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Special Issue

Unconventional Nonlinear Input–Output Response in a Luminescent Molecular Switch by Inner Filtering Effects

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Nonlinear input–output relations are at the basis of the regulation of biochemical processes in living organisms and are important for the development of digital logic circuits based on molecules. In this article we show that a linear change of a chemical input can be translated into an exponential change of a luminescence output in a simple fluorescent acid-base switch based on 8-methoxyquinoline. Such unconventional behavior arises from the fact that part of the light emitted by the switch in its basic form is reabsorbed by the acid form, and is made possible by the particular spectroscopic properties of the two forms. Systems of this kind could act as noise filters in analog-to-digital conversion, and as control elements to increase the functional complexity of artificial molecular devices.

1. Introduction

Processing information is not only an important task for technology but also a fundamental activity for living organisms. In the latter, information is elaborated (gathered, transported, transformed, stored and retrieved) in an analog form by molecular or ionic substrates operating in soft environments.[1] Computer technology, on the other hand, is based on solid-state electronic circuits that operate on digital data. In the past two decades the search for novel paradigms for information processing alternatives to those exploited by silicon technology, in the awareness that molecules are tiny input/output devices that can be made-to-order, has led to the development of a new multidisciplinary scientific area—molecular logic—which nowadays engages dozens of research groups worldwide.[2–6]

Research on molecular logic has brought about significant conceptual innovation in chemistry[2,7] and a better understanding of complex biochemical phenomena.[8] Recent results have also shown that the implementation of complex logic operations within molecular systems can lead to the development of materials with advanced functionalities[9] as well as new products and processes for medical diagnostics[10] and therapy.[11]

The design of molecular logic gates takes advantage of the fact that molecules can act as sensors and switches, i.e., they change some of their physico-chemical properties (output) in response to physical or chemical stimuli (input).[12] In the case of chemically driven devices, such a response is typically based on a complexation equilibrium: for example, the association of a molecular or ionic substrate with a receptor.[13] This phenomenon leads to an input-output relationship such as that shown in Figure 1a: the input is linearly translated into the output until a plateau is reached upon saturation of the receptor by the substrate.

The analog-to-digital conversion is performed by applying a threshold to identify the output (and, consequently, input) ranges corresponding to digital zero and one. The accuracy of the conversion, however, is strongly affected by the experimental error in the input and/or output values near the threshold, because small fluctuations of the observed quantities can change the digital state. In other words, a noise on the analog data can result in a wrong digital representation.[14]

In this context, nonlinear input-output relationships such as those shown in Figure 1b and 1c are interesting. Systems exhibiting these responses could be used as filters to enhance the accuracy of the conversion into digital zero (Figure 1b) or one (Figure 1c). Even more appealing are systems characterized by a sigmoidal relationship (Figure 1d), as they can limit the effect of fluctuations on both low and high values. It should also be recalled that the nonlinear behaviour of (bio)-chemical systems in response to stimuli forms the basis of the regulation of many processes in living organisms.[15]

Nonlinear information processing has been demonstrated using biomolecular reactions (in most cases on enzyme-based systems), and logic operations with filtering functions that reduce noise have been obtained.[14,16]

As far as synthetic systems are concerned, while the responses shown in Figure 1b–d can be obtained with catalytic reaction networks,[17] their implementation with bistable com-

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An invited contribution to a Special Issue on Molecular Logic

