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Storage and Processing of Information Using Molecules: The All-Photonic Approach with Simple and Multi-Photochromic Switches

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Abstract. The use of photochromes for the implementation of molecular logic operations is a very promising approach toward molecular computing. This statement is based on (a) the possibility of operating such molecular devices exclusively with photonic signals and (b) the spatiotemporally and remotely controlled switching, which is characteristic for photochromes. In this account-style Review a brief overview of the application of simple photochromes and multi-photochromic conjugates for the small-scale functional integration of complicated logic circuits is given. This complements and extends the efforts of designing molecular photochromic memories for data storage which have been described by many research groups worldwide.

Keywords. Switches, photochromism, fluorescence, logic gate, memory

1. Introduction

Photochromic compounds are *par excellence* examples of molecular switches which change their optical properties (UV/vis absorption and fluorescence) upon applying a photonic stimulus. In the simplest situation a form A is transformed into B by means of a photochemical isomerization reaction. For achieving a real switching function, B should be convertible back to A by means of light irradiation with a different wavelength. Clear-cut conversions and photostationary states mainly composed of a single form (A or B) are achieved by fine-tuning the optical (UV/vis spectra) and photochemical properties (isomerization quantum yields) of the switches. Some of the herein discussed photochromic transformations are shown in Figure 1. The photochemical reactions may also be complemented by the possibility of acidochromic switching which enlarges the number of possible components in the switching network.

In this Account we will give a brief overview about some representative works where photochromic systems have been used for the processing or storage of binary information according to the principles of Boolean logic. These applications complement the extensive use of photochromic switches in the context of life sciences, chemosensing, and materials chemistry.[1] In the main part we will then concentrate on systems from our laboratories which have enabled us to achieve either a very high degree of functional integration or rather complex sequential logic. The outstanding characteristic of many of these systems is their all-photonic operation mode which means that exclusively photonic signals are used to address the system and to read its switching state in terms of the binary notation (0, 1). This has several advantages such as the possibility of spatiotemporal control and remote addressing. Resetting is possible without the accumulation of by-products which is a frequently encountered problem observed for systems with chemical input signals.

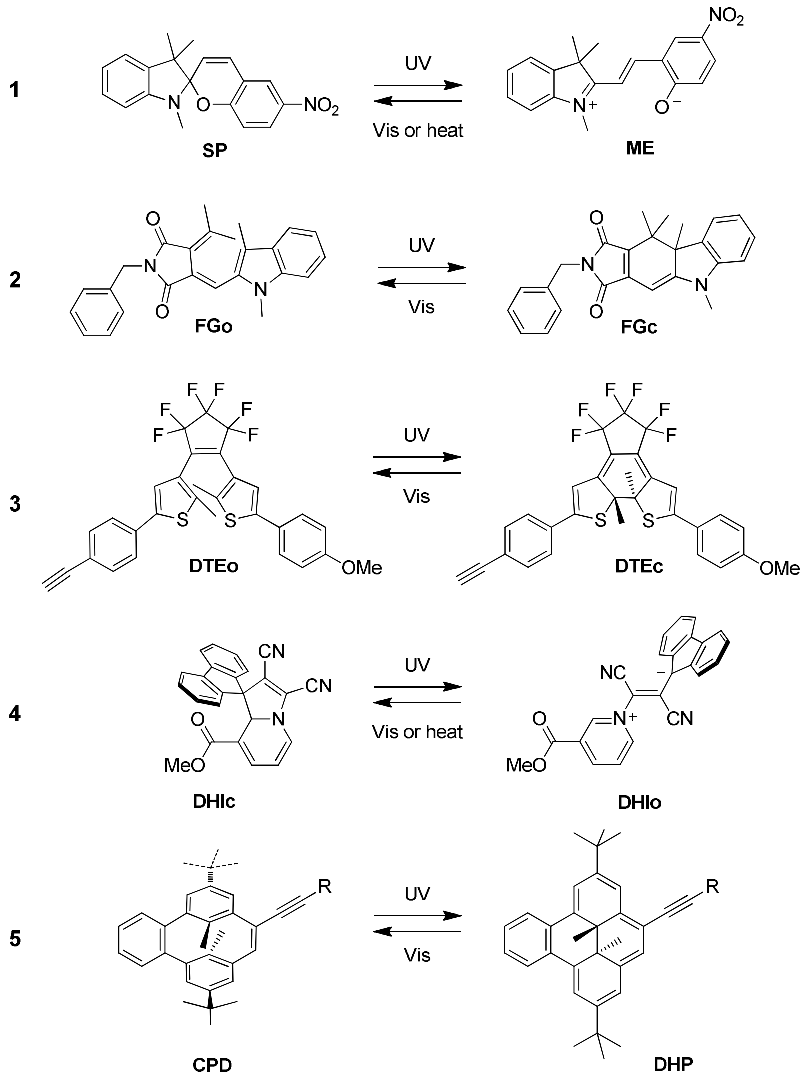


Figure 1

The idea to use photochromes for molecular information storage is in fact over 50 years old. It was Hirshberg in 1956 who suggested interpreting the switching of spiropyrans as a photochemical memory model.[2] Since then a large number of systems with similar characteristics have been reported in the context of information storage.[3] The often dramatic changes of the UV/vis absorption properties upon photoisomerization have been used to define the photonic signal indicating the binary state of the molecular device. However, the ease and sensitivity with which fluorescence can be measured makes it a preferred reporter signal for evaluating the binary state of the switch. Applying well-established design rules for the modulation of fluorescence by photoinduced electron transfer or energy transfer in donor-acceptor pairs, the switching of a large variety of photochromes can be translated into the change of an optical emission signal by integrating both entities (photochrome and fluorophore) into the same molecular architecture.[4]

In Figure 2 a small selection of fluorophore-photochrome conjugates that follow these principles is shown. These compounds have in common that they were explored as molecular bistable memories, allowing the writing, reading, and erasing of information.[5-8] The input information is provided by the light which is used to trigger the photochromic processes. The stored information is read out by detecting the fluorescence signal corresponding to the binary state. In order to guarantee the long-term storage of the written information it is desirable that the implicated forms of the photochromic switch show high thermal stability (no or very slow thermal isomerization reactions). The characteristic of high fatigue resistance (low yield of photodecomposition reactions) benefits the use of the memory in repeated write-erase cycles. These criteria can be achieved by an appropriate design of the photochrome itself and are often fulfilled by fulgimide (FG) or dithienylethene (DTE) photoswitches. However, the reading of the information through the measurement of a fluorescence signal bears a potential problem because light excitation has to be used to address the fluorophore. This light may be absorbed directly by the photochrome and cause its undesired back isomerization, leading to the partial loss of the written information. As a second possibility, energy transfer from the excited state fluorophore to the photochrome may sensitize the isomerization reaction. This is referred to as destructive readout and has been a problem of many early designs. In order to achieve non-destructive reading of the memorized information the following strategies have been used: a) separation of the fluorophore absorption spectrum from the photochrome spectra and b) use of photoinduced electron transfer communication between the fluorophore and the photochrome as a switchable quenching mechanism that does not sensitize any isomerization reactions.

