Molecule-Based Photonically Switched Half and Full Adder

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A single molecule logic gate using electronically excited states and ionization/fragmentation can take advantage of the differences in cross-sections for one and two photon absorption. Fault tolerant optically pumped half adder and full adder are discussed as applications. A full adder requires two separate additions, and the logic concatenation that is required to implement this is physically achieved by an intramolecular transfer along the side chain of 2-phenylethyl-*N*,*N*-dimethylamine (PENNA). Solutions of the kinetic equations for the temporal evolution of the concentration of different states in the presence of time-varying laser fields are used to illustrate the high contrast ratios that are potentially possible for such devices.

1. Introduction

There is much current activity seeking to construct molecular logic units.[1−3] A simple yet not trivial example is the logic circuit that implements a half adder. A half adder has two inputs, the two (binary) digits that need to be added. The device accepts the two inputs and produces two outputs that correspond to the (binary) sum and the carry digit. A carry digit is the output of a logical AND operation on the inputs. It has the value 1 only when both inputs have the value 1 or, in physical terms, when both inputs are "on". The sum digit is the output of a logical eXclusiveOR operation on the inputs. It has the value 1 when only one or the other inputs is on but not if both are on. Table 1 below illustrates the relation between inputs and outputs. A half adder is an important building block for molecular logic because by concatenating of two such "halves", one can build a full adder. A full adder accepts the two digits that are to be added and also a third input, namely, the carry digit from the previous addition. Using the diffusion of chemical species in solution, several schemes were proposed to implement half adders at the molecular level.[3]

TABLE 1: Truth Table for an Optical Implementation of a Half Adder

x (laser 1)	*y* (laser 2)	sum (XOR)	carry (AND)	(carry,sum)
0	0	0	0	(0,0)
1	0	1	0	(0,1)
0	1	1	0	(0,1)
1	1	0	1	(1,0)

In this paper, we discuss both a half adder and a full adder where the inputs are provided optically and their physical action is to excite a molecule. To be concrete, the entry "1" is coded as a laser being "on". The molecules in our sample act independently of one another, and we cannot make sure that every molecule absorbs the laser light. So it is not the case that a single molecule suffices to provide a reliable readout. If we are willing to work with a finite number of molecules, then we do not need a strict "yes" or "no" from each molecule. What is needed is to excite enough molecules so as to pass the threshold for detection of light absorption. Ions are easy to detect, so by monitoring the absorption by photoionization of the molecule it is sufficient if only a small number of molecules respond to the input. The price of detection by ionization is that the molecule self-destructs at the end of the computation. On the plus side, the time scale for the computation is pretty short. An optically addressed full adder[4] or a half adder[2] that can be cycled has been reported.

A full adder is often described as a concatenation of two half adders. This manner of constructing a full adder requires the logic coupling of two molecules.[4,5] In this paper, we present and discuss a design for a full adder by operating on a single molecule. The photophysics of what we do can be thought of as intramolecular transfer. As we show, constructing a full adder (see section 6) in this way is both more efficient in terms of physical resources and more efficient in terms of computational resources. To do so, we need to contrast the two manners of operating a full adder and so we need to begin with the operation of a half adder (section 4). The discussion of the half adder (section 5) will also allow us to show how our design is fault tolerant. We provide the input by optical signals that are to be absorbed. The efficiency of light absorption need not be high. It just needs to be detectable. The concept that we propose is in principle general for aromatic and conjugated molecules. We have chosen 2-phenylethyl-*N*,*N*-dimethylamine (PENNA) as a model molecule, because it is extensively investigated[6−8] (see section 3 for a summary of the photophysics of PENNA), has a high absorption cross-section, a long S_1 lifetime, and two local sites, which can provide two different fragment ions, depending on the laser color used. We present numerical solutions of the rate equations for the populations of the different optically accessible levels of PENNA in section 7 so as to show that even low, by today's standards, light intensity is sufficient for

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our needs. The results of the simulations are general and not limited to PENNA. They highlight the major problems that arise in the implementation of logical functions in molecules by resonant multiphoton excitation schemes. They illustrate what can be implemented in the gas phase for a large number of high absorption cross-section aromatic molecules. Concluding remarks are provided in section 8.

2. Molecular Logic by Photophysics

There are two logic operations that need to be implemented on the two (binary) inputs in order to realize a half adder: an AND operation (a binary product) that yields the carry digit and an XOR (eXclusiveOR) operation that yields the binary sum digit. The relation between input and output of a half adder is given as a "truth table" (Table 1). We input the data by switching two nonidentical lasers. We reiterate that the logical value 1 is physically realized as laser on, whereas 0 is laser off. Table 1 defines what logical operations we need to perform in order to implement a half adder and relate these operations to the physical state of both lasers. As we discuss below, the critical aspect is how to detect the logical sum because it is to have the value 1 if and only if just one laser is on. If both lasers are on, the sum is to have the value 0 because we are adding to base 2. If both lasers are on and only then, it is the carry that is to have the value 1.

As shown in Table 1, the sum of the two inputs is the logic eXclusiveOr operation while the carry digit is the result of the logic AND operation. The Boolean equations that generate the binary sum (addition modulo 2, denoted by $\oplus$) and the carry (binary product, denoted by $\otimes$) are given by

$$\text{sum} = x \oplus y \tag{1}$$

$$\text{carry} = x \otimes y \tag{2}$$

A molecular realization of the logical XOR operation is challenging. An XOR gate produces an output only when either input x or input y, but not both, is applied. In contrast, an AND operation is easier: An output is produced only if both x and y are applied and so any reproducible experiment, which requires two inputs to generate an output, implements an AND gate.[9] The difficulty with realizing an XOR gate by optical inputs is that it is an eXclusive OR: No output is to be produced when both inputs are applied.

