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## Intermolecular and Intramolecular Logic Gates

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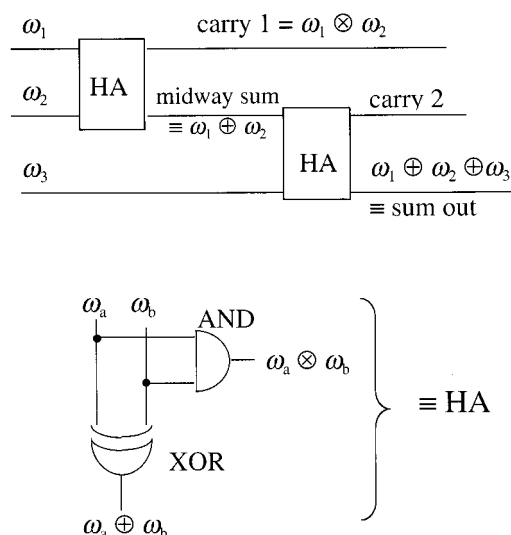
Logic circuits operating on different molecules or on different parts of the same molecule can be connected. As an example, a circuit known as a full adder is described. It is made up of two circuits, a half adder on a donor (rhodamine 6G) and another half adder on an acceptor (azulene). The signal, (an intermediate sum), is moved from donor to acceptor by electronic energy transfer. The concatenated logic arrangement is described, and potential applications using other bichromophoric molecules are outlined. Polychromophoric molecules will allow a fanout operation.

## Introduction

Charge and electronic energy transfer (ET and EET) are well-studied<sup>1–4</sup> examples whereby different molecules can signal their state from one (the donor, D) to the other (the acceptor, A). This transfer is often studied as an intermolecular process, but it can also occur intramolecularly, that is, between two bridged parts of a molecule. In this letter we propose to use this transfer as a way of connecting between logical operations that are implemented on different molecules. With such a concatenation one can begin to think of the construction of larger scale integrated logic circuits, made up of many molecules. In particular, the already demonstrated EET in trichromophoric molecules<sup>5</sup> ensures that a fanout operation, that is, the communication of a given output as input to more than one circuit, will be possible. Although we shall not make use of it, the scheme discussed in this letter can exhibit a bidirectional transfer so that feedback is also possible.

The present work is in molecular electronics.<sup>6,7</sup> Rather than trying to make molecules that can act as wires,<sup>8,9</sup> switches,<sup>10–14</sup> and other building blocks of conventional electronic circuits, in this work individual molecules are instructed to implement already nontrivial logic tasks. We show, and this is the point of this letter, that one molecule can communicate its logic output as input to another molecule. This transfer is achieved as an electronic energy transfer from a donor to an acceptor. We do discuss a specific pair for which there is considerable data, but the scheme is general enough to allow a wide choice of D and A pairs. The results are for an intermolecular transfer in solution, but many similar D–A pairs that are bridged, D–B–A, have been studied.<sup>1,15</sup> Indeed, a rigid bridge will make the energy transfer much more efficient<sup>16,17</sup> so that the rigid concatenation required for a circuit board is an advantage. A bridged pair is a particular example of our general suggestion that a reactive molecular coordinate can act as a bus.

In the background to the discussion is the proposal<sup>18</sup> that entire logic gates, and even circuits,<sup>19</sup> can be represented by



**Figure 1.** Logic circuits of a full adder (top panel) and of a half adder, HA, (bottom panel).  $\omega_1$ ,  $\omega_2$ ,  $\omega_3$  are Boolean variables. Their values are 0 (for laser off) and 1 (for laser on).  $\oplus$  is addition of Boolean variables, sometimes known as addition modulo 2. XOR is the eXclusive OR gate that evaluates the Boolean function  $\omega_1 \oplus \omega_2$ . The AND gate evaluates the Boolean product  $\omega_1 \otimes \omega_2$  that is unity if both lasers are on. The lines are drawn for clarity so as to indicate which variables are the inputs and outputs. The full adder is drawn as if it has three outputs carry 1, carry 2, and sum out. Either carry 1 or carry 2 will provide the value of the output carry bit. (If so desired, one can feed them into an OR gate, a one-photon broad absorber,<sup>18</sup> so as to get an answer that can be communicated to the next circuit.) The graphical notation for the AND and the XOR gates is a standard one.

the spectroscopy of a single molecule. When the logical output is achieved by ionization, as few as 10 molecules, acting independently, are sufficient to provide a signal above the noise level.<sup>19</sup> Detecting fluorescence will require more excited molecules. Chemical and electrochemical pumping of molecules has also been discussed,<sup>12,14,20–24</sup> and higher concentrations are then needed.

