ACCOUNTS
of chemical research

Surface-Confined Assemblies and Polymers for Molecular Logic

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RECEIVED ON JANUARY 5, 2011

CONSPECTUS

Stimuli responsive materials are capable of mimicking the operation characteristics of logic gates such as AND, OR, NOR, and even flip-flops. Since the development of molecular sensors and the introduction of the first AND gate in solution by de Silva in 1993, Molecular (Boolean) Logic and Computing (MBLC) has become increasingly popular. In this Account, we present recent research activities that focus on MBLC with electrochromic polymers and metal polypyridyl complexes on a solid support.

Metal polypyridyl complexes act as useful sensors to a variety of analytes in solution (i.e., H_2O, $Fe^{2+/3+}$, Cr^{6+}, NO^+) and in the gas phase (NO_x in air). This information transfer, whether the analyte is present, is based on the reversible redox chemistry of the metal complexes, which are stable up to 200 °C in air. The concurrent changes in the optical properties are nondestructive and fast. In such a setup, the input is directly related to the output and, therefore, can be represented by one-input logic gates. These input−output relationships are extendable for mimicking the diverse functions of essential molecular logic gates and circuits within a set of Boolean algebraic operations. Such a molecular approach towards Boolean logic has yielded a series of proof-of-concept devices: logic gates, multiplexers, half-adders, and flip-flop logic circuits.

MBLC is a versatile and, potentially, a parallel approach to silicon circuits: assemblies of these molecular gates can perform a wide variety of logic tasks through reconfiguration of their inputs. Although these developments do not require a semiconductor blueprint, similar guidelines such as signal propagation, gate-to-gate communication, propagation delay, and combinatorial and sequential logic will play a critical role in allowing this field to mature. For instance, gate-to-gate communication by chemical wiring of the gates with metal ions as electron carriers results in the integration of stand-alone systems: the output of one gate is used as the input for another gate. Using the same setup, we were able to display both combinatorial and sequential logic.

We have demonstrated MBLC by coupling electrochemical inputs with optical readout, which resulted in various logic architectures built on a redox-active, functionalized surface. Electrochemically operated sequential logic systems such as flip-flops, multivalued logic, and multistate memory could enhance computational power without increasing spatial requirements. Applying multivalued digits in data storage could exponentially increase memory capacity. Furthermore, we evaluate the pros and cons of MBLC and identify targets for future research in this Account.

I. Introduction

The increasing information load requires new approaches for data processing. The present methods are governed by a *top-down* approach in which one strives toward miniaturizing known (logic) devices.[1] Current technology allows for fabricating chips with 32 and 22 nm size transistors, which is used in the latest computer processors. Further miniaturization, however, comes with additional problems.[1,2] For instance, heat dissipation and electrical conductance are problematic below certain size thresholds.[2] Molecular

Published on the Web 06/16/2011 www.pubs.acs.org/accounts
10.1021/ar200002v

(Boolean) Logic and Computing (MBLC) offers a great degree of controllability and versatility over the intrinsic properties of the used material.[3] Therefore, a chemist's *bottom-up* approach toward information processing might be an attractive alternative.[1−5] In this regard, molecular sensors perform a form of information processing since they can detect changes in their environment and transfer this information into an interpretable output. Thus, they often initiate the information processing cascade and display classical input/output behavior required for logic operations. Their inputs are binary in nature, for example, the absence (0) or presence (1) of an analyte. In addition, the output signature of molecule-based sensors (variation in the absorbance, fluorescence, etc.) is also binary in nature, either absent or present. This elementary behavior can be described by the YES gate. This basic one-input logic gate has an output that follows the nature of the input: present or absent. Although they have limited application in digital circuits, the observation that their behavior can be described in binary terms led to the development of the first molecular logic gates.[6] These principles were later extended to mimic more complex logic circuitry and logic gates. In this Account, the use of surface-confined polypyridyl complexes of osmium and ruthenium and poly(3,4-ethylenedioxythiophene) (PEDOT) for MBLC will be discussed (Scheme 1).

II. Molecular Sensors

Our group has used surface-confined monolayers of osmium and ruthenium complexes (Scheme 1A) for the selective detection and quantification of H_2O, NO^+, $Fe^{2+/3+}$, Cr^{6+}, and NO_x in various matrixes (i.e., water, organic solvents, air).[7,8] The basis for this robust sensory platform is the transfer of electrons between the immobilized metal complexes and the analyte. The subsequent change in the formal oxidation state of the osmium complex (from M^{2+} to M^{3+} or vice versa) is accompanied by a significant reduction in the metal-to-ligand charge-transfer (MLCT) band at $\lambda_{max} \approx 500$ nm and the ligand-to-metal charge-transfer (LMCT) band at $\lambda = 317$ nm (Figure 1). These properties have been used for developing a new method for detecting part-per-million (ppm) levels of highly toxic Cr^{6+} in water.[9] This test can be performed in as little as 1 min and can be used in natural systems. The molecular-based sensor is reset to its original state by washing with water. It is highly selective and stable under various conditions. Moreover, dual sensing was demonstrated with the same monolayer since Fe^{3+} can be detected under neutral conditions, whereas the detection of Cr^{6+} requires acidic conditions.[9] Since a binary number can be represented by any system capable of existing in two exclusive states. The value of the binary digit (1 or 0) can be experimentally verified by assigning threshold values, with good ON/OFF ratios, to the output signature (e.g. absorbance or fluorescence) of the sensor; making it a suitable setup for MBLC.

