Molecular Encoder

DOI: 10.1002/anie.201203342

Orthogonal Addressable Monolayers for Integrating Molecular Logic**

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George Boole's "An Investigation of the Laws of Thought" has proven to be invaluable in the fields of mathematics and computer science.[1] The fact that any system capable of being in two states can be analyzed in these terms is of much importance. For instance, the cooperative behavior of transistors in electronic circuits is analyzed in terms of Boolean algebra.[2] Nonetheless, it was not trivial that the same rules could be applied for molecular information processing. In 1974 Aviram and Ratner proposed that molecules could be used as rectifiers in molecular electronics;[3] whereas de Silva et al. demonstrated in 1993 that molecules could mimic the in/output behavior of an AND logic gate.[4] A variety of molecular logic gates have been demonstrated since.[5] The mimicry of meaningful logic circuits requires predesigning a logic function with a molecular setup. Hitherto molecular equivalents of adders/subtractors,[6] encoders/decoders,[7] multiplexers/de-multiplexers,[8] flip-flops,[9] and keypad locks have been demonstrated.[10] Despite these advancements, most operations are performed in solution, which results in a buildup of chemical entities. A chemically addressable all-solution-based platform might be difficult to operate and to reset. Gust, Akkaya, and their co-workers reported recently exciting examples that use light to address molecular logic gates in solution.[6a,11] The individual control of each logic component in the circuit is difficult. As a consequence, molecular logic relies heavily on functional integration, rather than on physical integration of logic gates as is common for current silicon technology. Recently, a few examples demonstrate physical integration (cascading) of logic gates with molecular components.[12] The physical integration of logic gates with enzyme-based logic is more common.[13]

The key idea is to use molecular monolayers as universal chips that act as individual logic gates; combining their in/output sequence results in meaningful logic arrangements. This approach has many advantages because monolayers are physically separated, do not show interference, and can be read-out independently. By choosing the proper molecular chips, logic circuits can be mimicked, rather than synthesizing new molecules for each logic function. In addition, siloxane-based monolayers are thermally stable, and are robust to a wide variety of environmental conditions. The question remains, why not use such a methodology for molecular logic?

We demonstrate here that a combination of two orthogonal addressable monolayers can be used as molecular chips for mimicking a functional logic circuit, with subsequent control over the individual logic gates therein. The monolayers M1 and M2 are generated by covalently anchoring 5,10,15,20-tetra(4-pyridyl)porphyrin and $[Os(bpy)_2(mbpy\text{-}py)][PF_6]_2$ from solution to a quartz surface (Figure 1).[14] These molecular chips can be addressed chemically and behave as individual parts of the logic arrangement. Combining the optical output of these monolayers defines the overall operation as such. This setup enables, for the first time, to mimic the in/output behavior of a molecular encoder on a solid support. Since the encoder functionality is only displayed when both chips are active, it resembles the plug-and-play principle introduced by de Silva (see Figure S1 in the Supporting Information).[15]

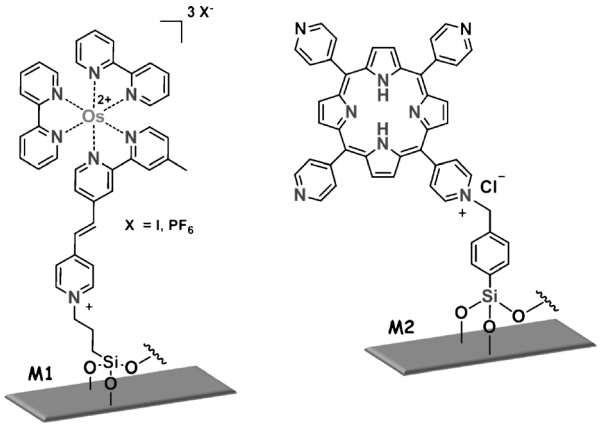

Figure 1. Molecular monolayers (chips) composed of $Os(bpy)_2(mbpy\text{-}py)][PF_6]_2$ (M1) or 5,10,15,20-tetra(4-pyridyl)porphyrin (M2) on quartz surfaces.

A molecular encoder is a device that can compress information, effectively storing the same amount of information in fewer bits. For instance, a 4:2 encoder converts the amount of information present in four bits into an output of only two bits. Therefore, we use four different inputs—with the restriction that they cannot be active at the same time—and two outputs (A and B).[16] In addition, there is also extra output that is called the validation output. This validates the active operation of the encoder when one of the inputs is active, that is, it gives a logic 1 when one encoder is "ON", and

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[**] This research was supported by the Helen and Martin Kimmel Center for Molecular Design, the Minerva Foundation, and the Israel Science Foundation (ISF). M.B. is the incumbent of the Bruce A. Pearlman Professorial Chair in Synthetic Organic Chemistry.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201203342.

