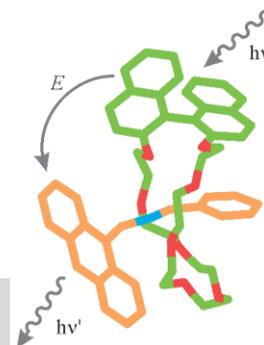


# Molecular Photochemionics\*\*

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Dedicated to Fraser Stoddart on his 65th birthday

Suitably designed molecular and supramolecular species are capable of combining light and chemical inputs to perform functions that mimic those of macroscopic devices. This paper describes the working principles of molecular-level photochemionic devices for i) chemical switching of photonic input/output signals, ii) chemical tuning of photonic input/output signals, and iii) the transformation of chemical and/or optical signals for logic operation.



## 1. Introduction

The miniaturization of components for the construction of silicon-based electronic computers is currently pursued by using the top-down approach. This approach, which is in the hands of physicists and engineers, consists in manipulating progressively smaller pieces of matter by using photolithography and related techniques. Although semiconductor devices of 65 nm are already on the market,<sup>[1a,b]</sup> and devices of 45 nm have been reported,<sup>[1c]</sup> it is becoming clear that the top-down approach is subjected to drastic limitations for dimensions smaller than 100 nm because of cost issues.<sup>[2]</sup> Furthermore, fundamental scientific problems (e.g., current leakage and heat dissipation) arise when bulk-semiconductor components approach the dimension of a few nanometers.<sup>[1b]</sup>

An alternative strategy towards technology at the nanometer scale is offered by the bottom-up approach, which starts from molecules and builds up to nanostructures.<sup>[3]</sup> Chemists are in an ideal position to develop bottom-up strategies for the con-

struction of nanoscale devices since they are able to manipulate molecules, the smallest entities of matter with distinct shapes and properties. In fact, the molecule-by-molecule bottom-up strategy is nothing other than supramolecular chemistry, a discipline extensively developed by chemists in recent years.<sup>[4]</sup>

Fraser Stoddart, to whom this issue is dedicated, has been a pioneer in this field.

## 2. Molecular Electronics

In current computers, information processing takes place at logic gates that employ electronic input and output signals (i.e., fluxes of electrons). Data manipulation relies on the binary digital (bit) nature of these signals that are elaborated by means of the Boolean logic.

In an attempt to develop bottom-up electronics (molecular electronics)<sup>[5]</sup> in the last few years there has been an increasing interest in using molecules to construct miniaturized electric circuits that would be much smaller than the corresponding micrometer-scale digital logic circuits fabricated on conventional solid-state semiconductor chips.<sup>[6]</sup> Many investigations on electrical conductivity and electrical-switching properties of molecules and supramolecular systems have been performed<sup>[7]</sup> and the construction of gates based upon molecular diodes has been proposed.<sup>[8]</sup> Such molecular gates would be about one-million times smaller in area than the corresponding logic elements fabricated on a semiconductor chip using transistor-based circuits. If this approach is successful, it will be possible to construct ultrahigh-density molecular circuitry that would

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have great impact in computer science (a Pentium on a pin-head).

In nature, fundamental processes like the initial events of green-plant photosynthesis involve electron transfer in supramolecular arrays.<sup>[9]</sup> A great number of electron-transfer processes in artificial supramolecular systems have been investigated and the fundamental principles that govern the occurrence of these processes in solution have been elucidated.<sup>[10]</sup> In molecular electronics, however, the molecular components have to perform their task (e.g., to conduct, switch, or rectify an electric signal) in the solid state and the function of the device originates from the architecture of the molecular array. Despite the efforts of many laboratories, much remains to be learned about the behavior of molecular wires, switches, and rectifiers in the solid state, as well as about the means of manipulating, bonding, and ordering molecules in circuitlike structures and on interfacing them with the macroscopic world.<sup>[5d]</sup> Experimental results in this field are difficult to obtain, and special care has to be taken to achieve reproducible measurements<sup>[11]</sup> and avoid artifacts related to the experiment setup.<sup>[12]</sup>

### 3. Molecular Photonics

An alternative possibility to the use of electron fluxes as a means of information processing (electronics) is that of using photon fluxes (photonics). In several macroscopic devices electrical cables have already been replaced by optical fibers. The advantage offered by optical signals with respect to electric signals for transmission of information at the macroscopic level relies on the fact that propagating light beams of different wavelengths in an optical fiber do not interfere, thereby allowing transportation of a large number of signals along a single fiber.

At the molecular level, photons can be used as power to make a system work and as input/output signals to be processed, this is what happens with electrons in molecular electronics. In nature, vision is based on a light-induced chemical reaction<sup>[13]</sup> and in the photosynthetic process light harvesting takes place by migration of the excitation energy within molecular arrays.<sup>[14]</sup> In artificial systems, manipulation of photons by

molecules can be used to transmit (molecular wires<sup>[15]</sup>), harvest (antenna systems<sup>[16]</sup>), store (photochromic systems<sup>[17]</sup>), disclose (fluorescent sensors<sup>[18]</sup>), and process (switching<sup>[19]</sup> and logic<sup>[20]</sup>elaboration) information. In most cases, however, the experiments have been performed on bulk solution systems.

Until now little attention has been devoted to the development of solid-state photonic technology at the molecular level. One reason is that the wavelength of light in the IR, visible, and even UV spectral regions is by far greater than the molecular dimensions, so that spatially selective excitation of a specific molecule in a supramolecular array is prevented. Devices for guiding electromagnetic radiations on a scale below the diffraction limit would also be needed for designing molecular-level optical circuits. Progress in near-field optical techniques<sup>[21]</sup> and electromagnetic energy transport in metal nanoparticle plasmon waveguides<sup>[22]</sup> might open this possibility. It should also be noted that energy transfer from a donor to an acceptor can occur along a molecular wire “waveguide” without any problem.<sup>[23]</sup>

### 4. Chemionics

Instead of electrons or photons, molecules and ions can be used as input/output signals to process information by using a molecular substrate. Indeed, information processing in nature is usually based on exchange of chemical signals. For example, in our brain, neurons process signals relying on the behavior of ions in solution, and in cells RNA molecules carry information from DNA to the machines that create new protein molecules.<sup>[24,25]</sup>

Chemical processes occur at the molecular level by their own nature and usually take place in solution. The fundamental features in chemionic information systems are molecular recognition and changes in the molecular structure. These interconnected processes, ubiquitous in nature,<sup>[24,25]</sup> have been extensively investigated in the last 30 years for artificial systems in the frame of the development of supramolecular chemistry.<sup>[4]</sup> Metal-ion coordination, host–guest pairs, and, more generally, a variety of adducts based on intermolecular forces (e.g., hydrogen bonds and donor–acceptor interactions) have been thoroughly studied and also exploited to perform a vari-



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ety of useful functions. In artificial systems, the most common reagents to process signals are acids and bases, but metal ions and molecules can also be used.