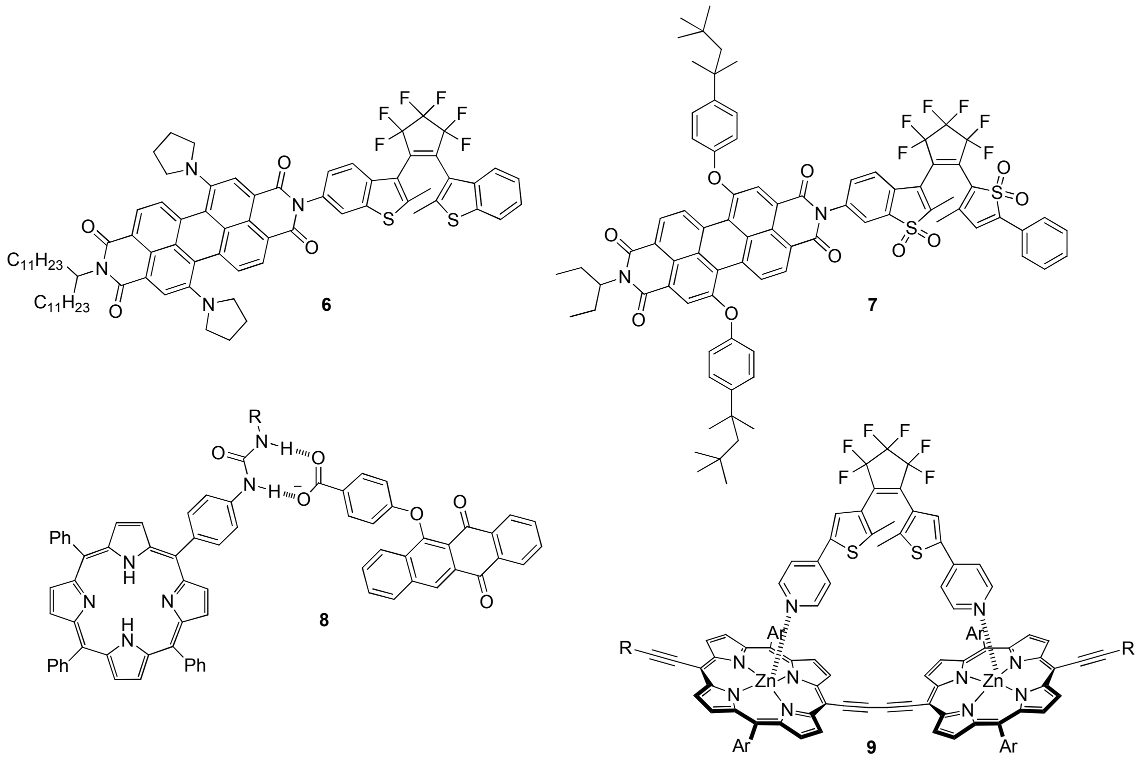


Figure 2

All systems shown in Figure 2 allow for non-destructive readout. In the case of **6** and **7** photoinduced electron transfer between the perylenediimide fluorophore and the ring-closed dithienylethene was operative.[5, 6] Switch **7** was shown to work even at the single molecule level.[6] Compound **8** also builds on photoinduced electron transfer communication.[8] In system **9** a porphyrin dimer was combined with a DTE unit through supramolecular interactions. The geometrical changes of the DTE upon switching from the open to the closed form led to a modulation of the binding mode with the porphyrin dimer which was conveniently and selectively read by characteristic changes in the absorption spectrum and also in the fluorescence spectrum of the porphyrin dimer.[7]

While the realization of the molecular memory function with photochromes is quite intuitive, photochromic switches have also been used for the processing of molecular information. This led to the molecular implementation of logic gates and functionally integrated logic circuits. These systems can be subdivided by the mode of their input operation: a) photonic inputs, b) photonic inputs coupled with heat as input, and c) photonic and chemical inputs. In all cases, photonic signals in form of UV/vis absorption or fluorescence changes were employed to read the output of the systems. The systems **10/11-17** are excellent examples of all-photonic molecular logic switches.[9-17] The bandwidth of logic functions achieved with these molecules reach from half-adders[9, 12, 15] (**10/11-13** in Figure 3) and 2:1 multiplexers/1:2 demultiplexers[10, 11] (**14**) to keypad locks (**15**);[13] see Figure 4. System **16** is an example of the use of photochromic reactions which generate a chemical output. The protons which are released by ring closure of the protonated merocyanine form were used to establish the switch-to-switch communication with a pH-sensitive ruthenium complex.[16] The DTE derivative **17** is an example of an optical organic transistor, making a link between molecular logic and organic electronics.[14]