Two photon resonance-enhanced absorption by aromatic chromophores has been used by us as an effective way to implement an XOR operation on optical inputs at the molecular level.[4,9,10] The two photons (each of a somewhat different color and therefore distinguishable) represent the possible inputs. We adopt the convention that the value 1 codes for light on and 0 for off. The following physical considerations enter in showing how the eXclusion needed for an XOR gate is physically realizable. First, for aromatic molecules or for molecules with aromatic chromophores, the resonant level, typically the first optically bright electronically excited state, S_1, has a fairly broad absorption band consisting of many vibronic transitions. So two photons of different frequencies, and therefore distinguishable, can be absorbed with a similar cross-section. Regarding the two beams of different frequencies as two distinct inputs, the resonant absorption to S_1 provides the OR part of the XOR gate.[11] If laser light of either frequency is on, the output can be identified as the fluorescence. Next comes the eXclusive part: It is often the case that having absorbed one photon, the cross-section of an aromatic chromophore to absorb a second photon is higher. That the bottleneck for two UV photon absorption is often the absorption of the first photon has been realized since the earliest days of visible/UV multiphoton ionization/dissociation[12] and has been used extensively since that time. What this means for us is that when two light pulses are applied the system need not remain in S_1 for a significant length of time because it can absorb a second photon. Whether it preferentially does so depends on the particular molecule. In the presence of two photons, the fluorescence from S_1 (a rather slow, >5 ns scale, process in PENNA) can go down but the high fidelity detection of the presence of both input beams is the increase of the number of ions. Either input laser can excite from the ground state to S_1. Therefore, the fluorescence signal will increase when both lasers are on. The input in this case is 1,1, and from Table 1, we need to detect the output 1,0. While the input 1,1 can cause a reduced electronic fluorescence, a better detection for the presence of both input beams is an increase of the number of ions. Increase rather than pure onset because a single laser can also cause ionization, but this occurs with low intensity. High ionization intensity corresponds to a simultaneous input of both lasers. In practice, the two events "high ionization efficiency" and "low ionization efficiency" can be easily distinguished by discriminators and analogue electronics. In section 7, we provide a simulation of the temporal response of the molecule to the laser pulses so as to show that this is possible. To conclude, we identify the 1,1 input as a high ionization signal.

Electron-donating or -withdrawing substituents on the aromatic ring can be used to fine-tune the ratio of the cross-sections $S_0 \rightarrow S_1$ to $S_1 \rightarrow$ ion. The molecule that we discuss below is expected to be similar in this respect to toluene for which the ratio is lower than 1:3.

The use of two lasers of different colors is dictated by the need to represent two distinct inputs, but there is a clear physical advantage if the two frequencies differ by more than a vibrational frequency in S_1: Because the S_1 and the S_0 vibrational frequencies are not exactly the same, the down pumping by the other laser is not resonance enhanced and thus improbable as shown schematically in Figure 1. For ionization, however, both lasers can ionize the S_1 population created by the other laser. This scheme simplifies the rate equations and optimizes the ionization probability because the intensity of ionization, for say two lasers of equal intensity, is 4-fold the intensity if only one laser is on (see section 7 below).

3. Photophysics of PENNA

As mentioned in the Introduction, the proposed logic schemes could be implemented in general in any substituted benzenes or other aromatic molecules. We here demonstrate our approach by designing a half adder and a full adder on the basis of the extensive recent studies[6−8,13] of the photochemistry of the PENNA molecule (Figure 2). We will compare two ways of implementing a full adder, directly, as proposed here, or by concatenation of two half adders[4] in section 6 and discuss the advantages and disadvantages of each scheme.

PENNA is an interesting molecule for molecular logic for several reasons: (i) It has only one conformer populated in a supersonic expansion.[6] Thus, all molecules in the interaction volume can be addressed by one resonant wavelength. This isomer is stretched, which allows for local excitation and ionization (see iii below). (ii) It has a nanosecond S_1 lifetime,[13] which allows the observation of fluorescence and enables efficient two laser, two color ionization. No relaxation processes such as charge transfer have been observed in neutral PENNA so far.[7] (iii) It has two well-separated functional groups, the amine group and the phenyl group, which allow local excitation

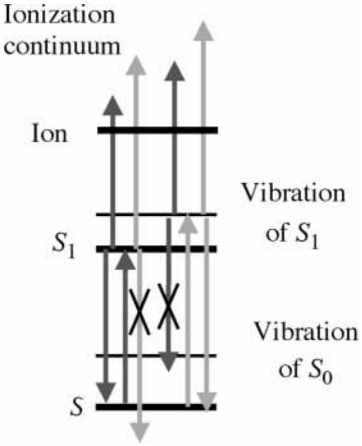

Figure 1. Detailed level scheme for an aromatic chromophore that performs the optical eXclusiveOR logical operation. The two binary inputs are represented by photons of somewhat different colors. The value 0 is coded by light off, and the value 1 is coded by light on. The input (0,0) generates no signal. Either one of the two inputs (1,0) or (0,1) generates fluorescence from the first electronically excited state, shown as a down arrow. For a typical aromatic chromophore, the input (1,1) preferentially pumps the molecule up to the ionization continuum. The figure shows how ionization is optimized for the input (1,1). After the absorption of the first photon during the first laser input, the second laser input cannot stimulate a down transition, a so-called "dump". By making one photon pump to a vibrationally excited state of S_1 and because the vibrational frequencies differ in S_0 and S_1, there will *not* be a resonance-enhanced down transition, as indicated by an ×.

