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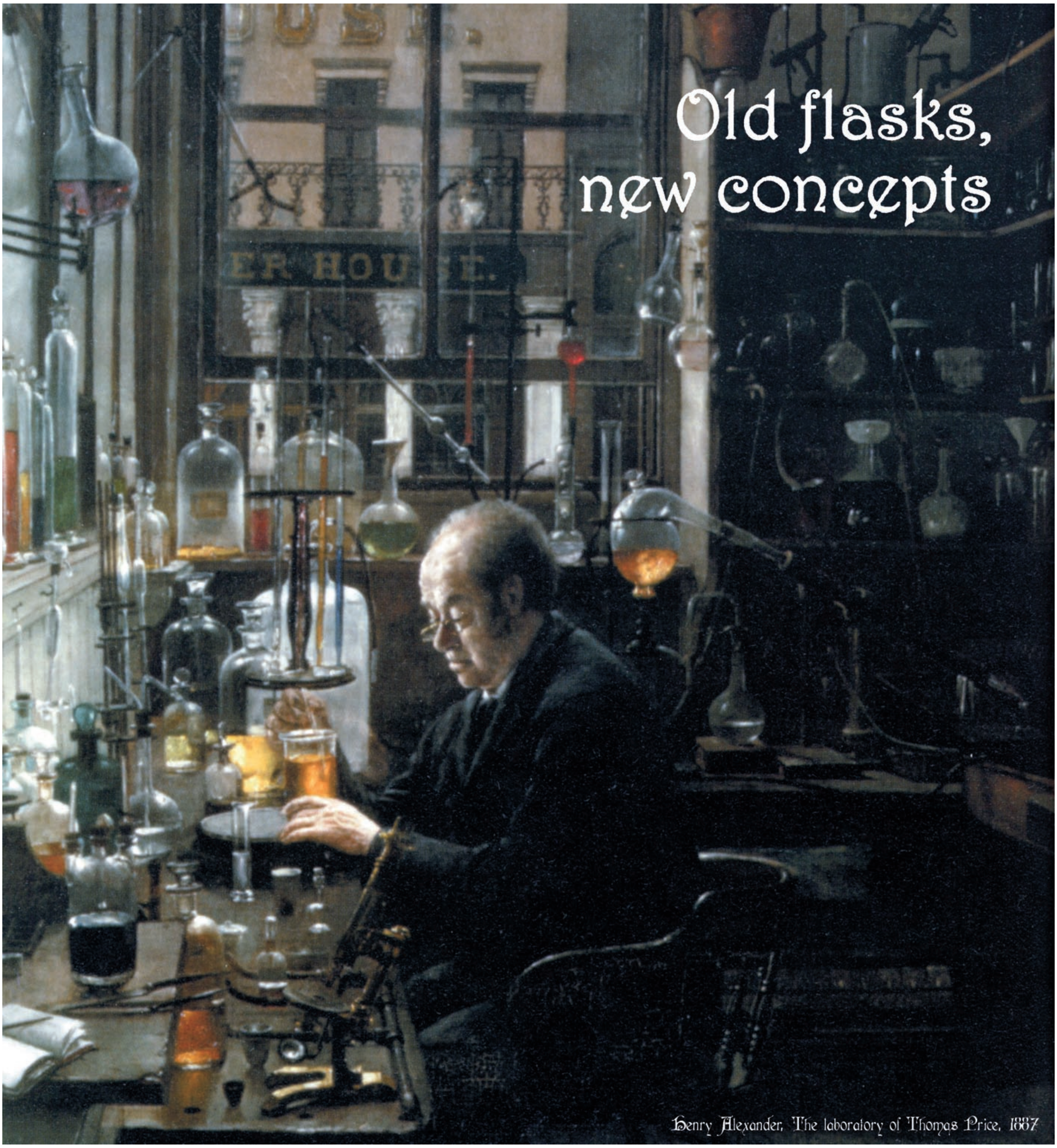
Processing Energy and Signals by Molecular and Supramolecular Systems

Vincenzo Balzani,* Alberto Credi, and Margherita Venturi[a]



Henry Alexander, The laboratory of Thomas Price, 1887

Abstract: Any kind of device or machine requires a substrate, energy, and information signals. If we wish to operate at the nanometer scale, we must use molecules as substrates. Energy- and signal-processing at a molecular level relies on cause/effect relationships between the input supplied and the kind of process obtained. We have classified energy- and signal-processing at the molecular level according to the nature of the input (electronic, photonic, or chemical) and the nature of the obtained effect (electronic, photonic, or chemical process that follows). By coupling the three kinds of inputs with the three types of resulting processes, nine types of molecular-based processes (electronic, photonic, chemionic, electrophotonic, electrochemionic, photoelectronic, photochemionic, chemiophotonic, and chemioelectronic) can be identified. In this concept article, looking at molecular transformations in an unconventional way, we have tried to give a flavor of some of the new features that project the old science of chemistry towards novel achievements.

Keywords: chemionics · electron transfer · energy transfer · molecular devices · molecular electronics · molecular photonics

Introduction

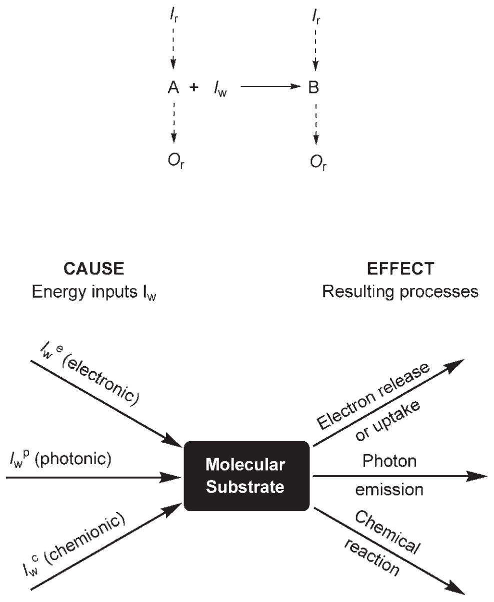
Chemistry is one of the oldest sciences. At the beginning, "… chemistry was the art of making substances change, or watching their spontaneous transformations. Ice turned into water, water could be made to boil. Grape juice or sugar cane mash turned into alcohol, and if you didn't intervene, it turned again, into vinegar. The colorless fluid in the gland of a Mediterranean sea snail, when exposed to air and sunlight, turned yellow, green, and finally a purple that could dye a skein of wood and hold fast".[1]

In the past century chemistry became the science of molecules: natural molecules discovered in the world in which we live, artificial molecules invented by chemists in their laboratories. Until ten years ago it was thought that "the most creative act in chemistry is the design and creation of new molecules".[2] In the meantime, the concept of supramolecular chemistry[3] began to permeate a substantial part of chemical research. Today, spontaneous transformations are still investigated and synthesis continues to be the most important field of chemical research. In the last ten years, however, quite new aspects of chemistry have also emerged. A variety of molecular devices and machines powered by chemical, photochemical, and electrochemical inputs have been constructed,[4] and novel conceptual interpretations[5] of old classes of chemical reactions have opened new scenarios on the potentiality of chemistry for signal-processing at the molecular level. In this concept article, looking at molecular transformations in an unconventional way, we have tried to give a flavor of such new features that projects chemistry in the fields of information science and nanotechnology.

Inputs and Outputs

Any kind of device or machine requires a substrate, energy, and information signals. If we wish to operate at the nanometer scale, we must use molecules as substrates. Molecules are nanometer-size entities that can exploit energy and signals to operate as devices and machines, particularly when suitably assembled in supramolecular systems.