## 5. Molecular Computers

Miniaturization down to the nanometer scale, performed by a bottom-up approach starting from molecules, could open the way to the design and construction of “molecular computers” much smaller and much more powerful than the presently used silicon-based computers. The term molecular computer still sounds weird to most chemists in spite of the fact that already 20 years ago the Pimentel report was explicit and optimistic in this regard: “There are those who dismiss as far-fetched the idea of man-made molecular-scale computers. ... But since we know that molecular computers are routine accessories of all animals from ants to zebras, it would be prudent to change the question from whether there will be man-made counterparts to questions concerning when they will come into existence and who will be leading in their development. The when question will be answered on the basis of fundamental research in chemistry; the who question will depend on which countries commit the required resource and creativity to the search.”<sup>[26]</sup>

Electronics, photonics, and chemionics can all operate at the molecular level and can thus be used to develop molecular computers. Recent advances in chemical synthesis have indeed enabled the design and construction of supramolecular systems in which a discrete number of structurally integrated functional components can perform quite complex functions.<sup>[41,27]</sup>

From the above discussion, it becomes apparent that there are two philosophically different approaches to molecular level information processing. The first one is to mimic, at the nanometric level, the operational principles of the solid-state computers presently in use. Molecular electronics and, perhaps, molecular photonics can help in this way. The other approach, which takes inspiration from information processing in living organisms, is based on chemionics, which operates in solution and can be complemented by photonics, since chemical and light input/output signals, as we will see below, can be easily coupled. It can thus be expected that the bottom-up approach will move science and technology of information processing not only from the micro- to the nanoscale, but also from electronics to photonics and chemionics and from solid-state to solution and soft matter. This change of paradigm concerning the material basis of the information processing systems does not necessarily mean that the use of Boolean logic will be abandoned.

The top-down approach has enabled the construction of current computers and of a variety of solid-state microelectronic devices (MEDs) and microelectromechanical systems (MEMS).<sup>[28]</sup> In the next few years, the bottom-up approach is likely to lead to a wealth of nanodevices in which photonics, chemionics, electronics, and mechanics will be integrated to a different extent, depending on the function that the device has to perform. We shall then become accustomed with new acronyms like NED (nanoelectronic device), NPD (nanophotonic device), NCD (nanochemical device), NPCD (nano-photo-

chemical device), NPED (nano-photoelectronic device), NEMS (nano-electromechanical system), NPEMS (nano-photoelectromechanical systems), and so forth.

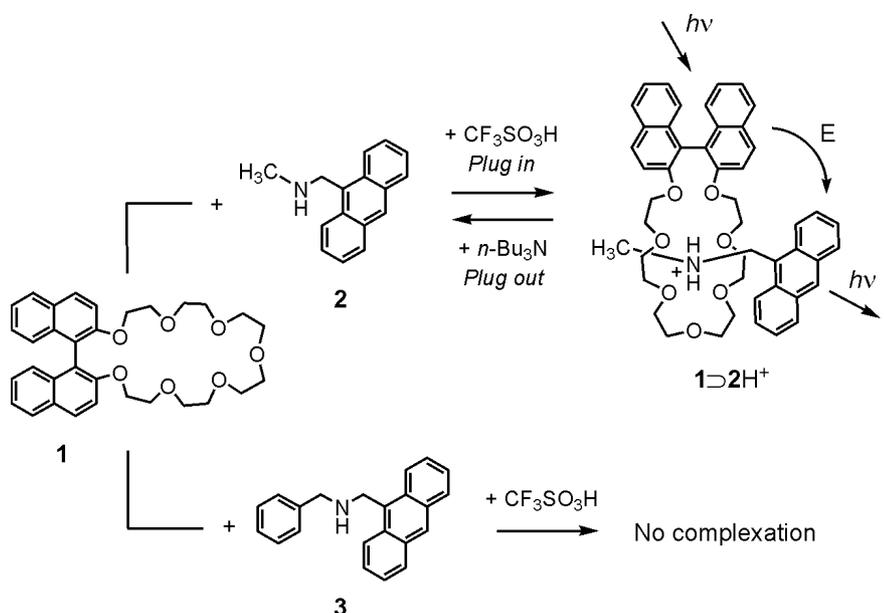
Apart from futuristic applications, the development of a set of components for information processing by molecular photonics and chemionics is an interesting scientific challenge. In this paper we will review some recent achievements of our laboratory in the design and construction of molecular-level systems that, in solution, are capable of transferring, switching, collecting, storing, and elaborating light signals, and we will show that molecular chemionics and photonics can be profitably combined (photochemionics) to obtain systems capable of information processing in solution.

## 6. Chemical Switching of Photonic Signals in Self-Assembling Supramolecular Systems

Supramolecular species, whose components are connected by means of noncovalent forces, can be disassembled and reassembled<sup>[29]</sup> by modulating the interactions that keep the components together, thereby allowing switching of energy- or electron-transfer processes. Two-component systems of this type are reminiscent of plug–socket electrical devices and, like their macroscopic counterparts, must be characterized by i) the possibility of connecting/disconnecting the two components in a reversible way, and ii) the occurrence of an electron or electronic energy flow from the socket to the plug when the two components are connected. Hydrogen bonding interactions between ammonium ions and crown ethers are particularly convenient for constructing molecular-level plug–socket devices, since they can be switched on and off quickly and reversibly by means of acid–base inputs.

### 6.1. A Molecular Plug–Socket System

A plug–socket system which deals with the transfer of electronic energy is illustrated in Figure 1.<sup>[30]</sup> The absorption and fluorescence spectra of a  $\text{CH}_2\text{Cl}_2$  solution containing equal amounts of binaphthocrown ether **1** and amine **2** indicate the absence of any interaction between the two compounds. Addition of a stoichiometric amount of acid causes profound changes in the fluorescence behavior of the solution, namely i) the fluorescence of **1** is quenched, and ii) the fluorescence of **2-H<sup>+</sup>** is sensitized upon excitation with light absorbed exclusively by the crown ether. These observations are consistent with the formation of a pseudorotaxane-type adduct wherein very efficient energy transfer takes place from the binaphthyl unit of the crown ether to the anthracenyl group incorporated in the component containing the dialkylammonium ion. Such a pseudorotaxane can be disassembled by the subsequent addition of a stoichiometric amount of base, thereby interrupting the photoinduced energy flow, as indicated by the fact that the initial absorption and fluorescence spectra are restored. Interestingly, the plug-in process does not take place when a plug component incompatible with the size of the socket, such as the benzyl-substituted amine **3**, is employed (Fig. 1).