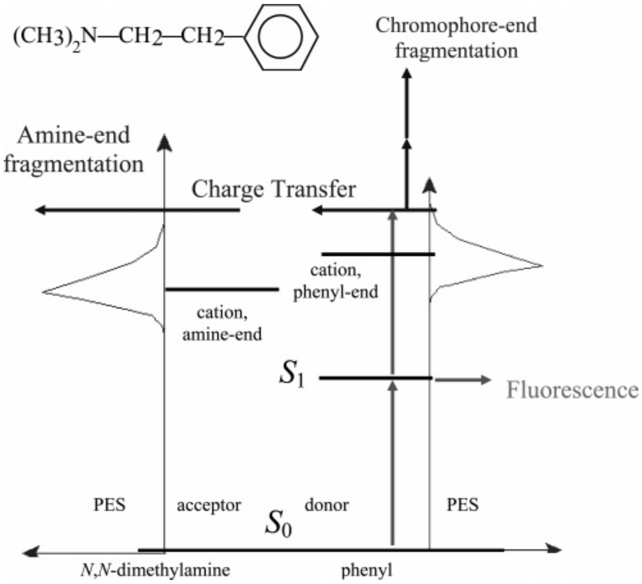

Figure 2. Level scheme for the photochemistry of PENNA. The essential part for performing the operation of a half adder is only the aromatic chromophore. Its absorption can distinguish between no photons at all, just one photon (resulting in fluorescence from S_1), or two photons (resulting in ionization and fragmentation at the N end). The side chain shows how charge migration can communicate the AND output, the presence of two photons, to the other end of the molecule. In ref 4, we used energy (rather than charge) transfer to implement a full adder. Here, the full adder is implemented using the fragmentation at the chromophore end induced by excitation of the phenyl cation by two green photons.

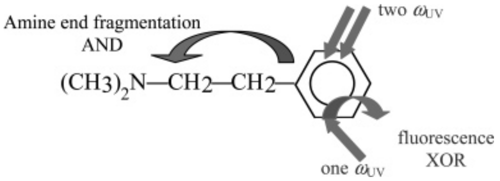

Figure 3. Schematic representation of the two photon excitation scheme used to implement a half adder on PENNA.

and ionization (see Figure 2).[6,7] (iv) The cation absorption of the two functional groups is different and leads to different fragmentation products. One of the channels is driven by an ultrafast charge transfer directly after ionization.[8] (v) PENNA is flexible, and the large density of vibrational states already acts as a heat bath, which cools the phenyl chromophore, for example, after relaxation processes and ionization with excess energy. This cooling ensures that the absorption of PENNA will be not strongly influenced by internal vibrational energy (for example, after an internal conversion process) and stays predictable at all excitation stages. (vi) PENNA offers a second ionization route by 2 + 1 multiphoton ionization at the amine chromophore,[7] a feature that is, however, not used here. In this work, we do not make use of all photophysical properties of PENNA but surely profit from its complexity.

The implementation of logic functions in the gas phase and the observation of fragments as outputs might seem impractical for application. Note, however, that ions and photoproducts can be detected with an efficiency of 1, leading to stable reproducible output signals. The experimental full realization of the here proposed molecular logic scheme is difficult only because of the three tuneable lasers needed. Such experiments are currently in preparation.

The experimental conditions for the realization of above proposed logic units are similar to those described in refs 6−8. In short, a time-of-flight mass spectrometer is used to allow the recording of the full mass spectrum for each laser shot sequence. A typical repetition rate could be 100 Hz. The readout of the result is finished after several tenths of microseconds. The molecules are brought into gas phase by thermal heating and cooled by a supersonic expansion. The cooling allows the observation of sharp spectra, as needed for the scheme in Figure 1. The cooling also ensures close to 100% vibrational ground state population and thus the addressability of all molecules by a single resonant laser radiation. Such excitation conditions are in principle impossible to realize in solutions. Typical laser requirements for the implementation of the half adder (ionization is the last excitation step) are UV nanosecond laser pulses with pulse intensities of 10^6 W/cm^2. Typically, 5−10% of the neutral molecules in the interaction volume between laser and molecular beam can be ionized and detected. The laser energy resolution should be below 1 cm^{-1} to match the widths of the S_0-S_1 resonances. For the full adder, the situation becomes more complex because of the ultrafast charge transfer after ionization. To allow a phenyl excitation by VIS light in the cation, which can compete with the charge transfer, femtosecond laser pulses must be used to provide the inputs.[8] The femtosecond laser intensities should be kept low to ensure resonant excitation. The resulting small ion and fragment ion signal for one pump−probe cycle can be easily compensated by repetition rates up to several kHz.

4. Implementation of a (Fault Tolerant) Half Adder

For the half adder as represented in Table 1, the two outputs, the sum (result of the XOR logic operation) and the carry (result of the AND operation), are to be detected. The direct way of doing this is to assign to each one of them a different experimental probe. For the sum digit, the experimental probe is fluorescence from S_1 while for the carry digit, the output is the result of the two photon absorption process (see Figure 3). (Depending on the chromophore and the wavelengths, this