A general scheme for the operation of molecule-based devices and machines is shown in Scheme 1 (top). We start with a species A, the properties of which can be monitored (read) by a suitable input, input reading I_r(A) (e.g., absorption spectroscopy), that generates an output, output reading O_r(A). Then, we write information on A by an energy input, input writing, I_w(A→B), that converts A into B. Since A and B are molecules, the writing process must be a chemical reaction.[6] Reading the system with I_r(B) after application



Scheme 1. Top: A general scheme for the operation of molecule-based devices and machines. I_r, and O_r are reading inputs and output that reveal the state of the system. I_w is a writing input that converts A into B. I_w can be an electronic (I_w^e), photonic (I_w^p), or chemical (I_w^c) input. Bottom: Schematic representation of the cause/effect relationships of energy inputs operating on molecular substrates.

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[a] Prof. V. Balzani, Prof. A. Credi, Prof. M. Venturi
Dipartimento di Chimica "G. Ciamician"
Università di Bologna, via Selmi 2, 40126 Bologna (Italy)
Fax: (+39) 051-209-9456
E-mail: vincenzo.balzani@unibo.it

of I_w yields an output, $O_r(B)$, that reveals the new state of the system.

In the case of a machine, I_w is responsible for the operation, while I_r and O_r monitor the machine movement.[4,7] In the case of a device for information processing, the performed function is based on the relationship among I_r, O_r, and I_w.[4,7,8]

The most important energy inputs to write on molecules are electronic (I_w^e), photonic (I_w^p), and chemical (I_w^c) in nature. The reading inputs I_r are multifarious; indeed, any kind of physical signals can be used but, for several reasons, electronic, photonic, and chemical outputs are most often used.

The operation of molecular devices and machines[4,7–9] relies on cause/effect relationships between writing inputs and kind of process obtained (as revealed by reading techniques). Therefore, it may be useful to categorize molecular devices and machines according to the nature of the cause (electronic, photonic, or chemical input) and the nature of the effect (electronic, photonic, or chemical process that follows). In the simplest case, input and resulting process have the same nature: an electronic input can generate release of an electron (molecular electronics), absorption of a photon can generate emission of a photon (molecular photonics), and a chemical input can generate a chemical reaction (molecular chemionics). It is also possible, however, to have molecules that convert an input into a process of different nature. For example, a chemical reaction can generate emission of a photon, and an electronic input can generate a chemical reaction. Furthermore, it is possible to stimulate a molecule (even better a supramolecular system) with a sequence of inputs of the same or different nature and to obtain processes of the same or different types. For example, a chemical reaction of a molecule followed by absorption of a photon can generate emission of a photon that would not have been emitted by the original molecule.

Therefore, besides molecular electronics, molecular photonics, and molecular chemionics, six cause/effect crossing couples can be considered, corresponding to: electrophotonics, electrochemionics, photoelectronics, photochemionics, chemiophotonics, and chemioelectronics (Scheme 1, bottom).

We will briefly illustrate, with a few elementary examples, the nine categories of systems obtained by coupling the three kinds of single writing inputs with the three types of resulting processes.

Molecular Electronics

Great effort is currently devoted to the design and construction of single-molecule electrical devices[10] and the subsequent fabrication of simple molecular-scale circuits.[11] Such electrical circuits would be much smaller than the corresponding micron-scale digital logic circuits fabricated on conventional solid-state semiconductor chips. For the sake of comparison, a typical organic molecule is around 0.3 nm wide, which means that it would take about 200 of these molecules, side by side, to span the 65 nm width of the metal wires used in advanced logic chips being made today.[12] By using molecules, it should be possible to make molecular gates about one million times smaller in area than the corresponding logic elements fabricated by using transistor-based circuits.[11a]

In principle, molecular electronics is based on electron-transfer processes between and through molecules. Such processes are well known to biologists and chemists. In nature, although they are not used for processing information, electron-transfer processes perform a most fundamental function in energy conversion. Green-plant photosynthesis, in which the energy of sunlight is converted into fuels, involves a sequence of photoinduced electron-transfer reactions that occur in suitably evolved supramolecular proteins arrays.[13] In chemistry, a great variety of electron-transfer processes have been investigated in solution, both between separated molecules and within supramolecular systems.[14] The principles that govern the occurrence of chemical and biological electron-transfer processes have largely been elucidated.

Molecular electronics can take advantage from this body of biological and chemical knowledge, but its task is much more difficult: molecules have to perform their role not in solution as in chemical experiments, but in the solid state, in which they have to be suitably oriented between and connected with at least two metal contacts to conduct, switch, or rectify an electric signal. Furthermore, the information-processing function does not depend on a single molecular junction, but on the architecture of the whole molecular array (Figure 1).

Recently, significant progress has been made in this field.[15] However, despite the efforts of many laboratories,

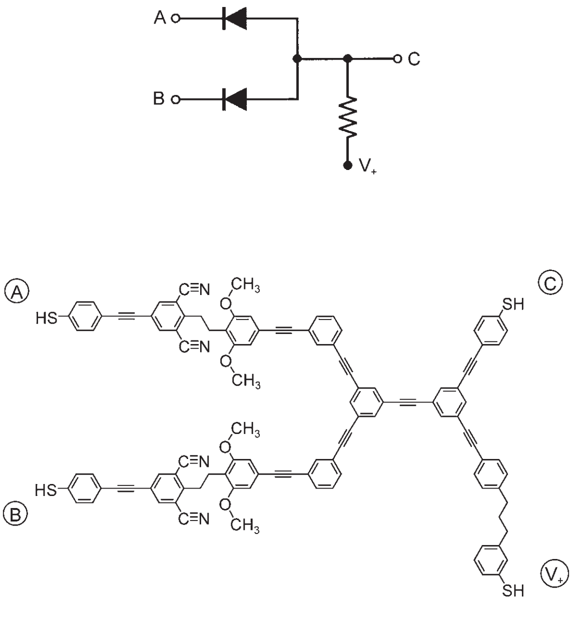


Figure 1. Molecular electronics: electronic circuit scheme (top) and molecular implementation (bottom) of a diode–diode AND logic gate.[11a]

much remains to be learned about the electrical properties of molecules and how these properties correlate with the molecular structure.[16] In a few instances it has been shown that the experimental current-voltage (i-V) curves have a true molecular origin and depend on the specificity of the molecular orbitals (Figure 2).[17] However, the nature of the molecule–metal contact and the specific geometry of the junction are often not controllable and interfacial or metallic effects can easily be confused with purely molecular mechanisms.[18–21] There are also difficulties concerning the means of manipulating, bonding, and ordering molecules in circuit-like structures. By analogy to conventional microelectronics, it should be determined how molecular components may be combined to realize useful electronic functions.[22–24]

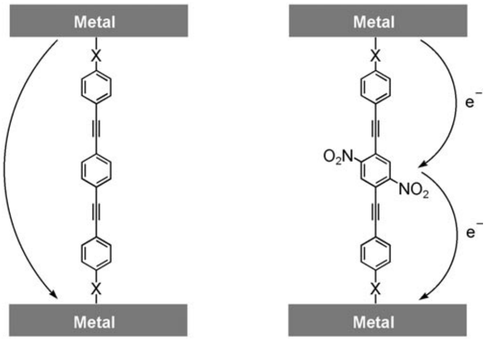


Figure 2. Molecular electronics: schematic representation of proposed models for electron transfer through monolayers. Left: tunneling through a molecule; right: tunneling through an intermediate molecular orbital on central substituted benzene ring.[17b]

Although the theoretical and practical barriers to designing molecular circuits may be formidable, the large number of degrees of freedom in molecular structure yields vast flexibility in how molecular electronic devices may be developed.

Molecular Photonics

An alternative possibility to the use of electron fluxes as a means for processing signals is that of using photon fluxes.[25] 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.

