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Molecular switches and logic gates for information processing, the bottom-up strategy: from silicon to carbon, from molecules to supermolecules

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The chemistry of molecular logic gates is a new science, which arose in the late 20th century at the intersection of chemistry, physics, electronics and Boolean algebra. The molecular gates differ from the currently used semiconductor elements by small size, multifunctional nature and variability of input and output signals. The review considers molecular gate operation mechanisms and design algorithms based on the compound structure and properties. The criteria to be satisfied by a molecular system to function as a molecular logic gate are outlined. The experimental data on the modelling of functions of logic gates at the molecular level are critically analyzed. Particular attention is given to photonic molecular gates, which can operate without any connecting wires or added chemicals, unlike molecular gates with chemical inputs or semiconductor gates. The problems of further development of molecular logic gates and options for their solution are discussed.
The bibliography includes 218 references.

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I. Introduction

Currently, operation of most of electronic devices ranging from toys and cell phones to supercomputers is based on digital processing of information, which is carried out by means of nano-sized logic gates based on semiconductor (SC) transistors. For half a century past, the development of SC electronics has followed the empirical Moore's law, according to which the complexity of chips, *i.e.*, the number of transistors in an integrated circuit, doubles approximately every two years.[1] So far, this was been achieved by decreasing the size of transistors and development of technologies, but the physical principle of their operation remained invariable. However, further miniaturization of SC elements inevitably reaches the physical and engineering limits associated with the problems of fabrication and thermodynamic instability of these elements, withdrawal of heat, loss of essential properties, *etc*. One presumptive way for overcoming these problems is switching from the level of micro- and nanocrystals and the top-down principles for chip fabrication (large element is split into smaller parts) to the level of single molecules and bottom-up fabrication principle [large element is formed upon (self)-assembly of smaller parts].

It has been suggested in the literature from time to time that minor atomic or molecular species could be used for supercompact information recording and fabrication of submicroscopic logic cells. The lecture of R.P.Feynman, the Nobel Prize winner of 1965, entitled 'There's Plenty of Room at the Bottom. An Invitation to Enter a New Field of Physics' [2] and theoretical papers of Aviram and Ratner [3, 4] are mentioned most often in this context. However, it is the paper of de Silva *et al.*[5] published in 1993 that is taken as the starting point for a new area of experimental chemistry, deliberately engaged in the synthesis, design and investigation of the molecular logic gates. As follows from analysis

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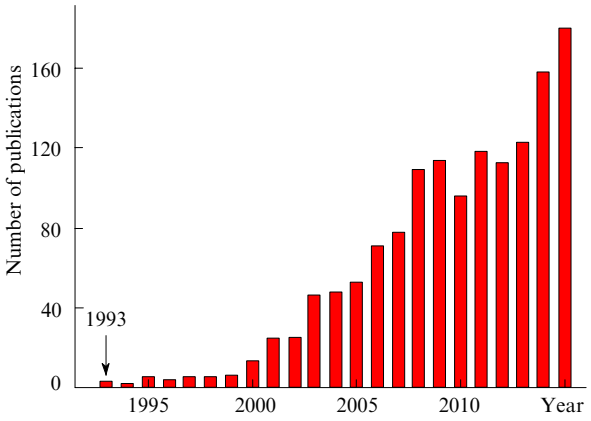


Figure 1. Change in the number of publications that include the key words 'molecular logic gate' according to the WEB OF SCIENCE data (http://apps.webofknowledge.com).

of publications on the subject 'molecular logic gate', initially, this paper did not arouse much of interest (Fig. 1). However, after some 'induction period', since the beginning of the 21st century, the number of publications has been steadily growing, this topic being addressed by more and more researchers. It became evident that further miniaturization of SC processors and development of information technologies require fundamentally new solutions and design and investigation of diverse molecular systems capable of operating as signal conductors, switches, diodes, memory elements, as well as logic gates. Therefore, a new area, that is, the chemistry of smart molecules — molecular logic gates (MLGs) — appeared at the junction of chemistry, physics, electronics and Boolean algebra.

Dozens of compounds that can function as MLGs have now been proposed. Unique potential of MLGs and the distinction between MLGs and SC analogues have been elucidated, but also obstacles to the practical use of MLGs for data processing have become obvious. Several reviews addressing particular aspects of the MLG chemistry appear every year.[6–40] Several monographs were recently published.[41–43] Note that this concerns foreign publications, while almost no works on this topic are published in Russia. This review aims to partially fill this gap.

The chemistry of MLGs is now at the stage of fundamental research and differs from organic electronics — a vigorously developing applied materials science.[44] The investigation objects of organic electronics (as well as optoelectronics, organic photonics, *etc.*) are π-conjugated electrically conducting polymers,[45,46] molecular diodes, transistors,[47] organic solar cells,[48] light-emitting diodes[49,50] and organic components of biocompatible and biodegradable (green) electronics.[51] This, already classic, organic electronics is often defined as molecular to emphasize that organic molecular analogues performing the same functions are employed instead of inorganic conductors and semiconductors.[52–54]

Thus, in the classic organic (molecular) electronics, the term 'molecular' characterizes the structure and composition; nevertheless, organic electronics is based on the same principles as inorganic electronics; therefore, the necessary function is still determined by the electronic band structure of the molecular crystal or the polymer film morphology, *i.e.*, by the properties of the whole bulk of the phase.[55]

In the chemistry of MLGs, the term 'molecular' characterizes not only the composition, but also properties. The necessary MLG function is attained exactly at the molecular level and is determined by the properties, structure and molecular orbital energies of a single molecule (*cf.* molecular machines[56–58]). Therefore, molecular gates possess properties that are in principle unattainable for the elements of classic inorganic or organic electronics.

The review deals with the principles of operation and chemical mechanisms of action of MLGs, requirements to a molecular system that should be met to perform logic operations and the algorithm of MLG design considering the existing molecular properties. The benefits and drawbacks of MLGs, the challenges of further development of this field of science and the ways to address them are discussed. Primary attention is devoted to fully photonic switches characterized by homogeneity of the input and output signals, which are represented by light quanta. The possibility to direct the output of one logic gate to the input of another one is needed in order to connect several MLGs into a single circuit and to ultimately fabricate a molecular computer.

In view of numerous existing reviews, the present paper surveys mainly publications of the last five years. Historically important earlier papers are cited to demonstrate the general principles and maintain the integrity of discussion.

II. Analogue and digital devices. Logic gate

The chemistry of MLGs appeared at the junction of several sciences and, hence, some terms used in this area are unfamiliar to chemists (beginning with the fundamental term 'logic gate'). Therefore, before discussing the operation of molecules as logic gates, we should pay attention to the terminology and find out what the differences are between positive and negative logic, combinational and sequential logic, and reversible and irreversible logic and between an analogue and digital signal and how one type of signal can be converted to the other.†

Analogue and digital signals. A digital signal can take only a discrete number of values, which are conventionally designated as 0 and 1 in the binary logic. An example of binary digital device is a switch, which can exist only in two positions (states) — off and on. An analogue signal can take an infinite number of values in a specified range, the dependence of the output signal on the input signal in an analogue device being described by a continuous function. An example of an analogue device is a rheostat, which smoothly regulates the voltage.

Positive and negative logic. If it is necessary to convert an analogue signal to a digital one, it is necessary to set some threshold value for the analogue signal. According to the positive logic, the digital signal is set to zero or one in the case that the analogue signal is below or above the threshold value, respectively. Conversely, in the negative logic, the digital signal is equal to zero (one) when the analogue signal is above (below) the threshold value. The design of MLGs is based, most often, on the positive logic, but examples of application of the negative logic are also available.

† Boolean algebra or Boolean logic is the modern symbolic logic created by George Boole and named after him. The laws of Boolean algebra are considered in detail, for example, in a review by Szacilowski.[19]

Table 1. Truth tables of some two-input logic gates.

Input		State	Output					
in1	in2		AND	NAND	OR	NOR	XOR	INH
0	0	(0,0) A	0	1	0	1	0	0
1	0	(1,0) B	0	1	1	0	1	1
0	1	(0,1) C	0	1	1	0	1	0
1	1	(1,1) D	1	0	1	0	0	0

Note. Logic functions: NAND means 'not – and', NOR means 'not – or', XOR means 'exclusive-or' and INH means 'inhibit'.

Logic gate is a digital device (switch), the input (in) and output (out) signals of which can be only either 0 or 1 (in binary logic), the ratio between the input and output being determined by the logic gate truth table. Binary logic has four simple single-input gates with one input and one output. Of these, especially important is the inverter — logical negation (NOT) gate, which takes the (output) value of 1 if the input value is 0 and 0 if the input value is 1.

The number of two input (two inputs, one output) gates is sixteen. The most important two input logic gates, including AND meaning logical product (conjunction) and OR meaning logical addition (disjunction), are summarized in Table 1.[13] Using these two logic gates supplemented by the inverter, it is possible to construct all other logic functions. The symbols used to designate logic gates are summarized in Fig. 2.

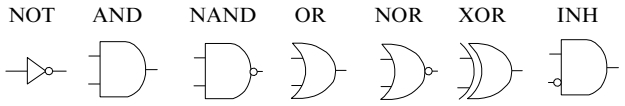


Figure 2. Symbolic designations of logic gates (ANSI standard).

Combinational and sequential logic. In the combinational logic, which is inherent in most MLGs, the output is unambiguously determined by the inputs. In the sequential logic, the output depends on the state of the logic gate, *i.e.*, on the prehistory of functioning of the digital device, and is dictated by not only the current input signal but also the input signals at earlier points of time. For memorizing the previous signal, a memory element is required, which is absent in the combinational logic. The current state of the gate is tested by means of feedback between the input and output signals.

Reversible and irreversible logic. All of the gates presented in Table 1 are irreversible, because it is impossible to restore the input signals from the output signal. For example, the AND logic gate has two bits of information at the input and one bit at the output, that is, one bit is lost upon the gate operation; if the output signal is 0, then any of the three pairs of signals, (0,0), (0,1) or (1,0), could be at the input. Hence, the same output signal can be obtained from more than one set of input signals. According to the Landauer principle, the loss of one information bit in a logically irreversible operation results in the release of heat in the quantity $k_B T \ln 2$ (k_B is the Boltzmann constant). At room temperature, this corresponds to $\sim 3 \times 10^{-21}$ J.[59–61] The smaller the MLG and the greater the number of gates contained in a chip, the more pronounced the heat release, and this is a severe problem for modern computers. In a reversible MLG, each set of output signals is matched by the only set of input signals and no information is lost during operation; therefore, this logic is referred to as conservative or adiabatic.

An example of simple single-input MLG widely used in chemistry is an indicator that is coloured (or bleached) in the presence of a reagent added (analyte), which corresponds to the signal – response function. In the binary code, this is 1 to 1 translation of the signal in both cases, but colouring involves the positive logic, while bleaching is based on the negative logic. If one applies the positive logic in the case of bleaching, this will give an inverter, which translates 1 to 0 and *vice versa*.

III. Principles of operation of molecular logic gates. Requirements for the properties of a molecular system

An electronic logic gate switches from one state to another under the action of electric field, *i.e.*, a flow of electrons serves as both the input and output signals. A molecular analogue of this gate is a molecular system that is able to switch from one state to another under the action of the input signal and this switching can be monitored by the change in the output signal. Unlike SC analogues, MLGs tolerate a large diversity of input and output signals.

Possible input signals include some chemical (change in the pH or addition of a salt solution or a neutral reagent) or physical (light irradiation, cooling, heating, change in the electric potential or magnetic field and so on) stimuli.

Output signals can also be diverse: release of a molecule or ion or a change in the absorption or luminescence spectrum, electrochemical potential, optical activity and so on. Any change in the properties of the molecular switch upon an external stimulus is expressed as appearance of a signal of a definite nature — chemical, optical, electrical, biological and so on.

In view of MLG functions, the following requirements are imposed on the structure and properties of a chemical compound suitable for performing logic operations:

— the presence of several (at least two) isomers (forms, states);

— stability of isomers;

— the possibility of reversible interconversion between two isomers upon an external stimulus (chemical or physical);

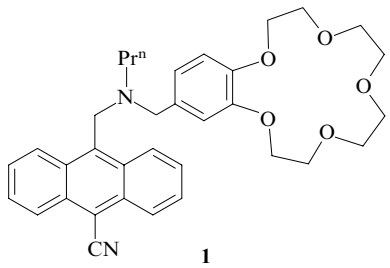
— different properties of the isomers.

The nature of the stimulus determines the type of MLG input, while the difference between properties of isomers dictates the type of the output. Since the response to the stimulus should occur particularly at the molecular level, transition from one state to another for MLGs always means a change in the molecular structure as a result of an intra- or intermolecular reaction. The transition of the molecule from one stable state (isomer, conformer) to another is very fast (over a period of chemical reaction); therefore, a molecular switch is a digital (or quantized) system, the number of discrete states of which is determined by the number of stable isomers. The most frequent case is a binary switch (based on two isomers).

As noted in the Introduction, the idea to analyze a chemical reaction in terms of the Boolean algebra was proposed by de Silva *et al.*[5] Considering this study, it is possible to follow the general mechanism of MLG operation.

In compound **1**, anthracene has two covalently bound functional groups: trialkylamino group and benzocrown ether. Both groups are electron donors and quench fluorescence of anthracene; therefore, fluorescence of free compound **1** is weak; the fluorescence quantum yield is $\varphi_{fl} = 0.011$.[5]

Structure 1



1

Protonation of the amino group or addition of sodium ions to crown ether entails a slight change of fluorescence ($\varphi_{fl} = 0.020$ and 0.013, respectively), that is, separate the addition of either a sodium salt or an acid does not bring about a noticeable effect, as it blocks only one electron transfer channel, while the other channel persists. However, the simultaneous addition of both reagents blocks both channels, and anthracene fluorescence is enhanced 6-fold ($\varphi_{fl} = 0.068$). If the absence of a reagent is taken as input of 0, the addition of a reagent is taken as input of 1 and the positive logic is applied, that is, a low fluorescence level is 0 and a high level is 1, then the output will be 1 only if both inputs are 1. This corresponds to operation of AND logic gate (see Table 1).

The operation of molecular logic gate **1** is based on the control over fluorescence quenching by the electron transfer mechanism. The crucial role is played by the ratio of the levels of frontier molecular orbitals (MO) of particular structural moieties of the molecular system and how they change in response to a stimulus.

In the general form, the mechanism of operation of the simplest switch — single-input MLG — and the control over the electron transfer is illustrated in Fig. 3. The switch consists of three structural moieties: fluorophore (F), spacer (S) and receptor (R). The receptor can exist in states A and B characterized by different levels of the highest occupied molecular orbital (HOMO). Figure 3 shows the case where in the initial state (A), the HOMO of the receptor is higher than the fluorophore HOMO (which becomes the lowest singly occupied molecular orbital in the excited state). Therefore, the R → F electron transfer takes place in the excited state and the fluorophore is quenched (see Fig. 3 *a*). Upon some stimulus, the receptor can switch to the other state (B) in which its HOMO level decreases to become lower than the fluorophore molecular orbital (Fig. 3 *b*). With this relationship, the electron transfer is impossible, the quenching channel is switched off, and hence the excited fluorophore emits light.

A two input MLG should perceive two external signals; therefore, it has two receptors, R1 and R2, linked

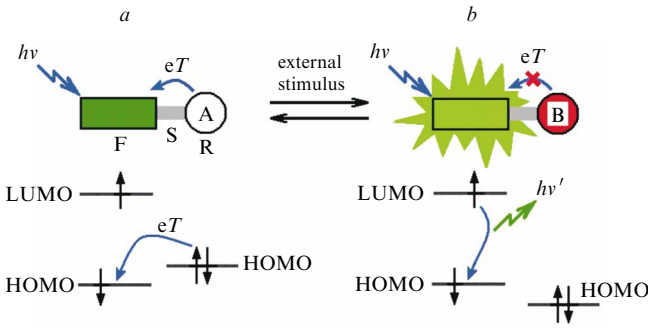


Figure 3. Diagram of operation of the molecular fluorescence switch by the electron transfer mechanism (e*T*).[30]

to the fluorophore *via* spacers S1 and S2. Switches of this type may have different architecture: the two receptors can be linked to the fluorophore either directly (R1–S1–F–S2–R2) or sequentially (F–S1–R1–S2–R2), as in compound **1**.

Figure 3 shows the case in which quenching is due to electron transfer from the receptor HOMO to the fluorophore; another possible case is electron transfer from the fluorophore to the lowest unoccupied molecular orbital (LUMO) of the receptor, the level of which depends on the receptor state. In any case, electron transfer quenches the fluorophore fluorescence in one of MLG states and this process can be controlled by stimulating the receptor.[62–68]

In the study of de Silva *et al.*,[5] the state of the receptor changed upon binding to a reagent added. Most switches operate according to this principle — these are MLGs with chemical inputs. If the receptor is a photochrome, its state can be changed by exposure to light; this operation principle is inherent in photonic MLGs (see below). There are examples of MLGs in which the added reagent (analyte) does not switch the receptor from one state to the other, but ruptures the bond between the fluorophore and the receptor, which also turns off the quenching process.[69]

Fluorescence quenching in a molecular switch can also occur by the energy transfer mechanism. The crucial factor for the control of this process is the arrangement of terms of lower excited states. As a rule, these are lower singlet excited states, but the participation of higher excited states in MLG operation has also been described. If the fluorophore and the receptor are separated by a spacer and their electron shells do not overlap, the electron transfer occurs by the dipole–dipole inductive resonance mechanism (Förster energy transfer).

