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Molecule-Based Photonically Switched Half-Adder

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Molecule-based approaches to computing are scientifically intriguing and have potential technological utility.[1−4] Molecular Boolean logic operators have been reported,[1−13] but mathematical calculations require several gates operating together. The half-adder, a combination of an AND gate and an XOR (exclusive OR) gate that share inputs, carries out binary addition; in combination, silicon-based half-adders perform the logic operations of modern computing. A few molecular half-adders have been studied previously.[14−16] As with most molecule-based logic elements, switching these pioneering constructs requires physical addition of chemical species that diffuse to a molecule and carry out reactions. Molecule-based logic gates with optical inputs and outputs would not require access for chemicals or wires and could operate on a fast time scale and in nonfluid media. Here, we report a molecule-based half-adder with all-photonic inputs and outputs that consists of two photochromic molecular switches and a third-harmonic-generating crystal (THG).

As shown in Table l, each input and output of a half-adder may be either *on* (designated *1*) or *off* (*0*). The AND gate gives an *on* response only when both inputs, *A* and *B*, are *on*. The XOR gate generates an *on* output when either input is *on*, but not when the inputs are both *on* or both *off*. In binary addition, the XOR gate output is the sum digit, and the AND gate output is the carry digit.

Figure 1A shows a schematic diagram of the molecule-based half-adder. An optical cuvette contains a solution of AND gate **1** and XOR gate **2** molecules (Chart 1). Triad **1** consists of a porphyrin (P) linked to a fullerene electron acceptor (C_{60}) and a dihydropyrene photochrome (DHP). We have previously shown[17] that, in the DHP−P−C_{60} form (**1c**), laser excitation of the porphyrin (e.g., at 650 nm) initiates photoinduced electron transfer to give a DHP−$P^{\bullet+}$−$C_{60}^{\bullet-}$ charge-separated state, which evolves by charge shift to $DHP^{\bullet+}$−P−$C_{60}^{\bullet-}$. This final state, whose lifetime is 2 μs, is detected optically via the transient absorption of $C_{60}^{\bullet-}$ at 1000 nm. When **1** is used in the AND gate, this transient absorbance signals the *on* state (vide infra). Visible (532 nm) irradiation of **1c** leads to photoisomerization of the DHP to the cyclophanediene (CPD), yielding **1o**. Laser excitation of **1o** produces a short-lived (<10 ns) CPD−$P^{\bullet+}$−$C_{60}^{\bullet-}$ state, but charge shift does not occur due to the high oxidation potential of CPD. Long-lived charge separation is not observed (gate *off*). Irradiation of **1o** with UV (355 nm) light converts the triad back to the DHP form **1c**. Thermal interconversion is extremely slow.

When **1** is used in the photochemical AND gate, it is set initially in the CPD form. Irradiation of **1o** with light from either input laser *A* (1064 nm) or input laser *B* (532 nm) does not lead to isomerization, and measurement of the transient absorbance generated by a readout laser shows no $DHP^{\bullet+}$−P−$C_{60}^{\bullet-}$ (output *X off*). However, simultaneous irradiation by both lasers generates 355 nm light via the third-harmonic-generating crystal, and **1o** is switched to the DHP form, **1c**. Long-lived $C_{60}^{\bullet-}$ absorbance due to $DHP^{\bullet+}$−P−$C_{60}^{\bullet-}$ is detected via the readout laser system, and output *X* is *on*. Experimental observation of these logic operations within the half-adder is demonstrated in Figure 1B. After a logic operation, the state of the gate may be read out once or several times prior to resetting the gate to **1o** by irradiation at 532 nm.

