Logic Operations at the Molecular Level. An XOR Gate Based on a Molecular Machine

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Abstract: A pseudorotaxane formed in solution by self-assembly of a wire-type electron acceptor (2,7-dibenzyl-diazapyrenium dication) and a macrocyclic electron donor (2,3-dinaphtho-30-crown-10) can be unthreaded and rethreaded by chemical inputs. Unthreading can be obtained by addition of stoichiometric amounts of acids or amines. After the unthreading process caused by addition of acid, rethreading can be obtained by addition of amine, and vice versa. The threading/unthreading processes are accompanied (and therefore can be monitored) by strong changes in the fluorescence properties of the system. The input (chemical)/output (fluorescence) characteristics of this molecular-level system correspond to those of an XOR logic gate.

Introduction

Current computers are based on semiconductor logic gates which perform binary arithmetic and logical operations.[1] Logic gates are switches whose output state (*0* or *1*) depends on the input conditions (*0* or *1*). Extension of information processing and computation to the molecular level will only be possible when molecular logic gates are available.[2−16] Apart from such futuristic applications, the design and construction of molecular systems capable of performing complex logic functions is of great scientific interest since it introduces new concepts in the field of chemistry and stimulates the ingenuity of the research workers engaged in the "bottom up" approach to nanotechnology.[4,7] Here we describe a chemical system (Figure 1) whose input/output characteristics correspond to those of an XOR gate.

YES and NOT single-input gates are the simplest logic devices.[1] A YES gate passes the input bits to the output without changes (input: *1*, output: *1*; input: *0*, output: *0*), while a NOT gate inverts any input data (input: *1*, output: *0*; input: *0*, output: *1*). Molecular systems that can perform such simple
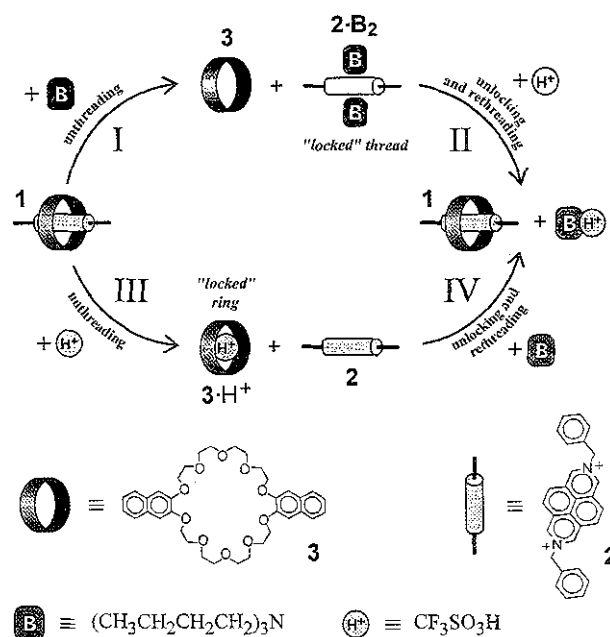
Figure 1. Schematic representation of the unthreading/rethreading pattern of pseudorotaxane **1**, which corresponds to an XOR logic function.

logic operations are very common and fluorescence is a particularly useful signal to monitor such operations.[14,15,17] A molecule that fluoresces (output) only in acidic media (i.e., in the presence of a proton input) acts as a YES gate. Conversely, a fluorescent molecule whose emission (output) disappears under the action of an input of protons can be regarded as a NOT logic device.

In order to perform more complex logic operations, carefully designed multi-component chemical systems are needed. Figure 2 shows schematically the changes which have to occur in a chemical system in order to perform the AND, OR, and XOR (eXclusive OR) logic operations under the action of two chemical inputs (X and Y). The truth tables of such operations and their classical representations based on electric circuit schemes are also shown.[1] An AND gate performs the logic

