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Anthraquinone-based demultiplexer and other multiple operations at the molecular level

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Abstract. Anthraquinone-based chemosensor **L** with pyridine units as additional functional groups has been found to show pH-dependent multiple coordination modes towards different metal ions (Co^{2+}, Ni^{2+} and Cu^{2+}). Based on these different absorption changes, this differential colorimetric chemosensor **L** has found promising applications as a multiple-mode molecular logic system, i.e., OR, three – input NOR, three – input INHIBIT, TRANSFER and 1:2 DEMUX.

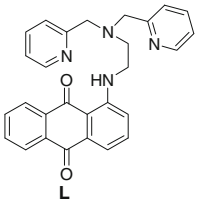
Keywords. Anthraquinone; chemosensors; molecular logic gates; demultiplexer.

1. Introduction

The chemical structure of small tailormade molecular scaffolds that can transform macroscopic properties with respect to external inputs have recently gained great importance to sustain the development of information science and new technologies.[1] Molecular logic gates or switches whose output (0 or 1) depends on the input conditions, play pivotal roles in molecular computation.[2] The possibility of mimicking the function of silicon chips and building electronic devices using organic/inorganic molecules, based on their spectral responses toward an external stimulus, has been much explored.[3]

A number of molecular-level machines, elementary electronic devices, fluorescent logic gates (AND, OR, INHIBIT, etc.) and arranged logic circuits incorporating single logic gates have been established recently.[4] Many different external physical signals, including optical,[5] electrochemical potential,[6] magnetic and sometime,[7] by chemical signals such as pH changes or metal cations additions were applied to activate chemical processes mimicking computational operations.[8,9] Mostly, chemical computing systems produce chemical output signals and these signals should be used as inputs for the next chemical computing operation when the individual chemical steps are connected in a complex chemical information processing network. In multifunctional systems, assembling of chemical computing units resulted in chemical devices performing basic Boolean operations such as NOR, XOR, XNOR, INH – and the most common combinational circuits, i.e., half– and full–adders and –subtractors, multiplexer, demultiplexer.[10–18]

An important function in information technology is signal multiplexing/demultiplexing. A 2:1 multiplexer (MUX) is a circuit with two data inputs, one address input and one output. The MUX selects the binary state from one of the data inputs and directs it to the output; the selected input depends on the binary state of the address input. Conversely, a 1:2 demultiplexer (DEMUX) is a circuit that possesses one data input, one address input and two outputs. The DEMUX routes the data input to one of the output lines, and the selected output is determined by the binary state of the address input. Hence, a multiplexer allows the encoding of multiple data streams into a single data line for transmission, and a demultiplexer can decode entangled data streams from a single signal. Molecules that can mimic the function of a 2:1 multiplexer or a 1:2 demultiplexer have recently been reported.[19–21] However, these systems either rely on carefully designed multicomponent species and coupling to an external optical device[20] or imply a dependence of the data input on the binary state of the address input.[19–21] Demultiplexers based on solid-state nanostructures have also been described.[22]



L

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In continuation with our earlier report anthraquinone-based molecular logic systems,[23] in this paper, we have shown that cation-induced modulations of the chemosensor's (**L**) absorption spectrum involve the appearance or disappearance of various bands in the visible region as well as different colour changes at different pH values. These different optical output signals (i.e., absorbance) can be used for construction of various molecular logic devices. More importantly, switching of the absorption properties at different pH values can form the basis for unimolecular 1:2 demultiplexer.

2. Experimental

A synthetic procedure for **L** and its detailed photophysical studies has already been reported.[24]

3. Results and discussion

3.1 *Metal ions switch*

In CH_3OH:H_2O (4:1), the absorption spectrum of **L** showed a band with λ_{max} at 510 nm. Addition of solutions of Co^{2+}, Ni^{2+} and Cu^{2+} showed a visible colour change from red to blue and their UV-vis spectra exhibited differently red-shifted (630–650 nm) absorption bands (figure 1).