a logic 0 when encoder is "OFF". This output, generated by the OR gate does not take part in the actual encoding of the information itself, but merely results from applying the inputs.[2] For correct operation of the 4:2 molecular encoder, the order in which the inputs are applied does not affect the operation of the molecular encoder. In our case this is evident as the monolayers that constitute the encoder are reset to their original state before applying the next input. The truth table and the corresponding logic circuit is shown in Table 1 and Figure 2, respectively. The inputs that are used for operating the encoder are defined as follows: input 1 (In_1) 0.1 mM KCl, input 2 (In_2) 2 M HCl, input 3 (In_3) $NOBF_4$ (saturated), and input 4 (In_4) K_2CrO_4 (50 ppm); see the Supporting Information. In our system, the two outputs, A and B, are represented by the optical absorption of the metal-to-ligand charge-transfer (^{1}MLCT) band and Soret band at $\lambda = 495$ and 465 nm from monolayers M1 and M2, respectively.

Table 1: Truth table of a molecular 4:2 encoder consisting of M1 and M2 operating with four chemical inputs: In_1 = 0.1 mM KCl, In_2 = 2 M HCl, In_3 = $NOBF_4$ (saturated), and In_4 = K_2CrO_7 (50 ppm). The outputs A and B correspond to the outputs of the two different logic gates in the logic circuit of the encoder (Figure 2).

Entry	Inputs				Output		
	In_1	In_2	In_3	In_4	Out_A	Out_B	V
1	1	0	0	0	0	0	1
2	0	1	0	0	0	1	1
3	0	0	1	0	1	0	1
4	0	0	0	1	1	1	1

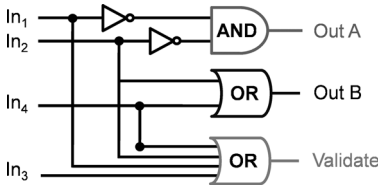

Figure 2. Logic circuit of an 4:2 encoder consisting of M1 and M2, operating with four chemical inputs In_1–In_4: In_1 = 0.1 mM KCl; In_2 = 2 M HCl; In_3 = $NOBF_4$ (saturated); In_4 = K_2CrO_7 (50 ppm), according to the truth table (Table 1).

Since the reactivity of M1 and M2 are orthogonal with respect to the selected stimuli (In_{1-4}), these monolayers will respond differently to the four applied inputs. The Os metal-centers in M1 ensure that this monolayer will be operated according to its redox chemistry, whereas the porphyrin in M2 can be addressed by (de)protonation of the pyridine moieties attached to the porphyrin core.[17]

For example, monolayer M1 is able to respond to various oxidizing agents.[18] The subsequent change in the oxidation state from $Os^{2+} \rightarrow Os^{3+}$ results in bleaching of the ^{1}MLCT band at $\lambda = 495$ nm. As illustration, monolayer M1 is oxidized by immersing the chip in a saturated solution of $NOBF_4$ (In_3) in dichloromethane for 3 minutes. This effect is optically visible and illustrated in Figure 3 A. The logic 1—in this system—is assigned if the difference of absorption before and after applying the input exceeds the threshold value: ΔA ($A_{before} - A_{after}$) $> 2 \times 10^{-2}$. This eliminates noise and ensures high ON/OFF ratios, and hence only occurs if the metal centers in M1 are in the higher oxidation state (Os^{3+}).

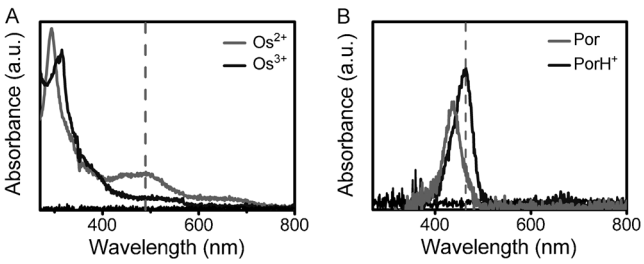

Figure 3. A) Optical response of the metal-to-ligand charge transfer (^{1}MLCT) band at $\lambda = 495$ nm of monolayer M1; before (gray trace) and after (black trace) immersion in saturated solution of $NOBF_4$ in dichloromethane for 3 minutes. B) Optical response of the Soret band at $\lambda = 465$ nm of monolayer M2; before (gray trace) and after (black trace) immersion in a 2 M aqueous solution of H^+ for 3 minutes. The dashed gray lines indicate the wavelengths ($\lambda = 495$ and 465 nm) that were used for assignment of the logic 1 or 0.

Similar results were obtained when the monolayer M1 was immersed in a strong acidic solution containing K_2CrO_7 at pH 0. However, since M1 is only responsive to changes in the oxidation state, it does not respond to changes in the pH value in the absence of oxidizing agents. Immersing this monolayer in a strong acidic solution (pH 0) does not lead to changes in the intensity of the ^{1}MLCT band.[18a] Accordingly, the monolayer M1 is in state 1 only if inputs In_3 and In_4 are applied. This data is summarized in Figure 4 A and Figure S2 in the Supporting Information.