In our proposal, the logic that can be implemented on a molecule is determined by the number of states of the molecule that can be spectroscopically pumped and probed. High-

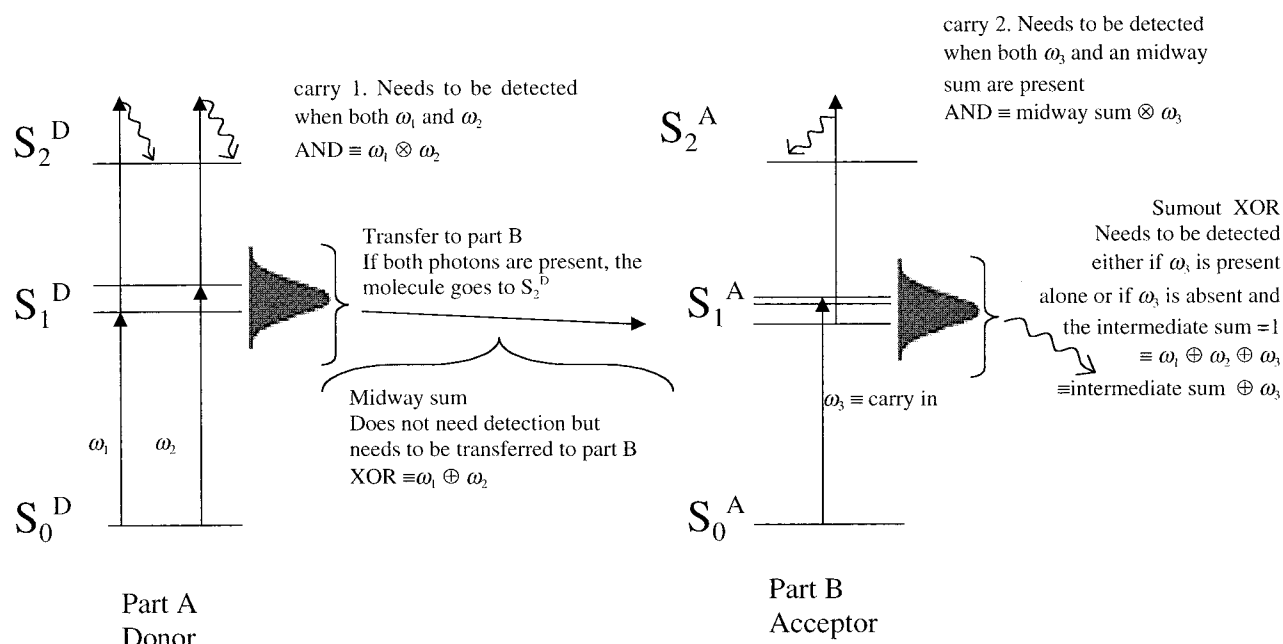
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**Figure 2.** Photophysical scheme that implements the logic circuit shown in Figure 1. The text specifically discusses the example where the donor is rhodamine 6G and the acceptor is azulene and provides the values of the frequencies, etc. The Boolean notation is defined in the legend to Figure 1.

**TABLE 1: Truth Table for a Full Adder**

$\omega_1$	$\omega_2$	carry in $\equiv \omega_3$	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

resolution work can make the number of states large, and this is one promising direction. The other possible route, and the one that is followed here, is to connect different molecules in the manner made familiar by connecting arithmetic units into larger chips. Note that we do not say “to connect different molecules in the manner made familiar by connecting transistors into larger circuits”. This is because of the considerable versatility of modern molecular spectroscopy, which allows the design of nontrivial circuits already on individual molecules. For example, either the donor or the acceptor that are here discussed implements by itself both an AND gate and an XOR (eXclusive OR) gate, see Figure 2 below. It takes several switches (= transistors) to build any one of these gates.

This letter discusses the photophysics of a full adder that is a circuit that receives two binary one-digit inputs plus the carry bit from the previous addition and yields as output the sum of the two inputs and a new value for the carry bit (= carry out). There are altogether eight possible inputs to the full adder, and these, together with the outputs, are given in Table 1. Table 2 shows how Table 1 can be broken into two separate tables, using an intermediate output that is labeled as “midway sum”. It is the (Boolean value of the) intermediate sum that is communicated between the donor and acceptor. The corresponding logic circuit is shown as Figure 1. It is shown in two panels. First shown is a full adder made by concatenating two-half adders (HAs), and below is shown a construction of a half adder using two gates, an AND gate (that performs a Boolean product of two variables,  $a \otimes b$ ) and an eXclusive OR gate (that performs a Boolean addition of two variables,  $a \oplus b$ , or addition modulo

**TABLE 2: Truth Table for Components of a Full Adder**

(A) First Half Adder Having Two Summands as Input <sup>a</sup>			
$\omega_1$	$\omega_2$	midway sum	carry 1
0	0	0	0
1	0	1	0
0	1	1	0
1	1	0	1
(B) Second Half Adder Having Midway Sum and the Input Carry Bit as Inputs			
midway sum	carry in $\equiv \omega_3$	sum out	carry 2
0	0	0	0
1	0	1	0
0	1	1	0
1	1	0	1

<sup>a</sup> The gate implements an XOR and an AND logic.