The photonic properties of single molecules are easily studied by spectroscopy.[26] Light-harvesting in the natural photosynthetic process takes place by migration of the excitation energy within molecular arrays.[27,28] Excitation transfer along molecular wire "waveguides" from an excited to a ground state molecule, which is equivalent to an input/output couple of photonic signals, is a well-known process that can occur by Förster or Dexter mechanism.[4,29,30]

Interesting molecular photonic wires are compounds in which the two chromophoric units, that is, the donor and the acceptor, are connected by rigid, modular spacers, as in the case of the $[\{Ru(bpy)_3\}^{2+}\text{-}(ph)_n\text{-}\{Os(bpy)_3\}^{2+}]$ (ph = 1,4-phenylene; $n = 2, 3, 4, 5$) species (Figure 3).[31] In such compounds, excitation of the $[Ru(bpy)_3]^{2+}$ moiety is followed by energy transfer to the $[Os(bpy)_3]^{2+}$ unit, as shown by the sensitized emission of the latter (CH_3CN, 293 K). The lowest energy level of the bridge decreases slightly as the number of phenylene units is increased, but always lies above the donor and acceptor levels involved in energy transfer. A further decrease in the energy of the triplet excited state of the spacer would involve such an excited state as an intermediate (hopping mechanism),[32] similar to what happens for photoinduced electron transfer.[33] In the series of compounds shown in Figure 3, the energy-transfer rate decreases with increasing the length of the oligophenylene spacer ($n = 2$, $k = 2.5 \times 10^{11}\ s^{-1}$; $n = 3$, $k = 5.9 \times 10^{10}\ s^{-1}$; $n = 4$, $k = 4.1 \times 10^{9}\ s^{-1}$; $n = 5$, $k = 4.9 \times 10^{8}\ s^{-1}$). Such rate constants are much higher than those expected for a Förster-type mechanism, whereas they can be accounted for by a superexchange Dexter mechanism, as suggested by the linear plot obtained for $\ln k$ against metal–metal distance, with a β value of 0.50 Å^{-1}. The values obtained for energy transfer in the

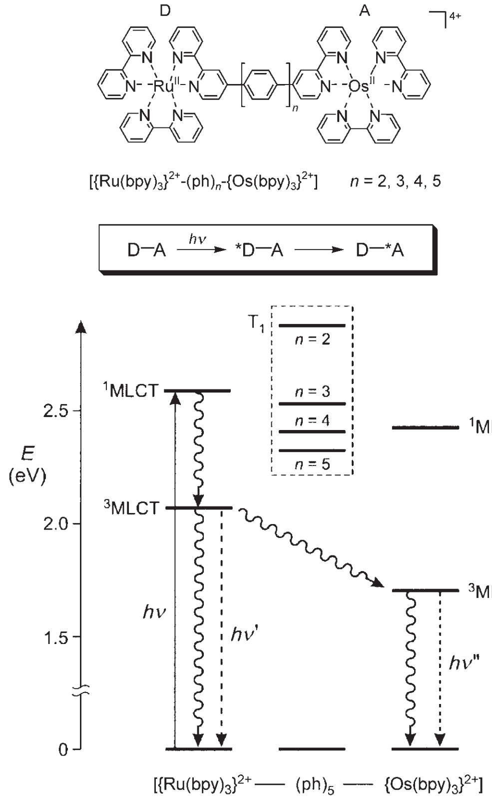


Figure 3. Structure of compounds $[\{Ru(bpy)_3\}^{2+}\text{-}(ph)_n\text{-}\{Os(bpy)_3\}^{2+}]$ and energy-level diagram for the energy-transfer process.[31]

series of compounds $[\{Ru(bpy)_3\}^{2+}\text{-}(ph)_nR_2\text{-}\{Os(bpy)_3\}^{2+}]$,[34] in which the central phenylene unit carries two hexyl chains, are much lower than those found for the unsubstituted compounds, most likely because the bulky substituents R increase the tilt angle between the phenyl units. A strong decrease in the rate constant is observed when the Ru-donor and Os-acceptor units are linked by an oligophenylene bridge connected in *meta*-position.[35,36]

Photons can excite molecules in the gas phase, in solution, and in the solid state. However, the position of the molecule in the sample, even in the solid state, remains ill-defined because the wavelength of light, including the ultraviolet spectral region, is by far greater than the molecular dimensions. Therefore selective excitation of a specific molecule in a supramolecular array is prevented. This is the reason why a solid-state photonic technology at the molecular level for information processing has not been developed. Devices for guiding electromagnetic radiations on a scale below the diffraction limit would be needed for designing molecular-level optical circuits. Progress in near-field optical techniques[37] and electromagnetic energy transport in metal nanoparticle plasmon waveguides[38] might open this possibility.

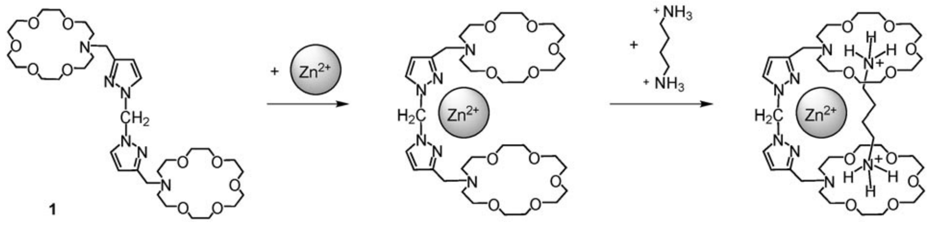
Molecular Chemionics

Instead of electrons or photons, chemical entities (molecules or ions) can be used as writing inputs on molecular substrates. Because chemical processes occur at the molecular level by their own nature, molecular chemionics could simply be called chemionics.

Chemionics is based on chemical reactions and therefore it usually concerns solution systems. Chemionics is the most important means for information processing in nature. Besides the information exchange between DNA and RNA, it should be recalled that in our brain neurons process signals relying on the behavior of ions, and that the activity of enzymes is regulated by the so-called allosteric effect; that is, by changes in shape produced by binding molecules or ions.[39,40] Two of the most important sensory systems, taste[41] and smell,[42] as well as pheromonal communication in vertebrates[43] and bacterial conversations[44] are based on chemical signals.

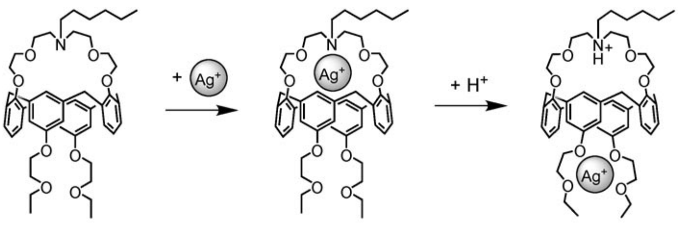
The most important features of chemionics are molecular recognition and changes in molecular structure. These interconnected processes, ubiquitous in nature,[39,40] have been extensively investigated in the last 30 years for artificial systems in the frame of the development of supramolecular chemistry.[3,45] Metal-ion coordination, host–guest pairs and, more generally, a variety of adducts based on intermolecular forces (e.g., hydrogen bonds, and hydrophobic and donor–acceptor interactions) have been thoroughly studied in relation with structural changes. Allosteric effects in artificial systems are also very common.[46] Chemionic signals govern a great number of threading/dethreading processes of molecular wires with molecular rings as well as of mechanical movements in molecular machines.[4,7] A few examples of chemionic processes will now be illustrated.