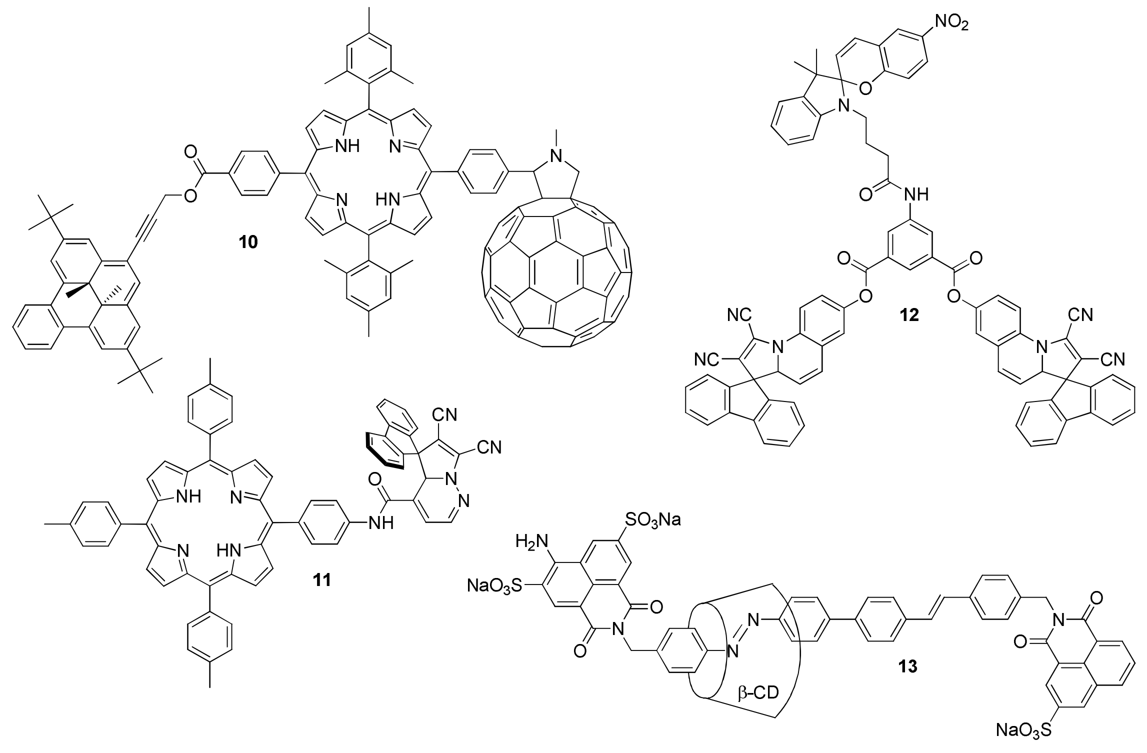


Figure 3

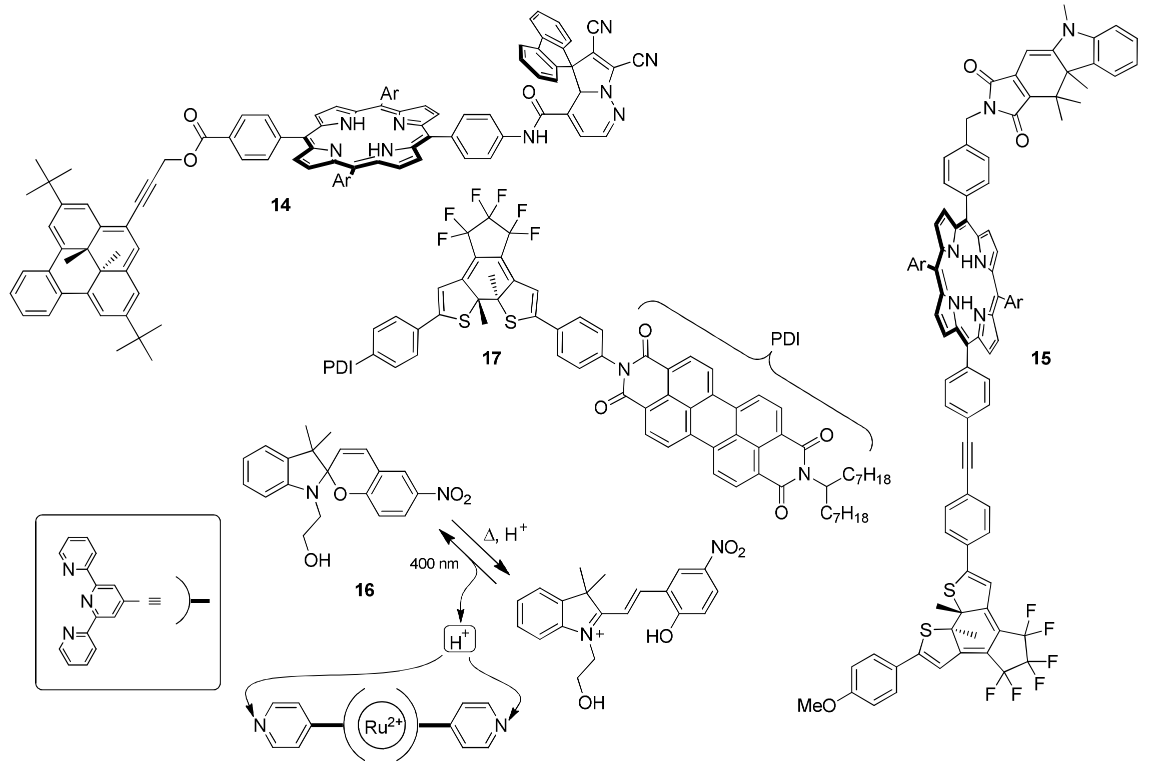


Figure 4

As discussed above, all-photonic switching has several advantages over the use of chemical inputs. However, both input types (light and chemicals) may be combined in order to increase the complexity of the switching network and to increment the diversity of logic operations which can be realized with the device. A very good example for this strategy is the use of spiropyrans. The photochromic process consists in the conversion between the ring-closed spiro (SP) and the open merocyanine (ME) form. Additionally, the merocyanine can be involved in acidochromic switching, which gives the corresponding protonated merocyanine (MEH). This three-state switch (**18** in Figure 5) was used extensively for the design of complex logic circuitry, including the optical networks of several chromophores.[18, 19] Other examples made use of addressing the open merocyanine form with Fe^{3+} cations leading to a half-adder or a three-input AND gate.[20, 21] When combined with properly designed receptors also DTE photochromes or therefrom derived compounds can be used as combined photo- and ion-sensitive switches (Figure 6). This was explored for example in the design of a mimic for a soft gear shift[22] (**19**) or the realization of a multifunctional logic platform[23] (**20**) implementing the operation of a half-adder, half-subtractor, demultiplexer, and encoder/decoder. However, it should be emphasized that logic devices which use chemical inputs come with a drawback. The chemical reversibility is gained at the price of the addition of auxiliary “reset” reactives (e.g., base in case of acidochromic systems or competing chelator for metal cation inputs) and the thereby formed waste products may compromise the long-term operation of the systems.