**Figure 1.** A molecular-level plug–socket system for energy transfer based on the reversible acid–base driven threading–dethreading motions in the hydrogen-bonded pseudorotaxane  $1 \supset 2\text{H}^+$  ( $\text{CH}_2\text{Cl}_2$ ; room temperature). The acid-driven threading of compound **3**, incorporating a bulky benzyl group, through the macrocyclic cavity of **1** does not occur [30]. Adapted from [27].

## 6.2. An Electrical Extension Cable at the Molecular Level

The plug–socket concept described above can be used to design molecular systems which mimic the function played by a macroscopic electrical extension cable. The operation of an extension cable is more complex than that of a plug–socket system, since it involves three components that must be held together by two connections that have to be controllable reversibly and independently; in the fully connected system, an electron (or electronic energy) flow must take place between the remote donor and acceptor units (Fig. 2).

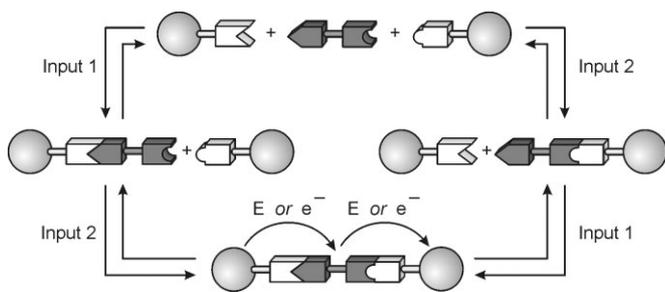
A system of this type, made of the three components  $4^{2+}$ ,  $5\text{-H}^+$ , and  $6^{2+}$ , has been recently obtained and studied (Fig. 3a).<sup>[31]</sup> Component  $4^{2+}$  consists of two moieties:<sup>[32]</sup> a  $[\text{Ru}(\text{bpy})_3]^{2+}$  unit, which behaves as an electron donor under light excitation, and a dibenzo[24]crown-8 macrocycle, capable

of playing the role of a hydrogen bonding first socket. The extension cable  $5\text{-H}^+$  is made up<sup>[33]</sup> of a dialkylammonium ion that can insert itself as a plug into a dibenzo[24]crown-8 socket by virtue of hydrogen bonding interactions, a biphenyl spacer, and a benzonaphtho[36]crown-10 unit, which fulfils the role of a  $\pi$ -electron-rich socket. Finally, the 1,1'-dioctyl-4,4'-bipyridinium dication  $6^{2+}$  can play the role of an electron drain plug. In  $\text{CH}_2\text{Cl}_2$  solution, reversible connection–disconnection of the two plug–socket junctions can be controlled independently by acid–base and reduction–oxidation stimulation, respectively, and monitored by changes in the absorption and emission spectra, owing to the different nature of the interactions (hydrogen bonding and  $\pi$ -electron donor–acceptor) that connect the components. In the fully assembled triad,  $4^{2+} \supset 5\text{-H}^+ \supset 6^{2+}$ , light excitation of the Ru based unit of  $4^{2+}$  is followed by electron transfer to  $6^{2+}$ , with  $5\text{-H}^+$  playing the role of an extension cable (Fig. 3b). The occurrence of this process is confirmed by nanosecond-laser flash-photolysis experi-

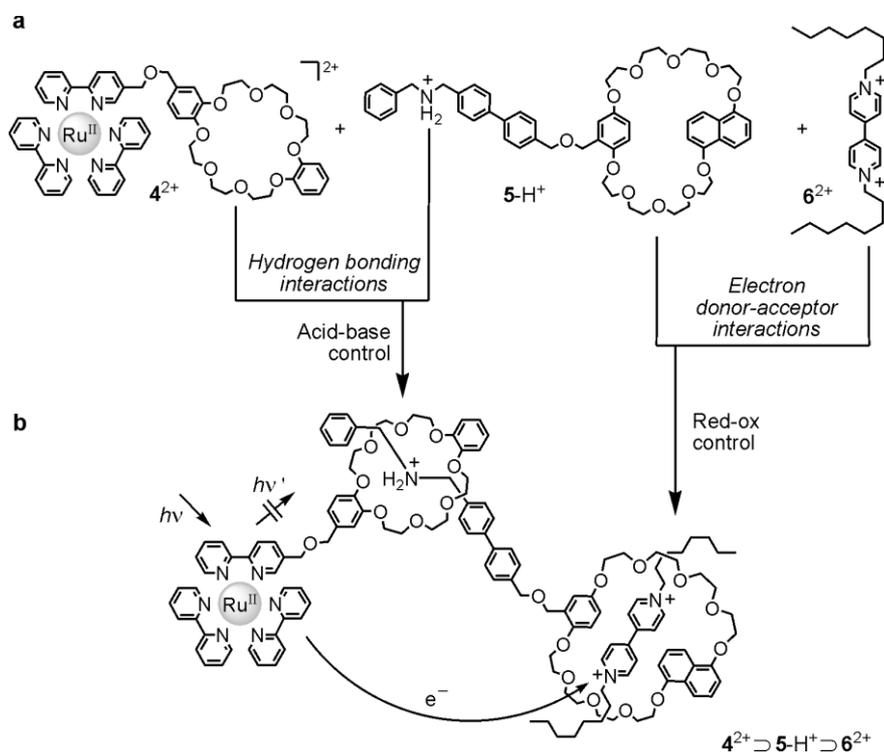
ments, showing a transient absorption signal assigned to the 4,4'-bipyridinium radical cation formed by photoinduced electron transfer within the self-assembled triad. Interestingly, the extension cable component  $5\text{-H}^+$  exists in a self-threaded conformation<sup>[33]</sup> that cannot host the electron drain until it is opened up by complexation with the socket unit of the source component. This feature, which can be viewed as a limitation because it reduces the efficiency, in fact plays the function of a safety-catch device. Moreover, the photoinduced electron-transfer process can be powered by sunlight because the  $4^{2+}$   $[\text{Ru}(\text{bpy})_3]^{2+}$ -type component shows a broad and intense absorption band in the visible spectral region.

## 7. Chemical Tuning of Output Photonic Signals

In suitably designed A–B supramolecular systems, light excitation of component A can be followed by energy transfer to component B, which can thus emit light. In such systems the input light signal is converted into an output signal of different wavelength, characteristic of the B species. In the case in which A is a dendrimer, it may contain several chromophores at the periphery, in the branches, or in the core, that can absorb light, and it is able to host a variety of luminescent B species ( $B_1, B_2, \dots$ ). Therefore, it happens that the same light input on A can be converted into output light signals of predetermined wavelengths, depending on the specific  $B_n$  species that is hosted into A. Chemical tuning of the input-to-output photonic signal can thus be achieved in these systems.