The principle of operation of the energy transfer-controlled switch is illustrated by Fig. 4. In the initial state of the receptor (A), its S_1 is below the S_1 level of the fluorophore; the latter is quenched *via* energy transfer to the receptor. Upon a stimulus, the receptor converts to the B state, its S_1 level rises above the S_1 level of the fluorophore. The energy transfer is switched off and fluorescence appears.[70–74]

The fluorescence switching on and off corresponds to the operation of a digital switch. The experiment on the controlled intramolecular energy transfer in dyad **2a**,**b** (here and below the letter F inside the ring means a perfluorinated moiety) was used to confirm the statement that a molecule is a digital device in its nature.

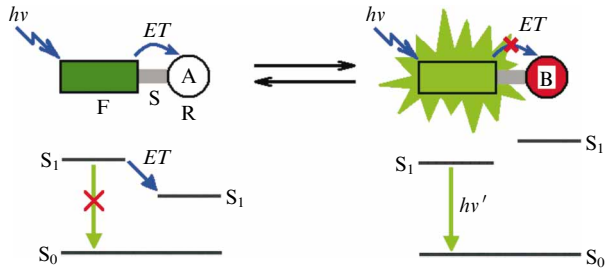
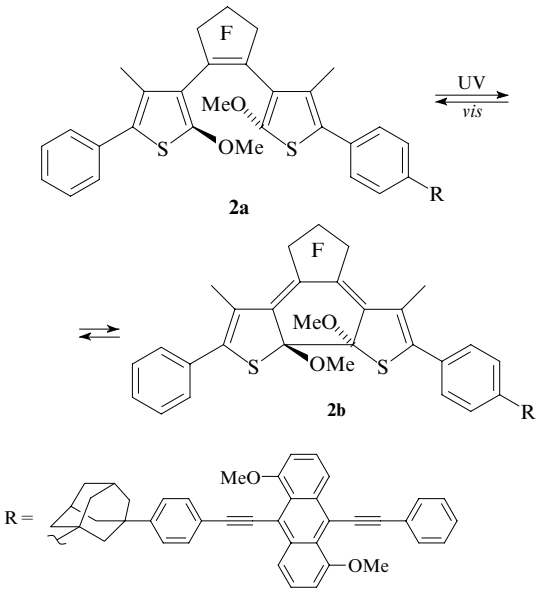


Figure 4. Diagram of operation of the molecular fluorescence switch by the energy transfer mechanism (*ET*).[30]
S_0 and S_1 are the levels of the ground and lower singlet excited states, respectively.

Structures 2



Dyad **2a**,**b** operates according to the F–S–R sequence; in this case, the anthracene derivative is the fluorophore and the adamantane group is the spacer; the receptor is a derivative of dithienylethene (DTE),[75,76] which is a photochrome; therefore the stimulus in this case is irradiation with light. On exposure to UV light, open-ring DTE form **2a** is converted to closed-ring form **2b** with a quantum yield of 0.12. The reverse reaction is induced by visible light and has a quantum yield of 8×10^{-5}. Form **2a** corresponds to the state B of receptor in Fig. 4. In this case, the S_1 level of DTE is higher than S_1 of anthracene; the energy transfer is impossible and anthracene emits light with the quantum yield $\varphi_{fl} = 0.73$. The closed-ring form **2b** corresponds to the state A of the receptor in Fig. 4; in this state, the DTE term is below that of anthracene, efficient energy transfer with a rate constant of 2.2×10^{11} s^{-1} takes place, and the fluorophore is quenched, $\varphi_{fl} < 0.001$.

When a solution of dyad **2a**,**b** was exposed to UV light, the anthracene fluorescence intensity smoothly decreased with the progress in DTE cyclization and formation of quenching molecule **2b** (Fig. 5 *a*). Quantitatively, the fluorescence signal declined in proportion to the degree of conversion of the open form to the closed form and arrived at a plateau as the photostationary state was reached. The reverse process of gradual fluorescence enhancement took

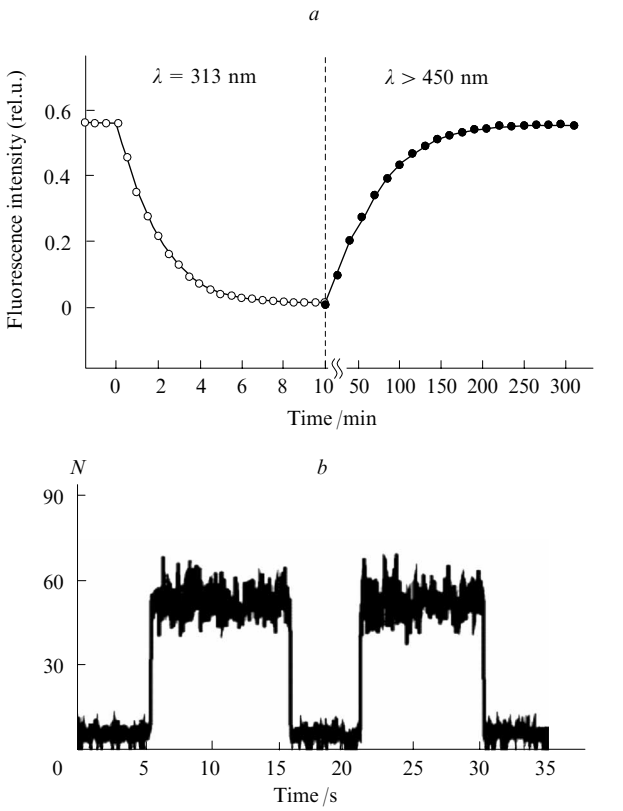


Figure 5. Change in the fluorescence upon irradiation of dyad **2** as a toluene solution (*a*) and as a single molecule in a polymer film (*b*).[76]
N is the number of photons observed in 20 ms.

place on exposure to visible light in parallel with the ring opening reaction. The shape of the curve in Fig. 5 *a* corresponds to a typical analogue signal, which can be converted to a digital one by setting some threshold value of fluorescence.

Then dyad **2a**,**b** was dispersed in a polymer film to reach a dilution level such that single molecules could be monitored by fluorescence. The fluorescence signal from a single molecule became digital: a molecule of the dyad either emits light or not, no intermediate states being possible (Fig. 5 *b*). The digital nature of the change in the fluorescence signal observed on monitoring of a single molecule being switched from one state to the other was also demonstrated using other examples.[77–80]

It is noteworthy that most experimental studies dealing with MLG chemistry are carried out in solutions with molecular assemblies. Since the fluorescence quantum yield is a parameter related to a molecule (because in the absence of a quencher, it depends on the ratio of rate constants for intramolecular photophysical and photochemical processes), then on going from model experiments with molecular assemblies to single-molecule experiments, the switch operability (output signal) is completely retained.

Not all compounds can exhibit fluorescence; therefore, the MLG output is detected, most often, by electronic absorption spectroscopy, which is the most convenient, accessible, and popular method for monitoring a chemical reaction. The measurable quantity is absorbance, *i.e.*, a value characterizing the properties of a solution. The

absorbance is determined by the molar absorption coefficient. The analogue of this value at the molecular level is the absorption cross-section; therefore, monitoring of a single molecule based on absorbance is theoretically possible. A comparison of the absorption cross-section of the molecule ($\sim 5 \times 10^{-16}$ cm^2) with the area of focused light beam demonstrated that one molecule absorbs less than one photon out of million, which is less than light intensity fluctuation (noise problem). Nevertheless, currently methods of this type are being developed, but this technique is far from being universally used.[81–83]

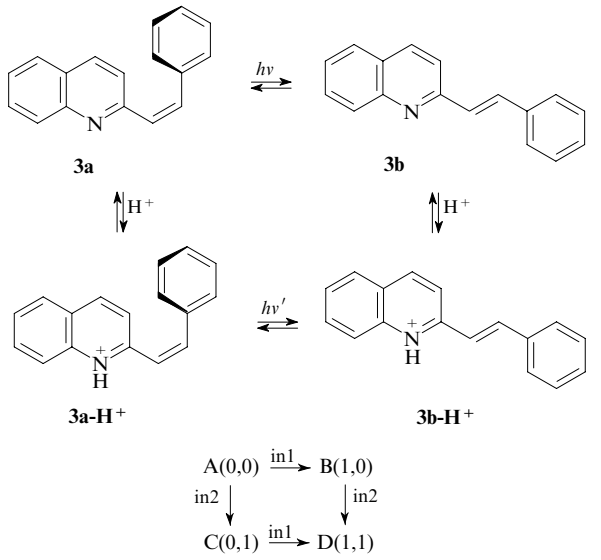
IV. Algorithm of the design of molecular logic gates

Formally, any, even irreversible, chemical reaction in which one compound is converted to another one with different properties can be considered as switching between states of a gate. These single-use irreversible MLGs are necessary for solving specific problems, *e.g.*, for diagnosis, targeted drug delivery and so on.

However, if MLG is considered as a multiple information processing unit, the gate must be capable of reversible operation. Having chosen a compound that meets the requirements of isomer stability and reversibility of isomer interconversions, one should determine what logic functions can be performed by this MLG and what will be the input and output signals. This can be done by means of a special algorithm, which will be considered here in relation to the design of two-input MLGs.[84,85] We will use two reactions that are encountered most often in the MLG chemistry — protonation and photoisomerization, as both are reversible, easily implementable, and, in the absence of side products, can be repeated many times. 2-Styrylquinoline (**3**), which can undergo both of the above reactions, will serve as the investigation object and the output will be based on absorption, which is the most frequent case.

A two-input gate can exist in four states (see Table 1); hence, the molecule must have two receptors and four isomers. The 2-styrylquinoline molecule has two functional moieties: the vinyl group, which is able to isomerize, and the quinoline nitrogen atom, which can be protonated.[86] Therefore, compound **3** can exist as four stable states (forms), that is, as neutral and protonated *cis*- and *trans*-isomers. The chemical interconversion cycle for 2-styrylquinoline and logical cycle of transitions between the states of the two-input gate are presented in Scheme 1. The switching between the states is induced by UV irradiation and protonation; this determines the nature of the MLG inputs.

Scheme 1



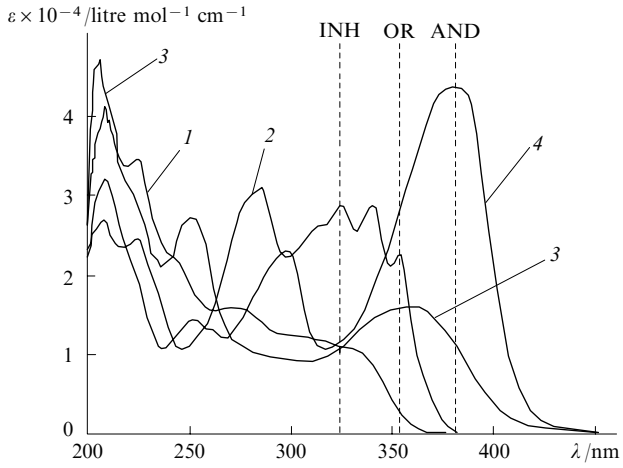


Figure 6. Absorption spectra of 2-styrylquinoline (**3**) in ethanol in neutral (*1*, *2*) and protonated (hydrochloride) (*3*, *4*) forms.[22] (*1*, *3*) *cis*-isomers, (*2*, *4*) *trans*-isomers; the vertical lines show the wavelengths, monitoring the absorbance at which gives the corresponding MLGs.

Next, it is necessary to define the type of the MLG output. Figure 6 shows the absorption spectra of all four 2-styrylquinoline isomers. Owing to the considerable difference between the spectral properties of the isomers, it is always possible to determine in which state the system occurs by measuring absorption. Therefore, the absorbance at a particular wavelength can conveniently be used as the output.

After choosing the molecular system and defining the input and output signals, it is necessary to find out what logic operations can be performed by this system. For this purpose, the interconversions of isomers should be represented as a cycle (see the upper part of Scheme 1). The truth table (see Table 1) and switching of the logic gate between the states should also be represented as a cycle, for which it is convenient to designate each state of the gate — (0,0), (1,0), (0,1) and (1,1) — by A, B, C and D (see the lower part of Scheme 1). Now these two cycles — logic and chemical ones — should be compared to match the states of the gate to the states of the molecular system.[22]

The initial state of the logic gate (A) can be matched to any 2-styrylquinoline isomer, as the isomer interconversion cycle is fully reversible. As a result, each isomer is assigned with a particular symbol and the input signal is correlated with a type of stimulus. In Scheme 1, the state A(0,0) of the MLG corresponds to neutral *cis*-isomer **3a**, B(1,0) corresponds to neutral *trans*-isomer **3b** and so on. From comparison of the two cycles, it can be seen that irradiation with light is the first input (in1) and the addition of an acid (in this case, HCl) is the second input (in2). The thus obtained match between the stimuli, the MLG states and the 2-styrylquinoline isomers is reflected in Table 2.

Table 2. Relationship between the stimulus acting on MLG, the state of the MLG (Scheme 1) and the corresponding 2-styrylquinoline isomers for the case where the *cis*-isomer is used as the initial state.[22]

Stimulus	MLG state	Isomer
–	A	**3a**
hv	B	**3b**
HCl	C	**3a-H**$^+$
hv + HCl	D	**3b-H**$^+$

Then it is necessary to find out, using the truth table, in which MLG states the absorbance should be different, *i.e.*, which of the isomers should have different properties. For example, operation of the AND gate for logical conjunction requires, according to Table 1, that the output be 1 only with the signal on both inputs (1,1) and be 0 in the three other cases. According to Table 2, the properties of the protonated *trans*-isomer **3b-H**$^+$, which corresponds to the state D(1,1) of logic gate, must differ from the properties of the three other isomers of 2-styrylquinoline, while the properties of these three isomers (corresponding to the states A, B and C) may be the same, as the output is 0 for any of these states. As follows from Fig. 6, this can be easily implemented using absorbance at $\lambda = 381$ nm, which is higher for isomer **3b-H**$^+$ (spectrum *4*) than for any other isomer.

In order to obtain the INH logic gate, the output has to be 1 only in the state B(1,0) corresponding to the neutral *trans*-isomer **3b** (see Table 2); in any other state, the output is 0. As can be seen in Fig. 6, this can be easily arranged at 325 nm where the absorbance of **3b** (spectrum *2*) is much higher than the absorbances of the other isomers. Similarly, the logic OR function can be obtained by measuring the absorbance at 353 nm, because the *cis*-isomer **3a** corresponding to the state A(0,0) has a lower absorbance at this wavelength (spectrum *1*) than the other isomers, and the output should be 0 in this state. The 325, 353 and 381 nm wavelengths at which the absorbance should be measured to obtain various 2-styrylquinoline-based MLGs are marked in Fig. 6 by vertical lines.

It is noteworthy that owing to reversibility of photoisomerization of diarylethylenes and overlap of the absorption spectra of isomers, it is impossible to completely convert the *cis*-isomer to the *trans*-isomer and back by irradiation with light. Actually, exposure to light at the wavelength λ results in the photostationary state PS_λ comprising a mixture of the *cis*- and *trans*-isomers. Taking advantage of the fact that the photostationary states attained upon irradiation, for example, at 313 and 365 nm (PS_{313} and PS_{365}, respectively) differ in the composition, they can be spectrally distinguished and used to perform logic operations.

Since photoisomerization and protonation reactions can occur not only in solution, but also in a solid matrix, the MLG based on 2-styrylquinoline can operate in a polymer film.[87] The variation of absorbance of a polyvinylbutyral film containing 2-styrylquinoline as a function of the external stimulus is depicted in Fig. 7. In this case, the photostationary state PS_{365} enriched in the *cis*-isomer was the initial MLG state (0,0). If the in1 signal is irradiation with light at 313 nm and in2 is treatment with HCl, then PS_{313} corresponds to the state (1,0) of the MLG, $PS_{365} \cdot HCl$ corresponds to the state (0,1), and $PS_{313} \cdot HCl$ is the state (1,1).

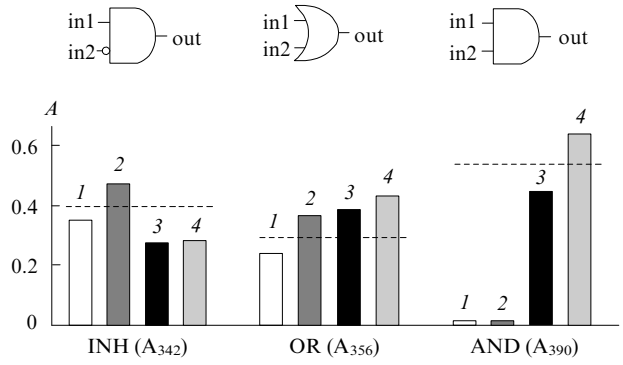


Figure 7. Change in the absorbance upon stimulation of a polyvinylbutyral film containing 2-styrylquinoline.[87]
The initial MLG state (0,0) is PS_{365} (*1*), PS_{313} corresponds to the state (1,0) (*2*), $PS_{365} \cdot HCl$ corresponds to the state (0,1) (*3*) and $PS_{313} \cdot HCl$ corresponds to the state (1,1) (*4*). The bars show the absorbances depending on the input signal. The dashed lines mark the threshold values for conversion of the analogue output signal to the digital 0 or 1. The designations of the corresponding logic gates are given above.

