Materials Letters 158 (2015) 355–358

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Construction of multiple logic gates based on anthocyanin derivative

Prem Jyoti Singh Rana, Harendra Tyagi, Amit Kumar, Pallavi Singh, Prasenjit Kar*

Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand 247 667, India

ARTICLE INFO

Article history:
Received 29 April 2015
Received in revised form
30 May 2015
Accepted 1 June 2015
Available online 6 June 2015

Keywords:
Anthocyanin
Sensor
Logic Gate
Spectroscopy

ABSTRACT

An optically active anthocyanin compound containing hydroxyl functionality was designed, synthesized and characterized. A change in optical absorption is observed on addition of excess Fluoride, H^+ or OH^- in methanol. Deprotonation of hydroxyl groups of quinonoidal form of anthocyanin derivative (AC) occurs after addition of excess fluoride ion. From optical absorption spectra it is revealed that flavylium cation of anthocyanin derivative (ACH^+) is formed either on addition of H^+ in AC or in deprotonated species generated by fluoride ion. We demonstrated multiple logic operations using different ionic inputs as H^+, Fe^{2+}, OH^- and F^-.

Logic gate is an elementary building block of a digital circuit [1]. Most logic gates have two inputs and one output. At any given moment, every terminal is in one of the two binary conditions low (0) or high (1), represented by different output signals. Mimicry of logic gate operation in molecular level has been developed after the pioneering study of de Silva in 1993 [2]. Many molecules can act as switches by changing their structures among two or more states as a result of stimuli. This phenomenon may be controlled to design molecules that respond to combinations of inputs in ways that correspond to Boolean logic operations, providing a potential basis for molecule-based computing. Chemical inputs are versatile and simple to implement in demonstrations of principle and require physical access to the molecules. Most of these logic gates are based on the outputs like absorption, fluorescence, electrochemical, or electrochemiluminescence signals [3–16]. Development in supramolecular chemistry shows great interest in the construction of simple electronic or photonic driven systems that function as molecular logic gate. This is achievable in molecules as in many ways, but the most common are based on switching the optical properties of the molecule.

On the basis of the above considerations, in the present study we have designed and synthesized an anthocyanin (AC) dye which may function as a molecular logic gate on addition of various inputs. AC was synthesized following reported procedure [17] (Supporting Information) and was characterized using different standard spectroscopic and analytical techniques. The electronic spectra recorded for AC in methanol is shown in Fig. 1C. The observed transition band at 500 nm was assigned to be predominantly intramolecular charge transfer (ICT) transition. When a large excess of F^- was added an intense broad absorption band at 530 nm appeared. The corresponding molar absorptivity value determined was 2.5×10^{-5} L mol^{-1} cm^{-1}. Any color change was not observed for CN^-, Br^-, Cl^-, I^-, or oxyanions. Literature shows that chalcone is formed in presence of OH^- in aqueous medium. We studied the effect of OH^- in methanol and found a drastic color change from orange to deep blue. This change in absorbance is attributed to the formation of phenolate and catecholate functionality in AC.

Fabbrizi et al. have shown that suitably substituted H-bond donor receptor functionality undergo deprotonation in the presence of excess F^-, leading to classical Brønsted acid–base chemistry [18–24]. Das et al. have shown that phenol/catechol functionality acts as colorimetric sensor for fluoride ion [25]. With greater delocalization of negative charge, the spacing between p-orbital energy levels is decreased, and the electronic absorption band shifts to longer wavelength. Interestingly a broad absorption band appears after addition of F^- with a new peak centered at around 530 nm. This absorption band is attributed predominantly due to the formation of $-OH\cdots F$ and subsequent formation of HF_2^- in AC. This absorption band disappears and a new peak is appeared at 488 nm upon addition of H^+ which exactly matches with the absorption spectrum of ACH^+ (Supporting Information). These electronic transitions open up a possibility to construct a logic operation.

