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Prospects of luminescence based molecular scale logic gates and logic circuits

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ABSTRACT

In recent years molecular electronics has emerged as a rapidly growing research field. The aim of this *review* is to introduce this subject as a whole with special emphasis on molecular scale potential devices and applications. As a particular example we will discuss all optical molecular scale logic gates and logic circuits based on molecular fluorescence and electronic excitation transfer processes.

Charge and electronic energy transfers (ET and EET) are well-studied examples whereby different molecules can signal their state from one (the donor, D) to the other (the acceptor, A).

We show how a half-adder logic circuit can be implemented on one molecule that can communicate its logic output as input to another half-adder molecule. This is achieved as an electronic energy transfer from a donor to an acceptor, thus implementing a molecular full adder. We discuss a specific pair, the rhodamine–azulene, for which there is considerable spectroscopic data, but the scheme is general enough to allow a wide choice of D and A pairs. We present results based on this pair, in which, **for the first time,** an **all optical** half-adder and full-adder logic circuits are implemented.

1. Introduction

The need for increasing miniaturization of logical circuits will soon reach the physical limit of Metal Oxide Semiconductor Field Effect Transistor (MOSFET) devices. The fabrication of small semiconductor based devices becomes more difficult and expensive as the nanometric scale is approached. Furthermore, bulk properties of semiconductors vanish at the nanometric level. Further miniaturization of electronic devices is expected to open the way to new technologies.

Since our research focuses on molecular-level devices, e.g. molecular logic gates, there is the need to define such a device. When extending the macroscopic concept of a device to the molecular level, one can define a molecular scale device as an assembly of a discrete number of molecular components designed to perform a specific function. Each molecular component performs a single act, while the entire supramolecular assembly performs a more complex function, which results from the cooperation of the various components. Such a molecular-level device operates via electronic and/or nuclear rearrangements and, like a macroscopic device, needs energy to operate and signals to communicate with the operator [1]. Single molecule based switches [2,3] rectifiers [4,5] and wires [6] have been reported already. The extension therefore to more complicated schemes, such as discussed in this paper, is only natural.

Organic molecules are promising candidates for the realization of electronic and photonic devices. They have nanometric dimensions and their properties can be tuned through chemical modifications. Organic molecules can be easily produced and are relatively cheap to make, even in large quantities. It is important to note that the operating mechanisms of a device based on organic molecules have little in common with a conventional electronic one. Switching systems based on acid/base reactions, on redox processes, on photochromic behavior, on optical control of chirality, on conformational changes, on electrochemically and photochemically induced changes in liquid crystals, thin films and membranes and in supramolecular structures, and on photoinduced electron and energy transfer have been synthesized and studied [7,8].

Logic gates of microprocessor systems are assembled by interconnecting transistors, and their input and output are electrical. However, the concepts of binary logic can be extended to chemical, optical or other types of signals. Thus, it may be necessary to design devices that would respond to signals in the same way transistors respond to the electrical stimulations. Data processing and communication require the encoding of information in electrical and optical signals in the form of binary digits. A threshold value and a logic convention are established for each signal. In a positive logic convention, a 0 is used to represent a signal that is below the threshold, and a **1** is employed to indicate a signal that

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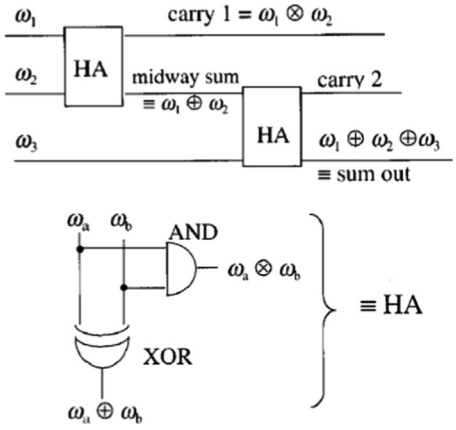

Fig. 1. Representation of a full adder constructed from two communicating half adders (HA) and the symbolic representation of a half adder.

is above it [9]. Each logic gate performs according to a set of rules arranged in so-called truth table, which is a list of gate outputs resulting from certain inputs. The ***AND*** gate executes a binary product, ⊗, while the ***XOR*** gate performs a binary sum, ⊕ [9].

The half adder is the basic component of computational arithmetic in digital computers. Its function is to add two one-digit binary numbers together. Thus, the ***AND*** and ***XOR*** are the two logic operations that need to be implemented on the two binary inputs in order to build a half adder, working in parallel. By concatenation of two such half adders, one can build a full adder. A binary full adder accepts the two digits that are to be added, and also the third input, namely the "carry in" digit from a previous addition, where the summation is completed. A full adder needs to produce two outputs, the so-called "sum out", which is the ***XOR*** sum of the two inputs, and an output called the "carry out", which is the ***AND*** product of these inputs that becomes the "carry in" for the next addition cycle.