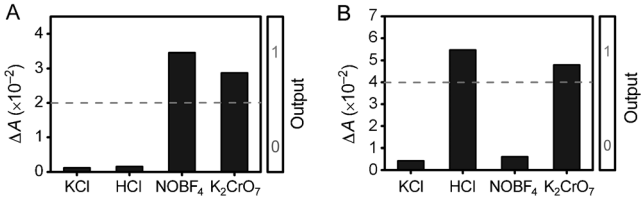

Figure 4. Response (ΔA) of the molecular monolayer M1 and M2 as a function of the four different chemical inputs (In_1–In_4) required for operating a molecular encoder (Figure 2). The dashed lines indicate the threshold level for assignment of the logic 1or 0.

In contrast, the monolayer M2 responds only to changes in the pH value. This property was recently exploited by Gulino et al. for the fabrication of a pH sensor on a solid support.[17] The consequent change in the optical absorption upon protonation of the pyridine groups of M2—after immersion in a 2 M aqueous solution of H^+ (In_2) for 3 minutes—is clearly visible in the optical absorption of the Soret band at $\lambda =$ 465 nm (Figure 3 B).

For M2, the logic 1 is assigned if the difference of absorption before and after applying the input exceeds the threshold value: ΔA ($A_{before} - A_{after}$) $> 4 \times 10^{-2}$. This eliminates noise and ensures high ON/OFF ratios, and hence the

output 1 will only occur if the monolayer M2 is protonated. This behavior pinpoints the orthogonality of M1 and M2, where the latter monolayer is responsive to strongly acidic solutions and not to the here applied oxidizing agents, as is the case with M1 (see Figures S2 and S3 in the Supporting Information). As a result the monolayer M2 only exhibits a logic 1, when inputs In_2 or In_4 are active. For In_1 and In_3 no change in the Soret band is observed. To ensure that both monolayers are responsive to In_4 (K_2CrO_7), we use the fact that the oxidation of Os^{2+} ions occurs predominantly at low pH values.[18a] Protonation of the nitrogen atoms of the inner core of M2 occurs under the strong acidic conditions as well ($pH < 1$).[19] Although one might argue in this case that In_3 will be active as well, the system responds in such a way that In_4 receive priority only over In_3, resulting in logic 1 for M1 and M2. The output of monolayer M2 upon applying In_1–In_4 is shown in Figure 4B and Figure S3.

As monolayers M1 and M2 are operated selectively with four identical inputs, the outputs of M1 and M2 (Figure 4) correspond to the outputs (Out_A) and (Out_B) of the 4:2 encoder (Table 1). Note that there is no special sequence or order in which the monolayer are read-out. Each monolayer M1 or M2 is addressed individually and read-out individually. As a result each monolayer performs a single simple logic operation in the logic circuit of the encoder. Thus, by plugging two independent molecular monolayers into an arrangement of four inputs, a fully functional and playable logic function results. The entire system can be reset by washing M1 and M2 with H_2O (pH 7.5) for 5 minutes.

With respect to molecular information processing, the simultaneous addressing of two types of molecules in solution has been demonstrated. Shanzer and de Silva were among the first to use this feat to cleverly design a molecular keypad lock,[10d] and to demonstrate molecular arithmetic.[20] In addition, parallel processing in solution has been shown as well.[21] Interestingly, the orthogonal reactivity of our chips to the applied chemical inputs allows specific addressing of M1 and M2 with an independent and interference-free read-out. It is reasonable to assume that the method presented here can be expanded to a plethora of different molecular chips that can be designed—when combined with other molecular chips—to produce functional logic schemes. The advantage of this is a large variety and degree of freedom in designing the logic function, without the need for synthesizing new molecules. Just combining two chips can lead to interesting integrated molecular logic. In addition, our siloxane-based monolayers are thermally, chemically, electrochemically robust, stable towards pH gradients, and to a wide variety of environmental conditions.[14,17–19,22]

In conclusion, we have shown a new method for fabricating functional logic schemes with a solid-state setup. The formation of the logic scheme depends on the combination of two different monolayers. Monolayers M1 and M2 were addressed with four different inputs and, by doing so, were able to mimic collectively a molecular encoder on a solid support. We envision that the presented plug-and-play approach[15] for fabricating logic schemes will lead to many more complex and useful functions, for diverse molecular monolayers can be plugged together into an assembly of inputs to produce intricate and complicated logic schemes.

Received: May 1, 2012
Revised: June 6, 2012
Published online: July 24, 2012

Keywords: molecular devices · molecular encoder · molecular logic · self-assembly

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