**Figure 2.** Schematic representation of the working mechanism of an electrical extension cable. Reproduced from [27].



**Figure 3.** A chemical system for mimicking an electrical extension cable [31]. Structural formulas of the three molecular components  $4^{2+}$ ,  $5\text{-H}^+$ , and  $6^{2+}$ , which a) self-assemble in solution ( $\text{CH}_2\text{Cl}_2$ ; room temperature) to give the  $4^{2+} \rhd 5\text{-H}^+ \rhd 6^{2+}$  triad shown in (b). In the fully connected system, excitation of the Ru-based unit of  $4^{2+}$  with visible light is followed by electron transfer to  $6^{2+}$ , with  $5\text{-H}^+$  playing the role of an extension cable.

### 7.1. A Luminescent Dendrimer Hosting Luminescent Metal Ions

Dendrimer **7** (Fig. 4) contains in the interior 18 amide groups, which are known to strongly coordinate lanthanide ions, and in the periphery 24 chromophoric dansyl units, which show intense absorption bands in the near UV spectral region and an intense fluorescence band in the visible region. We have investigated<sup>[34]</sup> the complexation of dendrimer **7** by six lanthanide ions ( $\text{Gd}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Er}^{3+}$ ) characterized by very different energy-level patterns (Fig. 5) and capable of exhibiting their own luminescence. Among these ions,  $\text{Eu}^{3+}$  and  $\text{Yb}^{3+}$  are rather easy to reduce ( $E^\circ = -0.35$  and  $-1.1$  V, respectively, versus the standard hydrogen electrode, in aqueous solution), whereas none of them can be easily oxidized.

Formation of the metal complexes  $\text{M}^{3+} \rhd \mathbf{7}$  is accompanied by a quenching of the fluorescent excited state of the dansyl units. The quenching effect is very large for  $\text{Nd}^{3+}$  and  $\text{Eu}^{3+}$ , moderate for  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$ , small for  $\text{Tb}^{3+}$ , and very small for  $\text{Gd}^{3+}$ . In the present context, the most relevant results are those obtained with  $\text{Nd}^{3+}$ ,  $\text{Er}^{3+}$ , and  $\text{Yb}^{3+}$ .

For  $\text{Nd}^{3+} \rhd \mathbf{7}$  and  $\text{Er}^{3+} \rhd \mathbf{7}$ , the observed quenching effect is accompanied by the sensitized near-IR (NIR) emission of the  $^4\text{F}_{3/2}$  ( $\lambda_{\text{max}} = 1064$  nm) and  $^4\text{I}_{13/2}$  ( $\lambda_{\text{max}} = 1536$  nm) excited state of  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$ , respectively. Energy transfer by a Förster-

type mechanism is more efficient in the case of  $\text{Nd}^{3+}$  because of the more extensive overlap between the dansyl emission band and the energy levels of the metal ion.

The case of  $\text{Yb}^{3+} \rhd \mathbf{7}$  is very interesting. A moderate quenching effect is accompanied by the sensitized emission of  $\text{Yb}^{3+}$  ( $^2\text{F}_{5/2}$ ,  $\lambda_{\text{max}} = 980$  nm, Fig. 5) at room temperature. On the other hand, in a rigid matrix at 77 K, no quenching of the dansyl emission and no sensitization of  $\text{Yb}^{3+}$  luminescence are observed. The interpretation of this result is not straightforward. In fact, whereas the moderate quenching ability on the dansyl fluorescence could be assigned to an electron-transfer quenching mechanism, which is thermodynamically allowed, the sensitization of the  $^2\text{F}_{5/2}$  emission is an unexpected result since energy transfer from the  $\text{S}_1$  excited state of the dansyl unit appears to be unlikely because of the lack of spectral overlap. It should be noted, however, that for  $\text{Yb}^{3+} \rhd \mathbf{7}$ , the  $\text{Yb}^{2+} \rhd \mathbf{7}^+$  electron-transfer level lies above the luminescent metal-centered level. Therefore, quenching by electron transfer can be followed by a back electron transfer leading to the formation of the lower lying, luminescent  $^2\text{F}_{5/2}$  level rather than the  $^2\text{F}_{7/2}$  ground

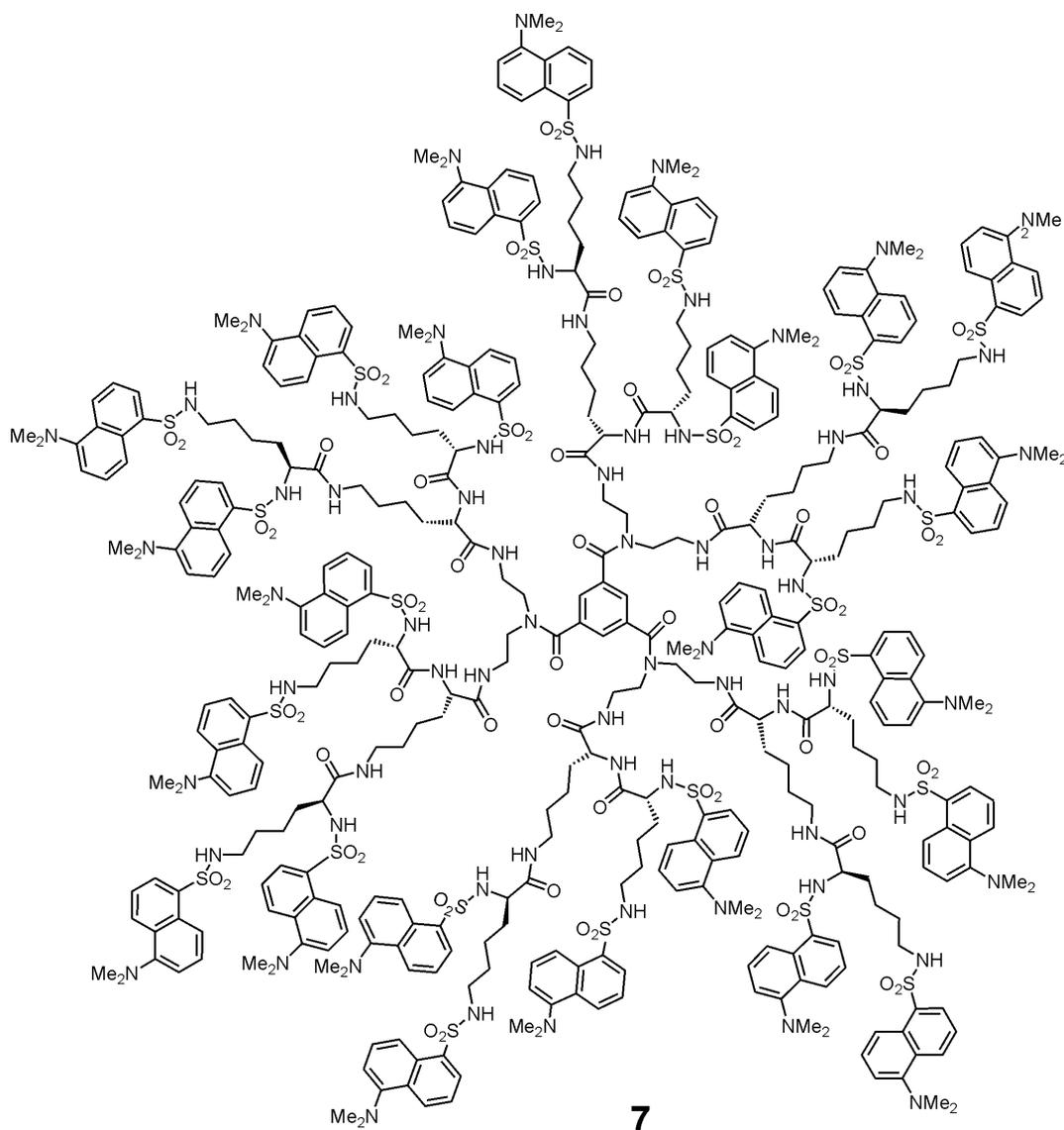
state. In a rigid matrix at 77 K, that is, under conditions in which the  $\text{Yb}^{2+} \rhd \mathbf{7}^+$  electron-transfer level moves to much higher energy, the quenching of the dansyl units and the sensitized emission of the  $^2\text{F}_{7/2}$  level of  $\text{Yb}^{3+}$  are no longer observed, confirming that the low energy  $^2\text{F}_{5/2}$  level cannot be populated by direct energy transfer from the  $\text{S}_1$  excited state of the dansyl unit.