However, on lowering the pH to 4.0, the solution of **L**, with addition of Co^{2+}, Ni^{2+} and Cu^{2+} gave respective blue (λ_{max} 620 nm), yellowish pink (λ_{max} 380, 460 and 510 nm) and yellow (λ_{max} 460 nm) colours (figure 2). Spectral fitting of the titration data of **L** against Co^{2+}, Ni^{2+} and Cu^{2+} showed the formation of 1:1 complexes with log β values of 6.8 ± 0.3, 5.9 ± 0.3, and 7.10 ± 0.72, respectively.[24]

At pH 7.0, the red shift in the case of Co^{2+}, Ni^{2+} and Cu^{2+} points to aryl NH deprotonation. However, under acidic conditions, i.e., at pH 4.0, the blue shift in the case of Ni^{2+} and Cu^{2+} and red shift in Co^{2+} shows differential mode of interaction of these metal ions towards sensor **L**. Here, aryl NH coordinates with Ni^{2+} and Cu^{2+} to cause hypsochromic shift, however, Co^{2+} coordination along with deprotonation results in increased electron-density and red shift of spectral band.

This pH-controlled switching between neutral and protonated forms of **L** was fully reversible and could be repeated many times with the same solution without any appreciable reduction in intensity in the absorption spectra. This particular spectroscopic behaviour and the chemical reversibility of the pH-switching can be used to obtain OR, NOR, INH, TRANSFER and 1:2 DEMUX functions.

3.2 *OR and NOR logic gates based on system **L** at pH 7.0*

The output of OR gate is normally switched on if either one or both inputs are turned on. As a consequence of observed absorbance of **L** (50 μM) at pH 7.0 in the presence of Cu^{2+} and Ni^{2+}, an OR gate can be easily applied by using Cu^{2+} (50 μM) and Ni^{2+} (50 μM) as two chemical inputs and absorbance at 620 nm as an output. In the absence of any of these cations, the absorbance at 620 nm of system **L** is relatively low (< 0.01, output 0), whereas absorbance values are high (> 0.1, output 1) in the presence of each or both of the two input. As a result, a two input OR logic gate is obtained according to the truth table in figure 3.

NOR gates (and also NAND gates) are of potential interest because they are considered as universal gates which enable the combinatorial creation of all other basic Boolean operations. In the present system **L** (50 μM), a three input NOR logic expression is yielded using absorbance output at 502 nm and 1 equiv. of Co^{2+}, Ni^{2+} and Cu^{2+} as the inputs. As seen in figure 4, there is relatively high absorbance at 502 nm (>0.30, output 1) when no ions are added. However, when one or both or all of the three inputs are operated, the absorbance of **L** is decreased (<0.2, output 0). This process can

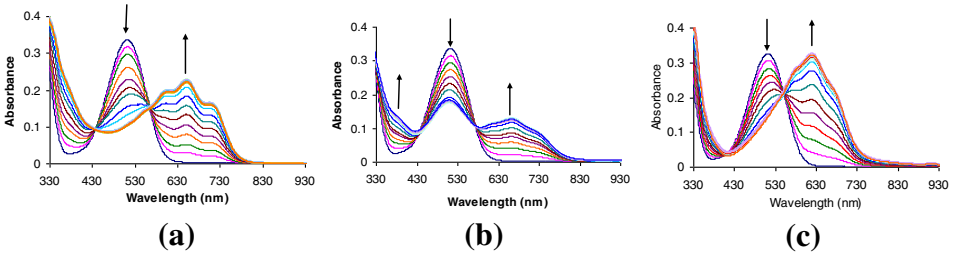


Figure 1. UV-vis spectra of **L** (50 μM; CH_3OH:H_2O 4:1; pH 7.0 ± 0.1) upon addition of different concentrations of (**a**) Co^{2+}; (**b**) Ni^{2+} and (**c**) Cu^{2+}.