TABLE 2: Implementation of a Half Adder on PENNA

x [UV(1)]	*y* [UV(2)]	sum (XOR)	carry (AND)	probe for XOR	probe for carry (AND)	probe for words (carry,sum)
0	0	0	0	no fluo from S_1	no N end fragment	no output signal (0,0)
1	0	1	0	fluo from S_1	no N end fragment	fluorescence from S_1 (0,1)
0	1	1	0	fluo from S_1	no N end fragment	fluorescence from S_1 (0,1)
1	1	0	1	no fluo from S_1	N end fragment	N end fragment (1,0)

output can be fluorescence from the S_2 state or a fragmentation or ionization.) This ideal situation corresponds to having a distinct probe for the third and the fourth columns of Table 1. As already mentioned, it is not exactly the case that the input of two photons fully quenches the fluorescence from S_1, meaning that a logical value of 0 in the last line of the third column cannot be achieved experimentally with high fidelity by the detection of fluorescence. We argue that it is still possible to implement a half adder. To do so, we group the combined result of the carry and the sum into a word (carry,sum) as shown in the fifth column of Table 1. We note that among the four possible output words that could be formed from two Boolean inputs, i.e., (0,0), (0,1), (1,0), and (1,1), only three are allowed, i.e., (0,0), (0,1), and (1,0). This is because the operation of half addition is such that when the carry is 1, the sum is necessarily 0, so that the output (1,1) is not a possible output for a half adder. Therefore, a half adder has four distinct possible inputs (0,0), (1,0), (0,1), and (1,1) but only three distinct outputs (0,0), (0,1), and (1,0). This observation allows mapping the two binary outputs in a different way, by encoding into a physical probe the combined result of the carry and the sum instead of encoding the carry and the sum separately. Note that in a half adder, the binary meaning of the word (carry,sum) is equal to the number of inputs that are equal to 1. This is also true of the full adder discussed below.[14]

Table 2 illustrates the two possibilities for implementing a half adder. The first option is the distinct experimental probes for the XOR and the AND outputs, and it is given by the fifth and in the sixth columns. As discussed above, probing XOR by fluorescence cannot always be implemented with high fidelity. Let us therefore assume a worst case scenario that such is the case for PENNA. Actually, this is not so but we want a scheme that will work even if the two photon absorption does not dominate. To do so, we assign an experimental probe directly to a word (seventh column) with the result that the requirements on the kinetic scheme for the S_1 population are far less severe. In other words, we illustrate for the case of PENNA how to design a fault tolerant half adder. If only one UV photon is present, the phenyl moiety will be selectively excited to the S_1 electronic state and fluorescence can be detected. When both binary inputs are 1, so that PENNA absorbs two photons, the molecule is selectively ionized at the phenyl ring. As discussed in refs 6−8, this selective ionization is followed by a charge transfer to the amine end and a rapid fragmentation into the *N*,*N*-amine cation fragment and a neutral benzyl radical. Detecting the fluorescence from the S_1 of the neutral PENNA with a level of N end fragmentation below the threshold means that the input was (0,1) or (1,0) so that the output word is (0,1), i.e., carry = 0 and sum = 1. Detection of the *N*,*N*-amine cation by mass spectrometry means that the input was (1,1) and the detection of N end ions is the signature of the output word (1,0). So whether there is or is not detectable fluorescence from the S_1 state, if we observe N end ions we report the output word (1,0), i.e., carry = 1 and sum = 0. Detecting the (0,0) word is with high fidelity since it means no fluorescence from S_1 and no ions. What we therefore are tolerant against is the extent of fluorescence from S_1 when both photons are on.

This half adder self-destructs at the end of any computation for which both binary inputs are 1, and the molecule ionizes. This does not allow for any further computing with the same molecule, but it does provide for a remarkable sensitivity because so very few ions can already be detected with good signal above the background. In other words, we deal with an ensemble of molecules not all of which will provide an answer. However, we need a response from only about 100 molecules to get quite acceptable statistics. Moreover, we get the answer on a rather short time scale.

A full adder with an input carry digit of 0 performs a half addition. So the simulations that we present below for the temporal response and threshold detection for the full adder include the half adder as a special case and so we do not show any separate simulations here.

5. Discussion of the Half Adder

If all one wants is a half adder, then sending the charge down the short side chain of PENNA is not necessary. Any suitable aromatic chromophore will implement a half adder, where the two outputs are fluorescence without or with ionization. What PENNA illustrates is the additional ability to send the output down a molecular bus. We will shortly take advantage of this option to implement a full adder.

Table 1 shows the implementation of an AND as well as an XOR logic gate. These are only two of the 16 possible Boolean functions of two inputs. There are 16 possibilities because for two Boolean variables (values 0 or 1) there are four possible inputs (0,0; 0,1; 1,0; and 1,1), and for each input, there are four possible outputs, each of which is Boolean. Using the vibrationally mediated photodissociation[15] of $HONO_2$ by Crim et al.,[16] we have shown how all possible Boolean functions of two inputs can be realized by optical inputs.[9] In these implementations as well as in the one discussed above, the read out of the two binary outputs is only partially optical, and at the end of the cycle, the molecule self-destructs and cannot be recycled.

Several other ways, partially optical, to implement adders and other combinational circuits on molecular systems were reported by us.[9,10,17] We have also shown how to operate a more elaborate logic circuit, known as a finite state machine,[18] in an all optical molecular context.[19] A finite state machine has an internal memory and so it can be programmed and we have provided rudimentary examples of such programming on a single molecule and for a machine that can be cycled.[19] Very recently,[20] we have shown how to operate a finite state machine in an all electrical molecular context. Here, we return to the full adder. This is still only a combinational circuit meaning that the output is fully determined by the input and there is no memory. Our purpose is to show how such a logic gate can be implemented on a single molecule.