In conclusion, the incident UV light input is converted into a NIR output, fine tuned by the nature of the coordinated metal ion.

### 7.2. Luminescent Dendrimers Hosting Luminescent Metal Complexes

Suitably designed dendrimers can be assembled as a second coordination sphere around a suitable metal complex. An interesting example involves the  $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$  complex and dendrimer **8** (Fig. 6), consisting of a 1,4,8,11-tetraazacyclotetradecane (cyclam) core appended with 12 dimethoxybenzene and 16 naphthyl units.<sup>[35]</sup>

$[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$  and **8** exhibit characteristic absorption and emission bands that are strongly affected by addition of acid. When an acetonitrile/dichloromethane 1:1 v/v solution, containing equimolar amounts of  $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$  and **8**, is



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Figure 4. Structure of the polylysine dendrimer **7** functionalized at the periphery with 24 dansyl units.

titrated by trifluoroacetic acid, or when  $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$  is titrated with  $(\mathbf{8}2\text{H})^{2+}$ , the  $\{[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-} \cdot (2\text{H}^+) \cdot \mathbf{8}\}$  adduct is formed (Fig. 6), in which the fluorescence of the naphthyl units is strongly quenched by very efficient energy transfer to the metal complex, as shown by the sensitized luminescence of the latter ( $\lambda_{\text{em}} = 680 \text{ nm}$ ). The  $\{[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-} \cdot (2\text{H}^+) \cdot \mathbf{8}\}$  adduct can be disrupted i) by addition of a base (1,4-diazabicyclo[2.2.2]octane), yielding the starting species  $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$  and **8**, or ii) by further addition of acid, with formation of  $(\mathbf{8}2\text{H})^{2+}$  and protonated forms of  $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$  (e.g.,  $[\text{Ru}(\text{bpy})(\text{CN})_2(\text{CNH})_2]$ ). In this system, UV input signals are converted into visible output signals. By using different metal complexes (e.g.,  $[\text{Ru}(\text{bpy})_2(\text{CN})_2]$ ), a fine tuning of the visible output signal can be achieved. As discussed below, this system can also be used as a logic gate.

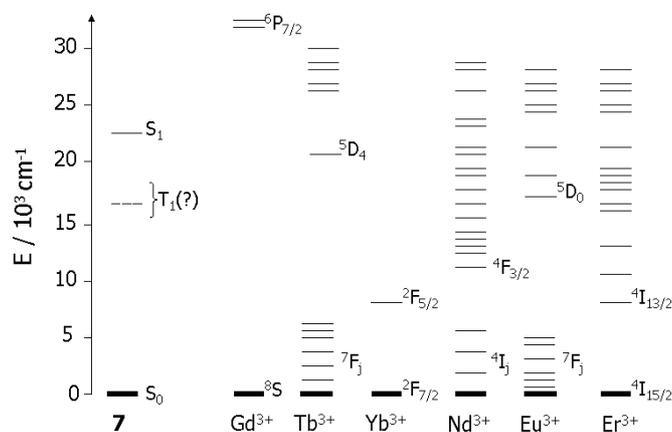
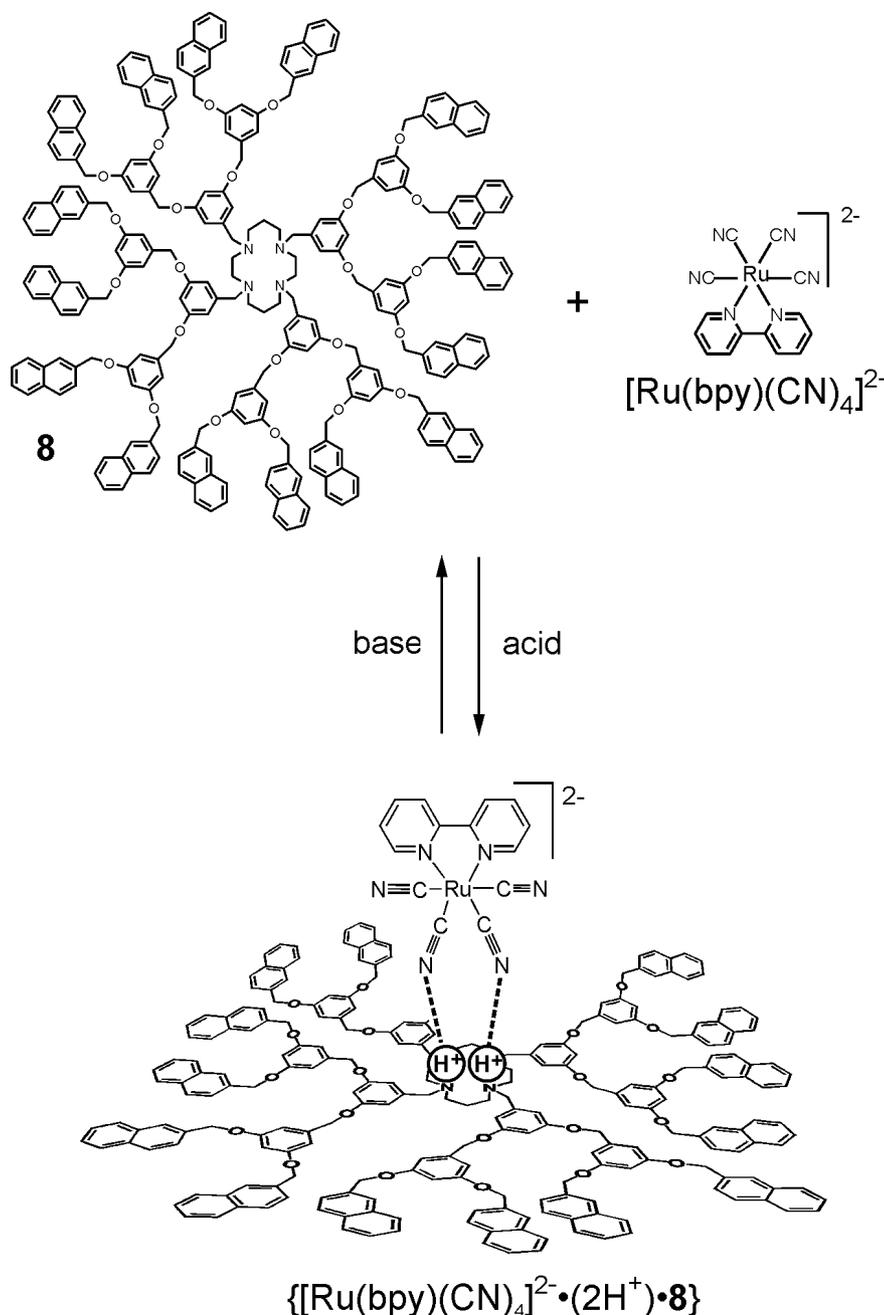


