A simplicity-guided approach toward molecular set–reset memories†

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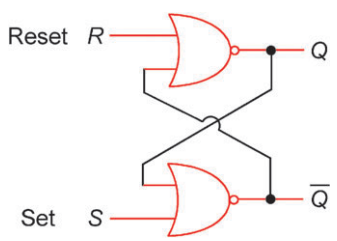
Photochromic switches fulfill the general molecular design criteria for the surprisingly straightforward small-scale integration of seemingly complex set–reset latches. The implications of this re-interpretation are discussed with the example of a dithienylethene photochrome. The concept is shown to be valid for a multitude of well-introduced bistable switches with clearly differentiated output signals, *e.g.*, optical signals for the presented example.

In light of the need for miniaturization and the increase of functional density in modern information technology, the designs of molecular devices as mimics for basic Boolean operations (AND, OR, XOR, INH, *etc.*) and logic circuits of increasing complexity, such as adders/subtractors, multiplexers/demultiplexers and encoders/decoders, have received considerable attention in recent years.[1–5] This has been also expanded towards alternative concepts such as reversible binary logic[6,7] and multivalued logic.[8,9] An emerging strategy in molecular logic is the realization of complex functionality through simplicity-guided approaches, also formulated as "old molecules, new concepts".[10] Recently, two intriguing examples have been reported that are exactly on this path. One is fluorescein, which was found to act as a molecular calculator (*moleculator*).[11] The other is $Ru(bpy)_3^{2+}$, a widely explored chromophore (labelling, sensing, electroluminescence, sensitizer, *etc.*), which was used recently for the molecular implementation of a 4:2 encoder/2:4 decoder combination.[10] In this Opinion article, we expand these lines of thought and provide a simple and generally applicable design principle for seemingly intricate molecular set–reset latches (S–R latches; see the electronic representation in Scheme 1).[12]

Most molecular logic functions have their combinational nature as a common denominator, *i.e.*, the input history has no importance in the outcome of the logic operation. On the contrary, sequential logic implies the existence of a memory function, and the actual state of the system is a determining factor for the final outcome of the logic operation. In conventional electronics, this is implemented by feedback coupling of the output with one of the inputs of the same logic gate. A prominent example for this type of circuitry is a keypad lock, for which molecular examples have been reported recently.[13–15]

Logic circuits with a memory function, such as S–R latches, play a fundamental role in electronics as building blocks of random-access memories (RAMs). This circuit requires the integration of two cross-coupled NOR or NAND gates (a circuit with NOR gates is shown in Scheme 1). The inputs are defined as set (S) and reset (R), and state Q of the system is read as the output. Importantly, Q exists with a certain current value $Q_{current}$ (the memorized state resulting from the input history of the logic device) and the related Q_{next}, which corresponds to the observed output based on the actual input application. Following the truth table (Table 1) of an S–R latch, only upon setting ($S = 1$) does the system switch from $Q_{current} = 0$ to $Q_{next} = 1$, while resetting ($R = 1$) yields the opposite change. Furthermore, the application of $S = 1$ while the system is in the 1 state ($Q_{current} = 1$) or use of $R = 1$ for $Q_{current} = 0$ does not have any effect. The same is true for $S = R = 0$, which corresponds to a "do nothing" situation that is translated into $Q_{current} = Q_{next}$. Notably, the concomitant setting and resetting ($S = R = 1$) of a system yields a physically meaningless indeterminate state. The combined



Scheme 1 An S–R latch as a circuit of two cross-coupled NOR gates; $\bar{Q}$ is the complement of Q.

Table 1 The truth table of a set–reset latch[a]

Entry	Set (S)	Reset (R)	$Q_{current}$	Q_{next}
1	0	0	0	0
2	1	0	0	1
3	1	0	1	1
4	0	0	1	1
5	0	1	1	0
6	0	1	0	0

[a] Q (see Scheme 1 and Scheme 2) is represented by the current memorized ($Q_{current}$) state and the following state (Q_{next}), which results from the actual input application.

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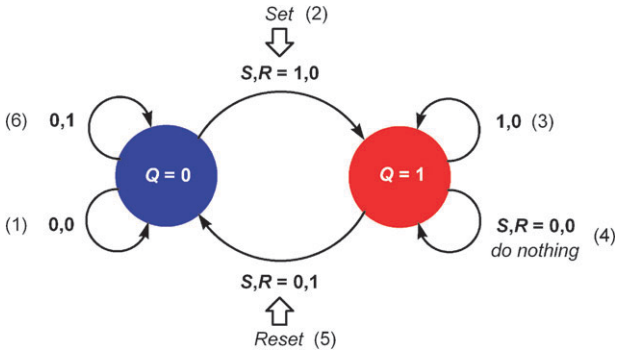


Scheme 2 The general representation of the logic function of an S–R latch. The corresponding entry of the truth table (Table 1) is indicated in parentheses.

