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A Half Adder Based on a Photochemically Driven [2]Rotaxane**

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Logic functions at the molecular scale are possible through a variety of approaches[1] that exploit the abilities of molecules to process information. The fundamental principles of logic operation have been demonstrated through detectable spectroscopic changes upon an ionic, electronic, or photonic input[1–6] and have led to the interpretation of complex molecular logic gates such as AND[2] and XOR functions.[3] Of course, mathematical calculations require the operation of several gates together. A half adder,[7] the combination of an AND gate and an XOR gate, could carry out elementary addition by using the XOR gate to generate the sum digit and the AND gate to generate the carry digit. Molecule-based logic gates with optical inputs and outputs would not require access for chemicals or wires and could operate on a fast timescale.[7d,f] Importantly, a single molecular platform that integrates multiple recognition sites for each input is expected to respond in parallel to a variety of reagents and thus provide logic functions at the molecular level.

Supramolecular systems[8–13] have attracted a great deal of attention in recent years because of their challenging construction as well as their potential application in molecular devices. Many supramolecular systems that function as simple logic gates have been reported.[1e,3,5] However, to the best of our knowledge, there has been no previous report of half adders based on a rotaxane system that uses light as an input. A rotaxane is a stable supramolecular system in which a linear subunit threads a macrocycle (wheel or bead) and is stoppered with two bulky end groups (dumbbell). Such a conformation is also similar to an abacus, the manual arithmetic calculator still used by some Chinese even today. Herein, we describe a new theoretical supramolecular half adder based on a [2]rotaxane, with optical inputs and outputs that can perform arithmetical functions directly by means of the position of the bead (wheel) on the axle. This abacus-type system can operate half-adder logic functions independently of any other reagents or chemical stimuli and may be the first step toward the construction of a supramolecular abacus for direct and complicated arithmetic.

[2]Rotaxane **1** comprises an α-cyclodextrin (α-CD) macrocycle locked onto a dumbbell that has two different photoswitchable binding sites, namely an azobenzene site and a stilbene site,[9,10a,13] and is end-trapped mechanically by two fluorescent naphthalimide moieties, 4-amino-1,8-naphthalimide-3,6-disulfonic disodium salt (stopper A) and 1,8-naphthalimide-5-sulfonic sodium salt (stopper B; Figure 1). The photoactive units can be switched independently by using light at different wavelengths (UV/Vis).[10c,14] The photochemical switching, which could mimic the function of a half adder that performs simple arithmetic addition, can be monitored by changes in the absorption of the supramolecular system and changes in the fluorescence of the end groups.

Molecular shuttle **1** is indeed a multistate [2]rotaxane that can be converted between a dynamic state and three static states in response to light and features dual fluorescence outputs. At room temperature in [D$_6$]DMSO, the state (*E*,*E*)-**1** as shown in Figure 1 is a dynamic state in which the α-CD bead moves back and forth between the azobenzene and stilbene units at a rate that cannot be followed on the NMR timescale. Rational nuclear Overhauser effects (NOEs)[14] can be observed between the resonances of the protons of the azobenzene and stilbene moities and protons H3 and H5 located inside the cyclodextrin annuli. This set of NOEs is not consistent with any single static geometry and shows that the cyclodextrin rapidly glides along the dumbbell. State (*E*,*E*)-**1** was converted into ($Z_{N=N}$,$E_{C=C}$)-**1** or ($E_{N=N}$,$Z_{C=C}$)-**1** by photoisomerization upon irradiation with at 380 nm or 313 nm, respectively. Finally, further irradiation of the $Z_{N=N}$,$E_{C=C}$ isomer at 313 nm or the $E_{N=N}$,$Z_{C=C}$ isomer at 380 nm can generate (*Z*,*Z*)-**1** (Figure 1).[15] Moreover, as shown in Figure 1, each photochemical reaction is fully reversible. The three *Z* isomers could be shifted back to the (*E*,*E*)-**1** isomer by irradiation with UV light of another wavelength, as shown in Figure 1, or by placing the sample in the dark for several hours. The initial *E*,*E* isomer could also be recovered upon heating solutions of each of the three *Z* isomers to 60 °C for 1 h and then cooling to room temperature. The various *E*→*Z* photoisomerization reactions of the [2]rotaxane **1** were also investigated by monitoring the changes in the ^{1}H NMR spectra and the two-dimensional ROESY spectra in [D$_6$]DMSO upon UV/Vis irradiation. Very different NOE patterns were observed for the three "Z" isomers,[14] consistent with the geometries of the three photostationary (PSS) states—$Z_{N=N}$,$E_{C=C}$ (PSS-ZE), $E_{N=N}$,$Z_{C=C}$ (PSS-EZ), and *Z*,*Z* (PSS-ZZ)—as shown in Figure 1. The NMR data[14] also support the idea that [2]rotaxane **1** can be photochemically converted between the dynamic-state *E*,*E* isomer (namely DS-EE)[16] and the three static states mentioned above.