Figure 5. Energy-level diagrams for the dansyl units of dendrimer **7** and the investigated lanthanide ions. The position of the triplet excited state ( $T_1$ ) of **7** is uncertain because no phosphorescence can be observed [34].



**Figure 6.** Self-assembly and disassembly processes ( $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$  1:1 v/v; room temperature) of dendrimer **8** and  $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$  complex controlled by chemical inputs [35].

## 8. Transformation of Chemical and/or Optical Signals for Logic Operation

In a solid-state transistor the current flowing from a source to a drain can be modulated by a gate potential. It is possible to design molecular-level photochemionic systems which work on a similar principle, except that the source is a light energy input, the drain is a light energy output (luminescence), and the gate is a chemical input (Fig. 7). This happens, for example, in the systems in which the luminescence signal can be

quenched by photoinduced electron-transfer (PET) processes, as schematically illustrated in Figure 8.<sup>[36]</sup> In this figure, F is a potentially fluorescent unit (e.g., an anthracene molecule), whose fluorescent excited state is quenched by PET from the highest-occupied molecular orbital (HOMO) orbital of an appended electron-donor receptor, D (e.g., an amine unit). When the HOMO orbital of the electron donor is engaged by a suitable added molecule or ion (in the case of an amine, e.g., by protonation), fluorescence can be observed, because the HOMO of the donor is lowered in energy and electron transfer can no longer occur.

These systems combine photonics with chemionics and therefore their working principles are closer to those that govern the processes of information transfer in living organisms, rather than to those exploited in artificial solid-state devices.

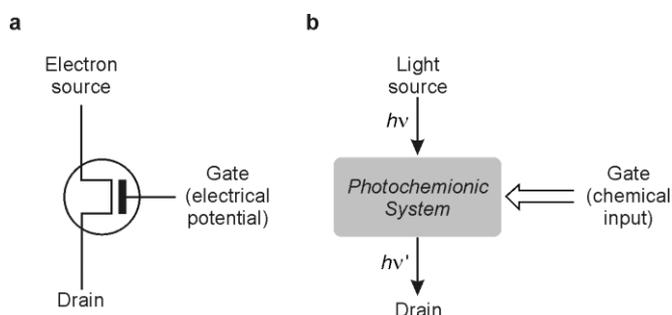
For the sake of space, we will only illustrate three examples of light powered, chemical input(s), optical output logic gates. For recent, exhaustive reviews on logic gates see the literature.<sup>[20,37]</sup>

### 8.1. An AND Logic Gate

The AND operator has two inputs and one output (Fig. 9a) and in a simple electrical scheme it can be represented by two switches in series. The above-discussed dendrimer **8** can be used as a substrate to construct an AND logic gate in acetonitrile/dichloromethane 1:1 (v/v) solution with two chemical inputs, namely one equivalent of  $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$  complex and two equivalents of  $\text{CF}_3\text{SO}_3\text{H}$  acid, and an optical output ( $\lambda_{\text{em}} = 670$  nm). Indeed, when both chemical inputs are present the  $\{[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-} \cdot (2\text{H}^+) \cdot \mathbf{8}\}$  adduct is formed (vide supra) and a sensitized emission of the  $\text{Ru}^{\text{II}}$  complex is observed upon excitation at 280 nm. A very weak emission at 670 nm is observed also when only the  $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$  chemical input is present, but its intensity is more than 20 times lower than in the adduct, under the same experimental conditions. Therefore, a threshold value can be chosen so that output is one only when both chemical inputs are present, as represented in the truth table of Figure 9b.

### 8.2. An XOR Logic Gate

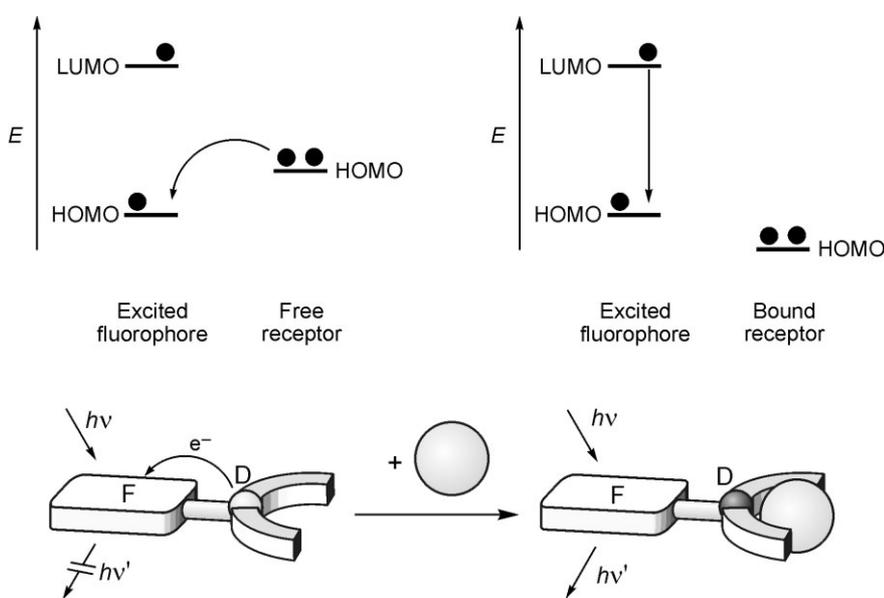
The XOR logic gate is particularly important because it can compare the digital state of two signals. If they are different an