A classical example of allosteric effect is that of compound **1** (Scheme 2),[47] which consists of two crown ethers linked by heteroaromatic rings. The two crown ethers can cooperatively interact with a suitable alkyldiammonium ion, whereas the two pyrazole rings can coordinate a metal ion like Zn^{2+}. The metal-ion coordination (input) affords a positive allosteric effect towards diammonium complexation.[47b]



Scheme 2. Molecular chemionics: a chemical input on compound **1** generates a reaction by positive allosteric effect.[47b]

Another example of single-input chemionic process is given by the so-called "molecular syringe" (compound **2** in Scheme 3),[48] which uses a 1,3-alternate calix[4]arene as a tube that carries a nitrogen-containing crown cap on one side and two ethoxyethoxy groups on the other side. An Ag^+ ion, which is coordinated to the azacrown ether, is pushed through the tube to the side carrying the twin ethoxyethoxy groups when the nitrogen atom in the crown cap is protonated. On deprotonation of the nitrogen atom, the Ag^+ ion is sucked back through the middle of the calixarene once again.



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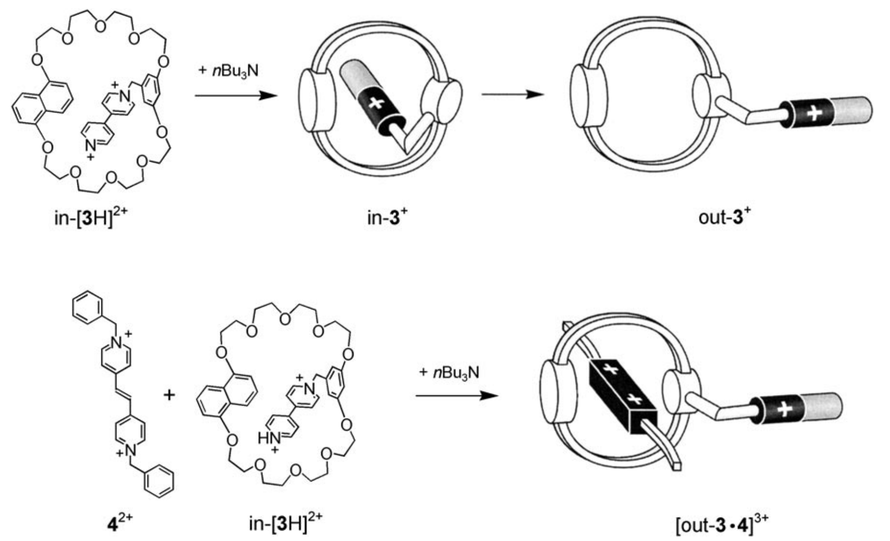
Scheme 3. Molecular chemionics: acid-based metal pumping in a "molecular syringe".[48]

An example of chemionic input governing threading/dethreading processes is given by compound $[\mathbf{3}H]^{2+}$ (Scheme 4, top) which is self-complexed (in-$[\mathbf{3}H]^{2+}$) in CH_2Cl_2 because of 1) the donor–acceptor interaction between the 1,5-dioxynaphthalene electron donor and the bipyridinium electron-acceptor moiety, and 2) the more favourable environment offered to the dication by the macro-



Scheme 4. Molecular chemionics: the base-induced dethreading of *in*-[**3**H]$^{2+}$ to give *out*-**3**$^+$ (top) and complexation of **4**$^{2+}$ by compound **3**$^+$ (bottom).[49]

cycle oxygens compared with the nonpolar solvent molecules.[49] Dethreading can be obtained upon addition of tributylamine which leads to the deprotonated compound in-**3**$^+$, that dethreads to give out-**3**$^+$. The process can be reversed quantitatively by adding trifluoroacetic acid. The base-driven dethreading can also be used to trigger the complexation of an external electron acceptor guest, **4**$^{2+}$, into the macrocyclic cavity of **3**$^+$ as schematically shown in Scheme 4 (bottom).[49]

Molecular Electrophotonics

Molecular electrophotonics concerns systems in which an electronic input I_w^e on (i.e., an electron transfer to) a molecule causes the emission of a photon. This is the realm of chemiluminescent processes based on electron-transfer reactions that can occur not only in solution, but also in the solid state.

Solution systems: It has long been known that, in solution, a luminescent excited state can be obtained upon outer-sphere electron-transfer processes involving suitable oxidizing or reducing species. For example, one-electron reduction of $[Ru(bpy)_3]^{3+}$ can lead to the luminescent $^*[Ru(bpy)_3]^{2+}$ excited state [Eqs. (1) and (2)]:

$$[Ru(bpy)_3]^{3+} \xrightarrow{+e^-} {}^*[Ru(bpy)_3]^{2+} \quad (1)$$

$$^*[Ru(bpy)_3]^{2+} \rightarrow [Ru(bpy)_3]^{2+} + h\nu \quad (2)$$

In the simplest example, the electron comes from a semiconductor electrode (Ta_2O_5) at a suitable potential.[50] In most cases, the strong oxidant and/or the strong reductant are species generated electrochemically. The latter systems could also be defined chemiophotonic, because the electron input derives from a molecule. The term chemiophotonics, however, can be reserved to systems in which the chemical input originates from a reaction that does not involve outer-sphere electron transfer (vide infra).

Solid state: Electrophotonics in the solid state is of the greatest interest, because it is the working principle of molecular light-emitting diodes.[51] In these devices an electron (hole) injected by an electrode into a solid-state matrix migrates to meet a positive (negative) ion, formed close to the other electrode, to generate an excited state that either undergoes radiative deactivation or sensitizes the luminescence of another species. In several cases, molecular species are used for electron and hole carriers as well as emitting species (organic light-emitting diodes, OLED, Figure 4).

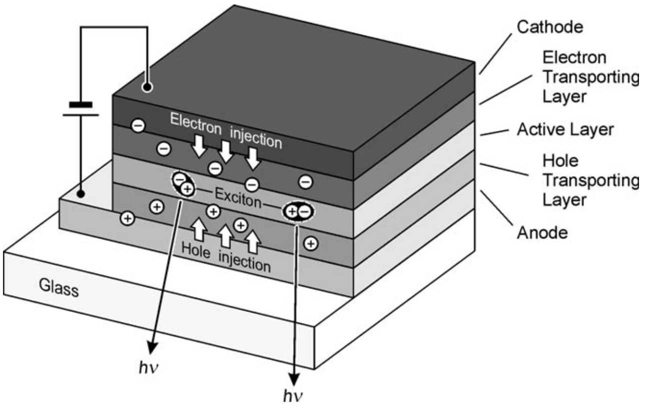


Figure 4. Molecular electrophotonics: working mechanism of an organic light emitting diode.

Molecular Electrochemionics

Molecular electrochemionics concerns systems in which an electronic input I_w^e on a molecule generates a chemical reaction. This is the field of electrochemical processes followed by a chemical reaction.

An example is given by the one electron reduction of $[Co(NH_3)_6]^{3+}$ [Eq. (3)] that in aqueous solution is followed by the release of the six NH_3 ligands [Eq. (4)]:[52]

$$[Co(NH_3)_6]^{3+} \xrightarrow{+e^-} [Co(NH_3)_6]^{2+} \quad (3)$$

$$[Co(NH_3)_6]^{2+} \rightarrow Co^{2+} + 6\,NH_3 \quad (4)$$

Another example of electro-chemionic process is illustrated in Scheme 5.[53] Receptor **5** consists of a hydrogen-bonding moiety linked to an anthracene unit and receptor **6** is an acylated diaminopyridine. Both hosts can undergo three-point hydrogen-bonding interactions with naphthalene diimide guest **7**. Owing to stacking interactions, in $CHCl_3$ receptor **5** binds **7** more than an order of magnitude stronger than **6** (Scheme 5a), whereas $\mathbf{7}^-$ exhibits a larger affinity for **6**, because of the stacking interactions between **5** and $\mathbf{7}^-$ are prevented (Scheme 5b). Therefore, upon one-electron reduction of [**5·7**], $\mathbf{7}^-$ translocates from **5** to **6** (Scheme 5c). Processes of this type can also occur on derivatized electrodes.[54]

An example related to molecular machines is illustrated by the switching of catenane $\mathbf{8}^{4+}$ (Scheme 6).[55] This compound is made of a symmetric tetracationic ring containing two electron-acceptor bipyridinium units and a nonsymmetric ring comprising two different electron-donor units, namely a tetrathiafulvalene (TTF) group and a 1,5-dioxynaphthalene (DON) unit. Because the TTF unit is a better electron donor than DON, as witnessed by the potentials values at which their oxidations occur, the thermodynamically stable conformation of the catenane is that in which the symmetric ring encircles the TTF unit of the non-symmetric one (Scheme 6a). On electrochemical oxidation in solution, the TTF unit loses its electron-donor power and acquires a positive charge (Scheme 6b). As a consequence it is expelled from the cavity of the tetracationic ring and is replaced by the neutral DON unit (Scheme 6c). At this stage, subsequent reduction of the oxidized TTF unit restores its electron-donor ability and the system goes back to its original conformation.