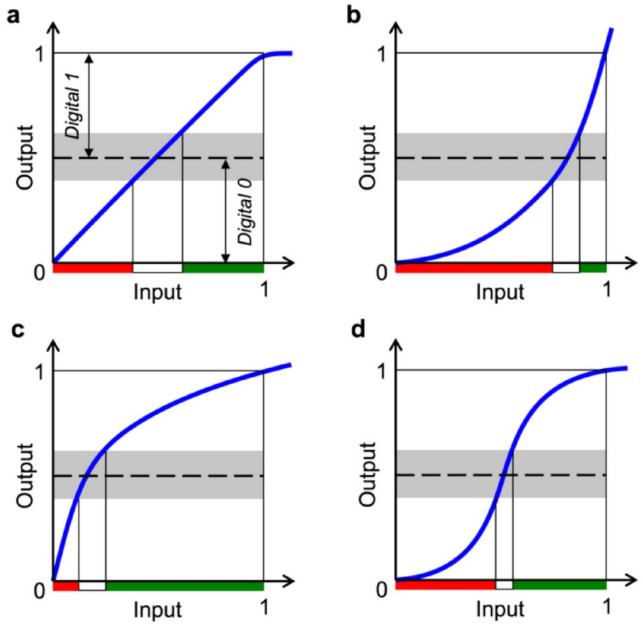


Figure 1. Different types of input-output relations: a) linear, b) concave, c) convex and d) sigmoidal. For simplicity, the input and output signals are normalized to the digital range from 0 to 1. The threshold for analog-to-digital conversion is shown as a dashed line, while the shaded area represents the experimental uncertainty on the output value. The corresponding input intervals yielding a digital output of zero and one are identified with red and green bars, respectively. The input values leading to an unpredictable digital output are highlighted with a white bar.

pounds working at equilibrium—a category that represents the vast majority of molecular switches—is challenging. Here we show that nonlinear relationships of this kind can be realized by exploiting the spectroscopic properties of a simple fluorescent molecular switch that responds to acid-base stimulation.

2. Results and Discussion

The investigated compound is 8-methoxyquinoline (**1** in Scheme 1),[18] an unsophisticated chromophore related to the widely used fluorogenic ligand 8-hydroxyquinoline.[19] In acetonitrile, **1** shows an absorption band with $\lambda_{max}=301$ nm (Figure 2) and does not absorb light for $\lambda>350$ nm; moreover it exhibits an intense fluorescence band with $\lambda_{max}=388$ nm (Figure 2). Upon addition of one equivalent of triflic acid to **1**, the protonated form **1**H$^+$ is obtained (Scheme 1). The absorption and luminescence properties of **1**H$^+$ are markedly different from those of **1**. Specifically, the absorption band at 310 nm becomes weaker and structured, and a new band with $\lambda_{max}=358$ nm appears (Figure 2). The emission band at $\lambda_{max}=388$ nm is replaced by a weaker fluorescence band peaking at 500 nm (Figure 2). The basic form **1** can be regenerated by adding one equivalent of tributylamine to **1**H$^+$ (Scheme 1); the acid-base controlled switching between **1** and **1**H$^+$ can be repeated many times with the same solution without appreciable loss in the absorption and luminescence spectra.

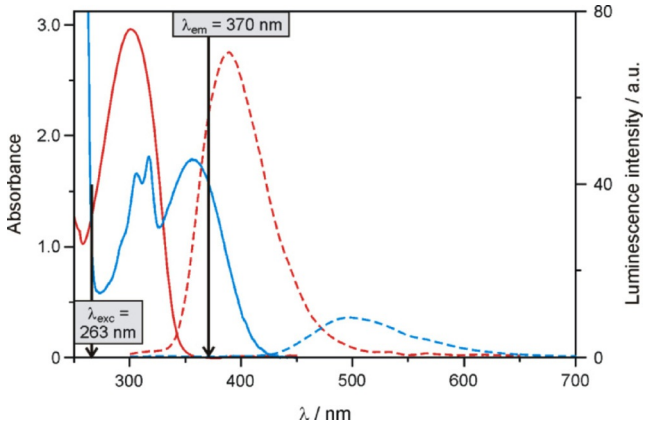
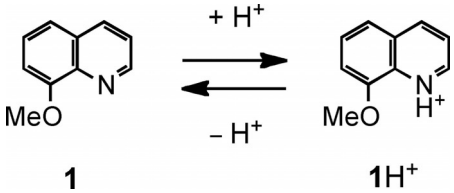


Figure 2. Absorption (full lines, left scale) and luminescence (dashed lines, right scale) spectra of **1** (red curves) and **1**H$^+$ (blue curves). The excitation (λ_{exc}) and emission (λ_{em}) wavelengths relevant for the discussion are indicated.