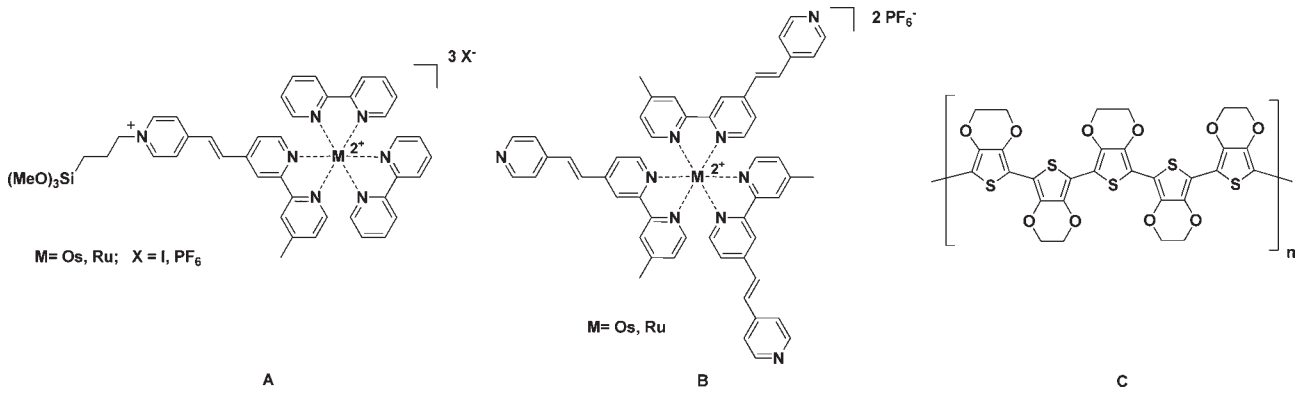
III. Molecular Combinatorial Logic Gates and Circuits

For logic gates with multiple inputs, the relationship between their inputs and outputs can be described by algebraic operations, as introduced by Boole. For two-input logic gates, this results in 16 distinct combinations, each representing a specific logic gate. The NOR and NAND gates act as natural primitive logic gates, in the sense that all other logic gates can be constructed from these gates.[10] In practice only the AND, OR, and NOT gates are used for constructing logic circuits because of their simplicity and cost effectiveness.

Our hexavalent chromium sensor only operates efficiently in the presence of H^+.[9] In other words, only if H^+ *and* Cr^{6+} are present will the surface-confined polypyridyl complexes change their current state within a given time period. The output at $\lambda = 516$ nm is equivalent to a logic NAND gate, where both inputs have to be high (1) in order to generate a negative (0) output (the initial state here is 1). According to De Morgan's theorem, the AND gate is created if one chooses the absorption band at $\lambda = 317$ nm, since this is complementary to the absorption band at $\lambda = 516$ nm. By changing the nature of the chemical inputs to, for example, a combination of $CoCp_2$ and H_2O, a NOR logic gate was constructed, while utilizing the same $Os^{2+/3+}$-based monolayer. In a similar manner, using different combinations of inputs, the formation of the AND, XOR and the INHIBIT gates were demonstrated, and by doing so, their complementary counterparts: NAND, NOR, and NXOR as well, according to De Morgan's theorem.[11]

Figure 2 shows one of the first examples that demonstrated that monolayers could be used for constructing logic gates/circuits that processed information provided by chemical inputs.[11] However, predesigning a desirable logic function or to introduce proof-of-principles, as shown recently in molecular gaming, photodynamic therapy, and/or medical diagnostics, is a major challenge.[12−15] A timeline is displayed in Figure 3 that gives a noncomprehensive overview when some concepts were introduced. From 1993 to 2000, combinatorial logic developed, and molecular logic gates and elementary arithmetic were demonstrated.[16,17] From 2007 onward, sophisticated logic circuits were designed, as in keypad locks,[18] de-/encoders,[19] (de)multiplexers,[20] and full adders/subtractors.[21,22] These

SCHEME 1. Polypyridyl Complexes (A,B) and Conductive Polymers (C) Used for MBLC on Solid Support (i.e., Silicon, Glass, and Indium–Tin Oxide (ITO) Coated Glass)[32,37,38,40]



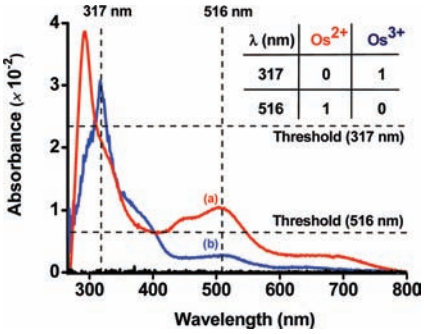


FIGURE 1. Representative absorption spectra of osmium-polypyridyl complexes (Scheme 1A) covalently bound to a quartz substrate when (a) reduced (Os^{2+}; red trace) and (b) oxidized (Os^{3+}; blue trace). The dotted lines indicate the threshold values that determine the value of the binary digits (1 or 0) at two selected wavelengths (317 and 516 nm). Adapted with permission from ref 11. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KgaA.

TABLE 1. Truth Table for the Combinatorial Logic Circuit (Figure 2) Operating with Three Chemical Inputs ($I_1 = Ce^{4+}$, $I_2 = H_2O$, and $I_3 = NO_2$)[11]

	chemical Inputs			
entry	Ce^{4+}	H_2O	NO_2	output
1	0	0	0	1
2	0	0	1	0
3	0	1	0	1
4	0	1	1	1
5	1	0	0	0
6	1	0	1	0
7	1	1	0	0
8	1	1	1	0

circuits were constructed with compounds that rely on the functional integration of logic gates; that is, one molecular based assembly represents an entire logic circuit rather than a gate.[23] This is unprecedented in silicon technology and underscores the potential power of MBLC.

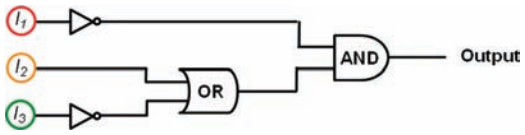


FIGURE 2. Logic circuit operating with three chemical inputs ($I_1 = Ce^{4+}$, $I_2 = H_2O$, and $I_3 = NO_2$), according to $F = \bar{A}[B + \bar{C}]$. Adapted with permission from ref 11. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KgaA.