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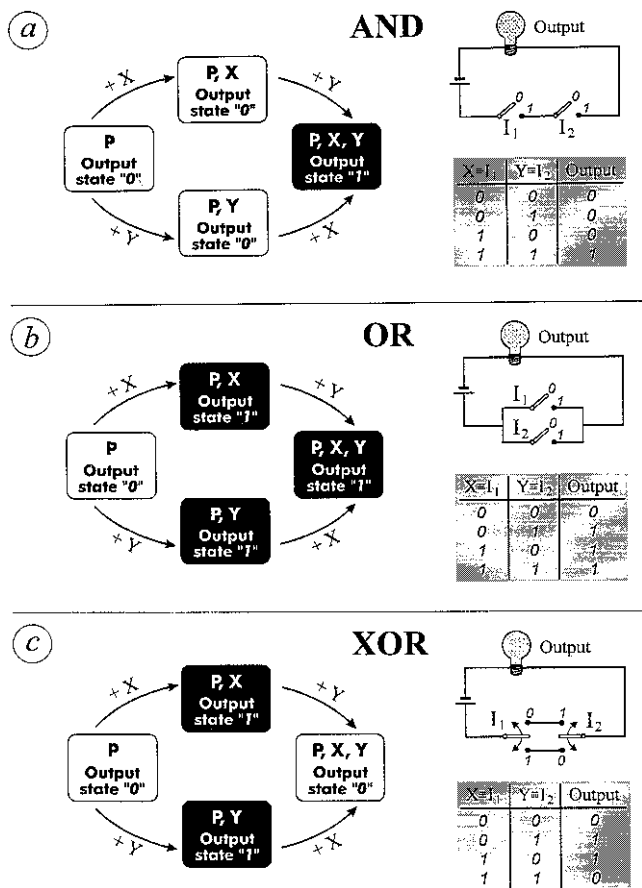
Figure 2. Schematic representation of a chemical system (P) which performs the AND (a), OR (b), and XOR (c) logic operations under the action of two chemical inputs (X and Y). The truth tables of such operations are also shown, along with their representations based on electric circuit schemes.

product between the inputs: the output signal is *1* provided that all the inputs are *1*. The equivalent circuit of the AND gate has switches in series (Figure 2a). An OR gate performs the logic sum between the inputs: the output is *1* provided that at least one of the inputs is *1*. Its equivalent circuit has switches in parallel (Figure 2b). Examples of chemical systems capable of performing the AND and OR logic operations have recently been reported by de Silva and co-workers.[12] An XOR gate is a much more complex device, as one can understand from the fact that its equivalent circuit contains two bipolar switches (Figure 2c). The familiar possibility to switch on/off the same bulb by either of two distinct switches of a room is based on this type of circuit. The truth table of the XOR operation is the same as that of the OR operation except that the output is *0* if *both* the inputs are *1*. In today's processors, addition is performed with an AND gate which gives the carry digit and an XOR gate which gives the sum digit. It is also important to notice that the XOR gate is actually a comparator because it can establish whether the two inputs have the same value.

Results and Discussion

Pseudorotaxanes (e.g., **1** in Figure 1) are supramolecular (multi-component) systems comprising at least one macrocycle ring threaded by an acyclic component.[18] In previous investigations we have shown that unthreading of pseudorotaxanes can be driven by photonic,[19] electrochemical,[20] and chemical[21] stimuli. An interesting aspect of these systems is that they

represent, together with other similar systems based on rotaxanes[22] and catenanes,[23] prototypes of simple mechanical molecular machines. Another interesting aspect, more relevant to the present paper, is that the unthreading and rethreading processes of pseudorotaxanes can be accompanied by readily monitorable differences in the absorption and luminescence spectra.[19−21]

The 2,7-diazapyrenium unit is a good electron acceptor capable of giving pseudorotaxanes with aromatic crown ethers.[21,24] The pseudorotaxane **1** schematized in Figure 1 results from self-assembly of the π-electron-accepting 2,7-dibenzyldiazapyrenium dication **2** with the crown ether **3** which contains two 2,3-dioxynaphthalene π-electron-donating units. In the pseudorotaxane structure, the electron-deficient diazapyrenium unit is sandwiched between the electron-rich 2,3-dioxynaphthalene units of **3**.[25] Because of the electron donor−acceptor interaction,[21] a low-energy charge-transfer (CT) excited state is formed which is responsible for (i) the presence of a weak and broad absorption band with λ_{max} around 400 nm, partially hidden by the bands of **2** (trace *a* in Figure 3), and (ii) the disappearance of the strong fluorescence (Figure 4) exhibited by the two separated components (λ_{max} = 432 nm for **2**, λ_{max} = 343 nm for **3**). In a CH$_2$Cl$_2$/CH$_3$CN 9:1 (v/v) solution containing 2 × 10^{-5} M **2** and 3 × 10^{-5} M **3**, about 85% of **2** and 60% of **3** are threaded in the pseudorotaxane structure **1** at room temperature. Upon addition of 6 × 10^{-4} M tributylamine (**B**, Figure 1), a 1:2 adduct[21] (**2·B$_2$**) is formed between the 2,7-dibenzyldiazapyrenium dication **2** and the amine, with the consequent unthreading of **1** (process I in Figure 1). This process causes large spectral changes, namely (i) the recovery of the emission band of **3** (Figure 4) and (ii) the appearance of a broad absorption (λ_{max} = 575 nm, ϵ = 6500 M^{-1} cm^{-1}; trace *b* in Figure 3) and emission (λ_{max} = 670 nm, Figure 4) band characteristic of **2·B$_2$**. A more detailed analysis of the absorption spectrum shows also the decrease in intensity of the CT band of **1**. From the recovery of the fluorescence of free crown ether **3**, one can estimate that 95% of the pseudorotaxane **1** undergoes unthreading. Subsequent addition of a stoichiometric amount (relative to the previously added amine) of trifluoromethanesulfonic acid unlocks **2** from the **2·B$_2$** adduct and allows rethreading between **2** and **3** to give back almost quantitatively (±10%) the pseudorotaxane **1** (process II in Figure