Molecular XOR gates are uncommon, and previous examples involve chemical diffusion.[1,6,9,18] Dyad **2**, in combination with the THG, carries out the XOR function with only light as inputs and output. A porphyrin is linked to a photochromic dihydroindolizine (DHI) to form P-DHI dyad **2c**.[19] Irradiation of the porphyrin of **2c**

Table 1. Truth Table for the Half-Adder

input *A*	input *B*	output *X* AND gate (carry digit)	output *Y* XOR gate (sum digit)	binary sum
0	*0*	*0*	*0*	*00*
1	*0*	*0*	*1*	*01*
0	*1*	*0*	*1*	*01*
1	*1*	*1*	*0*	*10*

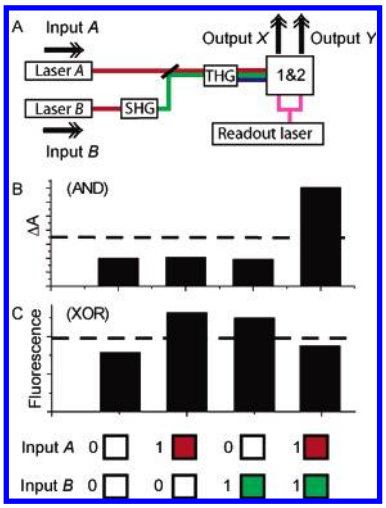

Figure 1. Half-adder and molecule-based logic gates. (A) The half-adder. Molecules **1** and **2** in 2-methyltetrahydrofuran reside in a cuvette labeled "1 & 2". Via pulsed (5 ns pulses at 10 Hz for 10 min) Nd:YAG lasers, the cuvette may be irradiated at either 1064 nm (input *A*) or 532 nm via a second-harmonic generator (SHG, input *B*). When both inputs are on, the sample is irradiated with 355 nm light from the third-harmonic generator (THG). Outputs *X* (AND gate) and *Y* (XOR gate) are the transient absorbance of the fullerene radical anion and porphyrin fluorescence, respectively. The readout laser (650 nm) provides light for the porphyrin excitation needed to produce these outputs. (B) Experimental output (absorbance change at 1000 nm) for AND gate triad **1** after exposure to inputs at 1064 nm (red squares) and/or 532 nm (green squares). The dashed line is a threshold level for detection of an *on* response. (C) Experimental output (fluorescence at 720 nm) from XOR gate dyad **2** after exposure to the inputs.

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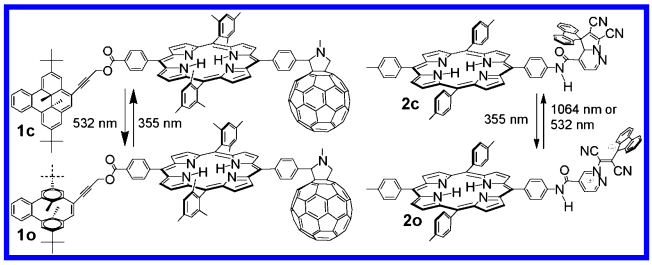
Chart 1. Structures of Molecular AND Gate **1** and XOR Gate **2**



leads to typically strong fluorescence at 720 nm (*on* output). Irradiation of **2c** at 355 nm opens the photochrome to the betaine (BT) form **2o**, which has a higher reduction potential than DHI. Light absorption by the porphyrin of P−BT is followed by rapid (50 ps) photoinduced electron transfer to yield $P^{\bullet+}-BT^{\bullet-}$, leading to strong quenching of the porphyrin fluorescence (output *off*). Irradiation of **2o** at 532 nm (photoisomerization) or 1064 nm (thermal isomerization) causes reversion to **2c**.

When dyad **2** acts as an XOR gate, the molecule is initially set in the **2o** state. The fluorescence readout of the gate (output *Y*) is *off* (Figure 1C). Excitation with input laser *A* (1064 nm) thermally isomerizes **2o** to DHI form **2c**, electron transfer ceases, and the readout laser induces strong porphyrin fluorescence; output *Y* switches *on*. Similarly, irradiation of **2o** with input laser *B* (532 nm) induces photochemical isomerization, and fluorescence output *Y* is turned *on*. However, if both input lasers are turned *on*, the 355 nm light does not induce net photoisomerization of **2o**, electron transfer still occurs, and the fluorescence output *Y* remains *off*. The requirements for an XOR gate are met. After a logic operation, the gate may be reset with 355 nm light.