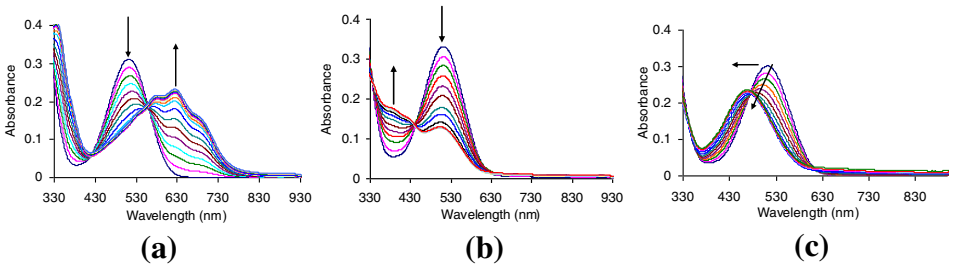


Figure 2. Response of absorption spectrum of **L** (50 μM) (H_2O, acetic acid-sodium acetate, pH 4.0 ± 0.1) towards different concentrations of (**a**) Co^{2+}; (**b**) Ni^{2+} and (**c**) Cu^{2+}.

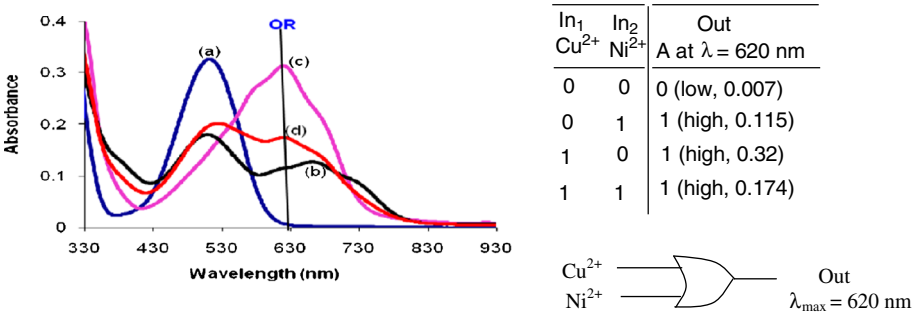


Figure 3. UV-vis spectra of **L** (50 μM; CH_3OH:H_2O 4:1; pH 7.0 ± 0.1) under different input conditions ((**a**) blank; (**b**) **L** + Ni^{2+}; (**c**) **L** + Cu^{2+} and (**d**) **L**+ Ni^{2+} + Cu^{2+}), the truth table and the OR logic scheme.

be referred to as a NOR logic system which integrates a NOT and an OR logic gate. Thus, the multiplicity of logic operations is also demonstrated for a three input photonic system. It should be noted that three inputs can provide much more information and show interesting behaviour at the molecular level such as the consequence of chemical congregations.

3.3 *TRANSFER and INHIBIT logic gates based on system **L** at pH 4.0*

The hypsochromic shift observed in case of system **L** on addition of Cu^{2+} brings another advantage. Shifting of observable wavelength from λ 620 nm (pH 7.0) to λ 410 nm (pH 4.0) in this case results in 'TRANSFER'[14e]

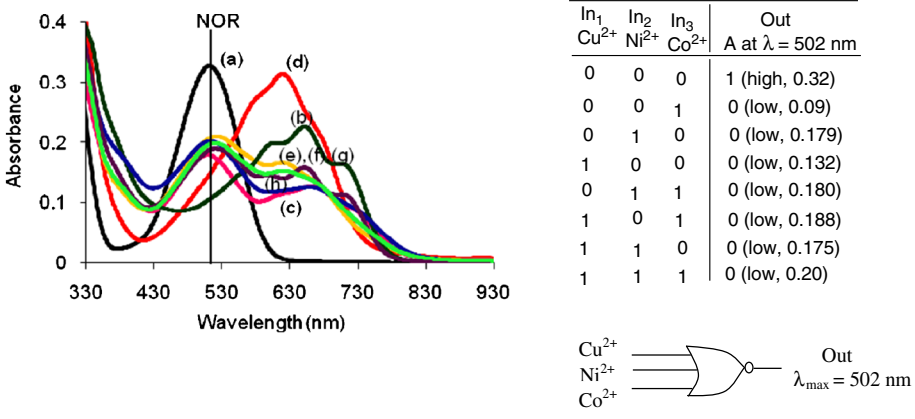
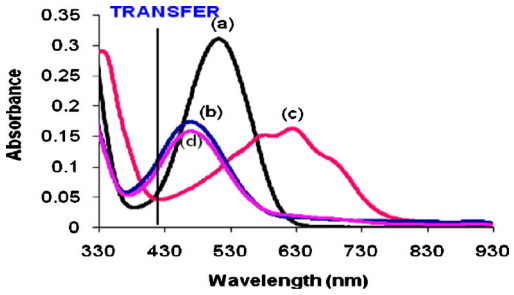