The last stage is the conversion of the obtained analogue output signal (absorbance) to the digital form. For each experiment and each particular wavelength, it is necessary to set a threshold value of the absorbance, below which the output will be 0 and above which it will be 1 (for positive logic). In Fig. 7, the threshold for each wavelength is marked by a dashed line. It can be seen that the output at 342 nm is equal to 1 only in the MLG state (1,0), while in all other states, the output is 0, which corresponds to the INH logic function. At the 356 nm wavelength, the output is 0 only in the MLG state (0,0), while in all other states, it is 1, which corresponds to the logical addition OR function. Finally, at the 390 nm, the output is 1 only in the MLG state (1,1) and 0 in all other cases, which corresponds to the logical product AND function.

The cycle of logic gate states has fixed initial and final states: the initial state (0,0) corresponds to the absence of a stimulus and the final state (1,1) implies the stimulus acting on both gate inputs. Conversely, the cycle of chemical reactions is variable as each reaction is reversible. Hence, any of the states (any of the isomers) of the molecular system is able to serve as the initial state A(0,0). For this purpose, the chemical cycle (see Scheme 1) should be rotated either clockwise or counter-clockwise and a new match between the MLG states and the isomers should be established. Also, one can interchange the positions of the diagonally opposing isomers. Then new inputs and outputs and new logic functions should be defined according to the presented algorithm.

For example, if *trans*-isomer **3b** is taken as the initial MLG state A (experimentally, this is the photostationary state PS_{313} enriched in this isomer), and the irradiation with light at 365 nm and treatment with HCl are taken as the in1 and in2 signals, respectively, the following match between the isomers and MLG states is established:

3b = A, **3a** = B, **3b-H**$^+$ = C, **3a-H**$^+$ = D

In this case, the 2-styrylquinoline MLG can additionally operate as the NAND, NOR and IMPLICATION gates.[87]

This example demonstrated the unique properties of molecular logic gates, namely, parallelism or superposability (several logic operations are performed simultaneously, being detected using different outputs) and reconfigurability (the same gate can be reconfigured to perform different logic operations by changing the input and/or output). These properties are, in principle, unattainable for the currently used semiconductor units in which a separate device is needed for each logic operation. The fundamental feature that underlies these properties is the diversity of the input and output signals of the MLGs, unlike the unified signal used in the SC gates. However, this advantage of MLGs turns into a drawback when attempts are made to connect several gates into a circuit (see below).

V. Molecular arithmetic. Moleculator

The information recording, storage and digital processing in the modern semiconductor processors are performed by means of logic gates using the binary number system. Compounds **1** and **3** are examples of two-input MLGs performing simple logic operations. Now we will consider how one can accomplish more complicated operations, for example, mathematical calculations.

The simplest arithmetic operation is the addition of the numbers 0 or 1 in the binary number system. This operation is performed by a half-adder (binary adder), which has two inputs (for two addends) and two outputs (the sum in a current digit position and the carry in the next higher position). The half-adder has the prefix 'half', as it does not take into account the carry from the previous addition, which appears upon the addition of multi-digit number. Two half-adders combined by an OR gate give a full-adder, for which the carry from the previous addition is the third input.

A half-adder can be constructed in several ways using various sets of logic gates. We will consider how this is done most often if the logic functions are performed by molecules. Table 3 presents the four possible options for the addition of two digits in the binary number system, the results in the customary decimal system and the half-adder states. As one can see, if addends are used as inputs 1 and 2, the lower digit position of the result (where the sum is placed) can be obtained as the output of the XOR gate, while the higher digit position of the result (where the carry is placed) is the output of the logic product (AND) gate. The simultaneous operation of these two logic gates gives a half-adder, the symbolic diagram for which is presented in Fig. 8 *a*.

Table 3. Binary addition (decimal sum in parentheses) and truth table of the half-adder.

Binary addition	Input		Output	
	in1	in2	AND	XOR
0 + 0 = 00 (0)	0	0	0	0
0 + 1 = 01 (1)	0	1	0	1
1 + 0 = 01 (1)	1	0	0	1
1 + 1 = 10 (2)	1	1	1	0

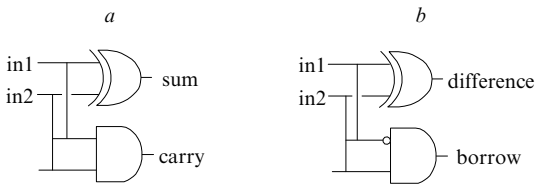


Figure 8. Diagrams of the half-adder (*a*) and half-subtractor (*b*).

Another simple arithmetic operation, the reverse of addition, is subtraction. This operation is performed by a half-subtractor, which has two inputs — in1 for the minuend and in2 for the subtrahend — and two outputs — one for the difference and one for the borrow. Table 4 shows the four possible options for the subtraction. It can be seen that the difference can be obtained as the output of the XOR gate. In other words, the digit in the lower position requires the same logic gate in both the half-adder and half-subtractor. The higher digit position of the half-subtractor contains the borrow, which is obtained as the output of the INH gate. The diagram of such half-subtractor is shown in Fig. 8 *b*.

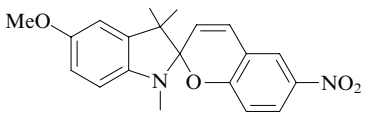
Table 4. Binary subtraction (decimal difference in parentheses) and truth table of the half-subtractor.

Binary subtraction	Input		Output	
	in1	in2	INH	XOR
0 – 0 = 00 (0)	0	0	0	0
0 – 1 = 11 (–1)	0	1	1	1
1 – 0 = 01 (1)	1	0	0	1
1 – 1 = 00 (0)	1	1	0	0

It is noteworthy that implementing the half-adder or half-subtractor function by means of SC elements requires a circuit consisting of several logic gates. Owing to the ability of MLGs to perform simultaneously several logic operations, both of the indicated functions can be performed by a single molecule.

However, the first arithmetic addition by a molecule was done by a bimolecular system in which the XOR and AND functions were performed by different MLGs.[88] They were combined in one molecule by using spiropyran **4**.[89] On UV irradiation (input 1), the spiropyran ring is opened to give mercocyanine, and on treatment with Fe^{3+} ions (input 2), the spiropyran is oxidized to the radical cation; in both cases, this results in an increase in the absorbance at 520 nm, where the sum is obtained (XOR gate). The action on both inputs (in1 and in2) yields a Fe^{3+} complex with mercocyanine, which absorbs at 420 nm, where the carry is obtained (AND gate).

Structure 4



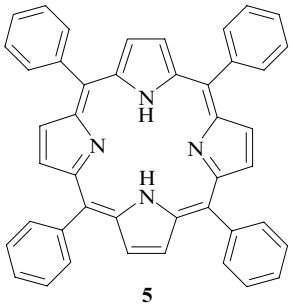
4

Both addition and subtraction require the XOR gate (see Tables 3 and 4). This is the non-equivalence gate, in

which the output is equal to 1 only provided that the two input signals are different, while in the case of identical input signals, the output is 0. One input signal is sort of annihilate with the other one; in chemistry, this is similar to neutralization. Indeed, the XOR function at the molecular level was first obtained using treatment with acid and base as the inputs.[90] Since for neutralization, the MLG initial state (0,0) and final state (1,1) correspond to the same structure, these states inevitably have the same output signal, which is determined by the properties of the same molecule. Hence, by using treatment with acid and base as the inputs and neutralization to obtain the XOR gate, one cannot obtain the AND gate at the same time, *i.e.*, it is impossible to add two digits (half-adder). However, since the properties of the acidic form usually differ from those of the basic one, the INH gate can be obtained simultaneously with XOR, and their combined operation may give a half-subtractor.

This was demonstrated for the first time in relation to tetraphenylporphyrin (**5**), which is amphoteric.[91] The absorption spectrum of compound **5** changes upon the addition of acid (HCl) or base (Bu^{t}OK), which are the input signals. The subtraction can be performed using porphyrin **5** if the difference (the XOR output) is found as transmittance at the 417 nm wavelength at which the absorbance of the ionized forms is substantially lower than the absorbance of the neutral form, while the borrow (the INH gate output) is found as the dianion fluorescence at 440 nm.

Structure 5

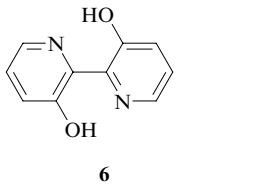


5

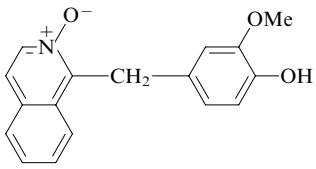
Subsequently, other molecular systems capable of performing addition or subtraction or even both have also been proposed. A half-subtractor with acid and base as input signals were obtained using 2,2′-bipyridyl-3,3′-diol (**6**),[92] substituted isoquinoline *N*-oxide **7**[93] and phenylimidazophenanthroline **8**.[94] The absorbance or fluorescence for compound **6**, fluorescence for compound **7** and absorbance for compound **8** were used as the outputs. Compound **8** can also function as a half-adder; for this purpose, the dication is taken as the initial state, a base serves as both inputs and fluorescence is used for the outputs.

A half-adder with the same input signals (alkali) and output signals based on absorption can be constructed using 2-(4-hydroxystyryl)quinoline (**9**) if its protonated form is used as the MLG initial state.[95] The neutral form **9** operates as a half-subtractor with acid and base treatments as inputs. A more complex quinoline derivative **10** substituted with a diethylamino group and a methylidenemalonic acid moiety can exist in the neutral and four ionized forms owing to the presence of two basic and two acidic groups.[96] The dication is the initial state for arithmetic operations and alkali serves as the input signals. The output signals are obtained by

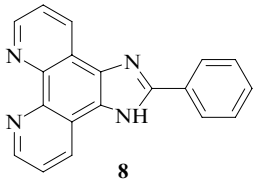
Structure 6 – 8



6



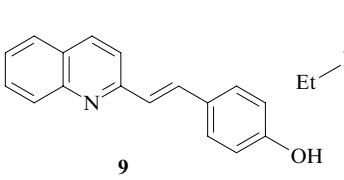
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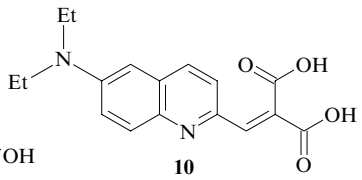
8

measuring the absorption at 400 nm for the AND gate and at 528 nm for the XOR gate; together, this gives a half-adder. The simultaneous measurement of the absorbance at 465 and 560 nm wavelengths gives two different INH gates; together with XOR, this operates as a bidirectional half-subtractor. A mixture of compound **10** with one more quinoline derivative may be used to construct a full-adder and full-subtractor.

Structures 9, 10



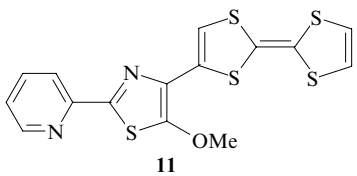
9



10

In compound **10**, all receptors of external stimuli (acid-base groups) are combined in a single conjugation chain; therefore, the system responds to the stimuli as a single whole, and the structures and energies of the common molecular orbitals change. A MLG based on substituted tetrathiafulvalene **11** has been designed differently.[97] The structure of this molecule corresponds to the F – S – R sequence. In this case, fluorophore F is the methoxypyridylthiazole moiety and receptor R is tetrathiafulvalene, which can be reversibly oxidized to the radical cation and the dication. Compound **11** operates *via* the mechanism of controlling the electron transfer (see Fig. 3). In the neutral and the radical cation form, the fluorescence of the fluorophore F is quenched, but it is enhanced when tetrathiafulvalene is oxidized to the dication; furthermore, all three forms have different absorption spectra. Using oxidants with different redox potentials — $NOBF_4$, $CuCl_2$ and $(NH_4)_2Ce(NO_3)_6$ — or using CF_3COOH, which can protonate pyridine (thus changing the absorption spectrum), as the input signals, it is possible to reproduce the half-adder and half-subtractor functions with molecule **11**. In both cases, the XOR gate is obtained by monitoring the absorp-

Structure 11



11

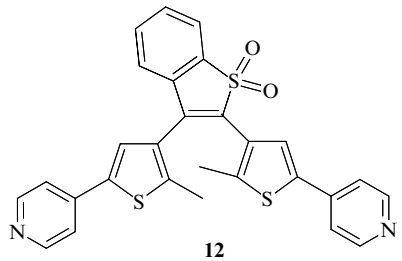
tion at 630 nm and the AND or INH gates are formed using fluorescence at the wavelength of 450 nm.[97]

A series of studies dealing with crown styryl dyes has been published.[98,99] These compounds possess the properties of photocontrollable ionophores and ion-controllable photochromes. These properties suggest that crown styryl dyes can potentially function as two-input MLGs; however, this possibility has not been tested experimentally. Modified thiacalixarenes operate as fluorescent MLGs with chemical inputs.[100]

We have already discussed dyad **2a**,**b** containing dithienylethene — a structural moiety widely used for the design of MLGs. This is a unique photochrome (see reviews [101–105]) capable of reversible and multiple interconversions between the open- and closed-ring forms; in addition, the ring can be opened upon electrochemical oxidation.[106] Dithienylethene by itself can operate only as a one-input switch, the state of which can be monitored either directly or *via* the fluorophore linked to it, as in dyad **2a**,**b**.

There are quite a few publications in which DTE is modified by attachment of functional groups able to respond to external stimuli. The greater the number of receptors in the molecule, the more logic operations it can perform. Apart from photocyclization, DTE derivative **12** containing benzothiophene and pyridine moieties can be protonated and can form 1 : 1 complexes with Hg^{2+} and 2 : 1 complexes with Cu^{2+}; this is accompanied by changes in the absorption and fluorescence spectra.[107] With various combinations of chemical and photonic inputs and the absorbance or fluorescence measurements as the output, compound **12** can operate as the AND, XOR or INH gate; this provides the functions of half-adder and half-subtractor as well as (4–2)-encoder, (2–4)-decoder and (1 : 2)-demultiplexer.

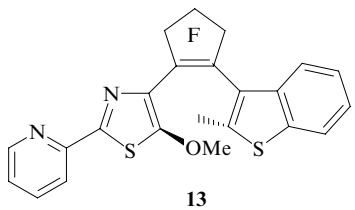
Structure 12



12

The unsymmetrical molecule of compound **13** can function as a half-subtractor using irradiation with light at different wavelengths and simultaneous addition of an acid or a base as inputs.[108] The output signals are monitored through fluorescence at 430 and 490 nm for the XOR and INH gates, respectively.

Structure 13

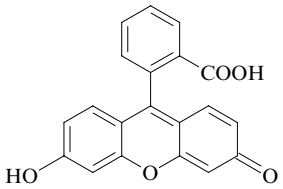


13

The most important feature of DTE, that is, the ability to undergo reversible photocyclization, is actively used in the design of supramolecular systems — dyads and triads that can function as fully photonic MLGs and contain DTE as a structural moiety. These compounds are considered in the next Section.

It has been noted above that, unlike the half-adder, the full-adder takes into account the carry from the previous addition operation and the full-subtractor involves the borrow from the previous subtraction operation; therefore, both these devices have three rather than two inputs. The functioning of a full-adder and a full-subtractor at the molecular level was demonstrated for the first time for fluorescein (**14**).[109] This indicator can exist in four forms: the neutral form, a cation, and singly and doubly charged anions; these forms have different absorption spectra. The interconversion between the forms is induced by treatment with acid or alkali, which are in this case chemical inputs. For the full-adder, the cation should be taken as the initial state (0,0,0) and treatment with alkali should serve as three input signals; the transmittance at 447 nm gives the sum and the absorbance at 474 nm gives the carry. The initial state for the full-subtractor is the neutral form and the inputs are an acid and a base. The difference is obtained as the absorbance at 447 nm and the borrow is viewed at 474 nm. Fluorescein is a model of the simplest molecular scale calculator (moleculator),[109] which combines the full-adder and full-subtractor functions.

Structure 14



14

The considered examples of arithmetic operations at the molecular level performed upon addition of one solution to another are important for the demonstration of MLG operation principles, but could hardly be used for real calculations. However, if only light quanta are used as input signals and the MLG state (output signal) is also monitored by means of light, as this is the case in fully photonic gates, a qualitatively new feature appears — the homogeneity of input and output signals; theoretically, this creates the prerequisites for the construction of complex circuits consisting of MLGs connected to one another. The advantages of photonic MLGs and problems arising in their functioning are discussed in the following Sections.

VI. Fully photonic molecular logic gates

Light is also involved in the operation of MLGs with chemical inputs if the output signal is found by measuring the absorbance or luminescence. However, if light is employed also as the input signal, this gives a fully photonic MLG, which has the following advantages over other types of MLGs:

— no need to add chemicals;

— no accumulation of reaction products during cyclic operation;

— no wires are required and no physical contact with the system is present;

— no diffusion restrictions (for the intramolecular photochemical reaction);

— photons can be used for both providing the system with energy and collecting information on the state of the system;

— homogeneity of the input and output signals, which enables connecting several MLGs into a circuit;

— high speed of operation: absorption of light takes femtoseconds and the lifetimes of the photoexcited states are pico- and nanoseconds;

— reversibility of many photochemical reactions;

— possibility of using various radiation sources (including solar light);

— possibility of functioning in a polymer matrix and in the solid state;

— possibility of attaining high spatial and temporal resolution of signals;

— possible design of devices with a three-dimensional architecture;

— reconfigurability of the same MLG to various types of logic operations utilizing the multi-wavelength nature of light;

— environmental friendliness.