**Figure 7.** Schematic illustration of the similarity between a metal-oxide semiconductor field-effect transistor (MOSFET) electronic transistor (a) and a photochemionic gate (b).

output 1 is given, whereas if they are the same the output is 0. This logic operation has proven to be difficult to emulate at the molecular scale, but some examples are now available.<sup>[38–40]</sup>

A light-powered, chemical-input(s), optical-output XOR logic gate is illustrated in Figures 10 and 11.<sup>[38]</sup> The electron-rich macrocycle **9** can be threaded by an electron-deficient wire-type molecule like  $10^{2+}$ . The resulting pseudorotaxane  $9 \supset 10^{2+}$  is held together by charge-transfer (CT) interactions. Assembling is signaled by as many as three different optical channels: i) appearance of a red color because of the presence of a CT absorption band in the visible region; ii) disappearance of the blue-green fluorescence of  $10^{2+}$ , and iii) disappearance of the UV fluorescence of **9** with  $\lambda_{\text{max}} = 343$  nm; the disappearance of the two fluorescent signals is due to the presence of the lower lying CT state in the complex. For the XOR function, protons and *n*-Bu<sub>3</sub>N are the inputs and the fluorescence of **9** at 343 nm is the monitored output. The working mechanism of this system is illustrated schematically in Figure 11.<sup>[38]</sup>



**Figure 8.** Schematic illustration of fluorescence switching through photoinduced electron-transfer (PET). Reproduced from [27].

**a**

**b**

| In <sub>1</sub><br>(H <sup>+</sup> ) | In <sub>2</sub><br>([Ru(bpy)(CN) <sub>4</sub> ] <sup>2-</sup> ) | Out<br>( $\lambda_{\text{em}}=670$ nm) |
|--------------------------------------|---|--|
| 0                                    | 0   | 0                                      |
| 0                                    | 1   | 0                                      |
| 1                                    | 0   | 0                                      |
| 1                                    | 1   | 1                                      |

**Figure 9.** Symbolic representation (a) and truth table (b) of an AND logic gate based on dendrimer **8** with two chemical inputs (acid and [Ru(bpy)(CN)<sub>4</sub>]<sup>2-</sup> complex) and optical output ( $\lambda_{\text{em}} = 670$  nm). Conditions: CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> 1:1 v/v; at room temperature.

As mentioned above, in the absence of the two inputs the fluorescence of **9** is quenched in the pseudorotaxane (output 0). When the Bu<sub>3</sub>N input alone is applied, the pseudorotaxane dethreads because of the formation of a stronger CT interaction between the amine and  $10^{2+}$ . Under such conditions, **9** is free and its fluorescence is not quenched (amine input 1, output 1). Application of the H<sup>+</sup> input causes protonation of **9** and, again, dethreading of the pseudorotaxane. Since protonation of **9** (presumably at the aliphatic ether oxygens) does not perturb its emission compared to the neutral form, the H<sup>+</sup> input 1 causes an output 1. Therefore, the output achieves logic state 1 in the two situations in which exclusively one of the two inputs is present.

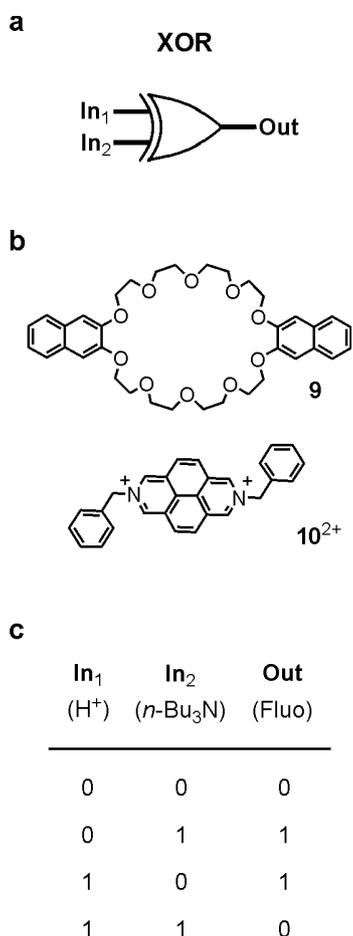
However, when both inputs are applied in stoichiometric amounts, acid–base neutralization results, the pseudorotaxane remains intact, and the 343 nm emission is quenched (output 0).

Also, in the previously described {[Ru(bpy)(CN)<sub>4</sub>]<sup>2-</sup>·(2H<sup>+</sup>)·**8**} adduct, stimulation with two chemical inputs (acid and base) leads to two distinct optical outputs (a naphthalene-based and a Ru(bpy)-based emission) according to an XOR and an XNOR logic, respectively.<sup>[35]</sup>

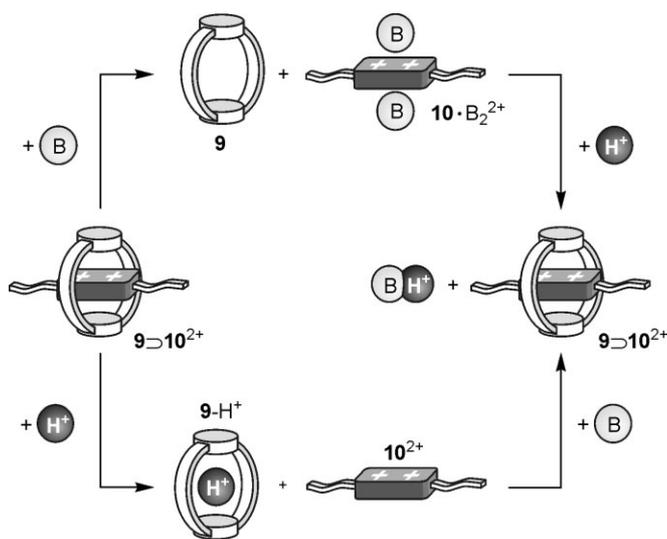
### 8.3. An XOR Logic Gate with an Intrinsic Threshold Mechanism

A system based on the photochemistry of a metal complex has been reported to mimic some elementary properties of neurons.<sup>[39]</sup>