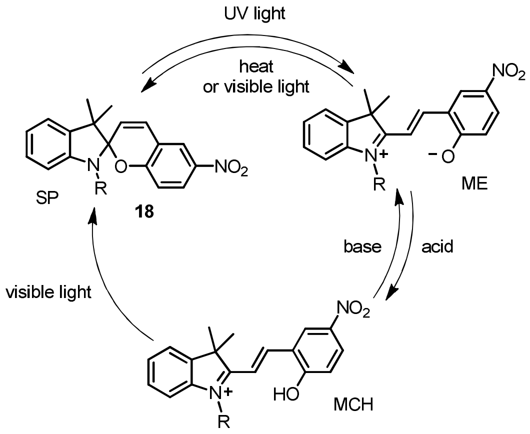


Figure 5

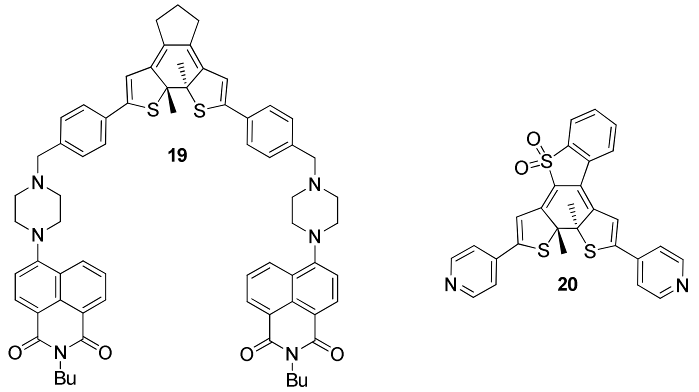


Figure 6

Finally, the photonic input can also be combined advantageously with other non-chemical inputs such as heat or an electrical field as external stimuli. Albeit less common there are some interesting examples for such systems. Among them the realization of basis logic gates[17] (AND, INHIBIT) and the first reported molecular 2:1 multiplexer[11] (Triad **14**, see Figure 4) with heat as one input as well as a logic AND gate with an electric field input (**4**, see Figure 1).[24]

2. The Dithienylethene Photochrome as Simplistic Design Model for All-Photonic Set-Reset (S/R) Latches

In principle any memory device which has been discussed in the Introduction can be re-interpreted as a Set-Reset (S/R) latch which is one of the most intuitive memory functions.[25, 26] An S/R latch corresponds to a circuit which is made of two cross-coupled NOR gates, as shown in Figure 7a. The function of the device is represented by the state diagram shown in Figure 7b. Basically, a bistable system with the states $Q = 0$ and $Q = 1$ is discussed. On application of a set input ($S = 1$) over the $Q = 0$ state the system flips to the $Q = 1$ state. On the other hand, the activation of the reset input ($R = 1$) over the $Q = 1$ state inverts the system to the 0 state. The application of S or R over the set ($Q = 1$) or reset state ($Q = 0$), respectively, does not change the binary value of the system. The same is true for the "do nothing" situation (S and R equal 0). In terms of molecular design the described function can be translated into the following essential criteria: *i*) the need of a bistable system with sufficiently differentiated output signal levels, *ii*) the S and R inputs have to interact with specific states of the molecular system, *iii*) the stored information must be long-term stable (thermal stability of the implicated forms), and *iv*) input accumulation must be avoided. These prerequisites are easily fulfilled for example by the DTE derivative **21** (see structure in Figure 7c).[27] The system is bistable, the output signal (Q) can be defined as absorbance at around 600 nm where the closed form **21c** is the only chromophore. UV light (302 nm, input S) leads to almost quantitative conversion of the open form **21o** to the closed form **21c** ($Q = 1$), and visible light (> 450 nm, input R) can be used to reset the system to **21o** ($Q = 0$). Finally, both forms are long-term stable which guarantees the non-volatility of the written information. The photochromic process is clean and fatigue-resistant, as has been shown for at least ten set-reset switching cycles. In conclusion, the straightforward implementation of S/R latching can be achieved with any photochromic system which fulfills the abovementioned simplistic design rules. This type of logic, where the outcome of the logic operation depends on the inputs *and* the current state of the system is called sequential logic.

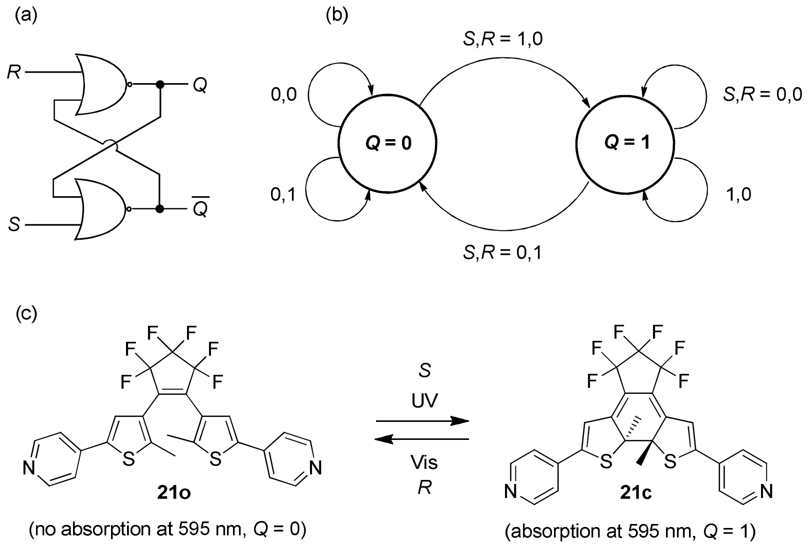


Figure 7

3. A Molecular Keypad Lock by Rational Design of Photochrome-Triggered Energy Transfer Switching of Fluorophore-Spiropyran Conjugates

The function of keypad locks is much related to day-by-day experiences of many people, be it through the use of automatic teller machines, door locks, or hotel room safes. This has doubtlessly increased the interest in mimicking such functions with molecular systems. The basic function of a keypad lock can be summarized relatively straightforward. Let be the device operated by just two chemical inputs I_1 and I_2 (i.e., building on a two-input priority AND gate). By only counting on activated inputs with a binary 1 value the system can be addressed by exactly two combinations (out of a total of eight possible ordered input combinations): first input I_1 and then I_2 and *vice versa*. Only the correct order will activate the system, which is expressed by a binary 1 output.