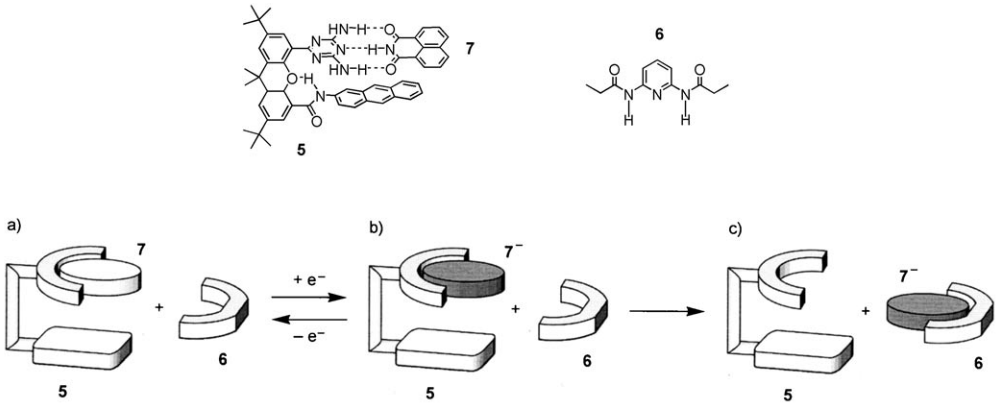
Molecular Photoelectronics

Photoelectronics in the solid state is of the greatest interest for a variety of applications (optoelectronics).[56] In these devices, photon fluxes are converted into electric current. Molecular photoelectronics concerns systems in which a photonic input I_w^p on a molecule causes the release of an electron (or hole). This process is quite common because an excited molecule is always a better reductant and a better oxidant than the ground-state molecule.[4,57]

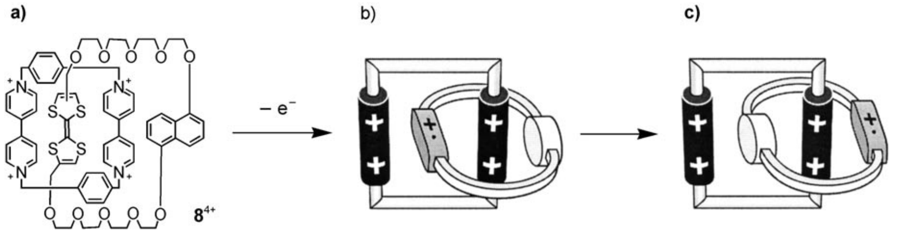
In the natural photosynthetic system, a photoexcited molecule (the so called "special pair" that can be excited directly by light absorption or indirectly by energy migration) transfers an electron to a nearby molecule, thereby initiating the charge separation process that ultimately leads to oxygen generation and carbon dioxide reduction.[13]

In artificial systems, photoinduced electron transfer (PET) has been extensively investigated in homogeneous and heterogeneous systems.[14] A few examples will now be illustrated.

Photoinduced electron transfer in homogeneous systems: In suitably designed multicomponent systems light excitation of a component leads to efficient electron-transfer processes. Extensive studies have been performed on electron transfer in donor–acceptor (D-A) systems in which the donor is a

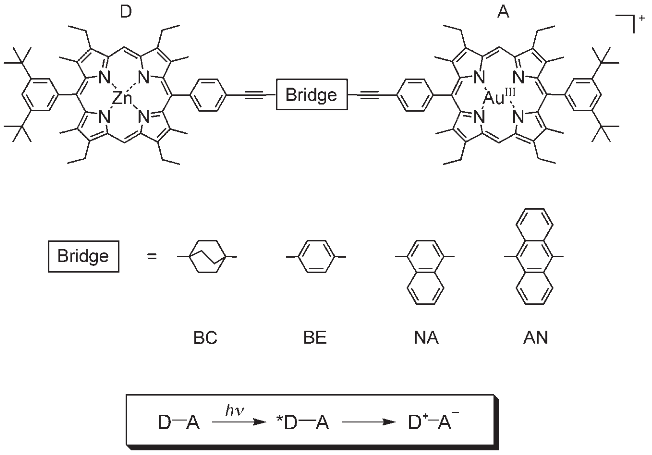


Scheme 5. Molecular electrochemionics: electrochemical control of the molecular recognition process involving receptors **5** and **6** and guest **7**.[53]



Scheme 6. Molecular electrochemionics: electrochemically driven switching of catenane $\mathbf{8}^{4+}$.[55]

zinc–porphyrin (ZnP) and the acceptor a gold(III)–porphyrin (AuP^+) linked by an aromatic conjugated bridge (Scheme 7).[58] When the bridge is NA, the photoinduced electron transfer occurs by a superexchange mechanism in a weakly polar solvent (2-methyltetrahydrofuran), whereas in polar solvents (butyronitrile and dimethylformamide) both superexchange and sequential (hopping) electron-transfer processes are observed. Comparison of the data obtained for the compounds in which bridge = BC, BE, NA, and AN have shown that both donor–acceptor distance and the barrier height (ΔE_{DB}) affect the electron-transfer rate constant.[59]



Scheme 7. Donor–acceptor porphyrin-based dyads linked by phenylethynyl-based bridges used for photoinduced electron-transfer studies.[58]

Photoinduced electron transfer in several dyads, triads, tetrads, and pentads is discussed in more detail in reference [4].

Photoinduced potential generation in heterogeneous systems: Conversion of photonic inputs into released electrons also takes place in dye-sensitized semiconductor cells.[60] These systems (Figure 5) are composed of a photosensitizer P (e.g., a complex of the Ru–bpy family) linked in some way onto a semiconductor electrode. The sensitizer, upon light excitation (step 1, Figure 5), injects an electron into the conduction band of the semiconductor (step 2).[61] In order to exploit this photoinduced potential generation, the oxidized sensitizer should be reduced by a relay molecule, which then diffuses to discharge at the counter electrode. As a result, a photopotential is generated between the two electrodes in open circuit conditions, and a corresponding photocurrent can be obtained upon closing the external circuit through an appropriate load (Grätzel cells).[60]

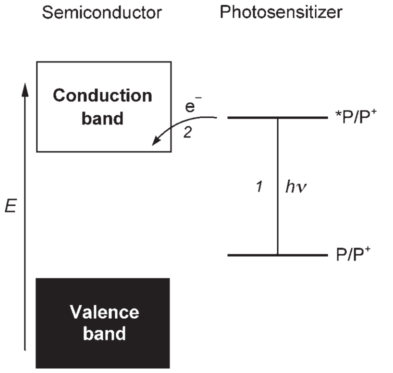


Figure 5. Molecular photoelectronics: working principle of a photosensitized (*n*-type) semiconductor cell. P is a dye linked onto a semiconductor electrode.[60]

Molecular Photochemionics

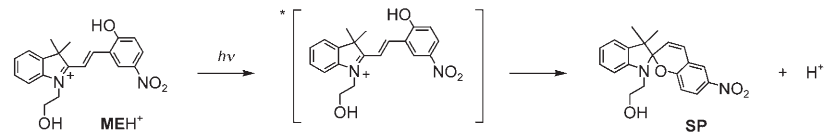
Molecular photochemionics relates to systems in which a photonic input $I^{\mathrm{P}}_{\mathrm{w}}$ on a molecule causes formation of an excited state that undergoes a chemical reaction. In principle, this kind of writing on molecules takes place in any photochemical reaction.