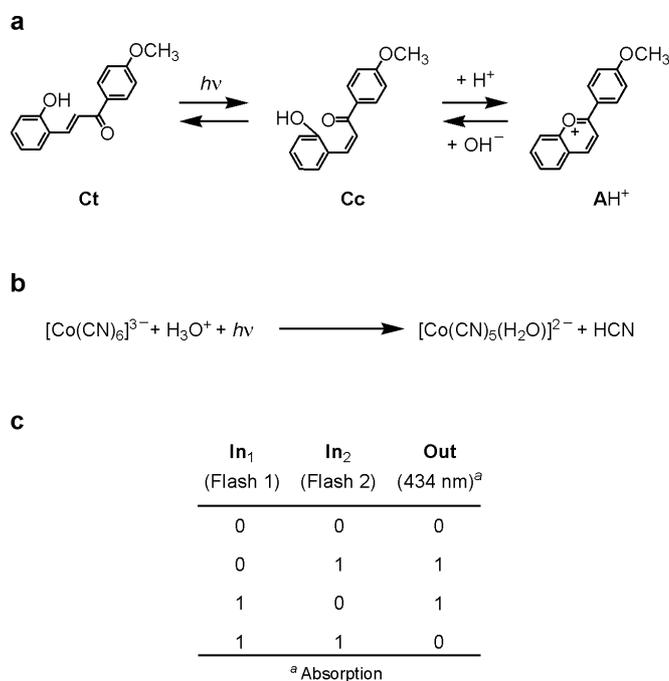
Such a system consists of an aqueous solution containing the trans-chalcone form (Ct, Fig. 12a) of the 4'-methoxyfla-



**Figure 10.** Symbolic representation (a), molecular implementation (b), and truth table (c) of an XOR logic gate [38]. The working mechanism of the system is fully illustrated in Figure 11. Conditions: CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN 9:1 v/v; room temperature. Adapted from [27].



**Figure 11.** Working mechanism of the XOR logic gate based on the compounds shown in Figure 10b [38]. Adapted from [27].



**Figure 12.** An XOR logic system under control of an intrinsic threshold mechanism: the two photoreactions involved (a and b), and the truth table (c) [39]. Conditions: aqueous solution; room temperature. Adapted from [27].

ylum ion (AH<sup>+</sup>), and the [Co(CN)<sub>6</sub>]<sup>3-</sup> complex ion (as a potassium salt). Excitation by using 365 nm light of Ct, which is the thermodynamically stable form of the flavylium species in the pH range 3–7, causes a trans → cis photoisomerization reaction ( $\Phi = 0.04$ ).<sup>[41]</sup> If the solution is sufficiently acid (< pH 4), the Cc isomer is rapidly protonated with conversion to the 4'-methoxyflavylium ion AH<sup>+</sup>, which is kinetically stable under such pH conditions and exhibits an intense absorption band with a maximum at 434 nm and an emission band with a maximum at 530 nm. At higher pH values, however, protonation does not occur and the Cc photoproduct is back converted to Ct. As far as [Co(CN)<sub>6</sub>]<sup>3-</sup> is concerned, excitation by 254 or 365 nm light in acid or neutral aqueous solution causes the dissociation of a CN<sup>-</sup> ligand from the metal coordination sphere ( $\Phi = 0.31$ ), with a consequent increase in pH (Fig. 12b).

When an acid solution (pH 3.6) containing  $2.5 \times 10^{-5} \text{ mol L}^{-1}$  Ct and  $2.0 \times 10^{-2} \text{ mol L}^{-1}$  [Co(CN)<sub>6</sub>]<sup>3-</sup> is irradiated at 365 nm, most of the incident light is absorbed by Ct, which undergoes photoisomerization to Cc. Since the pH of the solution is sufficiently acid, Cc is rapidly protonated (Fig. 12a), with consequent appearance of the absorption band with a maximum at 434 nm and of the emission band with a maximum at 530 nm, characteristic of the AH<sup>+</sup> species. On continuing irradiation, it can be observed that such absorption and emission bands increase in intensity, reach a maximum value, and then decrease up to complete disappearance. In other words, AH<sup>+</sup> first forms and then disappears with increasing irradiation time. The reason for the off-on-off behavior of AH<sup>+</sup> under continuous light

excitation is related to the effect of the  $[\text{Co}(\text{CN})_6]^{3-}$  photoreaction (Fig. 12b) on the **Ct** photoreaction (Fig. 12a). As **Ct** is consumed with the formation of  $\text{AH}^+$ , an increasing fraction of the incident light is absorbed by  $[\text{Co}(\text{CN})_6]^{3-}$ , whose photoreaction causes an increase in the pH of the solution. This change in pH not only prevents further formation of  $\text{AH}^+$ , which would imply protonation of the **Cc** molecules that continue to be formed by light excitation of **Ct**, but also causes the back reaction to **Cc** (and, then, to **Ct**) of the previously formed  $\text{AH}^+$  molecules. Clearly, the examined solution performs like a threshold device as far as the input (light)/output (spectroscopic properties of  $\text{AH}^+$ ) relationship is concerned.

Instead of a continuous light source, pulsed (flash) irradiation can be used.<sup>[39]</sup> Under the input of only one flash, a strong change in absorbance at 434 nm is observed, due to the formation of  $\text{AH}^+$ . After two flashes, however, the change in absorbance practically disappears. In other words, an output (434 nm absorption) can be obtained only when either input 1 (flash 1) or input 2 (flash 2) are used, whereas there is no output under the action of none or both inputs. This finding shows that the above-described system behaves according to an XOR logic, under control of an intrinsic threshold mechanism (Fig. 12c).

Two important features of the above system should be emphasized: i) intermolecular communication takes place in the form of  $\text{H}^+$  ions, and ii) the input and output signals have the same nature (light) and the fluorescence output can be fed, in principle, into another device.<sup>[27]</sup>

## 9. Conclusions

Information processing at the molecular level may be accomplished by using electrons, photons, or chemicals as input/output signals. Advances in these fields could lead to the design and construction of a molecular computer. To reach this goal, two philosophically different approaches can be pursued. The first one is to mimic, at the nanometric level, the operational principles of the solid-state computers presently in use. Molecular electronics and, perhaps, molecular photonics can help along this way. The other approach, inspired by information processing in living organisms, is based on chemionics which operates in solution and can be complemented by photonics, since chemical and light input/output signals can be easily coupled. In the last few years, the photochemionics approach has been strongly developed and a number of molecular and supramolecular devices capable of performing complex functions,<sup>[42]</sup> such as arithmetic operations,<sup>[40,43]</sup> have been designed and investigated. Regardless of the possibility of short-term applications,<sup>[44]</sup> the development of a set of components for information processing by molecular photochemionics seems a worthwhile investment.<sup>[26,27]</sup>

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