In this context, molecules which are addressed by chemical inputs and which deliver a defined photonic output (UV/vis absorbance changes, fluorescence modulation) only upon receiving the right order of inputs have attracted considerable interest in the last five years.[28-31] However, while these examples provide proof-of-principle, their practical value may be limited. Often the memory effect is based on kinetic differentiation, which makes the application of the keypad dependent on a time factor.[29, 32] Furthermore, the inputs have to be removed, masked or neutralized after each application. Simple acid-base neutralization is still practical, but the situation turns more complicated for metal cations and anions, which have been used as inputs with quite some abundance in keypad lock demonstrations.[33, 34]

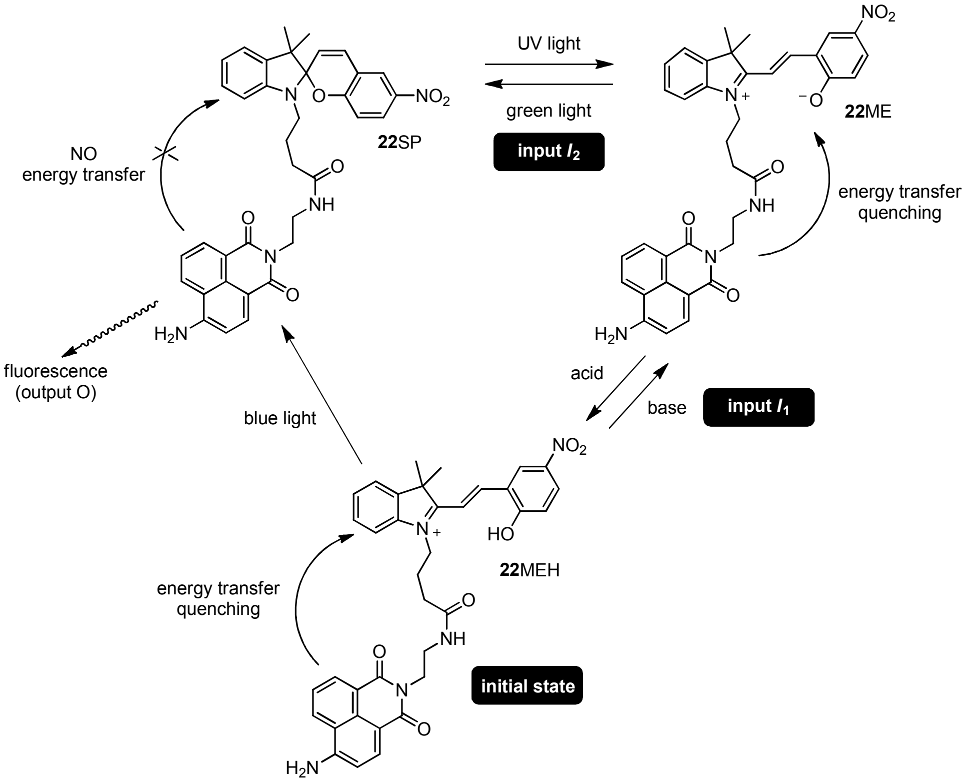
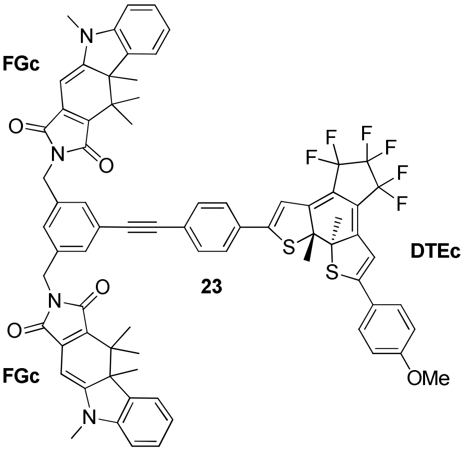


Figure 8

In an attempt to substitute the use of chemicals as inputs at least partially, we have drawn on the photo- and acidochromic switching of spiropyrans.[35] In the concrete case a nitrospiropyran was combined with a fluorophore (aminonaphthalimide, dansylamide, or perylene). The design principle relies on the use of energy transfer quenching of the fluorophore by some of the photochrome forms. As shown in Figure 8 for the example of the aminonaphthalimide-substituted spiropyran **22** the spiro form (SP) does not quench the aminonaphthalimide fluorescence due to a zero spectral overlap integral. However, the merocyanine (**22**ME) and the protonated merocyanine (**22**MEH) have considerable spectral overlap leading to efficient energy transfer. By starting with the **22**MEH form and applying a strong base (the phosphazene P_2-Et) and 530 nm green light as inputs I_1 and I_2, respectively, a keypad lock can be demonstrated. The lock requires the application of I_1 before I_2. In this case the sequence **22**MEH → **22**ME → **22**SP is followed, with the last form as the only fluorescent one (output $O = 1$, lock is open). If input I_2 is applied first and then input I_1, then the sequence stops at the non-fluorescent **22**ME (output $O = 0$, lock is closed). This is because the green light irradiation (I_2) does not alter the state of the system, i.e., **22**MEH maintains. In practice the system has a smaller dynamic switching range than could be expected from the quantitative energy transfer. This is because the SP to ME transformation used for the preparation of the system is limited by a photostationary state composition of *ca*. 50/50.