6. Optical Implementation of a Full Adder

A (binary) full adder has three inputs, the two binary numbers that are to be added, *x* and *y*, and the “carry in” bit from the previous addition. A full adder needs to produce two outputs, the so-called “sum out”, which is the XOR sum of the two inputs and of the carry in, and an output called the “carry out”, which

TABLE 3: Truth Table for the Implementation of a Full Adder on PENNA

x [UV(1)]	y [UV(2)]	carry in (vis, two photon)	sum out	carry out	output word (carry,sum)	probe for output word
0	0	0	0	0	(0,0)	no signal
1	0	0	1	0	(0,1)	fluorescence from S_1
0	1	0	1	0	(0,1)	fluorescence from S_1
1	1	0	0	1	(1,0)	N end fragment
0	0	1	1	0	(0,1)	fluorescence from S_1
1	0	1	0	1	(1,0)	N end fragment
0	1	1	0	1	(1,0)	N end fragment
1	1	1	1	1	(1,1)	C end fragment

for the next addition cycle becomes the carry in:

$$\text{sum out} = x \oplus y \oplus \text{carry in} \quad (3)$$

$$\begin{aligned}\text{carry out} &= (x \otimes y) + [(x \oplus y) \otimes \text{carry in}] \\ &= (x \otimes y) + (x \otimes \text{carry in}) + (y \otimes \text{carry in}) \quad (4)\end{aligned}$$

As in eqs 1 and 2, $\oplus$ means XOR (addition modulo 2), $\otimes$ means an AND gate, and + means OR. The carry out logic equation is also often written as

$$\text{carry out} = xy + x\,\text{carry in} + y\,\text{carry in} \quad (5)$$

It is the ability to take into account the carry in bit that makes a full adder a more complex combinational circuit than a half adder. The truth table of a full adder is given in Table 3 including the physical identification of the inputs and outputs. From this table, it can be seen that unlike the case of the half adder, for a full adder the output (1,1) is possible so that there are four distinct outputs for a full adder. On the other hand, just as for the half adder, the binary meaning of the word (carry,-sum) corresponds to the number of inputs that were 1.[14] This is used in an essential way for the physical implementation that we discuss below. The output word (0,0) means no input was 1, the output word (0,1) means one input was 1, the output word (1,0) means that two inputs were 1, and the output word (1,1) means three inputs were 1.

Just as in a half adder, the two digits to be added, x and y, are input as two UV photons, we code the third input, the carry in, by a green light that is intense enough for two green photon transition to access the first electronically excited state of PENNA, the S_1 level (see Figure 4), by a nonresonance-enhanced two green photon transition. The cross-section for this nonresonance-enhanced process is lower than for a one UV photon absorption and it is this smaller cross-section that sets the limit that we need at least 1000 molecules for reliable count statistics for the detection of fluorescence from S_1. In this paper, we implement a full adder by mapping each of the four distinct outputs, {(0,0), (1,0), (0,1), and (1,1)}, on a different experimental probe. These four probes, identified in Figures 4 and 5, are no output, fluorescence from S_1, fragmentation at the N end, and, as shown in Figures 2 and 4, fragmentation at the C end. This way of implementing a full adder, as summarized in Table 3, is similar to what was discussed in Table 2 for the half adder. Note however that because of the ultrafast charge transfer between the C and the N ends that is taking place in PENNA,[8] the implementation of the full adder requires femtosecond pulses, so that the absorption of the two green photons that leads to the fragmentation of the phenyl cation can compete with charge transfer to the N end. A physically different way of implementing a full adder is by concatenating two half adders, as was done in ref 4.

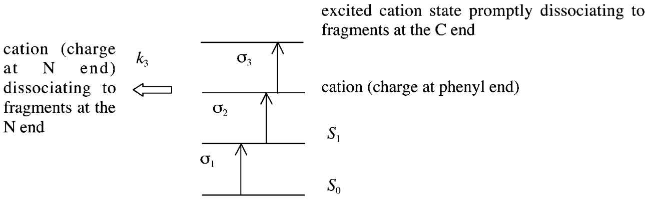

Figure 4. Inputs and states for the full adder. The σ's are the absorption cross-sections. k_3 is the rate constant for the intramolecular charge movement from the C to the N end. This transfer provides the carry out digit. Figure 5 shows the outputs of the adder.

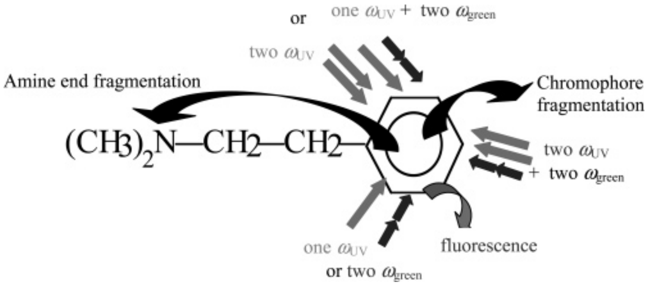

Figure 5. Three distinct outputs necessary to implement a full adder on PENNA. Fluorescence from the S_1 state of the phenyl ring codes for carry out = 0, sum out = 1, fragmentation at the amine end codes for carry out = 1, sum out = 0, and fragmentation at the chromophore end for carry out = 1, sum out = 1 (see also Table 3). The two binary digits to be added are encoded as the two UV photons being on or off. The carry in is encoded as excitation by two green photons.

The level scheme and the inputs used to implement a full adder are shown in Figure 4. The essential new feature that we make use of as compared to the implementation of the half adder is the two green photon absorption to the dissociative cation with the charge at the C end (see Figure 2).