Figure 4. UV-vis spectra of **L** (50 μM; CH_3OH:H_2O 4:1; pH 7.0 ± 0.1) under different input conditions ((**a**) blank; (**b**) **L**+Co^{2+}; (**c**) **L**+Ni^{2+}; (**d**) **L**+Cu^{2+}; (**e**) **L**+ Ni^{2+}+Co^{2+}; (**f**) **L**+Cu^{2+}+Co^{2+}; (**g**) **L**+Cu^{2+}+Ni^{2+} and (**h**) **L**+ Cu^{2+}+Ni^{2+}+Co^{2+}), the truth table and the NOR logic scheme.



In_1 Cu^{2+}	In_2 Co^{+}	Out A at λ = 410 nm
0	0	0 (low, 0.045)
1	0	1 (high, 0.101)
0	1	0 (low, 0.05)
1	1	1 (high, 0.092)

Figure 5. UV-vis spectra of **L** (50 μM; pH 4.0 ± 0.1) under different input conditions ((**a**) blank; (**b**) **L**+Cu^{2+}; (**c**) **L**+Co^{2+} and (**d**) **L**+Cu^{2+}+Co^{2+}) and the truth table.

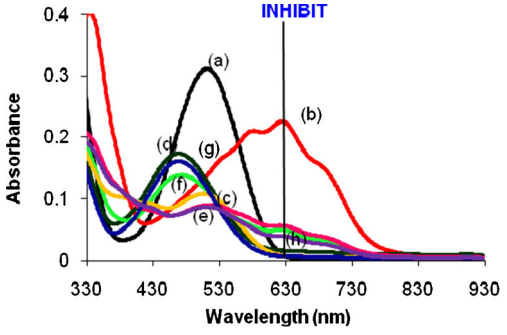
logic. TRANSFER logic requires that the signal is 0 when both inputs are 0 and when one of the two inputs is 1. However, when the other input is 1 or when both are 1, the output is 1. The free **L** (50 μM) (A 0.045) and addition of Co^{2+} (pH 4.0) (A 0.05) leads to low output at 410 nm. It is only in the presence of Cu^{2+}, the output is high (A 0.101, output 1) and remains high even after addition of both Cu^{2+} (50 μM) and Co^{2+} (A 0.092) (figure 5).

INHIBIT logic deserves some attention because it demonstrates a non-commutative behaviour, that is, one of the inputs can disable the whole system. Using the metal ions, Ni^{2+}, Cu^{2+} and Co^{2+}, an integrated logic circuit is constructed in system **L** (50 μM, pH 4.0) (figure 6). Only in the presence of Co^{2+} (1 equiv.), output at 620 nm is 1 (>0.20, output 1). In the presence of 1 equiv. of Cu^{2+} or Ni^{2+} or both of them, the resultant outputs are all 0 (< 0.04, output 0). This is a combinational logic circuit incorporating an OR and an INHIBIT logic gates where the output of OR gate serves as input for INHIBIT gate.