Thus, in fully photonic MLGs, the system is stimulated by irradiation with light at a specified wavelength and the output is based on absorbance and luminescence measurements. The cyclability of operation of photonic MLGs is provided by using photochromes that undergo reversible photochemical reactions, including photocyclization – photodecyclization of spiropyran, fulgimide, dihydropyrene, dihydroindolizine and dihetarylethene derivatives, photoisomerization of stilbene and azobenzene derivatives and photoinduced electron transfer.

Optical transitions in any photoactive compound that is converted to a product with distinct properties can be utilized to perform the AND and OR logic operations. The diagram of functioning of these photonic MLGs is shown in Fig. 9. In both cases, the input signals are laser pulses, the frequencies of which should meet the following requirements. The AND function is produced when the output is 1 if both inputs are 1; therefore, the reaction should proceed upon absorption of two photons, whereas in the case of separate irradiation (only one input is 1), the energy of photons should be insufficient to excite the molecule. The OR function is obtained when the output is 1 if at least one input is 1; therefore, the reaction should take place upon absorption of any of the two (or both) photons. Kompa and Levine [110] emphasized the exceptionally fast operation of these photonic MLGs: for example, the photoinduced ring opening in cyclohexa-1,3-diene to give hexa-1,3,5-triene takes place within ~100 fs and the complete cycle of photoinduced intramolecular proton transfer in 2-(2-hydroxy-5-methylphenyl)benzotriazole occurs in less than 1 ps.

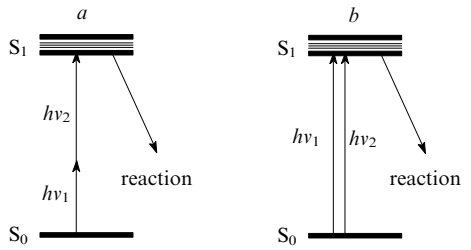


Figure 9. Schematic diagram of operation of photonic AND (*a*) and OR (*b*) logic gates with two laser pulses as the inputs. Adapted from Ref. 110.

In the considered example, the photochemical reaction product actually serves for recording of the output signal, and the logic function is achieved using photophysical laws of light absorption, which restricts the number of performed logic operations. Apart from the AND function, a photophysical MLG may perform the XOR function if the two-quantum excitation occurs to the higher excited states with intermediate population of the S_1 level, the fluorescence from which is measured to obtain the XOR output (the output is 1 only if one input is 0 and the other input is 1).

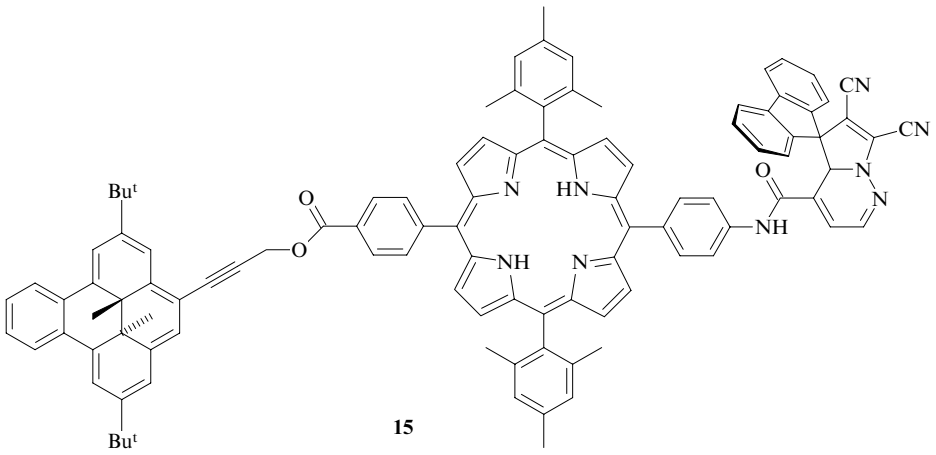
Unlike a photophysical MLG, a photochemical two-input gate is able to perform all of the 16 possible logic operations; for this purpose, it has to possess at least two receptors — photoactive compounds. Therefore, a photonic photochemical MLG is, most often, a supramolecular structure comprising two (dyad), three (triad) or more photochromes either bound by covalent bonds or associated. The molecule may also contain a fluorophore generating the output signal.

Triad **15** contains two photochromes and a fluorophore, *i.e.* operates according to the R1 – F – R2 sequence, where the fluorophore F is represented by tetraarylporphyrin and the photochrome receptors R1 and R2 are represented by dihydropyrene and spirodihydroindolizine. Dihydropyrene is able to isomerize to cyclophanediene, ring opening being induced by irradiation with light at $\lambda = 590 - 900$ nm and the ring closure is induced by irradiation at $\lambda = 366$ or 254 nm. Spirodihydroindolizine can isomerize to betaine; in this case, ring opening occurs on exposure to light with $\lambda = 366$ nm and the ring closure of the betaine is induced thermally or by IR irradiation (1064 nm). Owing to the presence of two photochromes, triad **15** can exist in four states (isomeric forms): R1o – F – R2o, R1c – F – R2o, R1o – F – R2c and R1c – F – R2c, where 'o' and 'c' refer to the open and closed forms of the photochrome receptor. Porphyrin does not quench the photochemical transformations in the receptors, but dihydropyrene and betaine are quenchers of the porphyrin fluorescence through the electron transfer mechanism (see Fig. 3). Triad **15** is able to operate as AND and INH gates [111] and serve as a (2 : 1)-digital multiplexer [112] and a (1 : 2)-digital demultiplexer.[113]

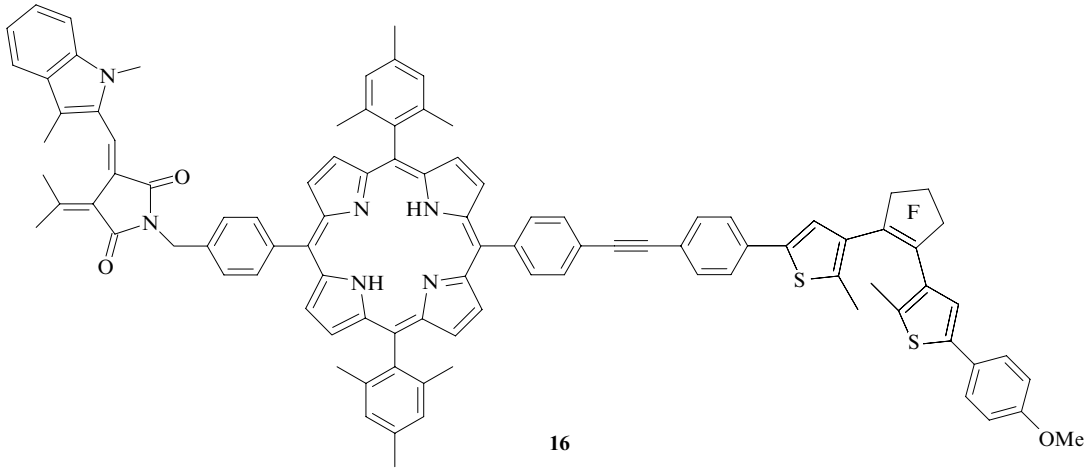
A similar sequence, R1 – F – R2, is inherent in triad **16** in which the tetraarylporphyrin is linked to other photochrome receptors — fulgimide and DTE. Triad **16** can also exist as four isomers (open and closed forms); irradiation at a wavelength of 366 nm induces cyclization of both photochromes, that at 310 nm results in cyclization of only DTE, and 410 nm light leads to cyclization of only fulgimide. Green light irradiation induces opening of both closed-ring forms and red light irradiation opens only the closed form of DTE. The closed form of DTE quenches the porphyrin fluorescence *via* energy transfer (see Fig. 4). Triad **16** can perform the XOR and NOR logic operations [114] and function as a 'keypad lock';[115] in both cases, the output signal is the porphyrin fluorescence monitored at 650 nm.

A different combination of DTE and two fulgimide units is implemented in triad **17**, which can operate as a (4 – 2)-encoder and a (2 – 4)-decoder.[116] The input for encoding is provided by light at $\lambda = 302$, 366, 397 and

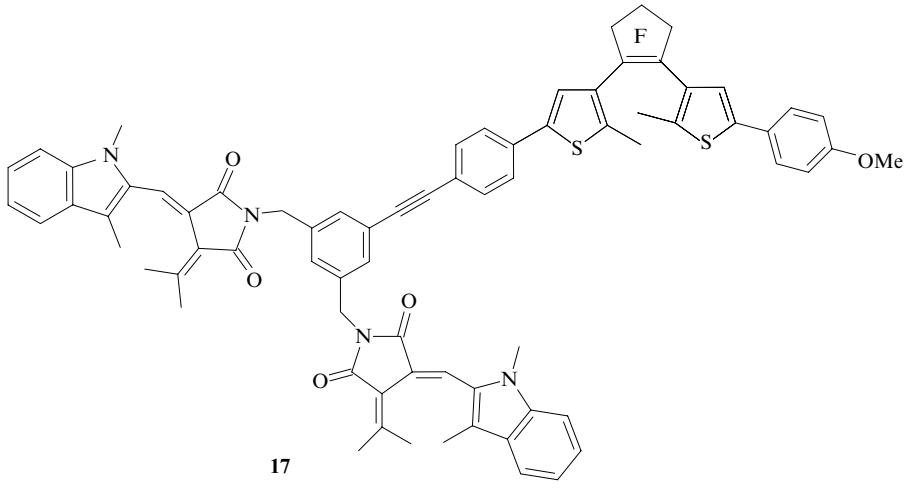
Structures 15 – 17



15



16



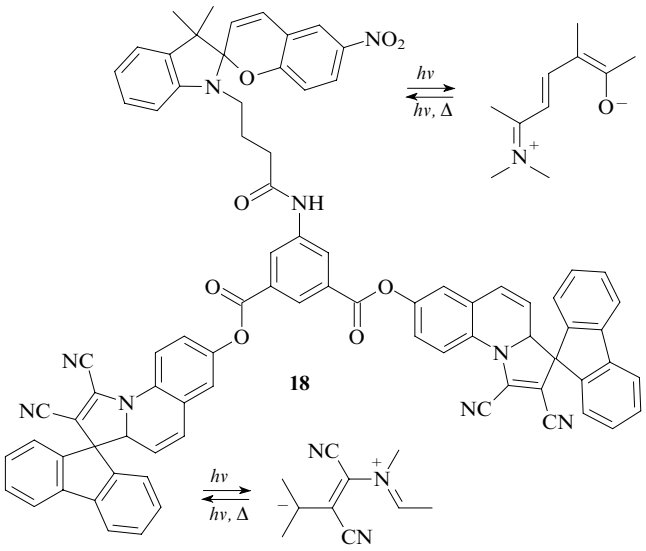
17

460 – 590 nm, while the output is absorbance monitored at 475 and 625 nm. For decoding, light with $\lambda = 302$ and 397 nm wavelengths is the input signal, while the output signals are the absorbances at 393 and 535 nm, transmittance at 535 nm and fluorescence at 624 nm (fluorescence is inherent in the closed form of fulgimide). In both cases, exposure to light with $\lambda = 460 – 590$ nm brings triad **17** back to the initial state. This triad can perform other logic operations, in particular, AND, XOR and INH, which provides for the half-adder and half-subtractor functions and some other functions.[117] In the number of operations it performs (at least 14), triad **17** is apparently the record holder among MLGs.[34] This is achieved by using six different input signals and different interpretations of five output signals based on absorption, transmission or luminescence.

A photonic molecular half-adder was implemented in triad **18**, which combines spiropyran and two spirodihydroindolizines. Scheme 2 shows the reversible reactions of the structural moieties of this triad.[118] Owing to the presence of three photochromes, triad **18** can exist as three isomers, of which only the fully closed isomer is thermally stable. The spiropyran open form — merocyanine —

absorbs light with λ = 579 nm and is a fluorophore emitting at 640 nm. The spirodihydroindolizine open form — betaine — absorbs light with λ = 659 nm; therefore, it quenches the fluorescence of merocyanine. Light with a 355 nm wavelength acts as the input signals (in this case, in1 and in2 coincide). A single irradiation of triad **18** (stimulation of one input) gives rise to merocyanine; as a result, both absorbance and fluorescence in the visible region increase. On further irradiation (stimulation of both inputs), betaine is formed. This results in further increase in the absorbance, but quenches the fluorescence. The absorbance at 581 nm is used as the output signal of the AND logic gate and fluorescence at 690 nm is the output signal of the XOR gate and, their simultaneous operation gives a half-adder.

Scheme 2

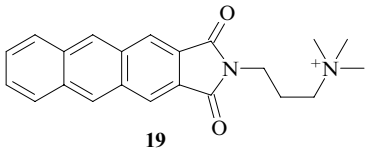


For pseudo[1]rotaxane in which azobenzene is linked to cyclodextrin by a covalent bond, the induced circular dichroism spectrum was found to change as a function of the isomeric state of azobenzene; this was used to model the INH photonic logic gate.[119] If phosphorescent α-bromonaphthalene able to enter the cyclodextrin cavity is used as the additional chemical input, it is possible to construct the AND gate with room temperature phosphorescence as the output.

In [2]rotaxane, in which the paraquat-phenylene ring can move along the chain containing tetrathiafulvalene, azobenzene and dioxynaphthalene, data recording (movement of the ring) is induced electrochemically and data locking occurs upon photochemical photoisomerization of azobenzene.[120] Note that rotaxanes (and catenanes) are used more extensively as molecular machines executing various types of motion rather than as MLGs.[56, 57]

Fluorescent anthracene derivative **19** with a covalently linked ammonium group forms 2 : 1 host – guest inclusion complexes with cucurbit[8]uril with the constant $K = 4.5 \times 10^{12}$ litre^2 mol^{-2} (Ref. 121). On exposure to light with λ > 395 nm, this supramolecular structure undergoes [4 + 4]-photodimerization to give the non-fluorescent dimer. 1-Aminoadamantane added to the system displaces the dimer from the cucurbituril cavity; after that, the dimer decomposes to the initial monomer on exposure to light (λ = 254 nm). The reversible reaction cycle was used to design a supramolecular keypad lock.

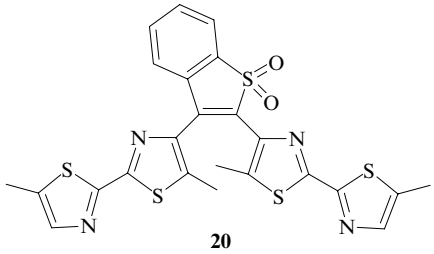
Structure 19



19

The quantitative reversible photocyclization of bis(dithiazole)ethene **20** in combination with high thermal stability of the open and closed forms were used to modulate a light flux.[122] A polymer film with embedded compound **20** is able to transfer the binary optical information from one light flux to another without an intermediate conversion of data to an electronic format. Particularly the binary information is transferred (by setting the appropriate threshold values); however, in this case, compound **20** operates at the level of a molecular assembly creating an analogue signal, that is, induced absorbance (absorption of the photocyclization product), rather than at the molecular level as a digital switch. The options of using photonic molecular switches in analogue devices are considered in a review.[123]

Structure 20



20

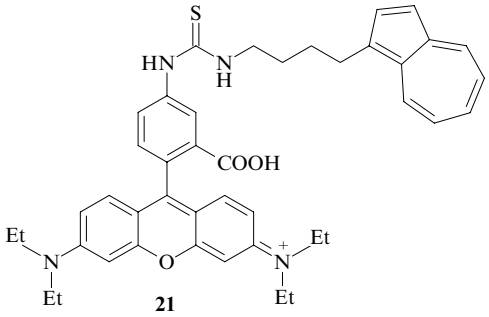
A theoretical model of ultrafast (switch off/on time of ~50 ps) fully photonic NOR and NAND gates based on graphene and a graphene oxide composite with metal porphyrins has been developed.[124] The operation of these gates is based on non-linear light absorption: the reverse saturable absorption is used. Picosecond laser pulses at 532 nm serve as the input signals for graphene and femtosecond laser pulses at 800 nm are used for the graphene oxide composite. For these materials, the excitation cross-section for the $S_1 \rightarrow S_n$ transition is greater than the cross-section for the $S_0 \rightarrow S_1$ transition; therefore, the absorbance increases with increasing light intensity and increasing population of the S_1 state. The output signals were based on a change in the transmittance at appropriate wavelengths and, depending on the chosen threshold value, the type of logic operation changes. The use of graphene in various logic devices has been considered in a review.[125]

Two-quantum photoionization and photodissociation processes were utilized to develop a failure-resistant photonic half-adder and adder based on dimethyl(2-phenylethyl)amine.[126] The output signal was monitored by fragment ions, *i.e.*, this MLG decomposes during operation and could not be used once again.