4. Multi-Functional Integration of Logic Gates and Circuits in a Unimolecular Platform

Until around 2010, functional integration was used in the design of molecules capable of mimicking more and more complex logic operations.[28, 32] Although examples of molecules that could perform more than one logic function were starting to emerge,[36] the vast majority of the reported examples were targeting a single function only, using a fixed set of input and output signals. These functions include those of the half-adder,[37] half-subtractor[38, 39] (constituting the moleculator if operated synchronized),[40, 41] 2:1 multiplexer,[11] 1:2 demultiplexer,[10] 4:2 encoder/2:4 decoder,[42] and keypad lock.[29] It can be shown that a molecular entity with the capacity to perform *all* the above functions must have a total of four or more distinct accessible physical states. For an all-photonic device, each of these states must have at least one unique spectral feature. In addition, these spectral features (used as output signals) must vary with the input signals according to the truth tables of the whole set of functions to be performed which adds even more complexity to the design criteria. The FG-DTE triad **23** shown in Figure 9 was our first candidate for this kind of multitasking molecular platform, and it proved to be able to perform no less than 13 different logic operations.[43]



23

Figure 9

In order to achieve this non-trivial task, a relatively large set of input and output signals was used altogether (five irradiation wavelengths as inputs and seven different photonic output signals). However, the individual functions were performed by using different subsets of input and output combinations. This is referred to as *reconfiguration* – a property of molecular logic devices that is not shared by the typical silicon-based equivalents where hard-wiring does not allow for any flexibility in the input-output definitions or device function.

The multi-photochromic triad **23** consists of two identical FG photoswitches and one DTE photoswitch covalently linked to a phenyl core. Both the FG and the DTE units (see structures of individual model photochromes **2** and **3** in Figure 1) exist in an open colorless form, FGo and DTEo, and a closed colored form, FGc and DTEc. This gives rise to four constitutionally isomeric forms (taking into account only the isomers in which the two FG units are in the same form): FGo-DTEo, FGo-DTEc, FGc-DTEo, and FGc-DTEc. As shown in Figure 10, 302 nm UV light induces selectively the closing reaction DTEo → DTEc, whereas 397 nm UV light is selective for FGo → FGc. 366 nm UV light triggers the closing reactions of both DTEo and FGo. As for the corresponding opening reactions, red light is selective for the reaction DTEc → DTEo, where green light opens both DTEc and FGc.

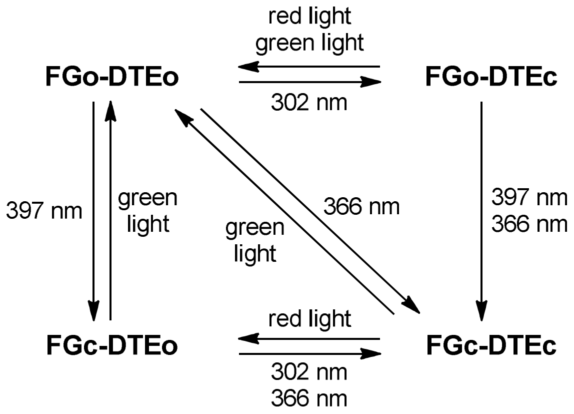


Figure 10

Due to the observed selectivity in the opening and the closing reactions, the triad can be highly enriched in all four isomeric states from any precursor state by the use of proper input combinations. The absorption and the emission spectra of these four states are shown in Figure 11.

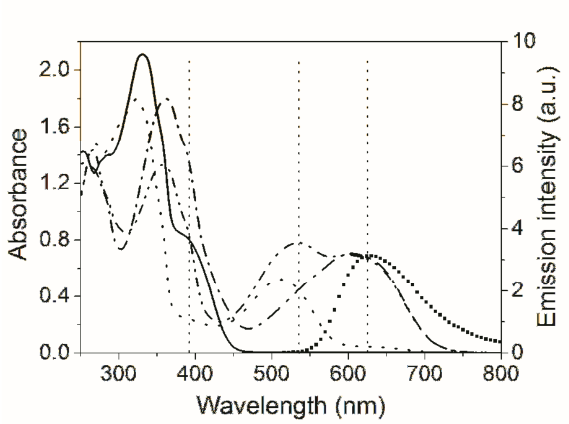


Figure 11

The vertical lines indicate the wavelengths where the four isomeric forms have their respective unique signature. These are high transmittance at 535 nm, high absorbance at 393 nm, intense fluorescence emission at 624 nm, and high absorbance at 535 nm for FGo-DTEo, FGo-DTEc, FGc-DTEo, and FGc-DTEc, respectively. The absorption/transmission features are easily traced back to the sum of the absorbance of the closed and the open forms of the individual photochromes at the respective wavelength. For the emission at 624 nm, FGc is the exclusive fluorophore. In FGc-DTEc, however, the fluorescence is quenched by DTEc in an efficient energy transfer process, so that significant emission is observed only for FGc-DTEo.

These different spectral "fingerprints" were used for example as output signals in the operation as a 2:4 decoder together with input signals at 302 nm and 397 nm. A 2:4 decoder together with a 4:2 encoder translates numbers in the binary to numbers in base 10 (encoder function) and back to numbers in the binary notation (decoder function). The truth tables for the encoder and the decoder are shown in Tables 1 and 2 and the electronic equivalents are represented in Figure 12.

Table 1. Truth Table of a 4:2 Encoder[a]

I_0	I_1	I_2	I_3	O_1	O_0	base-10	binary
1	0	0	0	0	0	0	00
0	**1**	0	0	0	**1**	1	01
0	0	**1**	0	**1**	0	2	10
0	0	**0**	**1**	**1**	**1**	3	11

[a] I_0: green light, I_1: 397 nm light, I_2: 302 nm light, I_3: 366 nm light, O_1: 625 nm (absorbance), O_0: 475 nm (absorbance).

Table 2. Truth Table of a 2:4 Decoder[a]

I_1	I_0	O_0	O_1	O_2	O_3	binary	base-10
0	0	**1**	0	0	0	00	0
0	**1**	0	**1**	0	0	01	1
1	0	0	0	**1**	0	10	2
1	**1**	0	0	0	**1**	11	3

[a] I_1: 302 nm light, I_0: 397 nm light, O_0: 535 nm (transmittance), O_1: 624 nm (emission), O_2: 393 nm (absorbance), O_3: 535 nm (absorbance).