Physical integration of molecular logic gates has proven to be difficult, especially because of inhomogeneity between inputs and outputs. This is of critical importance, as homogeneity allows for communication between (different) logic gates. There are a few examples of communication through molecular intermediates. One of these is the *three-phase test* where messenger molecules are generated by a polymer-bound material and detected by another polymer.[25] Credi et al. reported another example where the communication between a merocyanine derivative and an osmium terpyridyl complex by means of H^+ was demonstrated.[26] We explored the communication between Os^{2+}- and Ru^{3+}-based monolayers by means of a $Fe^{2+/3+}$ redox couple.[27] Subsequently, we used this to concatenate logic gates.[11,27,28] The electrochemical potential of Fe^{3+} is high enough to oxidize Os^{2+} but not Ru^{2+}. On the other hand, Fe^{2+} is able to reduce Ru^{3+} but not Os^{3+}; therefore, the redox couple can be used to transfer information from one monolayer to the other (Figure 4).

The communication was subsequently used to construct a logic circuit that relies on physical integration rather than on functional integration. Using Os^{2+}- and Ru^{3+}-based monolayers as information processors, in combination with Fe^{3+}, H_2O, and Ce^{4+} as inputs, a logic circuit is constructed by monitoring the output of the Ru^{3+}-based monolayer at $\lambda = 463$ nm (Figure 5A).

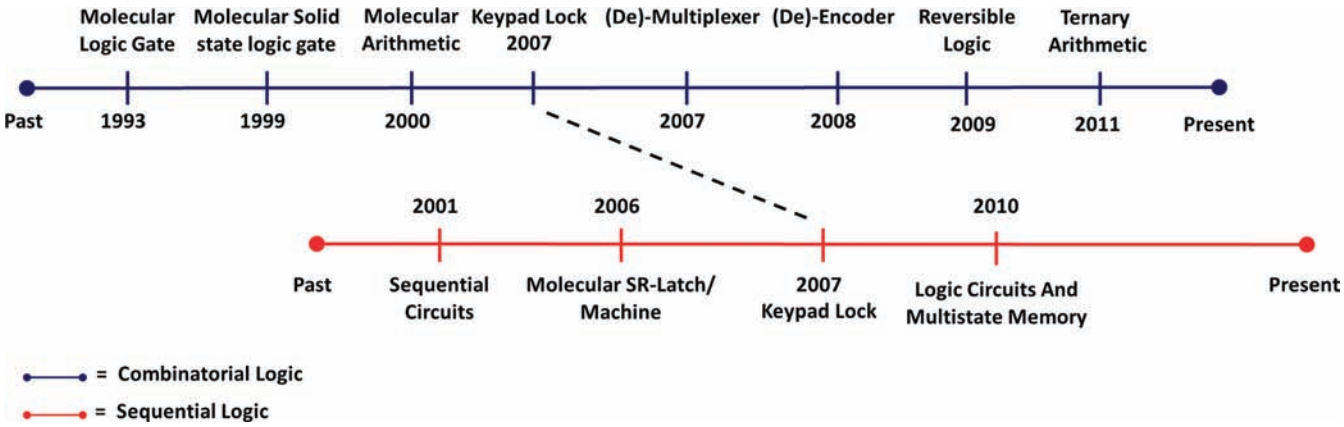


FIGURE 3. Representative milestones in molecular logic. The timeline does not include bioinspired systems.[24]

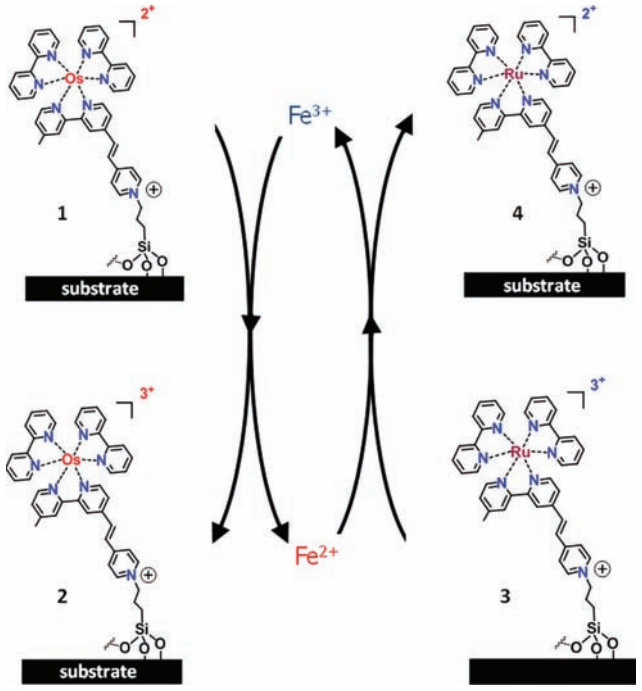


FIGURE 4. Representation of the information transfer, mediated by a messenger component ($Fe^{2+/3+}$), between Os- and Ru-based monolayers. Adapted with permission from ref 27. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KgaA.

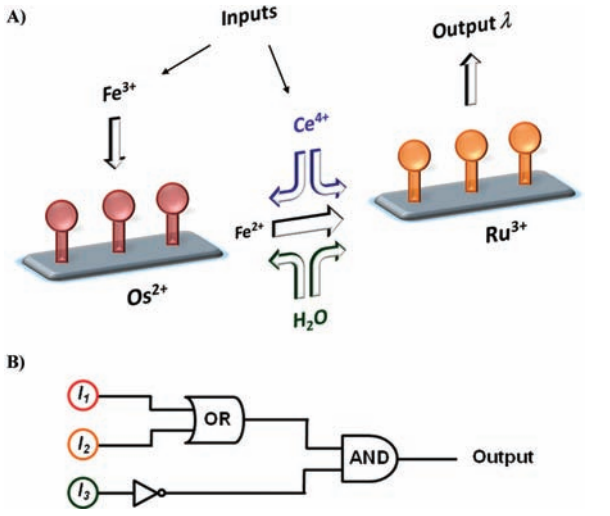


FIGURE 5. (A) Schematic representation of gate-to-gate communication between Os and Ru-based monolayers, mediated by Fe^{2+} as messenger and operating with three chemical inputs $I_1 = Fe^{3+}$, $I_2 = H_2O$, and $I_3 = Ce^{4+}$. (B) Corresponding logic circuit operating according to: $F = [A + B]\bar{C}$. Adapted with permission from ref 27. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KgaA.