The symbolic representations of the half and full-adder logic circuits are shown in Fig. 1. In Fig. 1 the full adder is made by concatenation of two half adders. Each half adder (**HA**) is constructed, using ***AND*** and ***XOR*** logic gates, where ω_1, ω_2 and ω_3 are Boolean input variables. In our study these will be laser inputs at specific frequencies exciting specific molecular electronic states. The ***XOR*** gate evaluates the Boolean function $\omega_1 \oplus \omega_2$, while the ***AND*** gate evaluates the Boolean product $\omega_1 \otimes \omega_2$, which is unity, if both lasers are on, and $\omega_1 \oplus \omega_2 \oplus \omega_3$ is defined as sum out. The full adder has three outputs: carry 1, carry 2 and the sum out. Either carry 1 or carry 2 will provide the value of output carry bit. The midway sum in our scheme will be communicated by energy transfer to the second **HA**. The corresponding truth tables for the above operations are given in Tables 1 and 2.

As mentioned above certain organic molecules change their structural and electronic properties due to stimulation by chemical (in the form of protons, metal ions, specific molecules, etc.), electrical (electrons or holes) or optical (photon) inputs. A molecule switches from one state to another when stimulated by an input signal. In photochemical stimulation the most common switching processes are related to photoisomerization or photoinduced redox reactions. If the input is electrochemical, the induced processes are redox reactions [10–12]. Compared with chemical stimulation, photochemical and electrochemical stimulations have the advantage that they can be switched on and off easily and rapidly. Most of the transformations are reversible: the chemical system returns to its original state when the input signal is turned off. In some cases the molecular switch produces a chemical, electrical and/or optical output that varies in magnitude with the switching process.

Table 1
Truth table for a full adder.

ω_1	ω_2	Carry in ⎔≡ω_3	Sum out	Carry out
0	0	0	0	0
1	0	0	1	0
0	1	0	1	0
0	0	1	1	0
1	1	0	0	1
0	1	1	0	1
1	0	1	0	1
1	1	1	1	1

Since both conventional logic gates and molecular switches convert input stimulations into output signals with intrinsic protocols, the principles of binary logic can be applied to the signal transduction operated by molecular switches [1,7]. The analysis of their logical behavior requires, first of all, the assignment of threshold values and logic conventions to their input and output signals. Making an analogy to CMOS logic circuits, the signal transduction protocol of a molecular switch can be programmed to execute specific logic functions simply by selecting the initial logic assumptions. Various molecular based logic schemes have been discussed. However, no ***all optical*** logic gates and schemes have been demonstrated. The most trivial gate would be a ***YES logic gate*** [13]. The ***NOT logic gate***, which inverts any signal received, is easily achieved in chemical systems because of the ease with which luminescence (output) can be quenched by chemical input. An example of ***NOT*** chemical gate based on fluorescence quenching by photoinduced electron transfer (PET) [14] was reported.

The first example of molecular scale logic gate especially designed to implement ***AND gate*** was reported by de Silva et al. [15]. As in the case of ***NOT*** molecular logic gate, the operation of the AND gate is based on PET process, where the inputs are chemical and the output are fluorescence signals. Similarly ***OR logic gate*** based on requirement of non-selective luminescence enhancement, e.g. a set of non-selective receptors giving a positive response upon binding has been demonstrated [16,17]. An example of ***XOR logic gate*** which functions with two chemical inputs and an optical transmission output has also been reported [18]. Recently Margulis et al. [19] reported a fully reversible ***molecular half adder***, based on controlling the absorption spectra of flourescein dye in solution by changing the pH conditions.

Molecular full-adder logic circuit is one of the great challenges in design of molecular logic. A simulation of a molecular full adder based on 2-phenylethyl-N,N-dimethylamine (PENNA) molecule, where the inputs were provided optically, was recently reported by Remacle et al. [20]. Threshold values for output reading were obtained by a numerical solution of the equations of motion for the population as a function of laser pulse duration. In their scheme three distinct inputs are necessary to implement a full adder on PENNA molecule: two UV photons (x and y inputs) and carry in input (excitation by two green photons). Fluorescence from the S_1 state of the phenyl ring codes for carry out = 0, sum out = 1; ion fragmentation at the amine end codes for carry out = 1, sum out = 0; and ion fragmentation at the chromophore end for carry out = 1, sum out = 1. Most of the outputs are detected due to photoionization of the molecule, which means that the molecule self-destructs at the end of the computation.

We have suggested that a molecular half adder can be implemented on molecules that have detectable one photon absorption and a detectable two photon absorption [21]. Fig. 2 depicts such a molecular half-adder scheme. Here the carry output is probed as $S_2 \rightarrow S_0$ fluorescence only when both ω_1 and ω_2 photons are present, whereas the sum output is probed as $S_1 \rightarrow S_0$