By examining the spectra shown in Figure 2 it can be noticed that the emission of **1** occurs in a spectral region in which the absorbance of **1** is negligible but that of **1**H$^+$ is significant. This means that in solutions containing both **1** and **1**H$^+$ (such as those obtained upon titration of **1** with acid or of **1**H$^+$ with base) the light emitted from the former is partially re-absorbed by the latter; as a result, the fluorescence intensity detected for **1** is lower than that actually emitted by the fluorophore. This phenomenon is known as inner filter effect[20] and needs to be taken into account when performing luminescence measurements on species characterized by a small Stokes shift, or in samples containing different chromophores.[21] As underlined in photochemistry textbooks,[19,22] the reabsorption of the emitted light is of great importance in the measurement of luminescence quantum yields and the determination of the correct spectral shape of an emission band.

In normal practice inner filtering is prevented by an appropriate choice of the experimental conditions; if this is not possible, the luminescence data can be corrected for the effect.[20] In the present case, however, we deliberately maximized the reabsorption of the emitted light and exploit it to obtain a nonlinear input-output response.

For our luminescence experiments we used the common setup of commercial spectrofluorimeters: the solution was contained in a quartz cell with a square section (1 cm), the excitation beam hit the cell perpendicularly to a face, and the emission was monitored along a perpendicular direction with respect to excitation (right angle geometry). Since during the acid/base titrations we excited the solution at an isosbestic



Scheme 1. Acid–base controlled interconversion between 8-methoxyquinoline **1** and its protonated form **1**H$^+$.

point (λ_{exc} = 263 nm, see dashed line in Figure 2), the intensity emitted by **1** is linearly correlated to its absorbance and hence to its concentration [Eq. (1)]:[20]

$$I(\lambda_{exc},\lambda_{em}) = \Phi \times I_0(\lambda_{exc}) \times A(\lambda_{exc}) = \Phi \times I_0(\lambda_{exc}) \times \varepsilon(\lambda_{exc}) \times d_{exc} \times [\mathbf{1}] \quad (1)$$

where Φ is the luminescence quantum yield of **1**, $I_0(\lambda_{exc})$ is the incident light intensity at the excitation wavelength, $\varepsilon(\lambda_{exc})$ is the molar absorption coefficient of **1** at the same wavelength, d_{exc} is the optical path length of the exciting light (in our case 1 cm) and [**1**] is the concentration of **1**.

For right angle geometry it can be easily demonstrated on the basis of the Lambert-Beer law that the fraction of emitted light at a wavelength λ_{em} which is transmitted through the chromophoric solution is expressed by Equation (2):

$$T(\lambda_{em}) = 10^{-\{\varepsilon(\lambda_{em})\times d_{em}\times[\mathbf{1}H^+]\}} \quad (2)$$

where $\varepsilon(\lambda_{em})$ is the molar absorption coefficient of the chromophore ($\mathbf{1}H^+$) at the monitored emission walevength, d_{em} is the average path length of the emitted photons across the solution,[23] and [$\mathbf{1}H^+$] is the chromophore concentration.

To determine the luminescence intensity emerging from the cuvette, and hence measured by the spectrometer, the emitted intensity I has to be multiplied by the fraction of transmitted light [Eq. (3)]:

$$I_{obs}(\lambda_{exc},\lambda_{em}) = I(\lambda_{exc},\lambda_{em}) \times T(\lambda_{em}) = \Phi \times I_0(\lambda_{exc}) \times \varepsilon(\lambda_{exc}) \times d_{exc} \times [\mathbf{1}] \times 10^{-\{\varepsilon(\lambda_{em})\times d_{em}\times[\mathbf{1}H^+]\}} = \text{constants} \times [\mathbf{1}] \times 10^{-\{\text{constants}\times[\mathbf{1}H^+]\}} \quad (3)$$

Since both [**1**] and [$\mathbf{1}H^+$] depend on proton concentration, Equation (3) shows that under the conditions discussed above a nonlinear relation exists between the concentration of H^+ (input) and the observed emission intensity (output). In order to maximize inner filtering, the emission was detected at a wavelength (370 nm) at which $\mathbf{1}H^+$ exhibits a strong absorption [i.e., $\varepsilon(\lambda_{em}) \gg 0$].