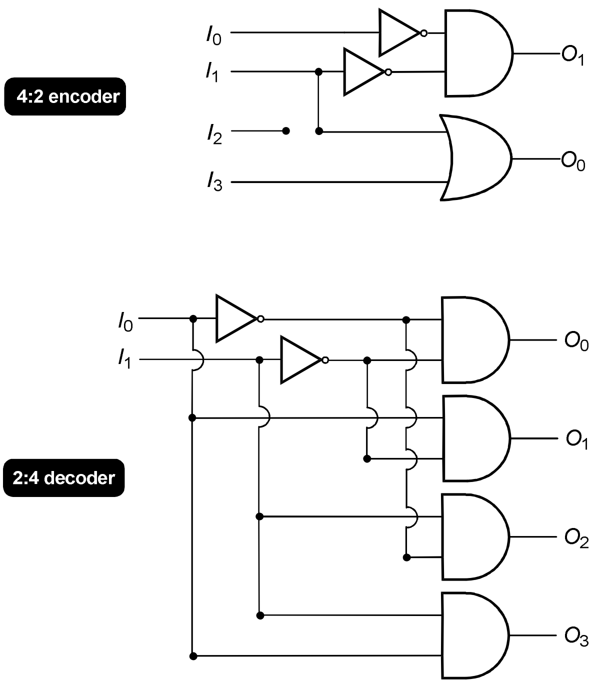


Figure 12

In the operation as the encoder, the triad is initially set to the FGo-DTEo form. The outputs of the encoder were read as the absorbance at 475 nm (O_0, mainly from FGc) and 625 nm (O_1, mainly from DTEc) after addressing the triad with four inputs at 302 nm, 366 nm, 397 nm, and $460 < \lambda < 590$ nm (green light). Application of I_0 (green light) leaves the triad in the FGo-DTEo form with no absorbance at the output wavelengths and both outputs (O_1 and O_0) remain in the off (0) state. This situation corresponds to 0 in base-10. I_1 (397 nm) enriches the triad in the FGc-DTEo isomeric form with high absorbance at 475 nm and low absorbance at 625 nm. This renders a situation where O_0 = 1 and O_1 = 0 corresponding to 1 in base-10. If instead I_2 is switched on (302 nm) the triad is isomerized mainly to FGo-DTEc with high absorbance at 625 nm and low absorbance at 475 nm, switching O_1 to the 1 state but leaving O_0 in the 0 state (2 in base-10). Finally, I_3 (366 nm) isomerizes the triad to the FGc-DTEc form, switching both O_0 and O_1 to the 1 state (3 in base-10). This completes the function of the 4:2 encoder.

In the operation as the 2:4 decoder, the triad is again set to FGo-DTEo in the initial state. As indicated above, I_0 at 397 nm isomerizes the triad mainly to the FGc-DTEo form, whereas application of I_1 at 302 nm enriches that sample in the FGo-DTEc form. Applying both I_0 and I_1 isomerizes the sample to FGc-DTEc. From Table 2 it is seen that the above input combinations in the decoder mode must switch on exclusively one of the outputs each, while leaving the other outputs in the 0 state. This is conveniently done by using the unique spectral “fingerprints” of the four isomers as the outputs of the decoder.

As described above, arithmetic operations (such as addition and subtraction) are examples of functions that also have been mimicked on the molecular scale.[41] Addition and subtraction of binary numbers are performed by half-adders (HA) and half-subtractors (HS), respectively. The function of the HA, i.e., calculating the binary sum $I_1 + I_2$, relies on the combination of an AND gate and an XOR gate, whereas the HS consists of an XOR gate and an INHIBIT gate. If a second, complementary, INHIBIT gate is used, the order of subtrahend and minuend can be switched. This allows for calculation of both $I_1 - I_2$ and $I_2 - I_1$. Although molecular versions of these devices are abundant, triad **23** is the first molecular species capable of performing the function of both the HA and the HS (a so-called moleculator)[40] using two inputs only. These inputs represent the two addends in the case of the HA, as well as the subtrahend and the minuend for the HS. For all other reported devices, input redefinition is necessary in switching between the two functions, i.e., more than two inputs are needed. The truth table for the HA and the HS is shown in Table 3 and an electronic representation of the circuit can be found in Figure 13.

Table 3. Truth Table of a Moleculator[a]

Inputs		Outputs			
I_1	I_2	**AND**	**XOR**	**INHIBIT1**	**INHIBIT2**
0	0	0	0	0	0
0	1	0	1	0	1
1	0	0	1	1	0
1	1	1	0	0	0

[a] I_1: 302 nm light, I_2: 397 nm light; output for AND: 535 nm (absorbance), XOR: 393 nm ($|\Delta A|$), INHIBIT1: 393 nm (absorbance), INHIBIT2: 624 nm (emission).

When triad **23** is used as a moleculator, the inputs I_1 and I_2 are defined as UV light at 302 nm and 397 nm, respectively. The outputs of the AND, XOR, and the two INHIBIT gates are read as the absorbance at 535 nm, the absolute value (modulus) of the absorbance change ($|\Delta A|$) at 393 nm, the absorbance at 393 nm, and the emission intensity of FGc at 624 nm. With the initial state as FGo-DTEo, it is evident from Figure 10 and 11 that all the prerequisite spectral changes for the HA and the HS are met.

For a complete and detailed description of the remaining logic functions performed by the triad, we refer to reference 43.

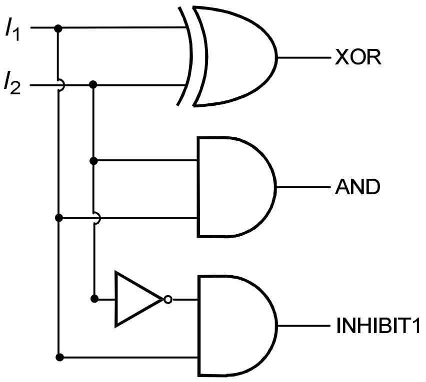


Figure 13

5. Photoswitchable Advanced Logic Memory Function: The D Latch

Just as for the S/R latch (see above), the D latch has two binary inputs and one binary output. The inputs are referred to as *Clock* and *In*. The function of the *Clock* input is to enable the *In* input, which means that the current output Q_{current} will remain unchanged as long as the *Clock* input is in the off state (*Clock* = 0). When *Clock* is applied (binary 1), the value of *In* is directly transmitted to the output as Q_{next}. The truth table of the D latch is summarized in Table 4 and the electronic representation is shown in Figure 14.