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(25) Association between a wire-type component like **2** and a crown ether like **3** could occur in principle according to a threaded or a U-shaped structure (refs 19, 21, 24, 26−27). For the adduct of **2** and 1,5-dinaphtho-38-crown-10 (which has a slightly larger cavity than **3**), ¹H NMR and X-ray experiments have demonstrated the formation of the threaded (pseudorotaxane) structure (ref 21). Even in the case of the adduct between 2,7-dimethyldiazapyrenium and dibenzo-24-crown-8 (which is smaller than **3**), a threaded structure is formed, as shown by ¹H NMR and X-ray analysis (ref 24). Therefore, there is little doubt that association between **2** and **3** occurs according to a pseudorotaxane structure (**1**). Even in the case of a U-shaped structure, the reported results and their discussion maintain full validity.
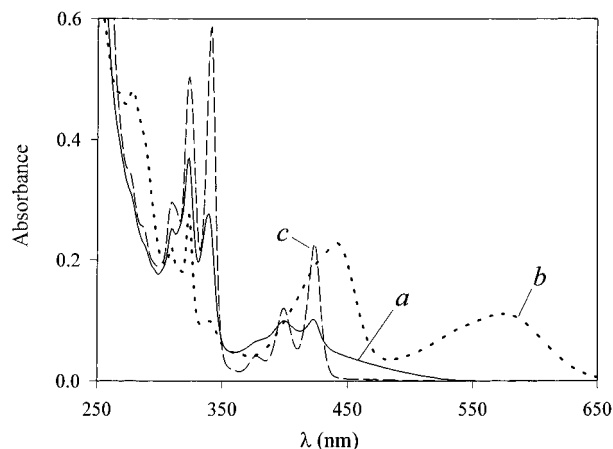
Figure 3. Absorption spectrum of a CH_2Cl_2/CH_3CN 9:1 (v/v) solution containing 2×10^{-5} M **2** and 3×10^{-5} M **3** (spectrum *a*). Spectra *b* and *c* refer to solutions obtained after addition of 6×10^{-4} M tributylamine and 6×10^{-4} M trifluoromethanesulfonic acid, respectively, to the solution giving spectrum *a*. Subsequent addition of stoichiometric amounts of trifluoromethanesulfonic acid to the solution giving spectrum *b* and of tributylamine to the solution giving spectrum *c* gives back spectrum *a* in both cases.
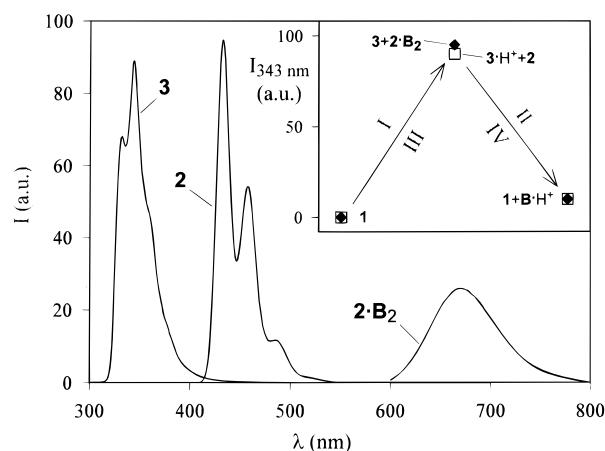

Figure 4. Emission spectra for **2**, **3**, and **2·B₂** in CH_2Cl_2/CH_3CN 9:1 (v/v). The emission spectrum of **3·H⁺** is almost identical to that of **3**. The inset shows the net changes in the emission intensity at 343 nm associated with processes I–IV shown in Figure 1 (excitation was performed at the isoabsorptive point $\lambda = 277$ nm; experimental error $\pm15\%$).