Put in simpler terms, two factors cause the observed luminescence intensity quenching at 370 nm upon addition of acid: i) a decrease of the concentration of the emitting species **1**, and ii) an increase of the concentration of the "filtering" chromophore $\mathbf{1}H^+$. While process (i) follows a linear relation [Eq. (1)], process (ii) is exponential [Eq. (2)].

The black circles in Figure 3 show the luminescence intensity changes measured at 370 nm for a 1.4 mM solution of **1** upon addition of increasing amounts of triflic acid. It can be noticed that the response of the emission intensity to proton concentration is strongly nonlinear and is in fact the complement to the curve displayed in Figure 1c. Conversely, as expected, the intensity corresponding to the light emitted by $\mathbf{1}H^+$, detected at 500 nm where no reabsorption occurs, increased in a roughly linear manner upon increasing the concentration of H^+ (white squares in Figure 3). The absorbance values (not shown) also exhibited the expected linear change as a function of the proton concentration.

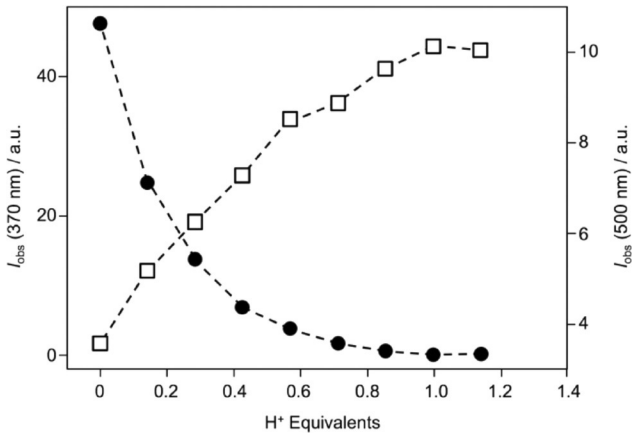


Figure 3. Emission intensity values detected at 370 nm (black circles, left scale) and 500 nm (white squares, right scale) on a 1.4 mM solution of **1** upon addition of triflic acid. The dashed lines connecting the points are a guide to the eye, not a fit. Conditions: acetonitrile, room temperature, λ_{exc} = 263 nm (isosbestic point).

Taking advantage of the reversibility of the reaction in Scheme 1, we titrated $\mathbf{1}H^+$ (obtained by adding one equivalent of triflic acid to **1**) with the base tributylamine (nBu$_3$N), and analyzed the spectroscopic consequences. Figures 4 and 5 show, respectively the absorption and luminescence spectral changes observed during the titration. As it can be noted in the inset of Figure 5 (black circles), the luminescence changes at 370 nm as a function of the base equivalents deviate significantly from linearity, because the inner filtering exerted by $\mathbf{1}H^+$ fades away as this species is scavenged by tributylamine. Interestingly, because of the saturation of the emission intensity reached after the addition of one equivalent of nBu$_3$N which quantitatively regenerates **1**, the observed curve (Figure 5, inset, black circles) has a sigmoid-like shape reminiscent of that shown in Figure 1d.

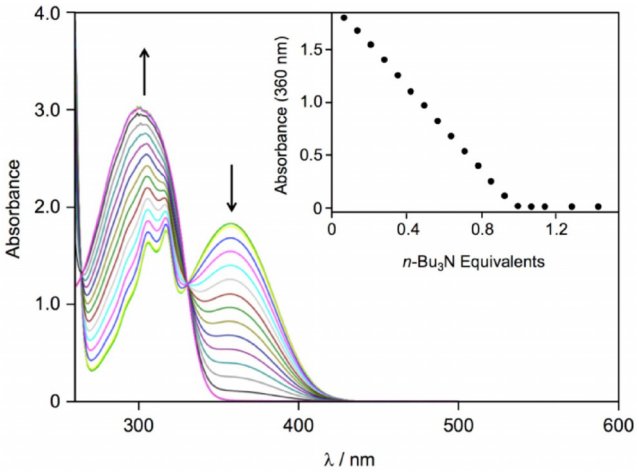


Figure 4. Absorption spectral changes observed upon titration of $\mathbf{1}H^+$ (1.4 mM, obtained by protonation of **1**) with tributylamine. The inset shows the titration curve obtained by monitoring the absorbance at 360 nm. Conditions: acetonitrile, room temperature.