Table 4. Truth Table of a D-latch[a]

entry	***Clock***	***In***	Q_{current}	Q_{next}
1	0	0	0	0
2	0	0	1	1
3	0	1	0	0
4	0	1	1	1
5	1	0	0	0
6	1	0	1	0
7	1	1	0	1
8	1	1	1	1

[a] *Clock*: 532 nm light, *In*: 1064 nm light, *Q*: 644 nm (emission).

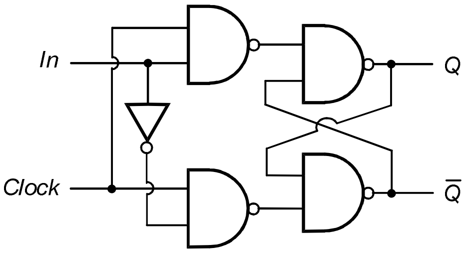


Figure 14

While the function of the S/R latch is relatively straightforward to implement on the molecular scale (see above), the realization of the corresponding D latch is a much more intricate task.[25, 44] Using a bistable molecular system where one state represents $Q = 0$ and the other state represents $Q = 1$, application of *Clock* alone must lead to the formation of the $Q = 0$ state regardless of the current form of the molecule, Q_{current}. Application of *In* alone must leave the molecule unchanged, i.e., the action of *In* should have no effect on either the $Q = 0$ state or the $Q = 1$ state. At the same time, application of both *Clock* and *In* must lead to the formation of the $Q = 1$ state, which may seem intuitively incompatible with the two previous input combinations (*Clock* or *In* applied alone). Inspired by this challenging task (and by unsuccessful attempts reported in the earlier literature)[45] we initiated a project aiming at the realization of an all-photonic version of a molecule-based D latch using a photochromic platform. Our first molecular candidate was the fulgimide derivative **2**, used previously in our laboratories, due to its excellent thermal stability, resistance to photodegradation, and the fluorescent nature of the closed colored isomer FGc.[46] The fluorescence from FGc at 644 nm was accordingly chosen as the output. This implies that *Clock* must be visible light, resulting in the FGo form displaying no emission ($Q = 0$, entries 5 and 6 in Table 4). *In* was chosen as IR light, as both isomeric forms of **2** are thermally stable so that IR light has no effect on the isomeric distribution between FGo and FGc (entries 3 and 4 in Table 4).

Finally (entries 7 and 8 in Table 4), applying both inputs must give $Q_{\text{next}} = 1$, i.e., visible light together with IR should isomerize the sample to FGc, which requires UV light. Here, the generation of UV light was assured by combining the first (1064 nm IR) and the second (532 nm vis light) harmonics from an Nd:YAG laser in a non-linear crystal (third harmonic generator, THG) which generates 355 nm UV light. In summary, the complete truth table of the D latch was demonstrated with the rather simple fulgimide switch **2**.

6. Summary and Outlook

The bistable switching of photochromic molecules provides an excellent platform for the implementation of molecular memories for data storage. However, by combining photochromes with fluorophores or integrating them in multi-photochromic conjugates even more sophisticated logic functionality can be achieved. In this Account we summarize the research efforts of our groups, which have led to novel and advanced molecular logic devices. Among them an unprecedented density of functionally integrated operations with a unimolecular, all-photonically addressable and readable molecular photochromic platform was described. Albeit still confined to solution-based operation, such sophisticated building blocks demonstrate the uniqueness of the photochrome approach. However, the use of synthetically easier accessible photochromic monomers like DTE or FG in combination with an adequate understanding of the logic operation and a proper molecular design can lead to sequential logic functions such as S/R or D latches. Research along these lines has recently attracted much interest in the steadily growing molecular logic community.[47]

In principle, photochromic switching is not bound to solution and all processes can be remotely and spatiotemporally controlled. No diffusion of chemical inputs or their neutralization/removal after finishing the operation is required in the all-photonic approach. Furthermore, long-term stable and fatigue-resistant switching is observed for many of the herein discussed photochromes. These advantages and characteristics should make it possible to integrate these functions on surfaces or in polymeric matrices. This would be the next step toward applications of all-photonic information processing with the ultimate (but realistically seen still distant) goal of molecular computing.

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Figure Captions

Figure 1. Examples of the different classes of photochromes and their switching which is discussed in this work. SP: spiropyran, ME: merocyanine, FG: fulgimide; DTE: dithienylethene, DHI: dihydroindolizine, CPD: cyclophanediene, DHP: dihydropyrene, open – o, closed – c

Figure 2. Examples of all-photonic memory devices. The DTE photochromes are shown in the open form.

Figure 3. Selection of all-photonic half-adders based on DHP (**10**)/DHI (**11**), a multi-photochromic DHI-SP conjugate (**12**), and an azobenzene-stilbene rotaxane switch (**13**).

Figure 4. Selection of photochromic switches as 2:1 multiplexer/1:2 demultiplexer (**14**), as keypad lock (**15**), in signal communication (**16**), and as all-photonic organic transistor (**17**).

Figure 5. Acido- and photochromic switching of spiropyrans.

Figure 6. Examples of logic switches with photonic and chemical inputs.

Figure 7. a) Electronic representation of an S/R latch. $\overline{Q}$ is the inverted output Q (not discussed in the text). b) State diagram of an S/R latch. c) Photochromic switching of the DTE derivative **21**.

Figure 8. Three-state switching of the aminonaphthalimide-spiropyran conjugate **22** and implementation of a keypad lock which only opens (high fluorescence output) when the inputs are activated in the order I_1 followed by I_2.

Figure 9. Structure of triad **23** in the all-closed FGc-DTEc isomeric form.

Figure 10. Photochromic switching between the FGo-DTEo, FGo-DTEc, FGc-DTEo, and FGc-DTEc forms of triad **23**.

Figure 11. Absorption and emission spectra of the different isomeric forms of triad **23**. Solid line: FGo-DTEo. Dotted line: FGc-DTEo. Dash-dot: FGo-DTEc. Dash-dot-dot: FGc-DTEc. The emission from FGc in FGc-DTEo is also shown (squares). The vertical lines indicate the wavelengths were the output signals are read.

Figure 12. Electronic circuits of 4:2 encoder and 2:4 decoder.

Figure 13. Electronic representation of a moleculator circuit (using AND, XOR, and INHIBIT1; see also Table 3).

Figure 14. Electronic representation of a D latch. $\overline{Q}$ is the inverted output Q (not discussed in the text).