Bichromophore dyad **21** with covalently bonded rhodamine and azulene can operate as a fully photonic adder making use of photophysical processes rather than photochemical reactions.[127, 128] Both these compounds can operate separately as photonic half-adders with fluorescence from the S_2 state as the output of the AND gate and

fluorescence from the S_1 state as the output of the XOR gate.[129] The full-adder operates *via* inductive resonance energy transfer from rhodamine to azulene within the dyad; however, the chromophores can also be non-bonded (free); in this case, intermolecular energy transfer is involved.[129]

Structure 21



21

A concept of the adder proposed in an earlier paper[130] consists in the following (Fig. 10). The light quanta with an energy sufficient for the $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_2$ transitions in both chromophores are the input signals; all three inputs are stimulated simultaneously, and the fluorescence from the S_1 and S_2 levels is used as the output signals. The first half-adder — rhodamine — perceives two input signals, in1 and in2 (two addends). If only one addend is 1 (one input quantum), then the S_1 state of rhodamine is populated, and the midway sum is transmitted by an energy transfer mechnism to the input of the second half-adder, *i.e.*, to the azulene S_1 level. If both addends are 1 (two input quanta), the S_2 state of rhodamine is populated, which gives the carry. The in3 signal (the carry bit from the previous addition, carry in) populates the azulene S_1 state if it has been free; this provides the output sum. If the azulene S_1 level is already populated (as a result of energy transfer from rhodamine), the $S_1 \rightarrow S_2$ transition is excited and the S_2 level of azulene is populated, which gives the carry (in this case, the S_2 level of rhodamine is vacant).

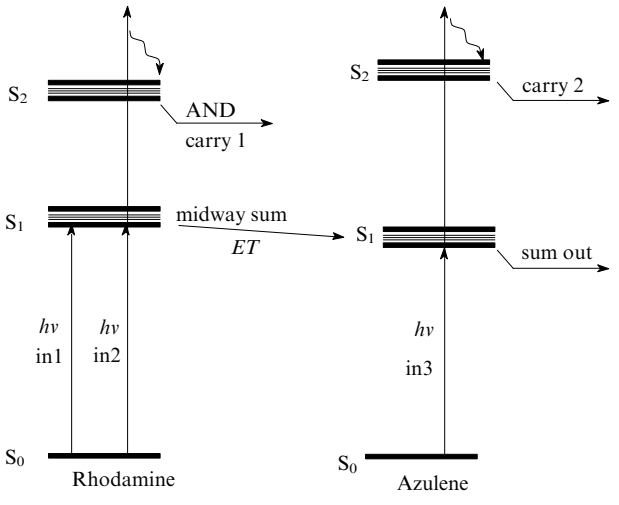
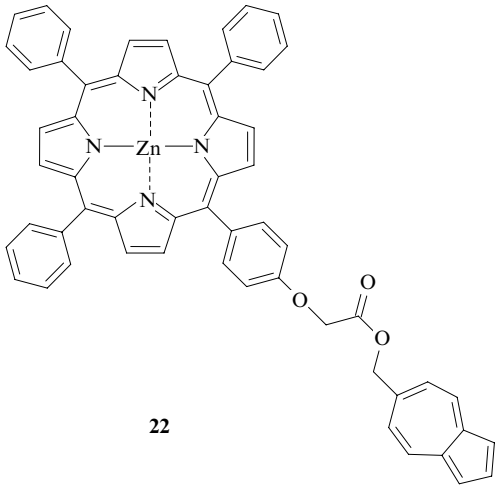


Figure 10. Schematic diagram of the rhodamine and azulene levels and operation principle of the photonic full-adder, *ET* is energy transfer. Adapted from Ref. 130.

In a real experiment, light with a frequency of 18 797 cm^{-1} was used (λ = 532 nm, second harmonics of the Nd : YAG laser) and the number of bits delivered to the adder input (one, two or three) was controlled by the laser radiation intensity. The measurement and comparison of the photophysical characteristics of molecular components (absorption cross-sections, excited state lifetimes, fluorescence quantum yields, rate constants for energy transfer) and kinetic analysis demonstrated that the energy donor and acceptor are not actually separate half-adders, as has been believed and is shown in Fig. 10, but the system as a whole operates as an adder.[127] We would like to emphasize that no chemical reactions are involved, and dyad **21** operates as an adder in the kinetic mode: the in2 and in3 signals should be delivered within the excited state lifetime, and a delay of one input signal would result in a failure of the adder operation.

A theoretical study deals with the possibility of constructing a photophysical MLG using cyclic energy transfer involving successively excited states S_2 and S_1 for a system in which azulene is the primary energy donor and the Zn porphyrin complex is the energy acceptor.[131] The experimental study of the azulene-Zn-tetraphenylporphyrin dyad **22** actually demonstrated the presence of cyclic energy transfer: the primary ultrafast ($S_2 - S_2$)-transfer from azulene to zinc porphyrin (rate constant $> 2 \times 10^{12}$ s^{-1}) was followed by the fast (2.2×10^9 s^{-1}) reverse ($S_1 - S_1$)-transfer to azulene with subsequent deactivation to the S_0 state.[132] Operation of dyad **22** as an MLG was not reported.

Structure 22

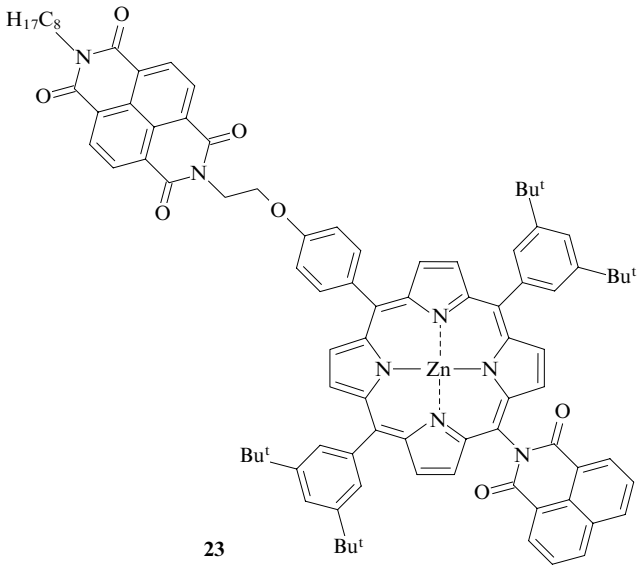


22

The optoelectronic switch, in which the direction of electron transfer from the central donor to side acceptors and the resulting dipole moment of the system depend on the irradiation wavelength, has been developed using unsymmetrical triad **23**.[133] The triad was prepared according to the A1 – D – A2 sequence where the electron acceptors A1 and A2 were represented by naphthaldiimide and naphthalimide, respectively, and the electron donor was a Zn porphyrin complex. The properties of acceptors and the bridges were selected in such a way that the excitation to the lower singlet excited state S_1 of Zn porphyrin (Q band) was accompanied by electron transfer to the acceptor A1, while the excitation to the higher state S_2 (Soret band) resulted in

the electron transfer to the acceptor A2. Detailed consideration of the induced absorption kinetics and spectra demonstrated that the charge separation in the S_2 state is followed by the ulrafast ($\sim$100 fs) recombination with population of the S_1 level of Zn porphyrin. The behaviour of triad **23** upon two-quantum excitation (two-input photonic gate) has not been studied.

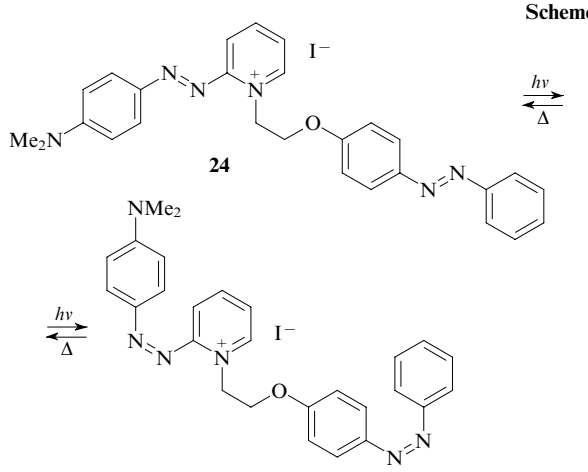
Structure 23



23

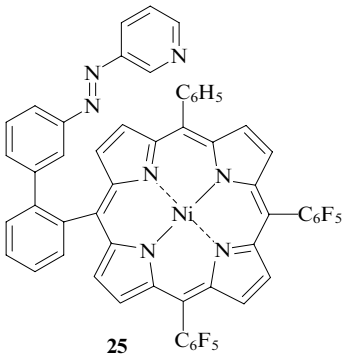
The bis-photochrome dyad **24**, in which 4-alkoxyazobenzene (absorption peak at 336 nm) and 4-aminoazopyridinium salt (absorption peak at 562 nm) are covalently linked, is a photonic switch operating in the kinetic mode.[134] Both azobenzene derivatives undergo *trans*–*cis* photoisomerization on exposure to UV light, while the reverse *cis*–*trans* isomerization is induced thermally (Scheme 3), and the thermal stabilities of the two *cis*-isomers differ by 15 orders of magnitude. The lifetime of the *cis*-isomer for alkoxyazobenzene is $\sim 3 \times 10^5$ s, while that for the azopyridinium salt is $\sim$200 ps (this is a uniquely low value for azo compounds). As shown by comparison with model azobenzenes, the thermal *cis*–*trans* isomerization of the azopyridinium component in the dyad is accelerated by a factor of 10^3, which is attributable to spatial proximity of the second azobenzene group. A similar effect was observed for the dyad with the azo group in position 4 of the pyridinium cation.

Scheme 3



In dyad **25**, photoisomerization of the azo group is induced by visible light (λ = 430 and 500 nm); as a result, a reversible photoinduced transition between the four-coordinate diamagnetic and five-coordinate paramagnetic states of the nickel complex takes place.[135, 136] Spin crossover is attained due to the ability of the 3-phenylazopyridine moiety as the *cis*-isomer to form the fifth coordination bond with nickel porphyrin. The photoinduced spin-crossover is currently actively studied for the possible use in the design of hybrid optomagnetic materials.[137 – 139]

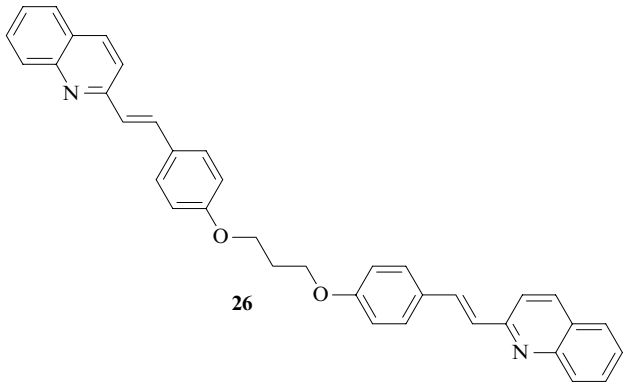
Structure 25



25

Unlike bis-chromophore dyad **24** containing azobenzene, in bis(styrylquinoline) dyad **26**, *trans*–*cis*- and *cis*–*trans* isomerizaton reactions can be induced only by light. According to a comparison with a model photochrome, high quantum yields of photoisomerization of styrylquinoline groups are retained in dyad **26**, although the kinetics of photolysis changes.[140] If photoisomerization reaction is used for switching between the states of the photonic MLG and absorption or luminescence is used as the output signal, dyad **26** is suitable for modelling the operation of the AND, OR, NAND, NOR, IMP and INH logic gates.[141]

Structure 26



26

In relation to dyad **26**, one can see a drawback of photonic MLGs in which identical photochromes function as external stimulus receptors. In these MLGs, it is impossible to selectively excite a specified photochrome, *i.e.*, stimulate a specified input, which reduces the number of possible logic operations performed by the MLGs.

VII. Problems of operation of molecular logic gates

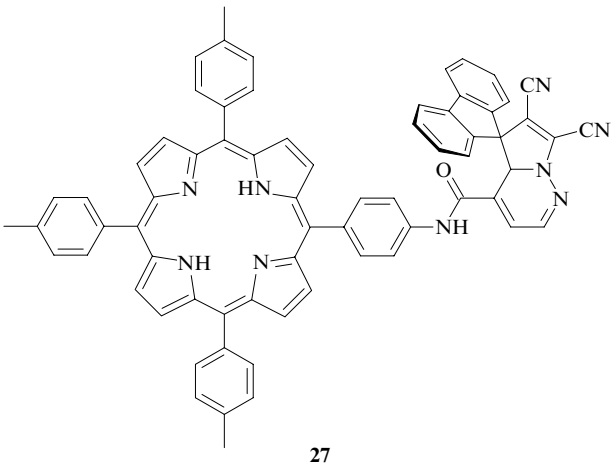
Among the problems of MLG operation, we would note the general input and output problem, the input – output inhomogeneity problem, the related problem of signal transmission between MLGs (signal transmission is necessary to construct circuits of several MLGs connected in series) and specific problems of operation of photonic MLGs.

VII.1. Input and output problem

In Section III, we defined the requirements imposed on the structure and properties of a chemical compound that can be used to perform logic operations at the molecular level. The type of input and output signals is determined during the MLG design considering the properties of compounds. It is clear that only an external stimulus that affects the molecular system and can switch it from one state to another can serve as the input signal. This simple rule is not always followed.

Dihydropyrrolopyridazine-porphyrin dyad **27** was claimed as a photonic MLG.[142] On exposure to UV light with $\lambda = 355$ nm, the spiro ring is opened to give betaine, which absorbs in the visible region and quenches porphyrin fluorescence (through electron transfer from the porphyrin to the betaine). By using absorption as the output signal, one can obtain the AND gate and using fluorescence gives the NAND gate. Light with 1064 and 532 nm wavelengths, that is, the first and second harmonics of the Nd : YAG laser, were indicated in the truth table as two inputs. However, neither of these wavelengths affects the dyad. For generation of UV light with $\lambda = 355$ nm (the third harmonics of the laser), which does affect the dyad, it is necessary to direct both light fluxes simultaneously onto a non-linear optical (third-harmonic-generating, THG) crystal placed ahead of the cell with the dyad solution. The crystal generates light with $\lambda = 355$ nm and exactly the crystal operates in this case as the AND logic gate, while the dyad is merely an actinometer measuring the effect of UV light.

Structure 27



27

A similar technique with a non-linear optical crystal was used for the operation of a photonic half-adder.[143] The functions of AND and XOR gates necessary to obtain the carry and the sum are supposed to be performed by the dihydropyrene-porphyrin-fullerene triad and the porphyrin-dihydroindolizine dyad, respectively. However, in reality, the functions of both gates are performed by the crystal located ahead of the cell with a solution containing both the triad and the dyad. When the crystal is simultaneously irradiated with a Nd:YAG laser at $\lambda = 1064$ and 532 nm, both beams annihilate (XOR gate) with generation of the third harmonics — UV light with $\lambda = 355$ nm (AND gate).

Fulgimide, which was claimed as a molecular photonic trigger, cannot operate without a non-linear optical crystal either.[144]

A technique consisting in the use of probe light as the input signal has been proposed in a number of publications. Usually the input signal acting on the MLG initiates a chemical reaction that switches the MLG from one state to another, while the probe light just reports the state of the chromophore (by absorption) or fluorophore (by emission). If the output of the fluorophore is taken to be 0 when the probe lamp of a spectrofluorimeter is off (the input is 0, the fluorophore does not emit) and to be 1 when the lamp is on (input is 1, the fluorophore emits), then filling of the truth table formally gives a certain logic operation. In this case, the output is determined by not only the state of the fluorophore but also by the state of the recording system (and the set threshold value). Actually, a similar situation is observed in the operation of dyad **21** when the input signal serves simultaneously as a probe signal to generate the output signal based on fluorescence.

A (2 : 1)-multiplexer – (1 : 2)-demultiplexer was developed using a simple compound — 8-methoxyquinoline.[145] The protonation and light from the probe lamp of a spectrofluorimeter served as the input stimuli. In all cases, when the lamp was off, the output was naturally 0, whereas with the lamp on, the output was 0 or 1, depending on the fluorescence intensity threshold set to convert the analogue signal to the digital one.

Substituted tetrathiafulvalene **11** considered above, which operates as a half-adder and a half-subtractor, can also function as a keypad lock, the probe light needed to generate the luminescence output signal was used as the input signal.[97]

Yet another approach was utilized for the operation of a (1 : 2)-demultiplexer based on isoquinoline *N*-oxide.[146] As in the case of 8-methoxyquinoline, the input signals are protonation (data input) and probe light (address input). Fluorescence at 380 and 479 nm, respectively, is used as the out1 and out2 signals and the probe light wavelength varies in the course of experiment: a half of the demultiplexer truth table (for output-1) is addressed by irradiation at $\lambda < 330$ nm and the other half (for output-2) is addressed by light with $\lambda > 360$ nm. Thus, there are two address inputs, *i.e.*, the (1 : 2)-demultiplexer function is not performed (this gate should have only one address input).

The input signal problem is related to the reset problem. The reset is an external stimulus that brings the system back to the initial state. Like an input signal, a reset signal should switch the MLG from one state to another. Therefore, during operation of especially photonic MLGs, the input signal and the reset signal often exchange places, depending on the chosen initial state of MLG and the logic operation performed. This is facilitated by reversibility of transformations of the photochromes used in MLGs.

Consider the output signal problems. In early stage of MLG investigations, during working out of the operation

principles, it was sufficient to detect changes in the state of a particular system and describe these changes by means of truth tables. Because of the procedural simplicity, this was done, most often, using light absorption (transmission) or emission. However, to obtain the 'final' output signals, the primary output signals were subjected to a fairly complex treatment.

Photocontrollable [2]rotaxane, in which a cyclodextrin ring is threaded on a dumbbell containing two photochromes, azobenzene and stilbene, can function as a photonic molecular half-adder.[147] On exposure to light with a certain wavelength (λ = 313 or 380 nm, input signals), a particular photochrome photoisomerizes, inducing movement of the cyclodextrin along the chain and a change in the absorption and fluorescence spectra. The output of the XOR gate is obtained from fluorescence, which is measured at different wavelengths for different MLG states (λ = 395 or 520 nm). The output signal of the AND gate is monitored by the change in the absorbance (ΔA); however, to obtain this value, it is necessary to perform several mathematical operations using absorbances measured at three different wavelengths

$$\Delta A = \frac{|A_{270} - A_{350}|}{A_{301}} \quad (1)$$

Thus, five output signals are actually measured, rather than two signals required for half-adder operation; futhermore, these five signals have to be additionally processed.