The metal center is only reduced (logical 1) when water *or* Fe^{2+} (generated by the Os^{2+}-based monolayer) is present *and* in the absence of Ce^{4+}, which is a strong oxidizing agent that keeps both the osmium and ruthenium in an oxidized state. The OR gate present in the circuit is generated partly by the Os^{2+}-based monolayer, which communicates its output as Fe^{2+}, toward the AND gate, represented by the Ru^{3+}-based monolayer. This corresponds to the logic circuit shown in Figure 5B. These findings have been extended by us to a system that amplifies its optical signature upon reaction with $FeCl_3$.[28] Covalently immobilized Os^{2+} complexes on a glass substrate are oxidized by Fe^{3+}, whereas the concurrently formed Fe^{2+} reduces a series of Ru^{3+}-based monolayers. The simultaneous readout of the light absorption intensities of the Ru^{2+}-based monolayers, which are placed in parallel to each other, provides the output. The gain can be controlled by the addition of a Fe^{2+}-chelating ligand such as 2,2′-bipyridine.

IV. Sequential Logic and Memory

In sequential logic, the output is determined by the current state of the system and the input currently present. The current state is usually a function of the previous input, and hence, the molecular-based system behaves as a basic memory element. In contrast, in combinatorial logic, the output solely depends on the current inputs. Consequently, sequential logic systems are commonly used in memory devices as well as infinite state

TABLE 2. Characteristics Table for the Combinatorial Logic Circuit (Figure 6) Operating with One Chemical Input ($I_1 = Cr^{6+}$)[32]

	input			
entry	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

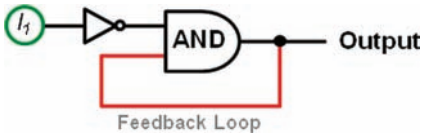


FIGURE 6. Sequential logic circuit based on the optical output of an Os^{2+}-based monolayer that operates according to Table 2. Adapted with permission from ref 32. Copyright 2010 Wiley-VCH Verlag GmbH & Co. KgaA.

TABLE 3. Characteristics Table of a Logic Circuit, Operating as a Flip-Flop[32]

	inputs				output
entry	S	R	current state	next state	*Q*
1	0	0	0	0	0
2	1	0	0	1	1
3	0	1	0	0	0
4	0	0	1	1	1
5	1	0	1	1	1
6	0	1	1	0	0
7	1	1	×	undefined	undefined

machines.[10] This sequential feature adds an extra level of complexity to the design and operation of such molecular-based logic platforms. Both combinatorial and sequential logic circuits are present in computers. However, molecular sequential logic has been less explored (Figure 3).[29−31] Remacle and Levine reported the potential use of single molecule spectroscopy for generating finite state machines.[29]

The sequential operations with our setup are also based on the presence or absence of an arbitrary chemical input, which is defined as a logical 1 or 0, respectively.[32] The generated output is dependent on the formal oxidation state of the system and is defined as Os^{2+} (1) and Os^{3+} (0). For example, a one-input sequential system was designed with an aqueous solution of Cr^{6+} (pH = 0) as the input. The four possible combinations were demonstrated with the same monolayer and are shown in Table 2. Only when Cr^{6+} is present and the osmium-based monolayer is in state 1 (Os^{2+}) does the logic gate change to state 0. Since the current state is variable, the output becomes dependent on the previous input of the logic gate. This corresponds to the sequential

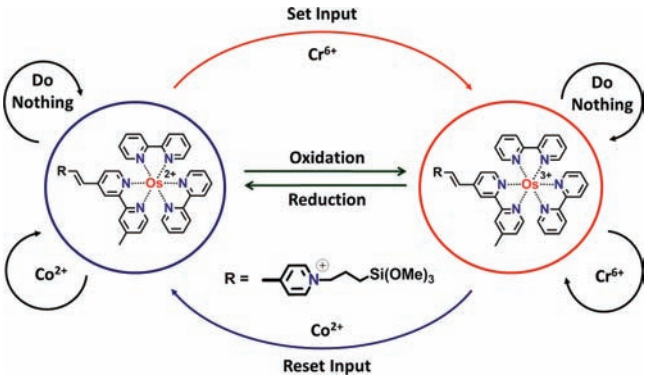


FIGURE 7. State diagram of the Mealy Machine (SR-Latch) generated with the Os^{2+}-based monolayer with Co^{2+} (Set) and Cr^{6+} (Reset) as inputs. The corresponding truth table and logic circuit are shown in Table 3 and Figure 14.[32]

logic circuit, as shown in Figure 6, and is equivalent to the operation of the Cr^{6+}-sensor without performing a reset.[9]

Building on those observations, we mimicked random access memory (RAM), in the form of a flip-flop device.[32] These devices consist of cross-coupled NOR gates that reinforce each other, so that only one input can be high (1) at the same time, and the output is stored even when the original input is switched to low (0). This kind of latching circuitry is the elementary unit from which static RAM (SRAM) is constructed.[10] The Set/Reset (SR)-Latch is operated with Co^{2+} (=Set) and Cr^{6+} (=Reset) as inputs to address the two internal states (Os^{2+}/Os^{3+}). The output, *Q*, is the absorption intensity of the $Os^{2+/3+}$-based monolayer recorded at $\lambda = 496$ nm (Table 3; Figures 7 and 14). The operation characteristics of our setup are equivalent to that of a conventional SR-latch: (i) State 1 (Os^{2+}) is written and preserved when the Set input is pulsed high (input = 1), and (ii) state 0 (Os^{3+}) is written and preserved if the Reset input is pulsed high (input = 1), after state 1 is eliminated. The simultaneous operation of inputs Set=1 and Reset=1 is not allowed, as this situation is undefined. Moreover, the state of the SR-latch is stored when both Set and Reset are kept low (input = 0). UV/vis spectroscopy indicated that the retention time of these states is 10 min with only minor signal reduction.