We start by discussing the implementation that maps the four distinct pairs of outputs for the carry out and the sum out onto four distinct experimental probes (see Table 3). For the outputs (0,0), (0,1), and (1,0), we keep the same coding as for the half adder. (0,0) is the simple case where all three inputs were 0, so that no signal can be observed. The output (0,1) means that one of the inputs was 1 while the two others were 0. Because the energy of the excitation by two VIS is equivalent to the energy of a UV photon, when one of the inputs is equal to 1, the S_1 excited state is populated and will fluoresce. The output word (0,1) is detected by fluorescence from S_1. The output word (1,0) means that two inputs were 1 and one was 0, so that PENNA received enough energy to ionize at the phenyl end and subsequently to fragment at the N end after an ultrafast charge transfer.[6−8] Significant N end fragmentation is the probe for the (1,0) output. The (1,1) output implies that all three inputs were one. In that case, PENNA received enough energy to ionize and fragment at the chromophore end. By using femtosecond pulses, fragmentation at the chromophore end can compete with fragmentation at the N end and this is detected by the presence of a benzyl ion (from molecules that ionized at the phenyl end). To observe fragmentation at the chromophore end is the signature of the (1,1) output. Note again that the detection of the four distinct outputs is unambiguous. (0,1) means significant S_1 emission and below threshold N fragment and number of benzyl ions; (1,0) means above threshold N fragment and below threshold ion count for the benzyl ions whatever is the level of fluorescence from S_1; and (1,1) means above threshold benzyl ion count, whatever is the fluorescence from S_1 and the amount of N fragment.

7. Simulation of Full Adder

We solve the equations of motion for the population as a function of time to demonstrate that robust threshold values can be specified such that clear-cut decisions are possible for reading the outputs. Time in the simulation is scaled by the duration of the laser pulse, which is taken to be the same for the three pulses used to provide the inputs. Therefore, the results presented below are general and valid both for a nanosecond pulse excitation scheme as is possible for the implementation of the half adder and for the femtosecond pulse excitation needed in the case of PENNA because of the ultrafast charge transfer. As outlined in section 5, a full adder requires three inputs, the two digits to be added, *x* and *y*, each coded by a UV photon being on or off, and also a carry in digit *z*. The carry in is the carry digit from the previous addition, and so this digit also has the values 0 or 1. We code this third input by a green light that is intense enough for a nonresonance-enhanced two photon transition to access the first electronically excited state of PENNA, the S_1 level. The cross-section for the nonresonance-enhanced process is lower than for a one UV photon absorption, and it is this smaller cross-section that sets the limit that we need at least 1000 molecules for reliable count statistics for the detection of fluorescence from S_1. The truth table for a full adder is shown as Table 3. The outputs are fluorescence from S_1 or two ions of different mass, resulting from dissociation at the two possible ends of the molecule.[6−8]

If the carry in is zero, the green laser is not on and the full adder acts as the half adder of Table 1. If the carry in is unity and the two digits to be added are zero, the green laser pumps the molecule to the S_1 level by a nonresonance-enhanced two photon process. The pumping to S_1 is detected as fluorescence. If only one of the two possible digits to be added is unity and there is a carry in, the molecule will ionize by absorption from S_1 and dissociate at the N end. The new channel that allows the full adder to act is when all three possible inputs are on and this leads to ionization at the C end as shown in Figure 4.

Equations of motion representing these transitions are

$$\frac{\mathrm{d}[S_0](t)}{\mathrm{d}t} = -(x + y + Q_1 z)\,\Phi(t)\,\sigma_1\{[S_0](t) - [S_1](t)\}$$

$$\frac{\mathrm{d}[S_1](t)}{\mathrm{d}t} = (x + y + Q_1 z)\,\Phi(t)\,\sigma_1\{[S_0](t) - [S_1](t)\} - (x + y + Q_2 z)\,\Phi(t)\,\sigma_2\,[S_1](t)$$

$$\frac{\mathrm{d}[\mathrm{PENNA}^+](t)}{\mathrm{d}t} = (x + y + Q_2 z)\,\Phi(t)\,\sigma_2\,[S_1](t) - (x + y + Q_3 z)\,\Phi(t)\,\sigma_3[\mathrm{PENNA}^+](t) - k_3[\mathrm{PENNA}^+](t)$$

$$\frac{\mathrm{d}[\text{ion C end}](t)}{\mathrm{d}t} = (x + y + Q_3 z)\,\Phi(t)\,\sigma_3\,[\mathrm{PENNA}^+](t)$$

$$\frac{\mathrm{d}[\text{ion N end}](t)}{\mathrm{d}t} = k_3\,[\mathrm{PENNA}^+](t) \tag{6}$$

The square brackets represent concentrations and PENNA^+ is the ground state of the cation.

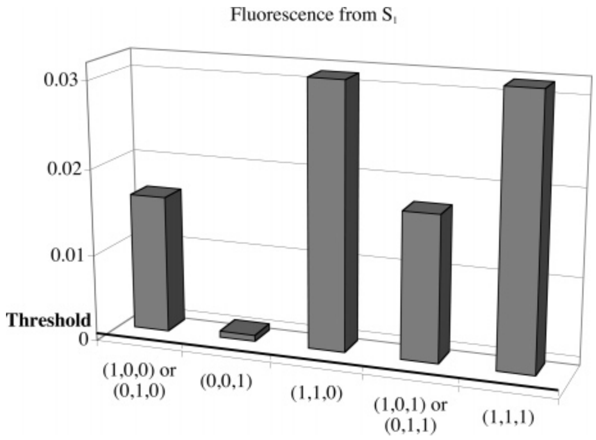

Figure 6. Histogram of the fraction of molecules that fluoresce from S_1 computed by integrating the kinetic equations for a time long after the laser pulse(s) have been switched on and then off and that the charge migration to the N end is essentially completed. The threshold value for detection is set, as shown, at 0.001. We could have made more molecules fluoresce by using higher power lasers. This however is not optimal because the full adder is based on our ability to distinguish one from two from three photon processes. At low laser power, these give rise to populations of excited states that scale roughly as I^n where I is the intensity and n is the number of photons. This provides the required discrimination. At higher powers, see Figure 7, the $S_0 \rightarrow S_1$ transition is progressively being saturated and thereby the selectivity is reduced.