Amelia *et al.*,[145] who used the probe light of a spectrofluorimeter as the input signal, observed an unusual effect while monitoring the output signal based on 8-methoxyquinoline fluorescence intensity (I_{fl}) at 474 nm. Upon excitation with light at 285 nm (in1), I_{fl} = 21 was measured, the excitation at 350 nm (in2) gave I_{fl} = 5.1, while both input signals (in1 + in2), *i.e.*, successive or parallel excitation at 285 and 350 nm (which is impossible in the standard spectrofluorimeter) resulted in I_{fl} = 26. Thus, two-quantum excitation resulted in an arithmetic increase in the probability of the $S_1 \rightarrow S_0$ emission, which contradicts the nature of fluorescence. According to the truth table, a similar 'summing-up effect' was observed for protonated 8-methoxyquinoline. Apparently, in both cases, the output obtained by the researchers[145] for (in1 + in2) was actially the artificial sum of two signals with separate action of in1 and in2, which does not correspond to the mechanism of logic gate operation.

In model experiments in solutions, the response to an external stimulus of a molecular assembly rather than a single molecule is measured as the output signal. This response is not always retained on going to a single-molecule level, which is easily understandable from the following experiment.

On dilution of a chromophore (fluorophore) solution, the absorbance (luminescence) decreases in proportion to the dilution. We will take an aliquot of the pure solvent as the input signal (both inputs are of the same type, *i.e.*, in1 = in2) and absorbance (luminescence intensity) as the output signal. The addition of an aliquot of the solvent to the solution (action of one input) dilutes the solution twofold, while the addition of two aliquots (in1 + in2) results in a threefold dilution; the output signal would decrease by the same factor. Depending on the set threshold value, the dilution procedure can be described in terms of the truth table of the NOR or NAND gates in the case of positive logic and OR or AND gates in the case of negative logic. Formally, the output uses the ability of the chromophore (fluorophore) molecule to absorb (emit) light, but this 'pseudo-MLG' evidently cannot operate at the single-molecule level.

The systems in which the molecular assemblies are used for the fabrication of 'optical shutters' (filters) cannot operate at the molecular level either. A method for the design of an optical shutter for switching off (modulating) the probe light was proposed in systems for physical integration of two or more logic gates. The essence of this approach is the following: an impact on one part of the system generates a non-transparent medium, which decreases the intensity of light that falls on the other part of the system. A spiropyran-based outer-filter system consisting of two cells was proposed: the first cell contained colourless spiropyran, which was converted to coloured merocyanine (generated an optical block) on exposure to light; as a result, the intensity of the optical signal that travelled through this cell and got to the other cell decreased. The second cell also contained spiropyran and the two cells together formed the NOR gate.[148] Formally the data on the state of the photochrome in the first cell is transmitted to the second cell, but it is evident that this transmission would be impossible at the single-molecule level.

A principle of fabrication of an inner filter was proposed for a mixture of two MLGs located in one cell. The first gate functioning as AND was the thionine dye, which was reduced to the colourless leuco form on exposure to the broadband white light and treatment with sodium ascorbate (input signals). The second gate — boron difluoride dipyrrolylmethene complex (BODIPY) — also performed the AND function with zinc ions and probe light at 560 nm as inputs.[149] The presence of the input (λ = 560 nm light) for the second gate depended on the state of the first gate (colourless or coloured). The authors called this phenomenon 'physical integration of chemical logic gates'; it is clear that such mixture of two gates does not operate at the molecular level, as one molecule cannot serve as the optical filter for another one.

The design of the optical shutter in a polymer film for modulation of one light flux and direct transmission of binary data to another light flux was considered above in relation to compound **20**.

It should be emphasized that the use of the output of one logic gate for photogeneration of an optical shutter for the other logic gate operates only at the macroscopic level. These systems cannot be scaled down to the single-molecule level, at which MLGs should operate by definition.

The OR gate based on the fluorescent organogel with exposure to light and heating as the inputs also operates only at the macroscopic level.[150] As the photonic signal receptor, the gel contains a DTE derivative, which cyclizes upon irradiation and the closed-ring form thus obtained quenches the fluorescence. The second input (heating) converts the gel to the sol, also resulting in fluorescence quenching, as the fluorescence of the gel is caused by aggregation-induced emission enhancement. This phenomenon is absent at the single-molecule level, that is, operation of this logic gate requires a bulk sample.

VII.2. Problem of signal transmission between the molecular logic gates. Circuits of several molecular logic gates

Despite the faulty solutions, the researchers cited above [148, 149] touched upon an important problem of signal transmission from one MLG to another. Currently, physical integration of elementary MLGs is the stumbling point hampering further development of this area.[36]

In the early phases of MLG design, primary attention was given to increasing the gate functionality and extension of the diversity of input and output signals. Some single polyfunctional MLGs can be used for special purposes. However, the design of data processing systems able to perform complex logic and computing functions at the molecular level require MLG assemblies in which the gates are connected into circuits, so that the output signal of one gate is delivered to the input of another gate. For this purpose, the input and output signals of MLGs should be homogeneous.

The inhomogeneity of input and output signals is the major challenge hampering the connection of several MLGs into a common circuit. The problem of signal inhomogeneity is absent in semiconductor devices in which an electron flow serves as both the input and output signal of each circuit unit.

The problem of signal inhomogeneity is partially solved owing to a unique feature of MLGs, namely, the ability of a single molecule to perform simultaneously several logic operations (parallelism). Therefore, a basically different circuit architecture is possible for MLGs. At the level of small computing units, the serial integration may be replaced by parallel one. Instead of connecting several logic gates to one another, at the molecular level, one can use the option of functional integration of several gates in one molecule by preparing a compound with a desired combination of properties. As an example, consider any of the half-adders mentioned above, the functions of which are performed by one molecular system, owing to simultaneous operation of the XOR and AND gates. In the case of semiconductor systems, a half-adder is assembled by serial-and-parallel connection of five NAND or NOR gates.

It has been noted above that logic gates at the molecular level use, most often, absorbance at a specified wavelength as the output. Absorbance is the logarithm of the ratio of incident to transmitted light. To find absorbance, it is necessary to measure two signals and make the appropriate calculations. These operations are carried out by a special instrument, a spectrophotometer. Despite the signal inhomogeneity, a sequence of gates with chemical inputs and optical outputs can be constructed in the following way: after addition of reagents into the cell (chemical inputs for the first MLG), depending on the instrument reading, which should be interpreted as output of either 0 or 1, reagents are added into the second cell (chemical inputs for the second MLG), and so on, until the required number of gates in the sequence is reached.

It is this method, but in an automatic mode, that was proposed for interconnection of an unlimited number of MLGs on microtiter plates.[151] These plates have been widely used recently for fast assays in medicine. Each well of the plate is filled by a pyrene-based fluorophore, which is quenched upon the addition of a bipyridinium salt and restores the emission upon addition of fructose. A special computer program (pipetting protocol) gives a command for adding a particular reagent into the next well depending on the fluorescent signal of the previous well. Formally, the fluorescent signal in each well changes as a result of complex formation at the molecular level, but in reality, this system cannot operate at the level of a single molecule. The operation of such a molecular computer requires a detection system for each well, a usual control computer and a power-driven pipette with a reagent kit.

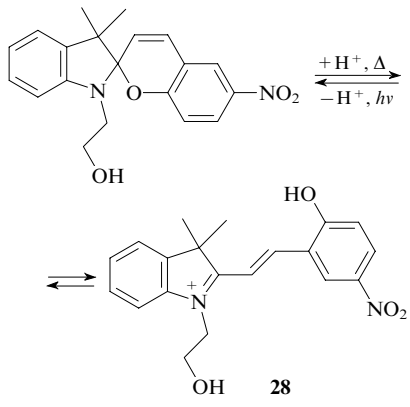
By analogy with a semiconductor chip containing millions of logic gates, this microtiter plate can be called chemical chip; functionally, this is the same, but, while retaining the formally molecular level, this device lacks the major MLG advantages: small size and fast operation.

In the chip with automated pipetting, the pipette actually functions as the signal converter for MLGs with heterogeneous input and output signals for the case where the output of one MLG cannot be directly connected to the input of another MLG. This approach is implemented in living organisms where signal converters are of molecular size. To continue the biomimetic analogy with living nature, consider the possible routes of information transfer from one molecule to another, namely, by means of chemical species — electrons, ions (in particular, protons), neutral molecules or electromagnetic field (energy transfer). All these routes have been practically implemented, but the size is restricted to two of three MLGs.

Osmium and ruthenium polypyridyl complexes deposited on glass plates as 1.5-nm thick monolayers [152] are able to separately operate as chemical MLGs performing a variety of logic operations *via* oxidation and reduction of the central ion.[153] If two plates with monolayers of these complexes are immersed into one solution containing iron ions, then Fe^{3+} ions oxidize the Os^{2+} ions attached to one plate, being reduced to Fe^{2+} ions, which then travel to the other plate (located at a 0.5 cm distance) where they reduce Ru^{3+} to Ru^{2+}. Thus, by means of iron ions, one MLG reports its state to another MLG. The output signal is derived from the absorbance in the metal – ligand (λ = 516 nm) and ligand – metal (λ = 317 nm) charge transfer bands.

A two-gate system in which a proton transmits a signal between the gates has been proposed.[154] The first gate is the photoacid, merocyanine **28**, the protonated open form of spiropyran, with an absorption peak at 401 nm. Upon irradiation at the absorption band wavelength, merocyanine is converted to closed-ring spiropyran with release of a proton (Scheme 4). Ruthenium complex **29** contains two terminal pyridine rings able to be protonated. Compounds

Scheme 4

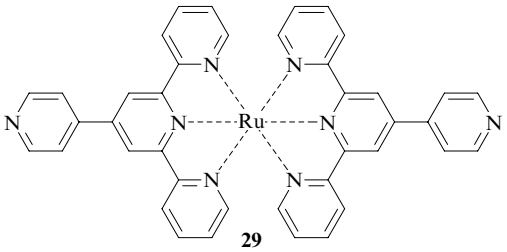


28

28 and **29** were mixed in 2 : 1 ratio; this gave an equilibrium mixture containing the photoacid and the non-protonated and monoprotonated complex in 7 : 3 : 1 ratio.

Irradiation with controlled doses of light (λ = 400 nm) needed for the release of one equivalent of protons with respect to the metal complex was used as two identical input signals. On successive irradiation of the mixture with controlled amounts of light, the photoacid released a proton, which moved towards the complex. The complex was, first, mainly monoprotonated and then diprotonated. The output signal was provided by the luminescence intensity of protonated forms at 732 nm; the whole system operated as photonic OR or AND gates depending on the threshold value. It is noteworthy that merocyanine actually functions, in this case, as a photonic to chemical signal converter rather than as a MLG.

Structure 29



29

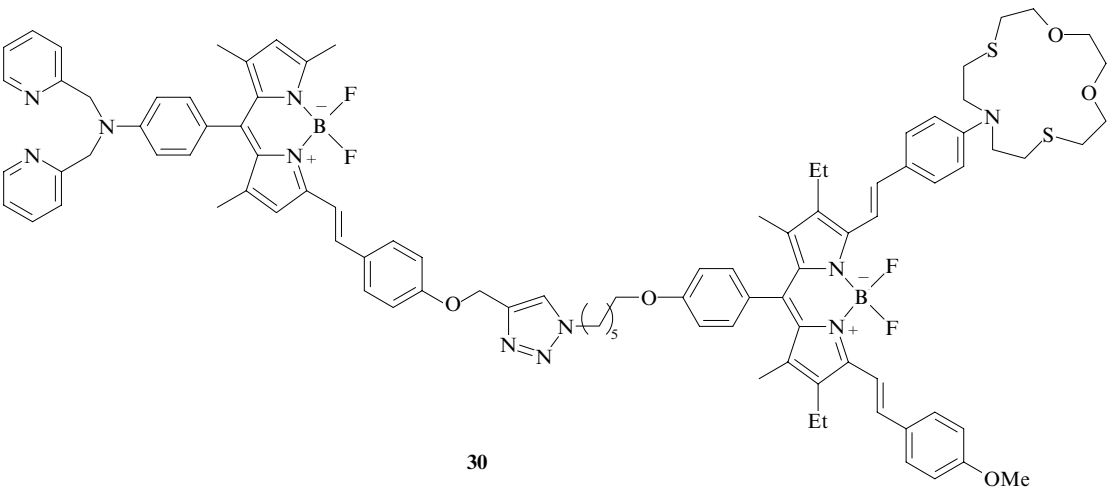
A specific feature of the system **28** + **29** (as well as other systems with spiropyran) is thermal instability: over a period of 5 days in the dark, the reverse reaction took place, namely, deprotonation of the complex and thermal spiropyran ring opening to give protonated merocyanine. The system conversion back to the initial state on heating was used for the reset function. The authors emphasized the inapplicability of this system for practical use, but noted its importance for the demonstration of the possibility of chemical bonding between two switches, which resembles the data processing in living organisms.

Singlet oxygen ($^1O_2$) generated during the operation of the first AND logic gate was proposed as a signal transmission agent in a single-use two-gate cascade.[155] The $^1O_2$ formed moves to the second MLG, represented by a dyad in which the fluorophore and the quencher are linked by a covalent chain containing a double bond. Under the action of $^1O_2$, the double bond is cleaved with intermediate formation of 1,2-dioxetane. This results in separation of the quencher and the fluorophore, which is detected as fluorescence enhancement at 537 nm (output signal). Thus, $^1O_2$ serves as an input for the second MLG. If the probe light (λ = 520 nm) is used as the second input, then the second MLG executes the AND function; if glutathione ($^1O_2$ scavenger) is added to the solution and the probe light is retained, this is interpreted as the INH function in a two-input MLG (however, actually this is a three-input MLG). Presumably, systems of this type could be useful as test systems for photodynamic therapy.

In the study cited above,[149] apart from the photochemical modulation of the inner optical filter, energy transfer was used for the signal transmission between MLGs. Dyad **30** containing two different complexes, BODIPY derivatives, was synthesized. Both complexes can function separately as the AND gates. For both MLGs, one of the input signals is the probe light, which excites fluorescence (output signal), while the second input signal is Zn^{2+} (for the complex with the dipicolylamino group) or Hg^{2+} (for the complex with azathiacrown ether group). The properties of the complexes were adjusted in such a way that the second complex quenched the fluorescence of the first one. Without metal ions, fluorescence of both complexes is quenched because of electron transfer from the appropriate receptors acting as electron donors for BODIPY. When receptors are bound to metal ions, electron transfer is suppressed (see Fig. 3) and both complexes exhibit fluorescence if they are not linked to each other. However, if the complexes are linked to form dyad **30**, fluorescence (at 660 nm) is observed only for the second complex as a result of energy transfer between the two BODIPY derivatives within the dyad.

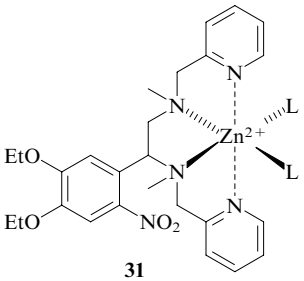
Dyad **30** was used to construct a three-gate logic circuit with two signal transfer stages; different transfer processes were used in each stage, *e.g.*, zinc ions were used in the first stage. Complex **31** functions as the INH gate with the addition of ethylenediaminetetraacetic acid and UV irradiation as the inputs and zinc ions as the output.[156]

Structure 30



30

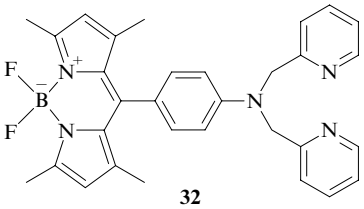
Structure 31



31

Complex **32** operates as the AND logic gate using Zn^{2+} ions and probe light (λ = 480 nm) as the inputs and fluorescence (λ = 510 nm) as the output. On UV irradiation of a solution containing both compounds, complex **31** releases Zn^{2+} ions, which add to complex **32**; this results in BODIPY fluorescence. In the initial state, the BODIPY fluorescence is quenched by the electron transfer from the covalently bound dipicolylamine.

Structure 32



32

Subsequently, dyad **30** was added, instead of compound **32**, to the cell with complex **31**.[156] This mixture operated as a logic circuit of three MLGs: first, zinc ions transmitted the signal between complex **31** and the complex **32** moiety of dyad **30** and then two BODIPY derivatives within the dyad communicated through energy transfer.

The data transmission between MLGs *via* energy transfer is a necessary stage of operation of dyad **21** considered above.[127] The case of this dyad demonstrates that the problem of signal homogeneity is automatically solved in fully photonic MLGs in which light quanta act as both input and output signals. However, photonic MLGs have other specific problems (see below).

To conclude this Section, we would like to note that bioluminescence data attest to the possible participation of biophotons in information processing and transmission in neural networks.[157] Therefore, it should be emphasized that energy transfer by the trivial re-absorption mechanism is of low efficiency, because emission of the energy donor occurs non-selectively in all directions, which brings about inevitable data loss, because only some of the emitted photons are absorbed by the acceptor.