Combinatorial logic with three chemical inputs, Cr^{6+}, Co^{2+}, and Ir^{3+}, was also demonstrated by changing the initial state before each operation. The system was operated with Os^{2+} (output A) as the starting state before each combination of inputs, and with Os^{3+} (output B) used as the starting state (Table 4). If the starting states are always formatted to the same value, they are independent of the previous input and combinatorial logic is performed. In this case with Os^{2+} (logic 1) as the starting state, the metal center only becomes oxidized if Cr^{6+} or Ir^{3+} is present. Consequently, this system mimics the behavior of the

TABLE 4. Truth Table for the Combinatorial Logic Operations of the Os-Based Monolayer Operating with Three Chemical Inputs and Two Different Starting States: Output A and Output B[32]

	chemical inputs				
entry	Cr^{6+}	Co^{2+}	Ir^{3+}	output A[a]	output B[b]
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]Output A: output generated with Os^{2+} as the starting state. [b]Output B: output generated with Os^{3+} as the starting state.

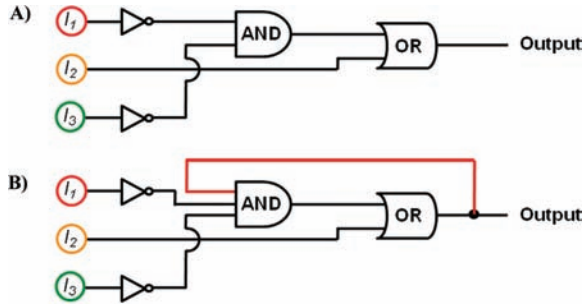


FIGURE 8. (A) Combinatorial circuit operating with three chemical inputs (Table 3) with a static current state (1, Os^{2+}). (B) Sequential circuit generated with a dynamic current state (Os^{2+} or Os^{3+}). Adapted with permission from ref 32. Copyright 2010 Wiley-VCH Verlag GmbH & Co. KgaA.

combinatorial logic circuit shown in Figure 8A. However, if Os^{3+} (logic 0) is used as the starting state, a YES gate is generated with respect to input-two (Co^{2+}). Therefore, a logic circuit and a gate can be mimicked with the same system, by changing the oxidation state of the system at the beginning of each entry. By doing so, all the possible combinations of inputs and previous states (whether the starting state is Os^{2+}/Os^{3+}) were tested, which are required for sequential logic. Interestingly, for the input string 0 0 0, the output is dependent whether the starting (previous) state was Os^{2+} or Os^{3+}. This reveals the sequential logic element that is present in this system, and the corresponding sequential logic circuit is depicted in Figure 8B. This circuit operates according to the combination of outputs A and B generated by the combinatorial logic circuit and the YES gate. *Although this is fundamentally one sequential logic circuit, it consists of two individually addressable combinatorial logic scenarios.*[32]

V. Multistate Logic and Memory

The above molecular logic gates and circuits are exclusively binary in nature. Base-2 has historically been used in silicon

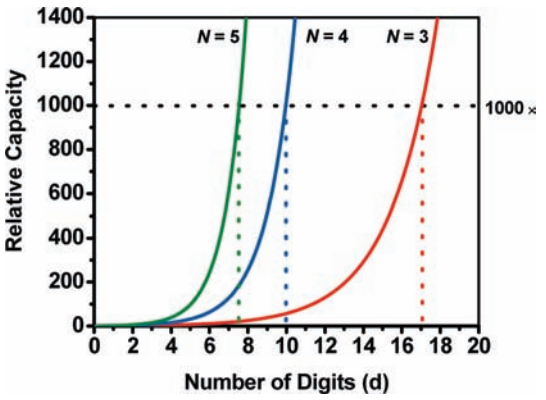


FIGURE 9. Relative memory increase, compared to binary memory, by increasing the radix (*N*). Adapted with permission from ref 40. Copyright 2010 American Chemical Society.

technology, as the first reliable devices were bistable. According to Keyes, only current binary transistor technology is feasible for computing, since transistors exhibit a large gain, can separate inputs from outputs, and act as amplifiers, so errors are nonaccumulative.[33] Moreover, they are self-correcting since the input potential range is much larger than their output range, which eliminates undesirable noise levels and small variances introduced by device fabrication.[10]

What is the advantage of using a different base? Information processing occurs with a certain information density that is determined by the base (or *radix*). If the information density is low, or the information is processed inefficiently, one needs simply more space to achieve a certain computational level. In this regard, a higher-valued radix is beneficial as it raises the information density per single logic operation. The most efficient radix for information processing is Euler's number 2.718.[34] Since integer numbers are used, ternary (base-3) is the most efficient. The number of digits required to represent any given number is $\sim$1.6$\times$ less in ternary than in binary, resulting in a significant increase in memory capacity. Changing from binary memory 2^d to multistate memory N^d leads to an exponential increase of $(N/2)^d$, where N is the radix and d is the amount of digits (Figure 9).