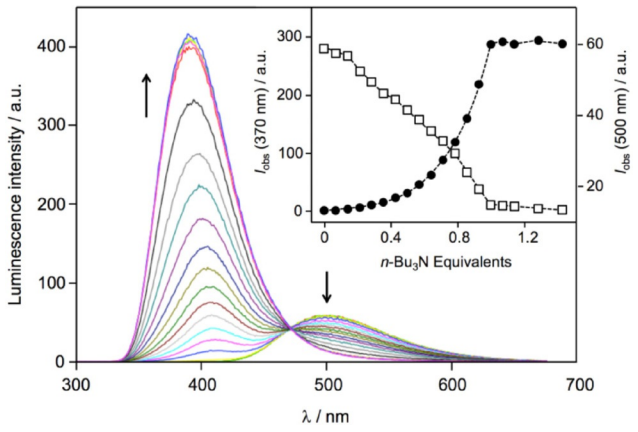


Figure 5. Luminescence spectral changes observed upon titration of $\mathbf{1}H^+$ (1.4 mM, obtained by protonation of **1**) with tributylamine. The inset shows the emission intensity values detected at 370 nm (black circles, left scale) and 500 nm (white squares, right scale) for increasing amounts of tributylamine. The dashed lines connecting the points are a guide to the eye, not a fit. Conditions: acetonitrile, room temperature, $\lambda_{exc} = 263$ nm (isosbestic point).

The emission signal of $\mathbf{1}H^+$ at 500 nm, unaffected by reabsorption phenomena, exhibits the expected linear decrease (Figure 5, inset, white squares).

In principle, the optical output of our ensemble at 370 nm could be fed as the input of another well-known molecular switch, namely, a protonated nitromerocyanine.[24] Upon absorption of light in the 350–450 nm region this compound behaves as a photoacid, generating the nitrospiropyran closed form and releasing protons into the solution. Such a concatenation of molecular switches[25] is interesting because it would enable the conversion of a linear rise of a chemical signal (proton concentration) into an exponential decrease of the same signal. In a proof-of-principle experiment the light emitted by the $\mathbf{1}H^+/\mathbf{1}$ ensemble in one cuvette was used to irradiate the protonated merocyanine in a nearby cuvette;[26] in our conditions, however, the emitted intensity was too weak to cause a significant transformation of the protonated merocyanine.

3. Conclusions

We have shown that the luminescence intensity can be nonlinearly modulated by the proton concentration in an acid-base switchable fluorophore. This result exploits the fact that the light emitted by the switch in one state is reabsorbed by the same switch in the other state. The strategy, based on the interplay of chemical (acid-base switching) and physical (light absorption) processes, is applicable to a large variety of luminescent compounds. Molecule-based systems exhibiting this kind of input-output relationship are conceptually interesting because they can act as noise filters in analog-to-digital conversion. Molecular switches such as **1** could be the forerunners of control elements that may be integrated with artificial chemical systems to increase their functional complexity. The general validity and the simplicity of the presented approach are factors of interest for further developments, which are underway in our laboratories.

Experimental Section

8-Methoxyquinoline (**1**) was available from previous investigations.[17] Acetonitrile Merck Uvasol™ was employed as the solvent in all the experiments. Triflic acid (CF_3SO_3H) and tributylamine (n-Bu_3N) were purchased from Fluka and used without further purification. Absorption spectra were recorded with a PerkinElmer lambda45 spectrophotometer in air equilibrated acetonitrile solutions at room temperature (ca. 298 K), contained in 1-cm spectrofluorimetric quartz cells. Luminescence spectra were recorded with a PerkinElmer LS50B spectrofluorimeter equipped with a Hamamatsu R928 phototube. Titrations were performed in the spectrofluorimetric cell by adding small aliquots (typically 5 μL) of a concentrated solution of either CF_3SO_3H or n-Bu_3N to a volume of 2.5 mL by using a microsyringe. The experimental errors are ±1 nm for the wavelengths and ±10% for the absorbance values, luminescence intensities, and concentrations.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: luminescence · molecular devices · molecular logic · molecular switches · photochemistry

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