VII.3. Problems of operation of photonic molecular logic gates

As shown in Section VI, photonic MLGs have numerous advantages over other molecular gates. However, operation of photonic MLGs is faced with a number of specific problems brought about by the very nature of light absorption and the properties of excited states of molecules. These problems have fundamental origin and some of them are in principle unavoidable, while the adverse consequences of some other can be minimized.

VII.3.a. Quantum yield problem

Quantum yield (φ) is a fundamental parameter of a photochemical or photophysical process; it is determined by the ratio of the rate constant for the process of interest (k) to the sum of rate constants (k_i) for all processes occurring in the excited state (including the process of interest),

$$\varphi = \frac{k}{\sum\limits_i k_i} \qquad (2)$$

Hence, the theoretical limiting value is $\varphi = 1$, but the quantum yield is usually lower than unity (often, much lower). For example, in the photoisomerization of diarylethylenes by the diabatic mechanism, the limiting φ value is 0.5; it is determined by the shape of the potential energy surface (PES) of the excited state and the distribution coefficient.[158] In ring opening reactions of hetero derivatives of dihydrophenanthrene (DTE cyclization products), φ can be several orders of magnitude lower than unity, being about 10^{-4} and less, because in the PES of the S_1 state, the closed-ring product is separated from the conical intersection with the PES of the S_0 state by an energy barrier.[158] The quantum yield of fluorophore emission is also seldom equal to unity, because of the competition of internal conversion and intersystem crossing.

When one deals with molecular assemblies, φ is a statistical characteristic. If a reversible photochemical reaction occurs in the system between two isomers A and B

$$\mathrm{A} \underset{\varphi_\mathrm{B}}{\overset{\varphi_\mathrm{A},\, h\nu}{\rightleftarrows}} \mathrm{B} \qquad (3)$$

then, depending on the irradiation dose, some molecules of the assembly are always being converted from one state to the other and the mixture contains both isomers. Finally, the system reaches a photostationary state (PS) in which the rates of the forward and reverse reactions are equal. The composition of the PS depends on the irradiation wavelength and is determined by the relation

$$(\varphi_\mathrm{A} \cdot \varepsilon_\mathrm{A} \cdot c_\mathrm{A})_\lambda = (\varphi_\mathrm{B} \cdot \varepsilon_\mathrm{B} \cdot c_\mathrm{B})_\lambda \qquad (4)$$

where φ_i and c_i are the photoisomerization quantum yield and concentration of isomer i, respectively, and ε_i is the molar absorption coefficient of this isomer at the irradiation wavelength λ.

When one deals with a single molecule, φ is a probabilistic characteristic. On exposure to light, a molecule occurring in the state A absorbs a light quantum and may switch to the state B with the probability φ_A or may remain in the initial state with the probability $(1-\varphi_\mathrm{A})$; the same is true for the reverse reaction. Thus, the lower the φ value, the higher the probability that MLG remains in the initial state after excitation and the longer the irradiation time (the greater the number of absorbed quanta) required for MLG switching.

The difference between the operation modes of an assembly and a single molecule is clearly seen in Fig. 5 in which fluorescence of the molecular assembly changes

smoothly as a particular isomer is being accumulated in the mixture and gradually enters the PS plateau. Switching of a single molecule from one state to the other is stochastic and occurs every time with random time intervals.

It is possible to pass from stochastic to deterministic switching mode by using an array of photonic MLGs operating in parallel. If the probability of switching for a single molecule is φ_A, then the probability of switching of at least one molecule in an array consisting of n molecules is $1-(1-\varphi_A)^n$ and for $\varphi_A = 0.7$, this is already 0.998 when $n = 5$.

VII.3.b. Energy dissipation problem

The energy dissipation problem is, to some extent, related to the quantum yield problem. If $\varphi < 1$, only part of the light quantum energy is spent for the chemical reaction, *i.e.*, for MLG switching, while the rest is released as heat upon vibrational relaxation (non-radiative deactivation of the excited state).

However, even if $\varphi = 1$, the energy dissipation problem inevitably exists in both photophysical and photochemical processes. If the fluorophore emits with a quantum yield of 1, the energy of the emitted quantum is still lower than that of the absorbed quantum (we do not consider the anti-Stokes luminescence). In the case of excitation and measurement at the absorption and emission peaks, respectively, this difference is determined by the Stokes shift $\Delta h\nu$ and depends on the shape of PES of the S_0 and S_1 states of the fluorophore (on the difference between the geometries and polarities of these states and on the solvent). Only the absorption and emission in the 0–0 band occur with the same energy. The $\Delta h\nu$ value can vary over a broad range, from several hundred reciprocal centimetres (for fluorophores with a rigid structure such as BODIPY) to several thousand reciprocal centimetres; the difference between the absorbed and emitted quantum energy is always released as heat.

Energy dissipation is also inherent in a photochemical reaction when $\varphi = 1$ and every quantum is spent for the conversion of the substrate to the product and it seems that no loss should be expected. This is due to the fact that the initial and final states of the molecular switch correspond to two isomers of the molecule in the ground (S_0) state. Therefore, after excitation of the substrate and completion of photoisomerization, even if it is adiabatic and the product is formed in the excited state, the system returns to the S_0 state as a result of radiative or non-radiative relaxation. The latter means that the energy of absorbed light quantum is released as heat. In addition, it is necessary to consider the difference between the heats of formation of two isomers. For example, the heats of formation of *trans*- and *cis*-isomers of diarylethylenes differ by ~ 5 kcal mol^{-1}. When the photoisomerization proceeds in the *trans*–*cis* direction, this value is subtracted from the energy of the quantum (endothermic reaction), while in the case of *cis*–*trans* photoisomerization, this value is added, thus increasing heat release (exothermic reaction).

If the functions of MLG are modelled in solution, the release of heat is unobservable; this can be evaluated in the following way. According to the formula $E = h\nu$, the energy of a single light quantum with a 365 nm (27 397 cm^{-1}) wavelength is 5.4×10^{-19} J. For the photochrome concentration of $\sim 10^{-5}$ mol litre^{-1} and the quantum yield $\varphi = 1$, the solution should absorb not less than $\sim 6 \times 10^{18}$ photon litre^{-1}, which corresponds to an energy of ~ 3.3 J litre^{-1}. For an average organic solvent heat capacity of ~ 2 kJ kg^{-1} K^{-1} and density of ~ 0.9 kg litre^{-1}, the temperature rise due to dissipation of the absorbed photon energy (without considering the reaction heat) is only ~ 0.002 K.

In close-packed molecular assemblies, the photochrome concentration may amount to 1 mol litre^{-1} (and more); operation of this system would lead to absorption of at least $\sim 6 \times 10^{23}$ photon litre^{-1} with an energy of ~ 330 kJ litre^{-1}, which should cause the temperature to rise by ~ 200 K. This is a formal calculation without taking into account that the irradiation is pulsed. When the photochrome concentration is ~ 1 mol litre^{-1} and $\varepsilon \approx 2 \times 10^4$ litre mol^{-1} cm^{-1}, a 1 μm-thick layer is sufficient for absorption of 99 % of light. If the response time of 1 ns is taken into account, the release of energy by this layer corresponds to a power of 33 MW cm^{-2}. For comparison, the dissipated power in modern processors is 100 W cm^{-2} (Ref. 59).

Although the input and output inhomogeneity problem is solved for photonic MLGs, the problem of heat release upon dissipation of the excitation energy may become one more stumbling point hampering MLG integration, like it is observed for SC chips due to the Landauer effect (which is also inevitable in molecular irreversible logic gates).

VII.3.c. Selective excitation problem

In an electronic SC switch, an input signal is applied by changing the voltage at the appropriate input pin. In a photonic molecular switch, signal application to an input occurs *via* excitation of the appropriate photochrome with light. For example, biphotochrome dyads are models of two-input switches. If the spectra of the photochromes overlap (if the photochromes are identical, the spectra fully coincide), selective excitation (switching) of a specified photochrome in such dyad is impossible. As a consequence, the MLG states (1,0) and (0,1) are indistinguishable: they have the same output signal, and this restricts the number of logic operations that can be performed by this MLG.

If we draw an analogy with voltage application to the required pin, then the excitation of a particular photochrome in a dyad requires that a light beam be focused down to the size of the photochrome molecule, which is unrealistic. Therefore, in photonic MLGs, selective excitation is achieved in a different way: by using unsymmetrical dyads in which two photochromes have different absorption spectra. Then the inputs can be separated and the specified photochrome can be excited (switched) by irradiating the dyad at the absorption band of this photochrome.[159] However, there are other problems inherent in unsymmetrical dyads.

A photochrome having a long-wavelength (LW) absorption band (LW-photochrome) can be switched selectively, as irradiation of the dyad with light around the LW band would selectively excite only this photochrome. However, a photochrome with a short-wavelength (SW) absorption band (SW-photochrome) cannot be selectively excited (switched), as the LW-photochrome always has absorption in the SW region (transitions to highly excited S_n states for the acceptor photochrome). Therefore, the LW-photo-

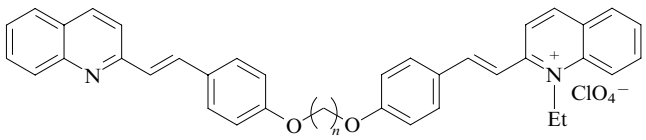
chrome would always be excited, to some extent, together with the SW-photochrome when the dyad is exposed to SW light. The excitation of the photochromes is proportional to their molar absorption coefficients at the irradiation wavelength.

In the case of modelling in solution using a molecular assembly, the problem of switching and monitoring a particular photochrome is solved if an isosbestic point for two isomers of the LW-photochrome is present in the absorption region of the SW-photochrome. In this case, the change in the absorbance at this wavelength depends only on the isomeric composition of the SW-photochrome, whereas a change in the isomeric composition of the LW-photochrome does not affect the absorption at the isosbestic point.[160] Irrespective of the irradiation wavelength (the input signal), the output signal monitored at the LW-band would depend only on the isomeric state of the LW-photochrome (because the SW-photochrome does not absorb in this region), while the output signal monitored at the wavelength of the isosbestic point of the LW-photochrome would depend only on the isomeric state of the SW-photochrome (since the LW-photochrome isomers have equal absorption at this wavelength). Thus, it is possible to selectively withdraw data from the required photochrome — a structural module of the MLG. However, this approach does not operate for the excitation of a single dyad molecule. In this case, photochrome photoisomerization occurs with a certain probability proportional to the quantum yield of the reaction and the absorption cross-section of the photochrome.

VII.3.d. Problem of quenching *via* energy transfer

Apart from the impossibility of selective excitation of an SW-photochrome, one more problem inherent in the use of dyads with two different photochromes is energy transfer, which occurs by the inductive resonance mechanism when there is no direct contact between the photochromes. This process is beneficial for data transmission between two MLGs but is adverse for unsymmetrical dyads, resulting in quenching of the SW-photochrome. For example, in styrylquinoline-merocyanine dyad **33a**, the energy transfer efficiency (quantum yield) is $\varphi_{ET} = 0.96$; therefore, the energy transfer from the styrylquinoline to merocyanine moiety virtually suppresses the *trans*–*cis*-photoisomerization of the former.[161]

Structure 33



n = 3 (**a**), 11 (**b**)

33a,b

According to the Förster theory, the rate constant for the singlet–singlet energy transfer by the dipole–dipole inductive resonance mechanism is determined by the equation (the term containing parameters that are not discussed here is omitted)

$$k_{ET} \sim \frac{\varphi_D \kappa^2 J}{\tau_D R^6} \qquad (5)$$

where τ_D and φ_D are the fluorescence lifetime and quantum yield of the donor in the absence of the acceptor, κ is the orientation factor, J is the overlap integral of the emission spectrum of the energy donor with the absorption spectrum of the energy acceptor and R is the distance between the donor and acceptor molecules.[162]

According to Eqn (5), the k_{ET} value (and, hence, φ_{ET}) can be decreased by several methods, namely

— by using a donor with a low quantum yield and high fluorescence lifetime;

— by decreasing the orientation factor;

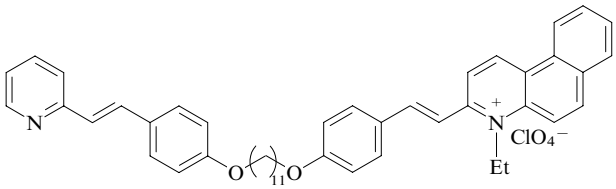
— by decreasing the overlap integral of the spectra (spectral separation method);

— by increasing the distance between the donor and acceptor molecules (spatial separation method).

The first and third methods require the synthesis (selection) of photochromes with appropriate characteristics. The second method requires that two photochromes be rigidly located in space, and this can decrease k_{ET} down to zero: according to the Förster theory, in the case of perpendicular arrangement of transition moment vectors in the donor and the acceptor, $\kappa = 0$ and energy transfer is impossible (however, interaction between the energy donor and acceptor *via* a covalent bridge should be taken into account). The fourth method requires fabrication of systems in which two photochromes are located as far as possible from each other.

The spatial separation of photochromes is used in dyad **33b** in which the polymethylene chain length has increased compared with dyad **33a** from 3 to 11 units, and the efficiency of energy transfer has decreased from 0.96 to 0.87.[156] Then spectral separation was added to the spatial one. To this end, the styrylquinoline moiety in dyad **33b** was replaced by a styrylpyridine moiety and the merocyanine was replaced by benzomerocyanine. In the biphotochrome dyad **34** thus formed, the energy transfer efficiency has decreased to 0.66; owing to the activity of both photochromes, dyad **34** can model the functions of any of the 16 possible two-input logic gates.[163]

Structure 34



34

The diagrams of photophysical and photochemical processes taking place in unsymmetrical dyads are shown in the general form in Fig. 11. The irradiation with LW light excites and induces a reaction of only the LW-photochrome. If the reaction quantum yield is $\varphi < 1$, radiative and non-radiative deactivation of the excited state can also be observed.

The SW irradiation may excite any of the photochromes, this is a probabilistic process. The excitation of both photochromes simultaneously (two-quantum excitation) requires intense laser pulses. The excitation of the SW-photochrome induces the energy transfer process in which the SW-photochrome is the donor and

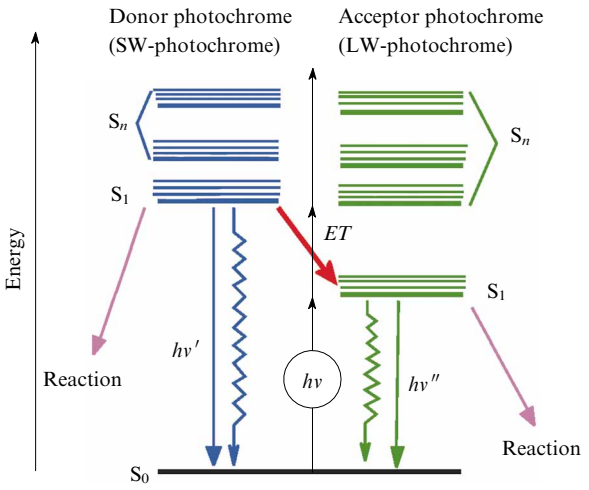


Figure 11. Diagram of terms for unsymmetrical dyad. Adapted from Ref. 164.
The radiative (straight arrows) and non-radiative (zigzag arrows) photophysical and photochemical processes in photochromes, *ET* is energy transfer from the donor photochrome to the acceptor photochrome.

the LW-photochrome is the acceptor. The energy transfer results in quenching of the donor (the quantum yield of its reaction can decrease to 0) and sensitization of the acceptor, so that its quantum yield can exceed 1. If a greater part of the incident light is absorbed by the SW-photochrome and is then transferred to the LW-photochrome, a major part of the latter is excited and participates in further transformations *via* sensitization rather than direct light absorption.[159]

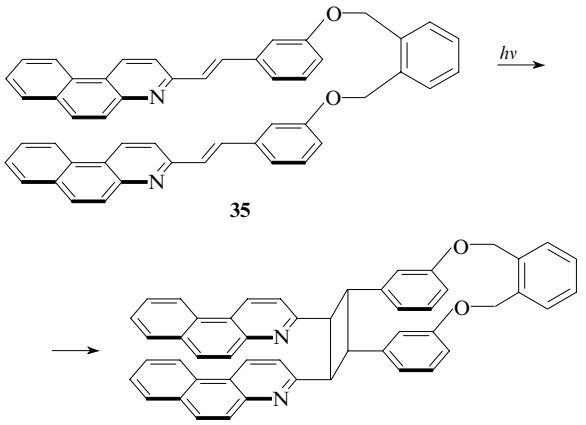
The problem of quenching of one photochrome as a result of energy transfer to the other photochrome is involved in the operation of symmetrical dyads, in the general case, multiphotochromic compounds containing identical photochrome groups if the product of the photochemical reaction has a longer-wavelength absorption spectrum that overlaps with the emission spectrum of the initial photochrome. After the phototransformation of the first photochrome, a symmetrical dyad becomes unsymmetrical, which may result in decreasing reactivity of the second photochrome, in some cases, down to complete deactivation. In particular, this effect is observed in the photocyclization of bis-DTE dyads[165–167] and multiphotochromic compounds containing three (trimer)[168] or four (tetramer)[169] DTE photochromes.

It is noteworthy that for multiphotochromic compounds with DTE photochromes, the quantum yield of the reverse, ring opening, reaction does not depend on the isomeric state of other photochromes, because the open form (*i.e.*, SW-photochrome) cannot quench the closed form (LW-photochrome) according to the energy transfer mechanism.