Within the framework of molecular logic, multivalued logic and data storage with molecule-based systems are relatively rare. In 2006, de Silva et al. utilized the principles of multivalued digits for molecular computational identification (MCID).[35] Combinations of dyes attached to polymer beads respond to different chemical environments, enabling multiple fluorescent states, that, when combined, operate similarly to radio frequency identification (RFID). Ternary logic gates were reported by Remacle and Levine who showed that three coupled quantum dots can be used to

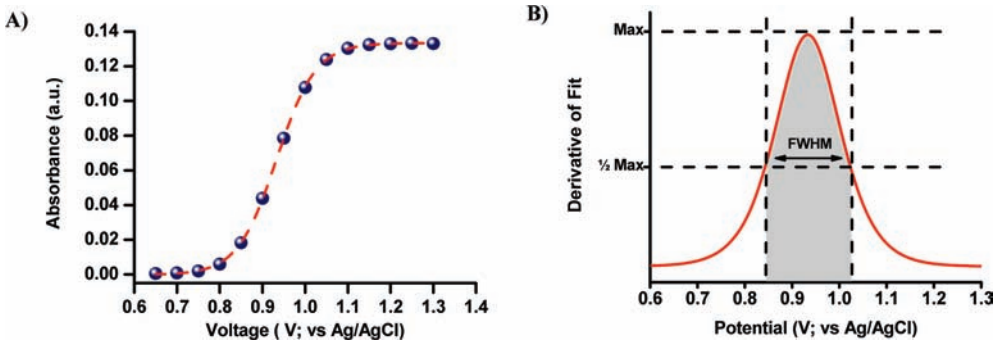


FIGURE 10. Optical properties of the SPMA. (A) Absorbance at $\lambda = 510$ nm as a function of the applied potential. The dashed line denotes a sigmoidal fit ($R^2 = 0.999$), with an inflection point at ($E_{1/2}$) 0.91 V. (B) Derivative of the sigmoidal fit and the corresponding full-width at half-maximum (fwhm). Adapted with permission from ref 40. Copyright 2010 American Chemical Society.

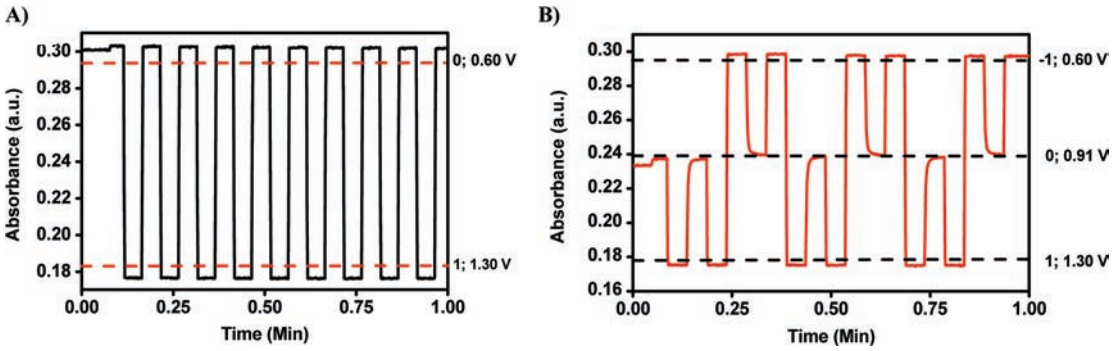


FIGURE 11. Multiple absorbance states at $\lambda = 510$ nm of the SPMA (A) when applying double-potential steps with 3 s intervals and (B) when applying triple-potential steps with 3 s intervals. The dotted lines represent the attainable memory states and the applied potential values. Adapted with permission from ref 38. Copyright 2010 Wiley-VCH Verlag GmbH & Co. KgaA.

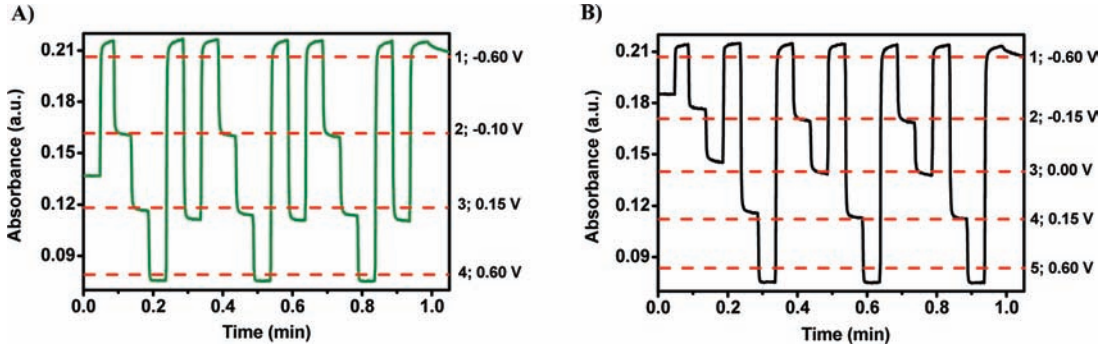


FIGURE 12. Multiple absorbance states at $\lambda = 630$ nm of the PEDOT-coated ITO. (A) Quadruple potential steps with 3 s intervals. (B) Quintuple potential steps with 3 s intervals. The dotted lines indicate the attainable memory states and the applied potential values. Adapted with permission from ref 40. Copyright 2010 American Chemical Society.

theoretically construct a complete set of ternary logic gates including the min and max operators, which are equivalent to the binary AND and OR gates.[36] We have focused on multistate memory with electrochromic materials. Initial steps toward achieving multistate memory were taken with a self-propagating molecular-based assembly (SPMA). The SPMA consists of an osmium polypyridyl complex (Scheme 1B) covalently grafted on ITO. Alternate immersion in a solution of $Pd(PhCN)_2Cl_2$ and the osmium component (B) results in an exponential growing network.[37] The molecular memory was constructed by using the optical absorbance of the SPMA at $\lambda = 510$ nm. When fully oxidized (Os^{3+}), the MLCT band is bleached and the system is in state 0. When the assembly is fully reduced (Os^{2+}), the absorbance is restored and the system is in state 1. Modulation of the oxidation state can be achieved electrochemically by