To make an unfavorable case scenario, the equations of motion include a term for stimulating the emission down from S_1 to S_0 even though for the lasers that we use this can be avoided as shown in Figure 1. For simplicity, we take all three lasers to have the same profile, a Gaussian centered at a common time. The number flux of photons in the pulse at the time t is $\Phi(t)$. The Q_i values weigh the two photon carry in signal differently than the one photon transition. Specifically, $Q_1 \ll Q_2$, Q_3 because the nonintermediate resonance-enhanced two photon transition $S_0 \rightarrow S_1$ has a significantly lower cross-section than the one photon resonant transition. The rate constant for the charge migration from the C to the N end is denoted by k_3. Note that this charge migration is one way because once the charge is at the N end the cation promptly dissociates. More details and other input parameters are specified in the appendix.

Figure 6 is a histogram of the computed fluorescence output for the five distinct inputs. These are listed below each column. As noted already in connection with Table 3, it is the input 0,0,1 where only the carry in is not 0 that requires that we specify a low threshold for fluorescence detection or, equivalently, that we use many (order of 1000) molecules per computation.

The need to operate at relatively low laser powers so as to ensure high contrast between one, two, and three photon processes is graphically emphasized in Figure 7. It shows, logarithmic scale, the power dependence of one and two photon markers.

As shown in Figure 6, if any one of the three lasers has been on [inputs (1,0,0) or (0,1,0) or (0,0,1); see Table 3], we detect fluorescence from S_1. If more than one laser has been on, we can detect fluorescence, but as we show next, we can then also detect ions and can take advantage of the sensitivity available for counting charges. Figure 8 shows the histogram for the two types of ions that differ by their mass. Detecting fragmentation at the N end verifies that either two lasers or all three have been switched on. As seen in Table 3, this means an output that is either 1,0 or 1,1. We use detection of ions at the N end

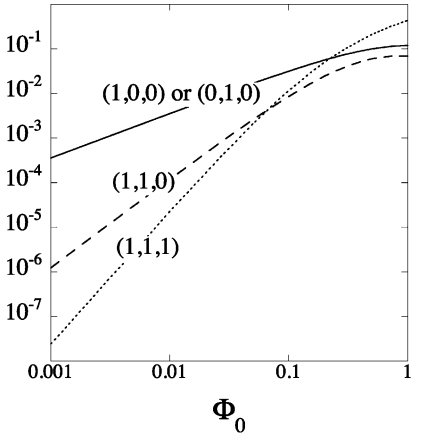

Figure 7. Yield, logarithmic scale, spanning the range of 0.1−10%, of fluorescence [for the input (1,0,0) or (0,1,0) and of ions (for the input 1,1,0) vs the laser power]. As seen, at lower power, the yield of ions increases with a higher slope. The plot is vs the power Φ_0 in reduced units, see Appendix, and in these units, Figures 6 and 8 are at $\Phi_0 = 0.05$. In reference to the kinetic scheme, eq 5, this corresponds to a one photon absorption rate of $R = 0.005w$ where w is the width in time of the laser pulse. This is not a very low power as seen from the result that about 2% of the molecules in the sample absorbed one photon. Discrimination is reduced when about 10% of the molecules are excited to S_1.

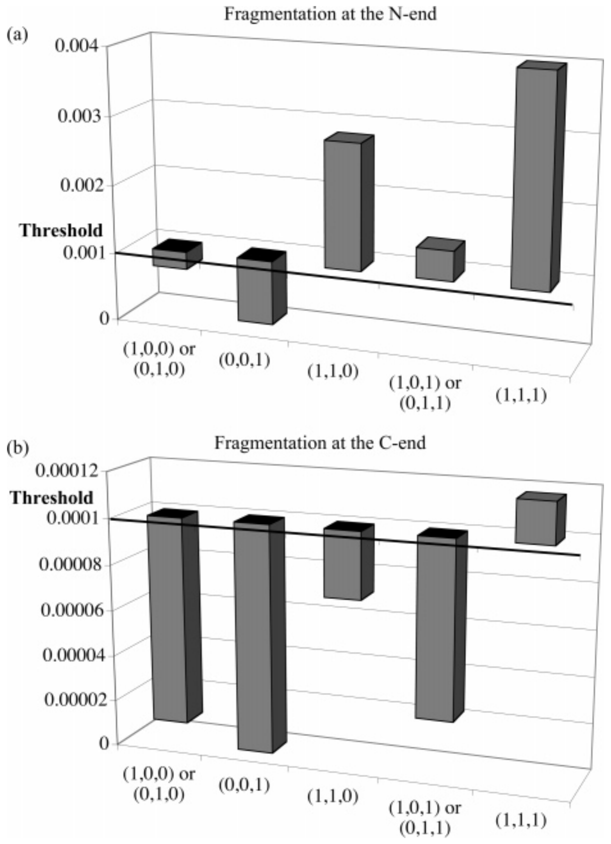

Figure 8. Histogram of the fraction of molecules that produce ions corresponding to (a) charge at the N end and (b) charge at the C end. The figure shows that (a) charge at the N end clearly discriminates between only one laser that was on or more than one. The threshold value is fixed at 0.001. The distinction between two or three lasers having been on is provided by case (b). The threshold value for the detection of C end fragments is fixed at 1×10^{-4}.

to code for the output 1,0 because, as very clearly seen in Figure 8b, detection of ions from the C end is uniquely correlated with the input 1,1,1 or, equivalently, the output 1,1.