In nature, the first step of the vision process is caused by a photon input that causes the *trans*→*cis* isomerization of a retinal molecule.[62] In artificial systems photochemical reactions have been extensively investigated in solution.

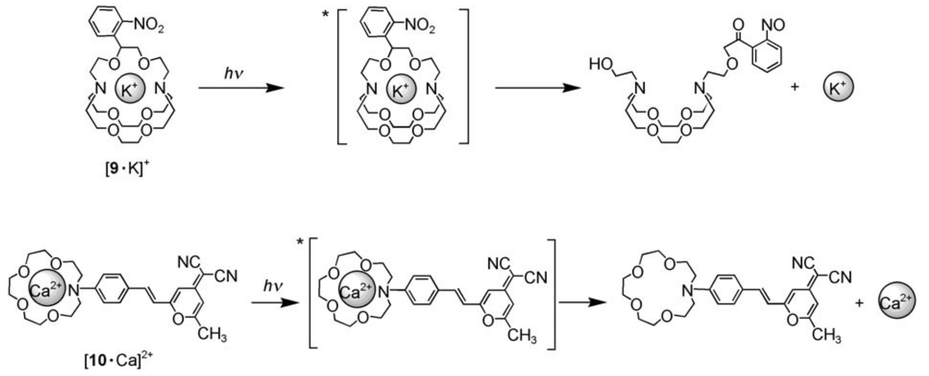
A few paradigmatic examples of chemical processes generated by photonic excitation of molecules or supramolecular systems will now be illustrated. Many other examples are available because photon inputs are used to supplying energy to a great variety of molecular devices and machines.[4,7,8,63]

Proton release or uptake: Photoexcitation of a molecule leads to electronically excited states that usually are stronger acids and bases compared to the ground state.[64] In most cases, proton release (uptake) from the excited state is immediately followed by proton uptake (release) upon deactivation to the ground state. However, when protonation–deprotonation is accompanied by changes in the molecular structure, protons can be permanently released or uptaken. For example (Scheme 8), the protonated merocyanine form (**ME**H^+) releases a proton upon excitation with visible light with formation of the stable spiropyrane derivative (**SP**).[65]

Metal-ion release: In artificial receptor systems, release of metal ions is possible as a result of photonic excitation. An example is shown by the cryptand [**9**·K]$^+$ (Scheme 9, top)[66] which, upon light excitation, undergoes irreversible decomposition. As a result, the free K^+ concentration increases permanently. By contrast, the photoreaction of compound [**10**·Ca]$^{2+}$ (Scheme 9, bottom) is reversible[67] and therefore leads to a transient increase in the Ca^{2+} concentration. Photonic excitation causes fast photoejection (picosecond time scale) of the metal ion, because the stability constant of the complex in the excited state is about two orders of magnitude lower than in the ground state, but after deactivation of the excited state the metal ion is again coordinated. Other examples have been reported.[68] This kind of photo-



Scheme 8. Molecular photochemionics: upon photoexcitation the protonated form of merocyanine, **ME**H$^+$, releases a proton giving the spiropyrane derivative **SP**.[65]



Scheme 9. Molecular photochemionics: photocleavable cryptand [**9**⋅K]$^+$ (top);[66] photoejection of Ca^{2+} from [**10**⋅Ca]$^{2+}$ (bottom).[67]

chemionic processes might be of biological interest because many physiological functions are controlled by localized fluctuations of intracellular metal ion concentration.

Anion release: Photonic inputs can also be used to obtain anion release. An example is given by the $[Co(CN)_6]^{3-}$ metal complex,[69] which upon excitation by 254 or 365 nm light [Eq. (5)], releases a CN$^-$ ligand from its coordination sphere [Eq. (6)]. In acid or neutral aqueous solution the CN$^-$ release is evidenced by an increase in pH of the solution because the free CN$^-$ undergoes protonation [Eq. (7)]. Compound $[Co(CN)_6]^{3-}$ can thus be considered a photobase. The reactions given in Equations (5)–(7) have been exploited in a more complex system to mimic some elementary properties of neurons.[69]

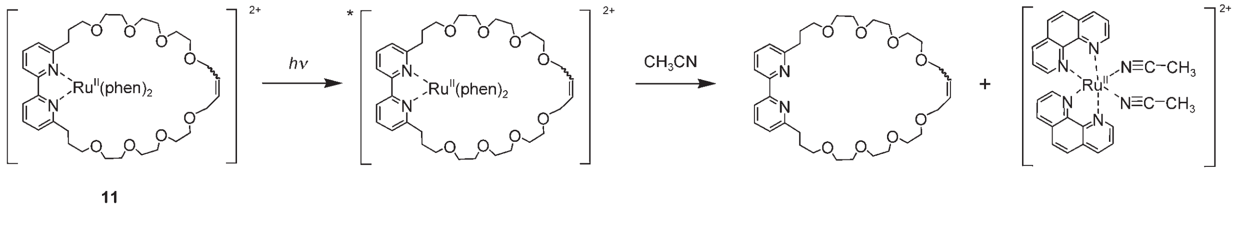
$$[Co(CN)_6]^{3-} \xrightarrow{+h\nu} {}^*[Co(CN)_6]^{3-} \qquad (5)$$

$$^*[Co(CN)_6]^{3-} \xrightarrow{+H_2O} [Co(CN)_5(H_2O)]^{2-} + CN^- \qquad (6)$$

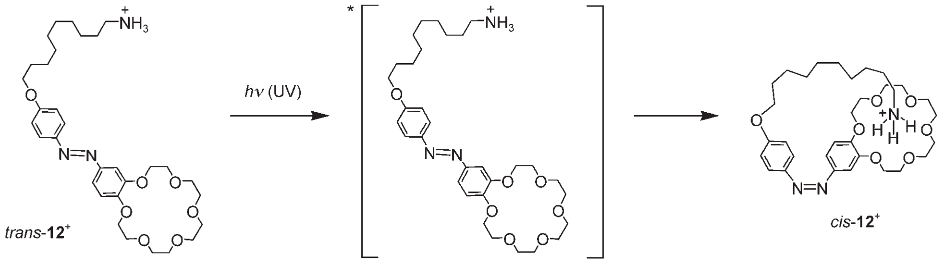
$$CN^- + H_3O^+ \rightarrow HCN + H_2O \qquad (7)$$

Molecule release: Photorelease of caged compounds is extensively used for control of cellular chemistry and physiology.[63] A simple example, taken from a different field, of reversible molecule release as a consequence of a photonic input is illustrated in Scheme 10. Compound **11** consists of a $[Ru(phen)_2]^{2+}$ fragment coordinated to a bipyridine ligand incorporated in a macrocycle.[70] Upon light excitation in acetonitrile, the macrocycle is released from the $[Ru(phen)_2]^{2+}$ fragment. The reaction can be reversed by replacing CH_3CN with ethylene glycol as a solvent and boiling the mixture for two hours. Extension of this photochemionic effect includes the replacement of the $[Ru(phen)_2]^{2+}$ fragment with other metal coordination centers[71] and of the macrocyclic ligand with other chelate ligands,[72] with the purpose of designing light-driven molecular machines.