VII.3.e. Problem of reactions between photochromes

The interaction between the photochromes located close to each other within the dyads may lead not only to energy (or electron) transfer but also to reactions between the photochromes. For example, the replacement of the trimethylene bridging group in bis(styrylquinoline) dyad **26** by a *o*-xylylene group induces stereospecific [2 + 2]-photocycloaddition to give a cyclobutane derivative.[170, 171] In bis(styrylbenzoquinoline) dyad **35** (Scheme 5), owing to the directing influence of the *o*-xylylene group and π-stacking interaction between the aromatic rings, the photocycloaddition and photoisomerization proceed with equal efficiency (the quantum yields are 0.18 – 0.19).[172]

Scheme 5



The photocycloaddition, like photoisomerization, is a reversible reaction and theoretically it could also be used for the design of photonic MLGs, especially in view of the considerable difference between the absorption spectra of the initial and final compounds. However, this possibility has not been tested experimentally.

VIII. Ideal molecular logic gate: extended set of requirements

Taking into account the mechanisms of action considered above and problems of MLG operation, which were identified following accumulation of experimental data, it becomes necessary to revise the requirements to the structure and properties of a chemical compound able to function as a logic gate. These requirements, listed in Section III, appeared at the early stage of research, but now some of them are not that obvious, while new requirements appear instead.

The key requirements are the presence of several stable isomers with distinguishable properties and the possibility of reversible conversion of one isomer to another under the action of some external stimulus. Only the latter is beyond doubt. Indeed, only an external stimulus that affects the molecular system and switches it from one state to another is suitable as the MLG input. Meanwhile, interpretation of the term 'state of the system' should be extended. In the case of MLGs with chemical inputs, different states of the gates are usually associated with different isomers of the molecular system and switching from one state to another corresponds to interconversion of isomers (see Scheme 1).

However, the mechanism of action of logic gates can be based on photophysical processes rather than chemical reactions, as shown by examples of using probe light as the input signal, in particular, the example of operation of dyad **21** as a photonic adder. The isomers of a molecule

are different states; however, the ground (S_0) and electronically excited (S_1, S_2, *etc.*) states of the molecule are also different states. Transitions between these states that do not require chemical reactions can also serve to perform logic functions. Theoretically, transitions between the vibrational and rotational levels could also be used for this purpose, but no such examples are available as yet.

The requirements imposed on isomers include stability and difference in properties. The latter requirement is indisputable, and it is always met for the ground and excited states of a molecule: these states, like isomers, possess different properties; therefore, it is always possible to find out in which state the molecule occurs. But there is still the stability requirement. How absolute is this requirement?

Above we considered dyad **24**, a photonic switch operating in the kinetic mode. The lifetimes of the *cis*-isomers of two azobenzene derivatives in this dyad differ by 15 orders of magnitude, being as short as ~200 ps for the azopyridinium salt. Nevertheless, this state is experimentally observable, which implies the possibility to obtain the output signal. The lifetimes of electronically excited states depend on the multiplicity and vary from femtoseconds for singlet-excited states to seconds for triplet-excited states, and this is also suitable as the output signal.

Thus, the 'absolute' stability of, for example, photochrome isomers is significant only for archive data recording where the time of read-out of the recorded signal is not defined. When MLGs are used for information processing at a rate of billion operations per second, the signal should be read-out the same number of times and after reading-out (transmission along the chain), the MLG should be returned to the initial state. Therefore, in this case, it is not the absolute stability that is significant, but the possibility to reliably record the output signal during the isomer (state) lifetime. Apparently, some threshold should be set for the lifetime, like for the value of analogue signal; for example, it should be an order of magnitude longer than the signal read-out time. For signal read-out over a period of 1 ns, it is sufficient that the isomer (state) lifetime be at least 10 ns. Owing to the high rate of photophysical transitions between states of the molecule, the signal read-out time and the recovery time of the initial state can be reduced; this is an advantage of photophysical MLGs over chemical ones. The same advantage is inherent in photochemical MLGs, because photoisomerization, photocyclization and ring opening reactions, depending on the molecular structure, can occur over a femtosecond range. Therefore, the whole cycle of functioning of photonic MLGs may be accomplished in a femtosecond to picosecond range. Also, one should take into account specific features of using ultrashot laser pulses, for example, the necessity of balancing the pulse duration and spectral width.[173, 174]

Nevertheless, the above-listed 'modified' requirements to be considered in the design of a single MLG are insufficient for the design of MLGs for information processing systems consisting of logic gate arrays connected in circuits. In this case, it is necessary to add the requirement of input and output homogeneity or to develop a MLG + converter complementary pair.

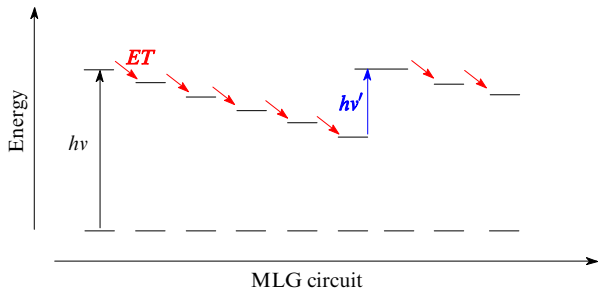


Figure 12. Vectorial energy transfer along the MLG circuit. Signal amplification takes place between the cascades *via* absorption of an additional light quantum, the energy of which is specified by parameters of the system.

For connecting MLGs into circuits, it is necessary to transmit information from one gate to another. This can be done by means of a chemical species or energy transfer. If the transfer of a chemical species, *e.g.*, proton, includes diffusion with exit from the solvent cage, this may entail, first, the loss of information and, second, retardation of the operation of the whole MLG circuit. Diffusion can be eliminated by using direct quasi-intramolecular proton transfer from the donor to the acceptor in a supramolecularly assembled system with an appropriate geometry. It is worth noting, however, that diffusion of ionic and molecular components is one of the stages of information transfer in living organisms.

To transmit information between MLGs *via* energy transfer, only the inductive resonance non-radiative mechanism is suitable, because trivial re-absorption is accompanied by information loss. Meanwhile, light emission may be envisaged for the last unit of the photonic MLG circuit, for example, to visualize the result.

The use of energy transfer between the gates brings about one more requirement: an intermediate signal amplification stage is needed. In the classic electronics, the direction of signal transfer is specified by current-carrying conductors and the voltage applied. The direction of energy transfer in the MLG circuit is specified by the positions of the excited states: the energy acceptor term should be lower than the energy donor term. Therefore, successive vectorial energy transfer in an MLG cascade requires that the terms of successive MLGs should gradually lower towards the direction of signal transfer (Fig. 12). In terms of physics, this means that the energy of a migrating exciton would decrease with movement along the chain. After a certain number of units, it would be necessary to raise the energy to the initial state in order to start a new energy transfer cascade. This can be done, for example, by means of singlet – singlet or triplet – triplet (T – T) annihilation. A control over T – T annihilation by means of a photochrome has been considered by Cui *et al.*[175] Yet another method is using an additional 'enhancement' quantum at the amplification stage. After absorption of the enhancement quantum, the exciton can continue the directed movement along the MLG circuit (start a new energy transfer cascade) (see Fig. 12).

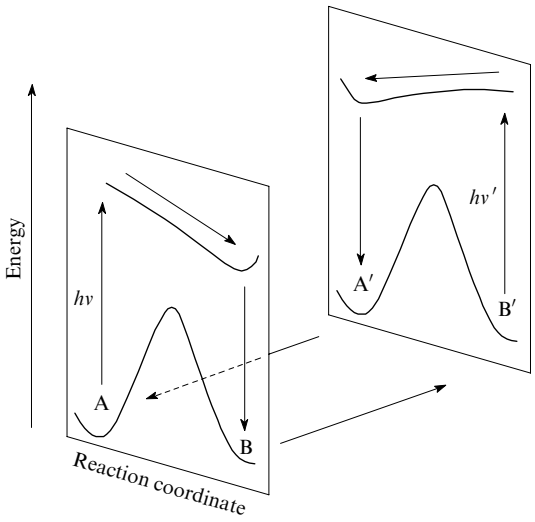


Figure 13. Adiabatic one-way photochemical reactions A → B and B′ → A′.

If switching between the MLG states occurs as a result of a photochemical reaction between the isomers A and B [see Eqn (3)], the optimal case is an adiabatic mechanism of the reaction A → B without considerable barriers in the PES of the excited state, as shown in Fig. 13. First, the quantum yield of this reaction can reach 1 and, second, the excited isomer formed can transfer the energy along the chain.

However, if $\varphi_A = 1$, this system can be photochemically returned to the initial state (reset function) only if the forward and reverse reactions follow different paths on the PES of the excited state. If it is the same minimum energy path, as shown in Fig. 13, then $\varphi_B = 0$ and the photochemical reaction B → A does not proceed. In this case, the reset function can be implemented only using an additional non-photochemical treatment. The best way is to switch the system to the new state A′, B′, in which photoisomerization in the opposite direction, B′ → A′, also follows an adiabatic mechanism (see Fig. 13). Switching of the predominant photoisomerization between the *trans*–*cis* and *cis*–*trans* directions is observed, for example, in the protonation of azadiarylethylenes.[176]

For selective excitation of photochromes in multiphotochromic compounds (for example, in unsymmetrical dyads), it is desirable that the absorption maximum of one photochrome should coincide with the absorption minimum of the other one.

All the necessary photophysical and photochemical properties of MLGs listed above, the structure and energies of molecular orbitals, the arrangement of excited state levels and the probability of transitions between them, the presence of appropriate functional groups capable of (self)-association and so on should be envisaged in the designed molecular system. However, it is impossible to unambiguously define the set of requirements for the design of ideal MLG, because each particular application requires a particular set of properties.

IX. Conclusion

The chemistry of molecular logic gates involved in their operation, *i.e.*, switching from one state to another interpreted as a logic operation, is based on simple one-step reversible chemical reactions — protonation, isomerization, cyclization, complex formation, oxidation and reduction. The structures of molecular and supramolecular systems considered here demonstrate the beauty and rationality of the design, but the complexity and art of the labourious multistage chemical synthesis of these molecules remain behind-the-scenes. The problems of development and optimization of synthetic routes for the preparation of MLGs require a separate discussion.

Quite a number of molecular systems able to function as MLGs have been found. Logic operations can be performed by not only complex supramolecular structures, but also by relatively simple molecules if they meet the appropriate requirements. The first MLGs were based on sensors and had chemical inputs. Most of new MLGs also belong to this type — owing to combination of several sensors for a variety of analyte molecules, cations and anions in one molecule, these compounds can function as logic gates with chemical inputs. The research along this line is in progress.[177–204] While analyzing these publications, one can notice some trend (or even a fashion) to end a paper dealing with a new sensor, for example, for mercury ions, with the remark that this system is promising for molecular computing. As shown in the review, in the case of modelling in solution, even a simple dilution can be described in terms of truth tables of logic gates. This is all the more possible for the operation of any sensor. The possibility to do this, in principle, was demonstrated back in the first study dealing with MLGs; now it is time to go ahead.

At the unity level, MLGs are able to perform simple logic and arithmetic operations. Performing more complicated calculations requires connection of MLGs into circuits in which the output signal of one gate is delivered to the input of the next one. This is possible if the input and output signals are homogeneous. However, for most MLGs, the input and output signals have different nature, which hampers direct connection of MLGs with one another.

The input and output inhomogeneity problem is one of the major obstacles for further development of MLGs for the information processing applications. Two options have been proposed for addressing this problem:

— homogenization of input and output signals: if the signals are of the same type, as in SC-electronics, the output signal of one MLG can be directly delivered to the input of another MLG;

— application of signal converters, which convert the output signal of the preceding MLG in such a way that it becomes of the same type as the input of the succeeding MLG.

The problem of signal inhomogeneity is, in part, solved taking advantage of the unique feature of MLGs — parallelism, that is, combination of several logic functions in one MLG. Functional integration allows one MLG to operate as several gates connected in a circuit. This parallel integration instead of serial one is possible for small computing units.

The problem of signal inhomogeneity is solved by itself for two types of gates — bio-MLGs and photonic MLGs. Bio-MLGs that use the principle of complementarity of nucleic bases have oligonucleotides as both inputs and outputs. Bio-MLGs of another type use the enzyme–substrate recognition principle. The mechanisms of operation of bio-MLGs differ from those of 'simple' MLGs and are discussed in specialized reviews (see, for example, Refs 205–209).

In view of input and output homogeneity, small size and fast operation, photonic MLGs (with photochemical or photophysical information processing principle) may make alternative to SC-devices. As shown by analysis, operation of photonic MLGs bring about their own problems, which could be partially solved by the synthesis of new luminophores and photochromes with appropriate properties.

The synthesis of supramolecular compounds is a sophisticated and labourious task. Nevertheless, this is incomparable with expenses for the fabrication of SC-chips. Actually, the number of MLGs that could be synthesized at the same time in a chemical solution exceeds the number of all transistors in all operating processors and those manufactured by all electronic manufacturing plants (this is a consequence of the enormous Avogadro's number: 6.02×10^{23} mol^{-1}).

In the case of large-scale application, one more advantage of MLGs is their commonality. In the manufacture of SC-elements, it is impossible to obtain two absolutely identical elements (to the accuracy of the number of atoms and their arrangement relative to one another in the nanocrystal). In molecular logic gates, this is achieved by itself: all molecules of a compound have the same structure.

There is a problem of selecting input and output signals in the MLG design. The input signal should affect a molecule and switch it from one state to another and the output signal should be measured as a value characterizing the molecule rather than molecular assembly in solution, crystal or film (*e.g.*, refractive index, viscosity and so on). Inappropriate choice of the input and output signals or the method of signal transmission between the gates results in pseudo-MLGs, which are either not molecular or cannot perform logic functions on going to the single-molecule level.

Apart from the input and output homogeneity problem, connection of MLGs into circuits brings about one more problem, which has not been discussed above but is mentioned in the literature, namely, the necessity to pass from solutions to structurally organized systems. For the fabrication of MLG arrays, it is desirable to use thermodynamically controllable association of molecules into supramolecular assemblies. By analogy with SC-computers, such assemblies (for example, Langmuir–Blodgett films) can be attached to the surface of a solid or a flexible film and by analogy with brain, a highly organized but not solid matter, these assemblies can be immobilized, for example, in a structured gel.

This review mainly focuses on photonic MLGs, which are potential working parts for computation at the molecular level. Chemical MLGs, which operate upon addition of chemicals, are not suited for this purpose. However, chemical MLGs — smart sensors — have their scope of applicability: placing coded labels on nano-objects, environmental protection, digital diagnostics in biology and medicine, targeted drug delivery and so on. For example, the multiaddressable AND gate with several receptors for biomarkers can serve for detection of diseases: the fluorescence of the gate would turn on only if the biomarker concentrations would exceed the threshold values. The greater the number of biomarkers to which the MLG is tuned, *i.e.*, the greater the number of inputs, the more accurate the diagnosis. This 'laboratory in a molecule' does not require skilled personnel. If this gate is used as a keypad lock for a nanocontainer with a pharmaceutical drug, it can not only report the presence of the disease but also start the therapy by opening the nanocontainer and releasing the drug at a particular site.[210–212] This principle is inherent in the developed selective sensitizer for photodynamic therapy.[213] A number of possible MLG applications not related to computing systems have been considered in the literature.[36, 214–217]

Irrespective of particular MLG application, further investigations are required, including the search, design and synthesis of new (supra)molecular systems able to perceive input signals of various types, process these signals in the context of truth tables of logic functions and produce output signals with desirable characteristics. Depending on results of this research, the moleculator able to add or subtract two binary digits would either remain just a toy for entertaining experiments in chemistry demonstrating the capabilities of molecules or become a working part of a molecular computer capable of fast processing of huge data arrays with minor expenses and, in some cases, with higher reliability: for example, molecular circuits are not prone to breakdown or destruction due to ionization under the action of radioactive radiation, which may cause failure of SC-devices. The drawback of the probabilistic nature of switching of a single photonic MLG can be eliminated in terms of a biomimetic approach by parallel use of several MLG circuits for solving one problem (massive parallel computations), like this takes place in neural networks.[218]

As noted in the Introduction, currently, semiconductor processors are fabricated according to the top-down principle *via* gradual decrease in the size of elements. The living nature uses a different, bottom-up approach, where single molecules are employed to construct supramolecular assemblies and complex hierarchically organized systems. It is this principle that is intended to be used for the design of MLG processors. Since carbon is located above silicon in the Periodic Table, the transition from semiconductor silicon systems to molecular carbon systems for information processing implies a bottom-up migration in the Table of Elements, thus extending the meaning of the bottom-up approach and providing it with a new shade.

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* * *

After this review was written and submitted for publication, awarding of the Nobel Prize of 2016 in chemistry for the 'design and synthesis of molecular machines' was

announced. Actually, the Prize winners, J.-P.Sauvage, B.Feringa and F.Stoddart, accomplished what R.P.Feynman imagined in the lecture mentioned above (see the Introduction): creation of mechanisms of infinitely small size. However, Feynman also dreamed of computers of exceptionally smaller size, which have not yet been created. Although particular blocks of molecular computers (adders, subtractors, *etc.*) have already been synthesized, integration of these units into a common circuit is faced with problems, which are outlined in the review. Solution of these problems and 'design and synthesis of a molecular computer' is a challenge for the possible future Prize Laureates.

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