The changes in absorption during the *E*→*Z* photoisomerism of [2]rotaxane **1** in solution were also investigated.[14] Compared with the absorption spectrum of the *E*,*E* isomer, those of the other three isomers were similar but showed an increased absorption at around 270 nm and a decrease in absorption at 350 nm with an isobestic point at 301 nm (A_{301} = 0.165). To indicate the magnitude of the change in absorption upon isomerization, the ratio of the difference in the

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

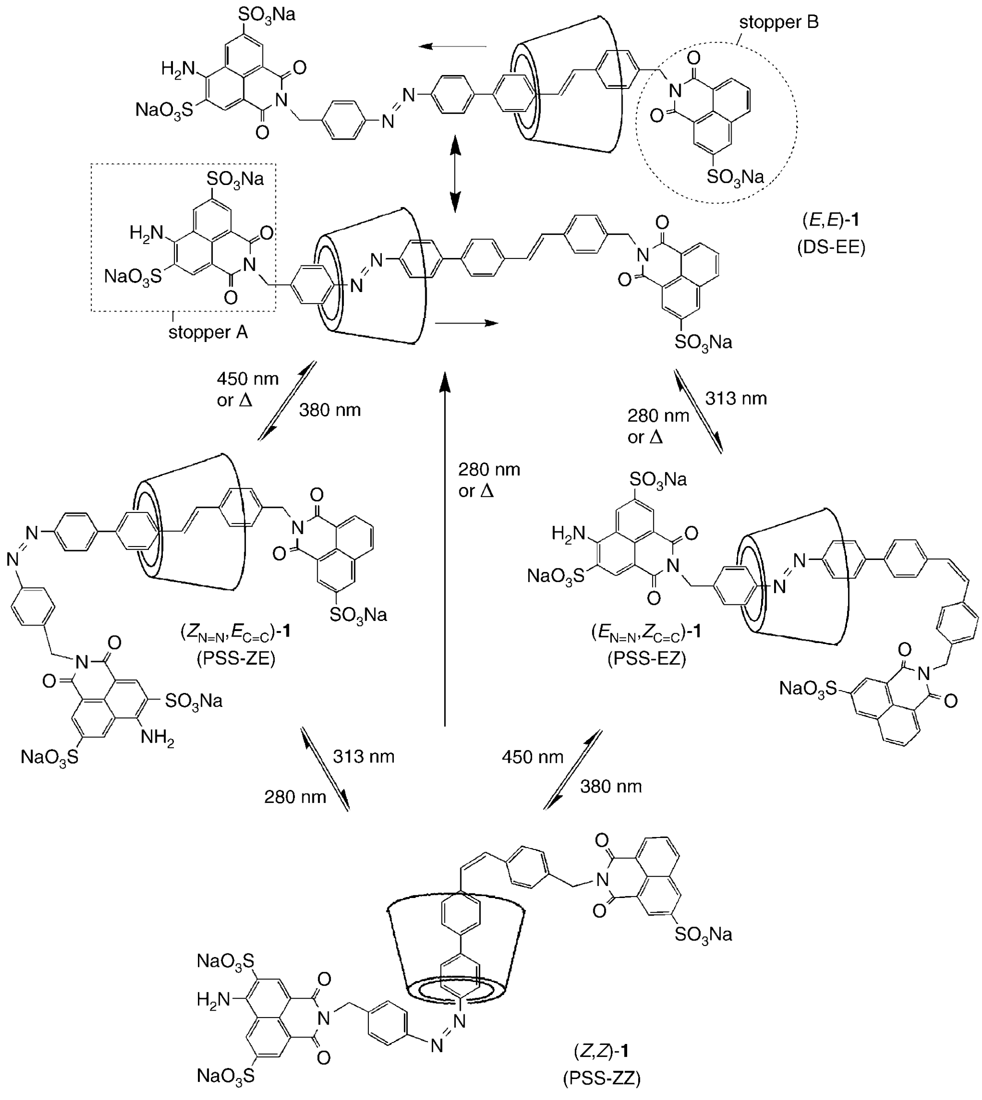

Figure 1. The intrinsic interconversion network of the α-cyclodextrin/azobenzene–stilbene [2]rotaxane **1** between the four states: one *E*,*E* isomer ((*E*,*E*)-**1**), two *E*,*Z* isomers (($Z_{N=N}$,$E_{C=C}$)-**1**), ($E_{N=N}$,$Z_{C=C}$)-**1**), and one *Z*,*Z* isomer ((*Z*,*Z*)-**1**). DS = dynamic state; PSS = photostationary state.

absorbances at 270 nm and 350 nm over the absorbance at 301 nm ($\Delta A = |A_{270} - A_{350}|/A_{301}$) was measured. For the *E* isomer, $\Delta A = 0.15$, whereas the values of ΔA calculated for the photostationary states (PSS-ZE, -EZ, and -ZZ) were 0.32 (PSS-ZE), 0.27 (PSS-EZ), and 0.73 (PSS-ZZ).[14]