Configurational changes: Photonic inputs can cause a variety of configurational changes in suitably designed molecules and supramolecular systems. For example, the photoinduced *trans*→*cis* isomerization of azobenzene induces intramolecular complexation in the self-complementary compound **12**$^+$ shown in Scheme 11.[73] This compound incorporates a macrocyclic polyether head bridged by a photoactive azobenzene unit to a linear tail bearing a terminal ammonium group. In the *trans* isomer, the ammonium recognition site is positioned away from the complementary macrocyclic head. Upon photoexcitation, however, *trans*→*cis* isomerization occurs, bringing the ammonium recognition site into close proximity with the crown ether head and allowing their intramolecular association.



Scheme 10. Molecular photochemionics: in compound **11** light excitation causes the detachment of the bipyridine-containing macrocyle from the $[Ru(phen)_2]^{2+}$ fragment.[70]

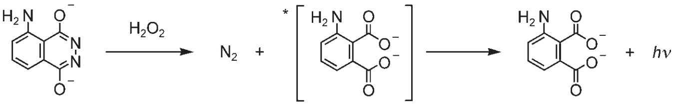


Scheme 11. Molecular photochemionics: the photoinduced isomerization of the azobenzene unit of $\mathbf{12}^+$ is accompanied by the motion of the cationic tail which can only interact with its macrocyclic head in the *cis* isomer.[73]

Molecular Chemiophotonics

Molecular chemiophotonics relates to systems in which a chemical input I_w^c on a molecule generates emission of a photon. As mentioned above, chemionic inputs imply the occurrence of chemical reactions, which usually occur in solution. Molecular chemiophotonics processes are more generally known as chemiluminescent processes. They are very common in nature (bioluminescence)[74] and have extensively been studied in artificial systems.[75]

A classical example is given by the chemiluminescent reaction of luminol.[76] The dianion obtained from luminol in basic solution (Scheme 12) reacts with hydrogen peroxide eliminating a molecule of nitrogen and producing the excited state of a dicarboxylate ion which undergoes radiative decay.



Scheme 12. Molecular chemiophotonics: the chemiluminescent reaction of luminol.[76]

Molecular Chemioelectronics

Molecular chemioelectronics concerns systems in which a chemical input I_w^c on a molecule causes the release of an electron (or hole).

The simplest case is that of a chemical input that causes a change in the redox potential of a molecular substrate. Such a behavior is usually observed in the electrochemistry of metal complexes, host–guest systems, and other adducts.

For example, in acetonitrile the Cu^+ ion does not undergo oxidation at −0.90 V relative to SCE [Eqs. (8)–(10)],[77] whereas upon complexation with the cyclam (1,4,8,11-tetraazacyclotetradecane) ligand it does:[78]

$$Cu^+ \overset{-0.90\,V}{\nrightarrow} Cu^{2+} + e^- \tag{8}$$

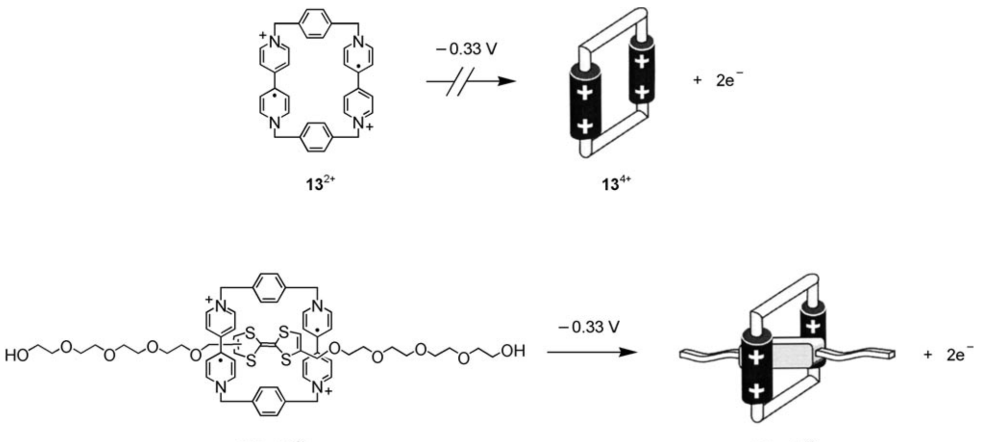
$$Cu^+ + \text{cyclam} \rightarrow [Cu^+(\text{cyclam})] \tag{9}$$

$$[Cu^+(\text{cyclam})] \xrightarrow{-0.90\,V} [Cu^{2+}(\text{cyclam})] + e^- \tag{10}$$

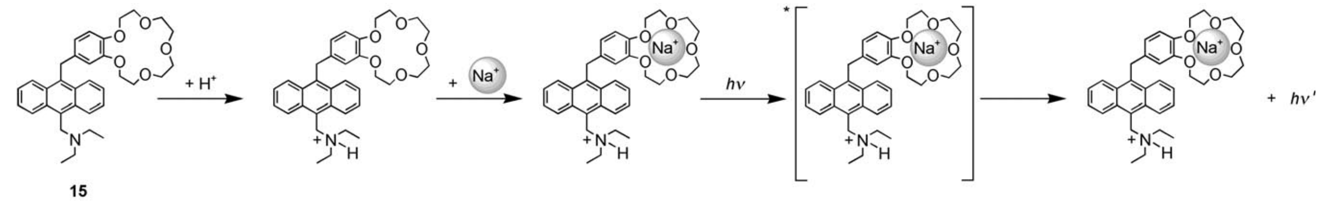
Another example is illustrated in Scheme 13. In acetonitrile the dicationic cyclophane $\mathbf{13}^{2+}$ cannot be oxidized to its tetracationic species $\mathbf{13}^{4+}$ at −0.33 V relative to SCE, whereas it does when threaded by the electron-donor wire **14**.[79]

Multiple Inputs/Processes

Multiple (in nature and number) inputs and resulting processes are also possible. An endless variety of electronic and/or photonic and/or chemionic inputs can indeed be con-



Scheme 13. Molecular chemioelectronics: the dicationic cyclophane $\mathbf{13}^{2+}$ cannot be oxidized to its tetracationic species $\mathbf{13}^{4+}$ at −0.33 V relative to SCE, but it does when threaded by the electron-donor wire **14**.[79]