2). An XOR gate is usually broken further into three simpler gates. The graphical notation for the gates is a standard in books on computer architecture.<sup>25,26</sup>

Our proposed full adder needs two-half adders such that one bit can be delivered from the first half adder to the second. A molecular half adder is available for molecules that have a detectable one-photon and a detectable two-photon absorption. This seems to go against Kasha's rule,<sup>27</sup> but in fact there are enough exceptions. Azulene and many of its derivatives provide one class. The emission from the second electronically excited state,  $S_2$ , is often as strong or stronger than the fluorescence from  $S_1$ .<sup>28,29</sup> More in general, emission from  $S_2$  is not forbidden, rather, due to competing nonradiative processes, it often has a low quantum yield but it is definitely detectable, particularly so because it is much to the blue as compared to the emission from  $S_1$ . If necessary, the emission from  $S_2$  can be detected by photon counting.

We draw attention to a relative paucity of photophysical information on absorption profiles and emission characteristics of  $S_2$  levels of potential donors and acceptors. While there is enough data to anchor our proposed scheme on firm observations, it would be useful to have more.

The concatenation between the two-half adders is performed by the fairly fast<sup>1</sup> intermolecular electronic energy transfer. Specifically, we propose the well characterized<sup>30–32</sup> transfer from the  $S_1$  level of rhodamine 6G to the  $S_1$  of azulene, Figure 2. There are many possible variations on this theme. While we shall not make use of it, we do mention that the scheme discussed in this letter can have bidirectional transfer so that the result of the logic implemented on what we call the acceptor can be returned to the donor. For example, the  $S_2$  level of azulene can transfer to a higher excited donor level. See, for example, ref 33 for a recent discussion of the role of the energy gap in the transfer.

The photophysical details of the full adder are as follows: <sup>30–32,34</sup> the  $S_1$  level of rhodamine 6G can be readily pumped with photons absorbed within the  $S_0 \rightarrow S_1$  band. For example, we take the frequencies  $\omega_1 = 18797 \text{ cm}^{-1}$  (the second harmonic of the Nd:YAG laser) and  $\omega_2 = 18900 \text{ cm}^{-1}$ . In fact, because  $\omega_1$  and  $\omega_2$  are Boolean variables, they can be the same frequency but from two physically distinct laser beams, say, using a beam splitter with a beam stop (to do the Boolean variable selection, 0,1  $\equiv$  on, off) in either beam line. We do not need it for the full adder, but the absorption to  $S_1$  can be detected through its emission at about  $17500 \text{ cm}^{-1}$ .<sup>30,31</sup> This emission is logically equivalent to  $\omega_1 \oplus \omega_2$  because if the intensity is high enough due to two photons being present, the donor will be pumped either directly to  $S_2$  or to higher levels followed by ultrafast nonradiative relaxation to  $S_2$ . The large absorption cross section of the  $2.5 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ <sup>35</sup> for the  $S_1 \rightarrow S_n$  ( $n \geq 2$ ) of rhodamine 6G ensures efficient pumping of  $S_2$ . The emission from  $S_2$  is at about  $23250 \text{ cm}^{-1}$  with a quantum yield of about  $10^{-4}$ .<sup>31</sup> It is this emission which serves to logically implement the left AND gate and it is equivalent to  $\omega_1 \otimes \omega_2$  (denoted as carry 1). The  $S_1$  level of the donor transfers the energy, via the Forster mechanism<sup>1</sup> to the azulene acceptor, whose  $S_1$  level is at  $14\,400 \text{ cm}^{-1}$ .<sup>34</sup> This level emits in the  $13\,400\text{--}11\,000 \text{ cm}^{-1}$  range.<sup>34</sup> The  $S_2$  level of azulene has its absorption origin at  $28\,300 \text{ cm}^{-1}$  and so it can be reached from  $S_1$  by a third photon of frequency  $14\,400 \text{ cm}^{-1}$ . The same photon can also pump ground-state azulene to its  $S_1$  level. Emission (or lack thereof) from  $S_2$  of azulene at  $26\,670 \text{ cm}^{-1}$ <sup>32</sup> provides the carry 2 bit while emission from the  $S_1$  level of azulene provides the sum bit.

If one wants error correction, then the emission from the  $S_1$  level of rhodamine 6G can be used as a check bit.

The energy transfer rate for a solution of  $10^{-3} \text{ M}$  of azulene, estimated using the  $S_1$  fluorescence spectrum of rhodamine 6G and the absorption spectrum of azulene, is about  $10^{10} \text{ s}^{-1}$ . This rate is sufficient for our needs but it can be increased<sup>16</sup> if the two chromophores are incorporated within a single molecular unit using a short bridge to connect them.<sup>1</sup> The increase in the rate will be particularly significant (5 orders of magnitude) if the bridge is rigid.<sup>16,17</sup> We emphasize that it requires a rigid bridge to get a very high rate. There are many other couples based on commonly used laser dyes as donors and azulene derivatives<sup>35,36</sup> that can be utilized for the implementation of the logic gate.

Electron transfer from a chromophoric donor to an acceptor is another way to achieve concatenation. Rather than a direct donor to an acceptor transfer, one can put a bridge in between. One typically thinks of either through-space transfer without any bridge involvement or of a bridge in terms of the “super exchange” mechanism.<sup>3,4,37,38</sup> There are however other options in which the bridge itself is actively involved. This allows one to tune the components of the bridge such that the transfer is facile or not.<sup>16,17,39,40,41</sup>

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