated Fe^{2+} ions reduce an analogous Ru^{3+}-based monolayer that was placed in the same solution (Figure 5). Alternatively, the Fe^{2+} ions can be trapped by 2,2-bipyridine.[8]

The combination of these chemically wired monolayers by the in situ generated Fe^{2+} ions offers a unique opportunity to design logic circuits based on gate-to-gate communication. For example, the Os^{2+}- and Ru^{3+}-based monolayers were

Table 2: Truth table and absorption data for the Boolean logic functions for the Os^{2+}- based monolayer operating with three inputs.

Input[a,b]			Output $\lambda = 516$ nm (A [$\times 10^{-4}$])	
IN1	IN2	IN3	OUT1[a]	OUT2[b]
0	0	0	1 (112 ± 05)	1 (103 ± 05)
0	0	1	0 (35 ± 02)	0 (28 ± 02)
0	1	0	1 (115 ± 09)	1 (109 ± 06)
0	1	1	0 (31 ± 03)	1 (96 ± 09)
1	0	0	0 (29 ± 03)	0 (35 ± 03)
1	0	1	0 (24 ± 02)	0 (27 ± 02)
1	1	0	1 (93 ± 07)	0 (31 ± 02)
1	1	1	0 (27 ± 02)	0 (25 ± 03)

[a] IN1 = NO^+, IN2 = H_2O, IN3 = Ce^{4+}. [b] IN1 = Ce^{4+}, IN2 = H_2O, IN3 = NO_2.

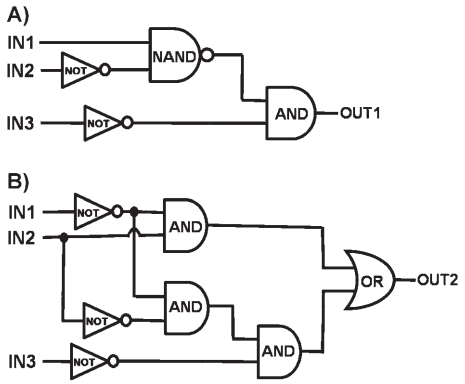

Figure 4. Logic circuits based the Os^{2+}-based monolayer and eight combinations of three chemical inputs (Table 2). A) IN1 = NO^+, IN2 = H_2O, IN3 = Ce^{4+}. B) IN1 = Ce^{4+}, IN2 = H_2O, IN3 = NO_2.

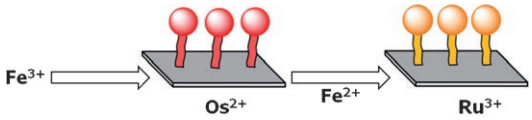

Figure 5. Redox-active monolayer setup used to demonstrate information transfer between two interfaces by metal ions as electron carriers coupled with optical readout.[9]

placed in one reactor and operated with one set of three chemical inputs: Fe^{3+}, H_2O, and Ce^{4+} (Figure 6 A). Table 3 shows the output of the Ru^{3+}-based monolayer at $\lambda = 463$ nm, which matches the performance of the multilevel circuit shown in Figure 6 B.

The electron-transfer-based logic gates immobilized on transparent substrates coupled with "contactless" optical readout are suitable as standalone systems or as operational parts in logic circuits. The large number of possible inputs allows the formation of a series of logic gates and circuits with wavelength-dependent optical outputs. Remarkably, a series of logic gates and circuits are possible with the same redox-active material. The large variety of polypyridyl complexes[12] should allow the formation of highly complex logic circuits. Apparently, this system has the option of a parallel readout and of the ability to combine logic gates into circuits by the proper choice of the absorption bands. An interesting feature

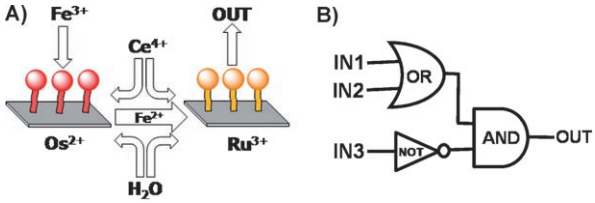

Figure 6. Gate-to-gate communication using both Os^{2+}- and Ru^{3+}-based monolayers. A) Redox-active Os^{2+} and Ru^{3+} monolayer setup. B) Corresponding multilevel circuit.

Table 3: Truth table and absorption data for the Boolean logic functions of a Ru^{3+}-based monolayer operating with three inputs.

Input[a]			Output (A [$\times 10^{-4}$])
IN1	IN2	IN3	$\lambda = 463$ nm
0	0	0	0 (22 ± 06)
0	0	1	0 (24 ± 02)
0	1	0	1 (121 ± 07)
0	1	1	0 (20 ± 01)
1	0	0	1 (116 ± 08)
1	0	1	0 (28 ± 02)
1	1	0	1 (100 ± 10)
1	1	1	0 (26 ± 04)

[a] IN1 = Fe^{3+}, IN2 = H_20, IN3 = Ce^{4+}.

of these monolayer-based logic gates is the ease by which they can be integrated into more complex logic circuits by using the solution as a communication medium.[9] The chemical output of one monolayer-based gate can serve as the input for another gate. These "wired" monolayers form multilevel circuits that can be expanded by using additional functional mono- and multilayers in the same network, as has been shown recently for immobilized DNA-based logic gates.[6b] These DNA systems and other multilevel chemical circuits were feed-forward (nonreversible).[6b,g] The system presented herein is stable up to 200 °C in air for 48 h,[8] and can be readily reused (as opposed to allowing the coordination complexes to be freely soluble components). However, the amount of Fe^{2+} generated by the Os^{2+}-monolayer is small and probably limits the wiring of several different gates. Therefore, future work will expand the monolayer chemistry to redox-active multilayer assemblies and explore other types of chemical wiring.

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