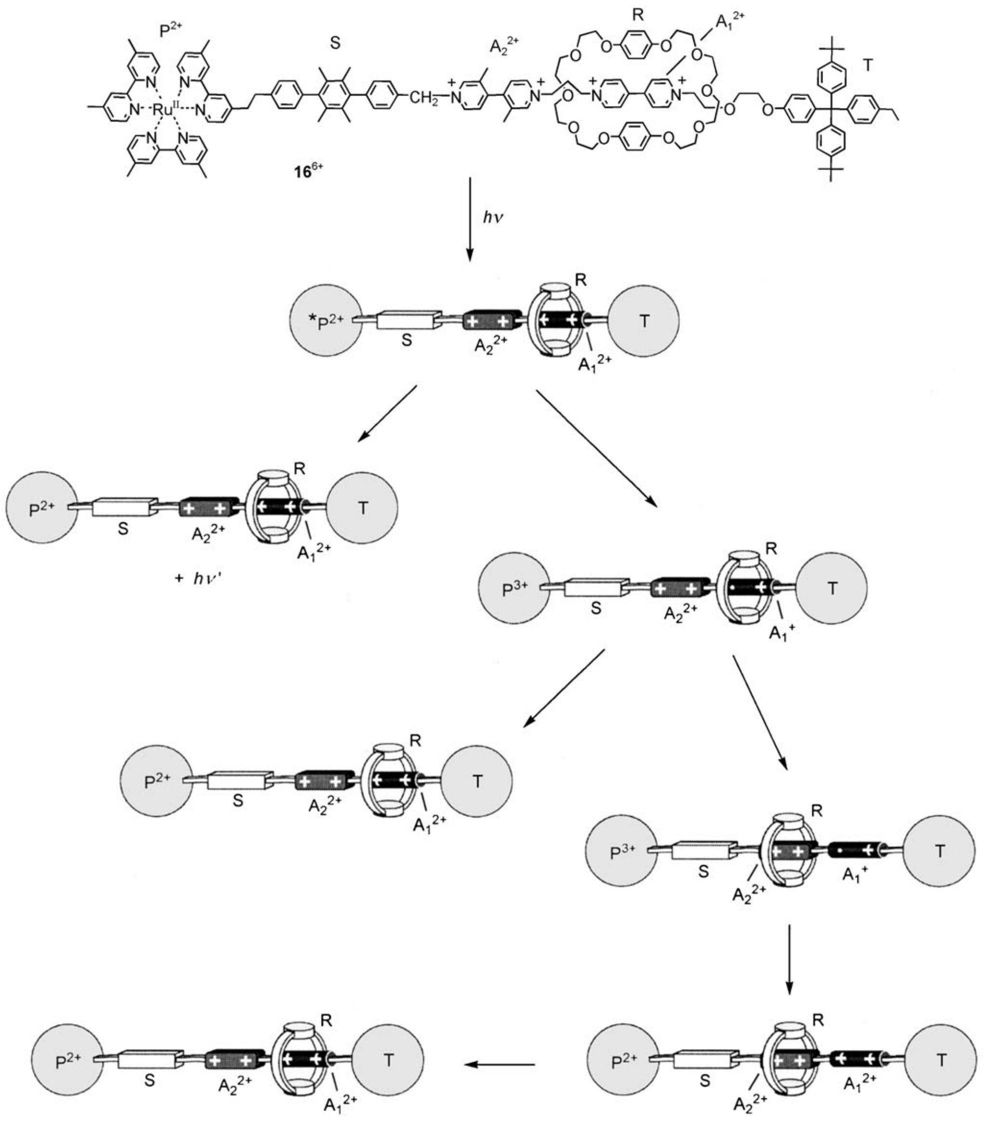


Scheme 14. A sequence of two chemical and a photonic inputs on compound **15** generates photon emission.[80]

ceived for designing functional molecular-level systems.[4,7–9] For space reasons, we illustrate only a few examples.

A sequence of two chemical and a photonic inputs generating photon emission: The anthracene derivative **15** (Scheme 14) does not exhibit an appreciable luminescence in methanol solution. Upon addition H^+ (chemical input I^c_{w1}) and Na^+ (chemical input I^c_{w2}), excitation with 377 nm light (photonic input, I^p_{w3}) generates luminescence at 428 nm.[80] This compound behaves as an AND logic gate. Systems of this kind have opened new avenues towards molecular logics,[5,8,81] molecular computation,[82] and molecular computational identification.[83]

Two electrochemical inputs in parallel generating a chemical and a photonic process in a sequence: This kind of behavior is shown by electrochemiluminescent reactions.[84] For example, in a solution of $[Ru(bpy)_3]^{2+}$ in acetonitrile, upon appli-



Scheme 15. Parallel and serial processes generated by a photonic input on rotaxane $\mathbf{16}^{6+}$.[86]

cation of an alternating potential (+1.5 V, I_{w1}^{c}, and −1.5 V, I_{w2}^{c}, relative to SCE), the species $[Ru(bpy)_3]^{3+}$ and $[Ru(bpy)_3]^{+}$ are generated [Eqs. (11) and (12)]; their comproportionation reaction leads to the formation of a $*[Ru(bpy)_3]^{2+}$ excited state [Eq. (13)] that gives rise to photon emission [Eq. (14)]:[85]

$$[Ru(bpy)_3]^{2+} \xrightarrow{-e^-} [Ru(bpy)_3]^{3+} \tag{11}$$

$$[Ru(bpy)_3]^{2+} \xrightarrow{+e^-} [Ru(bpy)_3]^{+} \tag{12}$$

$$[Ru(bpy)_3]^{3+} + [Ru(bpy)_3]^{+} \rightarrow *[Ru(bpy)_3]^{2+} \tag{13}$$

$$*[Ru(bpy)_3]^{2+} \rightarrow [Ru(bpy)_3]^{2+} + h\nu \tag{14}$$

A photonic input generating parallel and serial processes: In rotaxane $\mathbf{16}^{6+}$ (Scheme 15), which can behave as an artificial nanomotor powered by sunlight,[86] photoexcitation of the $[Ru(bpy)_3]^{2+}$-type moiety (photonic input, I_{w}^{p}) is followed by light emission of the excited $*[Ru(bpy)_3]^{2+}$ species, in competition with electron transfer from $*[Ru(bpy)_3]^{2+}$ to the $A_1{}^{2+}$ viologen unit. The latter species evolves by two competing processes: a back electron transfer from $A_1{}^{+}$ to the oxidized $[Ru(bpy)_3]^{3+}$ moiety, and a chemical rearrangement (displacement of the ring from $A_1{}^{+}$ to $A_2{}^{2+}$ unit). The species resulting from the rearrangement process undergoes back electron transfer leading the system to a translational isomer that then evolves to the original structure.

Conclusion

In the last ten years the marriage of the synthetic talent of chemists with an engineering mentality[87] and a clever use of chemical, photonic and electronic inputs to stimulate molecular and supramolecular species[3,4] have lead to the construction of a variety of molecular devices and machines capable of processing energy and signals.[4,7,9] At the same time, novel conceptual interpretations of old classes of chemical reactions[5,8] have opened new scenarios on the potentiality of chemistry for signal-processing at the molecular level.

Energy- and signal-processing at a molecular level relies on cause/effect relationships between writing inputs and kind of process obtained. We have classified molecular-level energy- and signal-processing according to the nature of the input (electronic, photonic, or chemical) and the nature of the obtained effect (electronic, photonic, or chemical process that follows). By coupling the three kinds of inputs with the three types of resulting processes, nine types of molecular-based processes (electronic, photonic, chemionic, electrophotonic, electrochemionic, photoelectronic, photochemionic, chemiophotonic, and chemioelectronic) can be distinguished (Scheme 1, bottom).

In this concept article we have briefly illustrated examples of the nine types of systems capable of interconverting chemical, photonic, and electrical inputs and outputs to give a flavor of some of the new features which project the old science of chemistry towards novel achievements.[88]

Acknowledgements

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[87] In the *Foresight Update 20*, Foresight Institute, Palo Alto, Cal, it is reported that Roald Hoffmann has reacted in this way when asked about the goal of nanotechnology: '*"I'm glad you guys (that includes women, of course) found a new name for chemistry." Now you have the incentive to learn what you didn't want to learn in college. Chemists have been practicing nanotechnology, structure and reactivity and properties, for two centuries, and for 50 years by design. What is exciting about modern nanotechnology is (a) the marriage of chemical synthetic talent with a direction provided by "device-driven" ingenuity coming from engineering, and (b) a certain kind of courage provided by those incentives, to make arrays of atoms and molecules that ordinary, no, extraordinary chemists just wouldn't have thought of trying. Now they're pushed to do so. And of course they will. They can do anything. Nanotechnology is the way of ingeniously controlling the building of small and large structures, with intricate properties; it is the way of the future, a way of precise, controlled building, with, incidentally, environmental benignness built in by design'.* (http://www.foresight.org/Updates/Update20/Update20.1.html#anchor176004 Accessed September 2007).
[88] This review is adapted from Chapter 2 of the book: V. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines—Concepts and Perspectives for the Nanoworld*, Wiley-VCH, Weinheim, in press.