A clear change was observed in the fluorescence spectra for [2]rotaxane **1** (see Supporting Information).[14] Relative to isomer (*E*,*E*)-**1**, the fluorescence intensity at $\lambda_{em} = 395$ nm (stopper B) increased by about 55% upon attaining the PSS-ZE state, while the fluorescence intensity at $\lambda_{em} = 520$ nm (stopper A) decreased by 14%. On the other hand, at the PSS-EZ state the fluorescence intensity at $\lambda_{em} = 520$ nm increased by about 52%, while a decrease of 15% in fluorescence intensity was observed at $\lambda_{em} = 395$ nm. For the PSS-ZZ state, the fluorescence intensities at both $\lambda_{em} = 395$ and 520 nm were similar to that of the *E* isomer but lower by 10%. The changes in the fluorescence spectra result from the rigidity of the α-CD ring. When the α-CD macrocycle is located near a fluorescent stopper, the vibrations and rotations of the methylene bonds between the stopper and the recognition site are hindered which leads to an increase in the fluorescence intensity of the stopper.[10] This was also confirmed by the weaker fluorescence observed for the lone dumbbell **2**, for which vibrations and rotations are relatively facile in the absence of the macrocycle.[14] Because of the total reversibility of the photoisomerization processes, the photoinduced shuttling motions of the α-CD ring on the dumbbell could be repeated and monitored by means of the reversible fluorescent output signals. By alternating irradiations at 380, 313, 450, and 280 nm, we verified that the photochemical processes are highly reproducible over more than 10 cycles.[14]