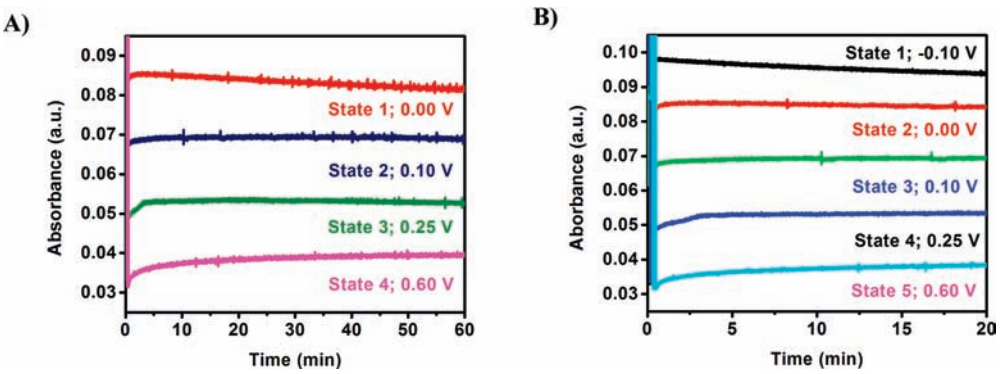


FIGURE 13. Retention times of the absorbance band at $\lambda = 630$ nm of the PEDOT-coated ITO after applying a multipotential step with 3 s intervals. (A) Quaternary memory and (B) quinary memory. Adapted with permission from ref 40. Copyright 2010 American Chemical Society.

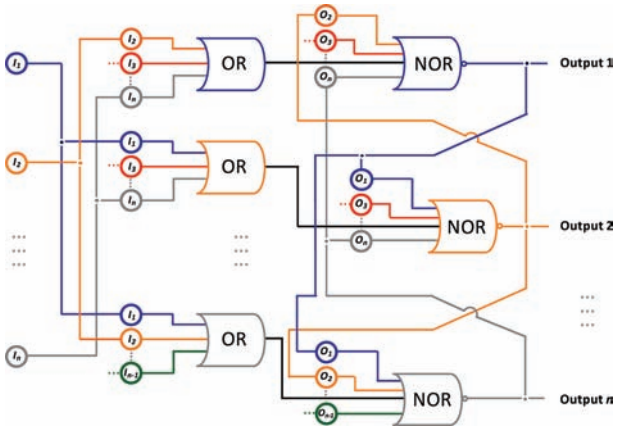


FIGURE 14. Generalized memory circuit capable of storing up to *N* different states in a single setup. Adapted with permission from ref 40. Copyright 2010 American Chemical Society.

applying a potential within the range of 0.60−1.30 V. The presence or absence of an applied potential is therefore defined as a logical 1 or 0, respectively. Although modulation of the oxidation state is binary in nature, the absorbance is a precise function of the applied voltage and can be used to create multiple states (Figure 10A). However, the multiple states are generated by the assembly as a whole, rather than by an individual molecule, which is binary.

The SPMA was used to demonstrate binary and ternary memory.[38] If the input potentials were chosen at 0.60 and 1.30 V, the assembly was cycled between its two oxidation states ($Os^{2+/3+}$) and binary memory was created (Figure 11A). In contrast, if a third input potential at 0.91 V is introduced, an intermediate state is accessible in which the assembly is not fully oxidized or reduced and the assembly is of mixed valency (Figure 11B). In this way, three accessible states are generated that allow the formation of ternary memory. A ternary device operating with individually addressable redox-active complexes would require three oxidation states. Nevertheless, our SPMA is able to achieve the same effect. In the absence of any inputs, the oxidation state of the SPMA is preserved within a certain time period and within predefined threshold values, and hence, no continuously applied potential is needed to maintain the current state. As indication, it takes ~25 min for full conversion from Os^{3+} to Os^{2+}, which can be extended by avoiding trace amounts of H_2O.[39] The observed retention times of the −1, 0, and 1 states of the ternary memory are 75, 110, and ∞ s, respectively. The electrical addressability is an improvement over our chemical addressable binary memory (vide supra)[32] and en route toward all solid-state systems. However, the maximum time (180 ms) it takes for the SPMA to change its output from *high-to-low* or from *low-to-high* is slow. Although, this propagation delay of the electrical addressable SPMAs has been decreased by a factor of 2.0×10^3 compared with the chemically addressable monolayers, a conventional logic gate has a propagation delay of nanoseconds or lower.

The observed dependence of the absorbance upon changing the potential is represented by a sigmoidal shape. Differentiating the obtained function results in a normal distribution centered on the $E_{1/2}$ of the electroactive material, which is expected (Figure 10B). Within this, the full-width at half-maximum (fwhm) of the response−potential characteristics is a useful benchmark. The fwhm describes the potential range in which the intended material is functional. If the range is too narrow, a small change in the potential leads to a large optical change. This is undesirable, since it introduces errors, making it difficult to differentiate between states. In contrast, a large fwhm makes each state easy to distinguish, although the potential range might be too large for practical applications. The SPMA has a relatively small fwhm of 0.17 V. In combination with the short retention times of the assembly, we were able to generate dynamic random

TABLE 5. General Characteristics for Multistate Memory[40]

#	Inputs				Output	
	I_1	I_2	···	I_N	AB ··· *N*	Overall
1	0	0	···	0	Store State	
2	1	0	···	0	10···0	1
3	0	1	···	0	01···0	2
⋮	⋮	⋮	⋮	⋮	⋮	⋮
N_{+1}	0	0	···	1	00···1	*N*

access memory (DRAM) that was able to reach four and five states. This type of memory needs a periodical potential pulse, typically in the millisecond regime, in order to maintain the current state. The memory properties might be improved by increasing the fwhm and the stability of the SPMA.