1). This process is of course accompanied by spectral changes opposite to those observed upon addition of amine (Figures 3 and 4). Processes I and II can be repeated on the same solution by repeating the addition of amine and acid.

The unthreading–rethreading cycle can also be performed by reversing the order of two inputs. Addition of 6×10^{-4} M trifluoromethanesulfonic acid causes protonation of the crown ether **3**, with the consequent unthreading of **1** (process III in Figure 1). This process again causes large spectral changes, namely (i) the appearance of the emission band of **3·H⁺** (which is practically the same as that of free **3**, Figure 4), (ii) the recovery of the emission band of **2** (Figure 4), and (iii) the disappearance of the CT band of **1** (trace *c* in Figure 3). From the intensity of the fluorescence of **3·H⁺**, one can estimate that 90% of the pseudorotaxane **1** undergoes unthreading. At this stage, addition of a stoichiometric amount (relative to the previously added acid) of **B** unlocks **3** from **3·H⁺**, thereby allowing rethreading between **2** and **3** to give back almost quantitatively ($\pm10\%$) the pseudorotaxane **1** (process IV in Figure 1), as indicated by spectral changes (Figures 3 and 4).

As shown in the inset of Figure 4, both processes I and III cause a strong increase of emission intensity at 343 nm, which

is cancelled by processes II and IV, respectively. Therefore we can conclude that *the chemical system described above shows the input/output relationships indicated by the truth table of the XOR logic gate* (Figure 2c). The strong fluorescent signal at 343 nm is present (output: *1*) only when either amine or H⁺ (inputs X and Y in the truth table) are added (i.e, X: *1* and Y: *0*, or vice versa); conversely, the fluorescent signal is absent (output: *0*) when none or both of the inputs are present (i.e., X = Y: *0* or X = Y: *1*).

Although the system shown in Figure 1 behaves as an XOR logic gate as the electric circuit shown in Figure 2c, it should be pointed out that a comparison between the characteristics of two XOR gates as different as a chemical system and an electric circuit should be made with great care. Under some aspects, such a comparison could also be inappropriate or impossible.

The described experiments concern an enormous number of molecules. The term *molecular machine*, however, seems appropriate because the system works at a molecular level. If and how such a machine can be used as a component of more extended logic systems is of course difficult to forecast.[8,11,13]

We would also like to emphasize that, besides the molecular logic aspect, the system described above exhibits some quite unusual features from a purely chemical viewpoint: (i) the pseudorotaxane **1** can be unthreaded by addition of reactants as different as acids and amines; this contrasts with the usual behavior of chemical systems that either remain unchanged or behave in opposite ways upon addition of acid or basic reagents; (ii) rethreading can occur either adding acids to amine-containing solutions or amines to acid-containing solutions; (iii) two distinct, reversible unthreading–rethreading cycles can be performed through two distinct sets of species (**2·B₂** and **3** or **2** and **3·H⁺**) which exhibit some *common* and some *specific* properties. A common feature is the 343-nm emission of **3** and **3·H⁺** (Figure 4), which is present or absent according to the above discussed XOR logic, whereas distinct features are the absorption (Figure 3) and luminescence (Figure 4) bands of **2·B₂** and of **2**. Such distinct features, not relevant for the XOR logic behavior, carry additional pieces of information that can prove useful for other purposes. For example, because of the different emission properties of **2·B₂** and **2**, **1** can be used as a sensor for both amines and acids.

Experimental Section

Chemicals. Merck Uvasol CH_2Cl_2 and CH_3CN were used as received. Tributylamine and trifluoromethanesulfonic acid were purchased from Aldrich and Fluka, respectively. 2,7-Dibenzyldiazapyrenium dication (**2**) (PF_6^- salt)[21] and 2,3-dinaphtho-30-crown-10 (**3**)[26] were previously prepared and characterized.

Absorption and Emission Spectra. Absorption spectra were recorded with a Perkin Elmer $\lambda6$ spectrophotometer; uncorrected emission spectra were obtained with a Perkin Elmer LS50 spectrofluorimeter. When necessary, inner filter effects due to spectral overlap have been taken into account. The experimental error on the luminescence intensity was $\pm15\%$. All the experiments were carried out at room temperature.

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