The above interconversions among the four states (*E*,*E*)-**1**, ($Z_{N=N}$,$E_{C=C}$)-**1**, ($E_{N=N}$,$Z_{C=C}$)-**1**, and (*Z*,*Z*)-**1** can be described with binary logic. The input (I) signals are UV light at wavelengths of 380 nm (I1) and 313 nm (I2). The difference in the absorption, ΔA, can be considered as one of the output signals, O1; O1 = 0 when ΔA is low (< 0.7), whereas O1 = 1 when ΔA is high (> 0.7). As mentioned above, only at the PSS-ZZ state does the photoisomerization about both azobenzene and stilbene occur. In this case, ΔA is high (> 0.7), but only upon simultaneous irradiation of both units at 380 nm and 313 nm (I1 = 1 and I2 = 1) is the output signal O1 = 1—otherwise, O1 = 0. Consequently, the difference in the change in absorption, ΔA, upon the external inputs of UV light at $\lambda = 380$ nm (I1) and 313 nm (I2) could be interpreted as an AND gate.

The change in the fluorescence intensity ΔF—defined as the difference in fluorescence intensity between two states at $\lambda_{em} = 520$ nm or at $\lambda_{em} = 395$ nm—of the rotaxane was selected as another output signal, O2. When the value of ΔF is low (< 50%), O2 = 0, whereas when the value of ΔF is high (> 50%), O2 = 1. Separate irradiation of the *E*,*E* isomer at either 380 nm (I1) or at 313 nm (I2) leads to the formation of either ($Z_{N=N}$,$E_{C=C}$)-**1** (PSS-ZE; $\Delta F = 55\%$ at $\lambda_{em} = 520$ nm) or $(E_{N=N},Z_{C=C})$-**1** (PSS-EZ, $\Delta F = 52\%$ at $\lambda_{em} = 395$ nm), respectively, and the ΔF output signal (O2) is high in both cases, that is, O2 = 1. Interestingly, under simultaneous irradiation at 380 nm (I1) and 313 nm (I2), (*Z,Z*)-**1** (PSS-ZZ) was formed and the resultant changes in the fluorescence intensity at $\lambda_{em} = 395$ and 520 nm were both small ($\approx 10\%$, therefore, O2 = 0). The changes in fluorescence (ΔF) in response to irradiation at 380 nm (I1) and 313 nm (I2) could be interpreted as an XOR gate.

The intrinsic network of the transformations of [2]rotaxane **1** between its four states leads to changes in absorption and fluorescence intensities of the two end groups, and these spectral changes can be interpreted as AND and XOR gates, respectively. The AND and XOR gates may function in parallel, as each photoswitchable unit (azobenzene or stilbene) in [2]rotaxane **1** can be switched with the inputs I1 and I2 independently.[14] Therefore, the spectral variations that result from the interconversion of the four states (DS-EE, PSS-ZE, PSS-EZ, PSS-ZZ) as shown in Figure 1 could be used to mimic the function of a half adder (Figure 2). Figure 2a shows a schematic diagram of the molecule-based half adder. In binary addition, the XOR gate output is the sum digit and the AND gate output is the carry digit. In the rotaxane-based half adder, the sum digit (n_S) is coded by the fluorescence change ΔF (O2) and the carry digit (n_C) is coded by the absorption change ΔA (O1). As shown in the truth table (Table 1) and Figure 2, each input and output of the half adder may be either ON (designated 1) or OFF (0). The AND gate gives an ON response only when both inputs I1 ($\lambda = 380$ nm) and I2 ($\lambda = 313$ nm) are ON. The XOR gate generates an ON output when either input is ON but not when they are both ON or both OFF. After the readout, the half adder could be reset to its initial state by using light (280 nm) or heat energy. Because of the full reversibility of the photoisomerization processes, the current half adder can be used repeatedly.

Table 1: Truth table for a half adder with the sum digit n_S and the carry digit n_C.