In our search for suitable materials and to expand the scope from molecular assemblies to polymers, we tested poly(3,4-ethylenedioxythiophene) (PEDOT; Scheme 1C).[40] This electrochromic polymer is robust and operates at low potentials, making it a suitable candidate for demonstrating multistate memory. Similar to our monolayers and the SPMA,[32,37,38] we used here the optical absorbance as output signal ($\lambda = 630$ nm) and various potentials as inputs. Also in this material, the absorbance is a precise function of the applied potential. The fwhm is considerably larger than that for SPMA (0.4 vs 0.17 V). Moreover, the observed $E_{1/2}$ is centered on −0.01 V, which ensures that a future device might work at a low power consumption. The good stability of the PEDOT, combined with a favorable fwhm, resulted in excellent retention times and, moreover, enabled us to demonstrate multistate memory beyond ternary.

For example, the use of four input potentials (i.e., −0.60, −0.10, 0.15, and 0.60 V) generates four distinct absorption values that represent the four states in the memory (Figure 12A). In addition, the memory could be expanded to quinary memory by adding a potential value at 0.00 V (Figure 12B). One might expand the number of states, provided that the ΔA of the absorption is sufficient; however, this would not be beneficial because the gain in efficiency (cost) decreases by incrementing the radix to a large extent.

The input potentials can be reconfigured to increase the retention times of quaternary and quinary memory. The absorbance values are particularly stable between 0.00 and 0.60 V. Therefore, choosing the four and five potentials within this range resulted in retention times of 60 min for the quaternary memory and 20 min for the quinary memory (Figure 13). These retention times approach the range needed for the design of nonvolatile memory. The presented memory is volatile (SRAM), and the information is eventually lost. In this respect, the retention times of the PEDOT are excellent. However, the propagation delay of PEDOT is only 500 ms, which is a possible drawback for device performance, and together with physical integration of molecular entities, are commonly encountered bottlenecks in molecular logic.

In the aforementioned examples, we demonstrated multistate memory that functions with I_N inputs, where *N* is the number of states ($N = 2-5$). Their behavior can be described by the truth table shown in Table 5 and belongs to the flip-flop family. These circuits contain at least two cross-coupled NOR gates that store the corresponding state. In our case, additional OR gates are required to correctly convert the inputs I_N to appropriate inputs for the NOR gates. For two cross-coupled NOR gates, the flip-flop circuit is obtained, which is the main constituent of static random access memory (SRAM). Increasing the memory state by one results in the functional integration of one extra NOR gate into the circuit (Figure 14). Multistate molecular random access memory has attracted much attention recently.[41,42]

VI. Conclusions and Future Outlook

Molecular logic has seen rapid developments in the past few years (Figure 3), and important logic gates and circuits have been demonstrated.[11−22] Proof-of-principles and some applications of molecular logic have been introduced.[12−15,35] Nevertheless, interesting and difficult challenges remain, including (i) a decrease in the propagation delay, (ii) homogenization of the input and outputs, (iii) physical integration of logic gates, (iv) increasing the fan-out, and (v) solid-state logic gates/circuits. The propagation delay is an essential figure-of-merit, because an input should remain active within this time frame. If an input change does occur, an error during the data processing/storage is introduced. For many chemical addressable logic gate/circuits, this propagation delay is in the order of minutes, which constitutes a bottleneck. For our electrical addressable flip-flops, we were able to reduce this delay to ∼180 ms, which is a step toward real-world applications.[38] It would beneficial to use entirely optical or electrical addressable logic gates/circuits. They have been shown to exhibit small propagation delays and have homogeneity between input and outputs, which allows for the possible concatenation of logic gates.

To achieve concatenation of logic gates, it is important that the inputs and the outputs are homogeneous. Redox-active films are of particular interest, as it was shown that

their electrochemical characteristics could be used to construct entire electrical systems.[43] Moreover, this theory could in principle also be applied to our systems to physically integrate logic gates. Chemical wiring of redox-active monolayers capable of operating as gates has been demonstrated.[11,27] Only few other systems are available.[25,26] Moreover, the fan-out (how many logic gates can be driven by another logic gate) for molecular logic systems has to be explored. A first step toward addressing this issue has been the simultaneous readout of the light absorption intensities of a series of Ru-based monolayers, which were chemically addressed by the output (Fe^{2+}) of another Os-based monolayer. Gain control was demonstrated by trapping the messenger component (Fe^{2+}) with a chelating ligand.[28]

Most molecular logic gates utilize solution-based chemistry. This results in amassing chemical entities and thereby limits the reversibility. En route toward all solid-state systems would be the controlled assembly of molecules on a solid support.[17,44] In turn, these molecules can be addressed in a reversible way, optically or electrically.

In conclusion, surface-confined polypyridyl complexes are highly versatile components for the chemical and electrochemical development of a wide range of logic gates, circuits, and memory elements. Static random access memory (SRAM) was demonstrated in the form of flip-flops. Moreover, both Boolean logic and sequential logic operations are possible with a single setup.[27,32,38] The concepts and principles are not limited to these metal complexes, as we were able to demonstrate the formation of multistate memory that was able to store up to five different states with a polymeric material.[40] These findings, the exciting progress made by others, and the numerous stimuli-responsive materials (SRMs) available could be used to solve some of the above-discussed challenges and move this field toward practical applicable systems.[45]

BIOGRAPHICAL INFORMATION

Graham de Ruiter obtained his B.Sc. (2006) and M.Sc. degrees (*cum laude*; 2008) in chemistry with Prof. Jan Reedijk at Leiden University, The Netherlands. He is currently a Ph.D. student in the group of Prof. Milko E. van der Boom at the Weizmann Institute of Science (Israel). He uses polypyridyl complexes as versatile platforms for optical devices, sensors, catalysis, and molecular logic gates.

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This research was supported by the Helen and Martin Kimmel Center for Molecular Design and the Israel Science Foundation (ISF). We acknowledge the persons who participated in the presented work. Their names can be found in the listed papers.

FOOTNOTES

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