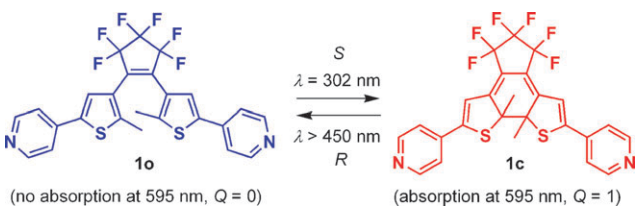
effects of S and R inputs, depending on the memory state Q of the system, are summarized in Scheme 2. Due to the importance of the S–R latch function in electronics, as well as the academic challenge of its molecular mimicking, its realization has recently received growing attention, but is documented only by a handful of examples. These include biomolecular devices,[16,17] a photo-electro switch,[18] an electrochemically-driven finite state machine[19] and a redox-active monolayer.[20]

At first glance, the scarcity of examples could be thought to reflect some very constrained pre-conditions for a molecular S–R latch. However, this is not the case, and it occurred to us that the molecular implementation of this logic function is far more general and based on just a few conditions. In essence, a bistable molecular system is needed, whose state, Q, can be read out through sufficiently differentiated signal levels. Optical signals in form of absorbance or fluorescence are very convenient from a practical point of view. Furthermore, the S and R inputs are expected to act state specifically, *i.e.*, the S input only has an effect on the $Q = 0$ state and the R input acts chemically only on the $Q = 1$ state. The stored information in form of the corresponding chemical species should be stable so as to guarantee that the "do nothing" situation ($S = R = 0$) is not accompanied by a change of the Q state. The application of the S or R input for $Q = 1$ or $Q = 0$, respectively, should not lead to input accumulation. This limits the use of chemical input signals. Finally, the switching process $Q = 1$ to $Q = 0$ and *vice versa* should be repeatable, and thus chemical reversibility is required.

As results from these few pre-conditions, the function of an S–R latch can be implemented in a simplicity-guided approach with surprisingly uncomplicated molecules such as photochromes.[21] Herein, we discuss a representative switch of this class (**1**, see Scheme 3) to illustrate the essential functional requirements for molecular S–R latches. It should be pointed out that the general lines of interpretation are not just limited to this concrete example, but can also be applied for a multitude of switches relying on similar principles. Thus, the core message of this contribution is the generalization of the molecular S–R latch concept.

Photochromic dithienylethene (DTE) switches are promising candidates to implement S–R memory functionality in an all-photonic manner, *i.e.*, optical inputs and outputs.[15,22] This is an advantage in front of the otherwise frequently encountered input–output inhomogeneity of molecular logic devices, which is a problem for their concatenation.[4,5] In our actual example, the well-used DTE photochrome **1** is employed (see Scheme 3).[23–25] On the one hand, 40 s irradiation with UV light ($\lambda = 302$ nm, *ca.* 1.5 mW cm^{-2}, $S = 1$) converts the open form **1o** (no absorbance at 595 nm, $Q = 0$) to the closed form **1c** (high absorbance at 595 nm, $Q = 1$).† On the other hand, the application of broadband visible light for 10 min ($\lambda > 450$ nm, *ca.* 100 mW cm^{-2}, $R = 1$) reverses this conversion. The corresponding isomerization quantum yields in methanol solution have been reported to be 0.57 and 0.014, respectively.[25] Extended irradiation of the closed form **1c** ($Q = 1$) with the S input wavelength after the establishment of the photostationary state has no effect, as is also true for irradiation of the non-colored open form **1o** ($Q = 0$) with the R input wavelength. The "do nothing" situation ($S = R = 0$) leaves the system in its present state ($Q = 0$ or 1), as derived from the extraordinary thermal stability of both isomeric forms (practically stable over months, herein tested with no detectable absorption changes over 88 h).[26] Hence, all six possible entries of the S–R latch truth table (Table 1) are fulfilled by this system.† The cycling between the Q states can be repeated many times (> 10 000 times, as shown for various DTE derivatives in the literature)[26] and is herein demonstrated as exemplary for 10 cycles.† The reading out of the Q state *via* its absorbance in the visible region, which may trigger partial back-isomerization from the closed to the open form and thereby destruction of the memorized bit, can be elegantly accomplished in a non-destructive manner by a recently reported supramolecular approach, including the use of a fluorescence output.[27]

Photochromes have been frequently suggested for applications in data storage,[21,28] typically in the context of write–(read)–erase cycles. However, it must be stressed that the specific implementation of S–R latches based on the all-photonic operation of photochromes is without precedent. In line with the initially mentioned "old molecules, new concepts" idea, this discussion should contribute to alternative views on generally accepted switching phenomena for the purpose of advanced molecular logic functions.



Scheme 3 The photochromic switching of system **1**.

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