3.4 *1:2 Demultiplexer in CH_3OH:H_2O (4:1)*

The system can be easily reconfigured to behave as a 1:2 demultiplexer by changing the optical input and output channels. The Boolean algebraic expression for a two output DeMUX switch is In#a(Out_1, Out_2), the # symbol denoting a demultiplexer function and '*a*' is address input. This expression says that, if $a = 0$, then the first argument (Out_1) equals In and the second argument (Out_2) is disabled; conversely, if $a = 1$, Out_2 is In and Out_1 is disabled. The variable preceding # is the input variable and the symbol following # is the control data variable. The variables in brackets are the output variables of the two output demultiplexer, which possesses one input (In = Cu^{2+}), one address input (a = pH) and two outputs (Out_1 = 620 nm and Out_2 = 401 nm).

The performance of chemosensor **L** as a molecular digital demultiplexer was assessed by using CH_3OH:H_2O (4:1) solution of **L** (50 μM) and measuring the absorbance values at the two output destinations (620 nm and 401 nm) for the Cu^{2+} input at different



In_1 Cu^{2+}	In_2 Ni^{2+}	In_3 Co^{2+}	Out A at λ =620 nm
0	0	0	0 (low, 0.005)
0	0	1	1 (high, 0.22)
0	1	0	0 (low, 0.004)
1	0	0	0 (low, 0.005)
0	1	1	0 (low, 0.056)
1	0	1	0 (low, 0.04)
1	1	0	0 (low, 0.009)
1	1	1	0 (low, 0.039)

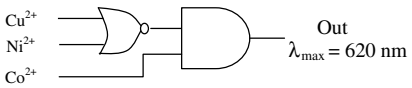
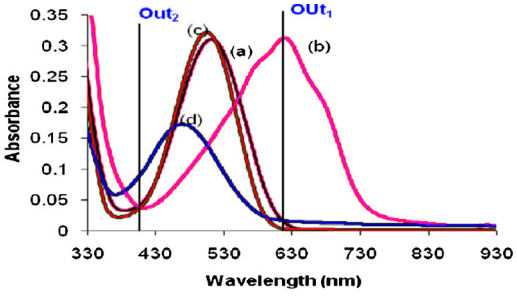


Figure 6. UV-vis spectra of **L** (50 μM; pH 7.0 ± 0.1) under different input conditions ((**a**) blank; (**b**) **L**+Co^{2+}; (**c**) **L**+Ni^{2+}; (**d**) **L**+Cu^{2+}; (**e**) **L**+ Ni^{2+}+Co^{2+}; (**f**) **L**+Cu^{2+}+Co^{2+}; (**g**) **L**+Cu^{2+}+Ni^{2+} and (**h**) **L**+ Cu^{2+}+Ni^{2+}+Co^{2+}), the truth table and the INHIBIT logic scheme.



In_1 Cu^{2+}	*a* (pH)	Out_1 (A) λ = 620 nm	Out_2 (A) λ = 401 nm
0	0	0 (low, 0.003)	0 (low, 0.036)
1	0	1 (high, 0.32)	0 (low, 0.037)
0	1	0 (low, 0.001)	0 (low, 0.03)
1	1	0 (low, 0.012)	1 (high, 0.083)

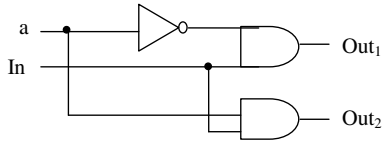


Figure 7. UV-vis spectra of **L** (50 μM) with Cu^{2+} as input having address input as *a* (pH = 7.0, *a* = 0; pH = 4.0, *a* = 1), the truth table and the DEMUX logic scheme.

pH values (pH = 4.0 and pH = 7.0) (figure 7). If the address input is 0 (pH = 7.0), the binary state of the data input is transmitted to Out_1 (620 nm) and when the address input is 1 (pH = 4.0), the binary data input is transmitted to Out_2(401 nm).

4. Conclusion

We have found that chemosensor **L** can carry out logic operations with multiply configurable multiple outputs by selecting the initial states and chemical inputs. As a result, OR, three-input NOR, three-input INHIBIT and TRANSFER logic gates are achieved at the molecular level. Also, the pH-driven modulations of absorption signals allows the implementation of 1:2 demultiplexer digital function.

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