8. Concluding Remarks

We began with a molecule-based fault tolerant half adder and on this basis showed how to realize a full adder using realistic photophysical data for PENNA. One remaining major challenge to molecular logic machines is concatenation, namely, the direct communication of the output from one molecule as an input to the next molecule. Our original full adder[4] was concatenated by intermolecular energy transfer, and other options[11] include electron and hole transfer and charge and energy transfers coupled to atom transfer.[21] More massive concatenation is yet to be demonstrated. In this paper, we explored a different option for the operation of a full adder. The entire Boolean operations were performed by one molecule. It is possible to do so because the four different outputs of a full addition, {(carry,sum) = (0,0), (0,1), (1,0), and (1,1)}, can be coded as four distinct actions by the molecule (no output; fluorescence from S_1; N end ionization/fragmentation; and C end ionization/fragmentation). This is both faster and more reliable, and it allows generalization because polyatomic molecules have a great multitude of states each of which has a distinct signature output.

In the future, it will be increasingly possible to progress beyond combinational circuits and to design finite state logic machines by optical input/output (see ref 19 for an early example). This is feasible because the action of a finite state machine depends both on the input and on the current state of the machine and that the optical response of a molecule depends on its present state is at the heart of photochemistry. Energy and/or charge and/or atom transfer can then be used for concatenation of different logic gates.

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Appendix: Photoexcitation Kinetic Scheme for the Implementation of a Full Adder

The electronic states of PENNA involved in the implementation of a half adder are shown in Figures 2 and 4. For the implementation of a full adder, we used an excited electronic state at the chromophore end from which ionization and fragmentation can occur (Figure 4). This gave us the third output necessary for the implementation of a full adder.

The optical inputs excite PENNA at the chromophore end by one or two UV photons, which code for the two inputs x and y, and two green photons whose combined energy roughly matches that of a UV photon. The two visible photon transition codes for the carry-in digit. If only one input is on, the S_1 state of the neutral is accessed; when two inputs are on, a low-lying state of the PENNA cation with a hole at the C end is reached while the excitation by the three inputs accesses a higher excited state of the same cation. The cross-section for one photon excitation from S_0 to S_1 is σ_1; for excitation from S_2 to the lowest state of PENNA ionized at the phenyl end, the cross-section is σ_2; and to the excited state of the cation, the cross-section is σ_3. The lowest state of PENNA ionized at the phenyl end undergoes a facile charge transfer to the N end that leads to the N end fragment with the rate constant k_3 while the excited state of PENNA ionized at the phenyl end undergoes a rapid fragmentation at the C end. The optical excitation is by a Gaussian pulse

$$p(t) = \exp[-(t - t_0)/2w^2] \tag{A.1}$$

centered at the time t_0. The same pulse shape is used for all three lasers. The number flux of photons, $\Phi(t)$ (in number of photons time^{-1} area^{-1}), of the input pulse is given by

$$\Phi(t) = (c/2\,\pi\,\hbar\,\omega)\,E_0^2\,p^2(t) \tag{A.2}$$

where $E_0\,p(t)$ is the electric field of the light at the time t. The energy flux of the light is $I(t) = \hbar\,\omega\,\Phi(t)$. We chose the power of the laser to be low so that the transitions are not saturated; see Figure 7. The kinetic rate of the transition is given by[22]

$$R = \sigma\,\Phi_0 \tag{A.3}$$

where σ is the absorption cross-section for a one photon transition. In terms of the number density of photons, n, $R = c\,\sigma\,n$. Note that the rate R has the dimensions time^{-1}.

In the full adder, the eight possible inputs (x, y, z) (see Table 3) therefore correspond to five distinct physical inputs: (1,0,0) and (0,1,0) are excitation by one UV photon, (0,0,1) is excitation by two green photons, (1,1,0) is excitation by two UV photons, (1,0,1) and (0,1,1) are excitation by a UV and two green photons, and (1,1,1) is excitation by two UV and two green photons. We write the input pulse

$$x + y + Q_i z \tag{A.4}$$

where x, y, and z can be either 0 or 1. $Q_i = (\delta_i\,/\,\sigma_i)\Phi_0$, $i = 1$, 2, 3, is the factor that takes into account that the excitation by the two green photons is a two photon transition, so that it scales quadratically with the flux and has a two photon cross-section δ_i.

In the simulations discussed in the text, the parameters are as follows: For the Gaussian pulse shape, eq A.1, its width w is taken to define the scale of time meaning that t/w is dimensionless. In this way, results that are valid both for a nanosecond or a femtosecond excitation scheme can be generated. $t_0 = 5w$. In units of w, the rate $R = \sigma\Phi$ is dimensionless. The peak flux $\Phi(t_0) = 0.05/\sigma$. The one photon cross-sections, see Figure 3, $\sigma_1 = 0.1$; $\sigma_2 = 0.5$; and $\sigma_3 = 0.5$. The dimensionless weights of the two photon transitions are $Q_1 = 0.1$, $Q_2 = 0.8$, and $Q_3 = 0.3$. Only a femtosecond laser can compete with the rate for the fast intramolecular charge transfer in PENNA, and we used $k_3 w = 1$. The other values of the parameters are also consistent with the photophysics of PENNA.[6−8]

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