I1 (380 nm)	I2 (313 nm)	O1 (ΔA) AND gate (n_C)	O2 (ΔF) XOR gate (n_S)	Binary sum
0	0	0	0	00
1	0	0	1	01
0	1	0	1	01
1	1	1	0	10

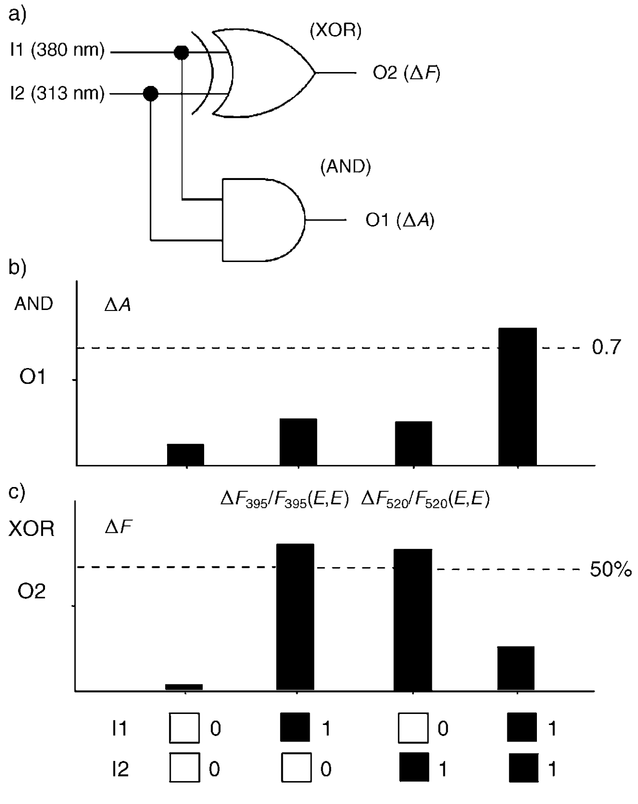

Figure 2. a) Schematic representation of the two-input half-adder logic circuit with [2]rotaxane **1** (I = input, O = output; *A* = absorbance, *F* = fluorescence). b) Experimental output O1 (ΔA) for the AND gate after irradiation of **1** at 380 nm (I1) and/or 313 nm (I2). c) Experimental output O2 (ΔF) for the XOR gate after irradiation at 380 nm (I1) and/or 313 nm (I2). The dashed line indicates the detection limit.

In summary, a photochemically driven (the inputs and the outputs are all photochemical) multistate [2]rotaxane that mimics a half adder with distinct AND and XOR logic gates has been demonstrated for the first time. After receiving inputs, the half adder remains in a static state for a while then gives rise to one of two optical outputs. The device can then be reset with light or heat, such that the half adder can be operated repeatedly. Most importantly, the realization that multistate [2]rotaxane operations which involve more than one logic expression are possible through a judicial choice of input and output signals has pointed a way to design complicated logic circuits based on one molecule. It is likely that by integrating these approaches, molecular logic gates with superior processing capabilities will emerge in the future.

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[14] The Supporting Information includes: ^{1}H NMR spectra, two-dimensional ^{1}H ROESY NMR spectra, and MALDI-TOF mass spectra of [2]rotaxane **1**; absorption and fluorescence spectra of dumbbell **2**, [2]rotaxane **1**, and the half-dumbbells; and detailed conditions for the photochemical reactions.

[15] The fractional conversion from (*E*,*E*)-**1** (DS-EE) to ($Z_{N=N}$,$E_{C=C}$)-**1** (PSS-ZE) is about 65%, and that to ($E_{N=N}$,$Z_{C=C}$)-**1** (PSS-EZ) is about 60%. The fractional conversion from ($Z_{N=N}$,$E_{C=C}$)-**1** (PSS-ZE) and ($E_{N=N}$,$Z_{C=C}$)-**1** (PSS-EZ) to (*Z*,*Z*)-**1** (PSS-ZZ) are slightly lower in comparison at about 53% and 57%, respectively.

[16] What station does the macrocycle prefer on the rotaxane: the azobenzene or the stilbene? The energy difference between the two translational isomers may determine the preferential location of the ring on one of the two sites. Fast shuttling of the ring between the two sites could make the determination of the population of the two translational isomers difficult, but if the entropy terms are sufficiently different then the relative binding affinity of the macrocycle for the two stations could be reversed by lowering the temperature.