The two molecular switches and the THG all work together as a half-adder (Figure 1A). The two shared inputs are laser beams at 1064 nm (input *A*) or 532 nm (input *B*). The output of the AND gate (output *X*, the carry digit) is the nanosecond transient absorbance of $DHP^{\bullet+}-P-C_{60}^{\bullet-}$ in **1c**. The output of the XOR gate (output *Y*, the sum digit) is the porphyrin fluorescence of ^{1}P-DHI in **2c**. (The porphyrin moiety in **1** is never significantly fluorescent.) Taken together, parts B and C of Figure 1 demonstrate the half-adder function experimentally. Initially, **1** is in the CPD−P−C_{60} form **1o**, and **2** is in the P−BT state **2o**. When both input beams are *off*, the outputs of both gates are also *off*. The output of the half-adder is the binary sum *00* (first row of Table 1). When input *A* is *on*, molecule **1** (AND) is not affected, but **2o** isomerizes to **2c**. The molecule fluoresces, switching the XOR output *on*. The output of the half-adder is *01* (1 in base-10). If instead input *B* at 532 nm is switched *on*, molecule **1o** is still not affected, and **2o** is again isomerized to P-DHI, leading to an *on* response for output *Y*. Again, the output of the half-adder is *01*. Finally, if both inputs *A* and *B* are switched *on*, the 355 nm light from the THG converts **1o** to **1c**, and long-lived charge separation gives an *on* response from output *X* (carry digit). Because the population of **2o** is not significantly affected by the 355 nm light, the XOR output remains *off*. The corresponding output of the half-adder is the binary sum *10* (2 in base-10), completing the truth table. After readout, the half-adder is reset to the initial state using 355 nm (**2**) and 532 nm (**1**) light. The rate of isomerization at 532 nm is about 50 times higher for **1** than for **2**, permitting the AND gate to be reset by the 532 nm light without significantly affecting the XOR gate. The results of photochemical cycling of **1** and **2** were investigated. Although triad **1** is unchanged after eight cycles, **2** undergoes some decomposition[19] (∼45%, see Supporting Information). Note that the THG provides a transient signal that affects **1** and **2** differently. The photochromes of **1** and **2** are molecular switches that record the inputs for later readout, and the remaining parts of **1** and **2** provide the readouts.

Due to equipment limitations, the experiments were performed with a single input laser. After input irradiation, the molecular response was determined using suitable instrumentation (fluorescence and transient absorbance spectrometers). This was possible because each state of the half-adder has a lifetime of ≥1 h at ambient temperatures. The photochemical events leading to the readouts for **1** and **2** have time constants ≤2 μs. The pulsed laser inputs *A* and *B* are applied for ≤10 min. Total irradiation time is ≤30 μs per input, and the half-adder is capable of relatively rapid cycle times.

Although the current device is not suitable for the construction of useful computers, it points the way to possible applications. The inputs and outputs are all optical, and no diffusional processes or bimolecular chemical reactions are required. Thus, this approach to molecule-based logic is suitable for nonfluid media, and the inputs and outputs do not require physical access, except by light. After receiving inputs, the half-adder remains latched in the resulting state for hours, facilitating single or multiple readouts, and can then be reset with light. The device is capable of cycle times on the order of tens of microseconds or less. Although half-adder function has been demonstrated here with optical outputs, both outputs are based on intramolecular electron-transfer reactions, and in principle could be detected electronically if the molecules were suitably "wired" into circuits.

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Supporting Information Available: Details and examples of data. This material is available free of charge via the Internet at http://pubs.acs.org.

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