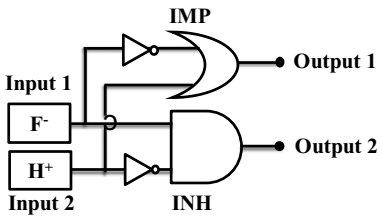
Herein we report multiple logic operations using anthocyanin derivative based on its optical and its emission response with different ionic inputs (OH^-, F^- and H^+). As shown in Fig.1 (A&B)

* Corresponding author.
E-mail address: kar.prasen@gmail.com (P. Kar).

http://dx.doi.org/10.1016/j.matlet.2015.06.004
0167-577X/

A

Input 1 (F^-)	Input 2 (H^+)	Output 1 (IMP) A_{488nm}	Output 2 (INH) A_{535nm}
0	0	1	0
1	0	0	1
0	1	1	0
1	1	1	0



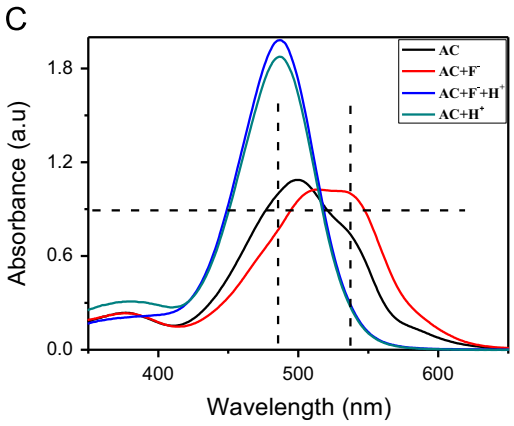


Fig. 1. (A) The truth table, (B) The Combinatorial logic scheme, (C) Absorption spectra of AC under different input condition F^- and H^+ with a horizontal line (dashed) that marks the threshold value.

the switching may be represented via a molecular IMPLICATION logic gate using H^+ and F^- as the inputs and absorption at 488 nm and 535 nm as output 1 and output 2 respectively. In case of output 1 and output 2 an absorbance of 0.8 has been taken as a threshold value; at 488 nm absorbance above 0.8 gives output = 1 and below of which gives output = 0. In presence of one input (F^-) the absorption intensity of solution is below the threshold value. In all other circumstances it remains in ON state. This logic operation resembles with IMPLICATION (Fig. 1A) logic gate and is represented in (Fig. 1B) as combinatorial logic scheme. The absorption intensity response at 535 nm is represented by INHIBITOR logic gate. The binary condition is high (1) at the output terminal in presence of excess F^-. However upon addition of H^+ the absorptions intensity is in OFF state (0). On simultaneous addition of both the inputs it remains in OFF state (0). This implies INHIBITOR (Fig. 1) logic operation. It is the complimentary of IMPLICATION logic gate.

As shown in (Fig. 2), IMPLICATION logic gate may be obtained using H^+ and OH^- as the inputs. Absorption at 488 nm, 580 nm (Fig. 2 C) and emission intensity at 597 nm (Fig. 2 D) was triggered as output 1, output 2 and output 3 respectively. In case of output 1 and output 2 an absorbance of 0.7 has been taken as a threshold value; In presence of OH^- the absorption intensity of solution is below the threshold value(0). In all other circumstances it remained in ON state (1). This logic operation resembles with IMPLICATION (Fig. 2 A) logic gate and is represented in (Fig. 2 B) as combinatorial logic scheme. The absorption intensity response at 580 nm may be represented by INHIBITOR logic gate as treatment with OH^- the absorption intensity was more than the threshold value. However in any other circumstances it remains in OFF state (0). The emission intensity at 597 nm was taken as output 3. The Emission intensity of 4.5×10^6 was considered as the threshold value. In absence of both inputs there was high emission (intensity is in order of 9×10^6). In all other circumstances, at this wavelength emission intensity was completely quenched. This output 3 channel encodes NOR gate.

In UV–vis absorption study, AC showed absorbance maxima at 490 nm. Significant changes in the absorption spectrum of AC were observed in the presence of Fe^{2+} with the appearance of a turn-on band at 540 nm and 650 nm. The absorption red-shift from 490 nm to 540 nm can be considered mainly due to extended conjugation of AC and electron delocalization due to the intramolecular charge transfer (ICT) after the encapsulation of Fe^{2+} (Supporting Information). Additionally the band appeared at 650 nm is attributed due to metal to ligand charge transfer transition. As shown in (Fig. 3D), the emission quenching by Fe^{2+} is most likely

due to an energy transfer occurred from AC to the open-shell d-orbitals and paramagnetic nature of Fe^{2+} exhibiting a faster and more efficient non-radiative decay of the excited states of AC.

As shown in Fig. 3 the switching may be represented via a molecular OR logic gate using Fe^{2+} and H^+ as the inputs and absorption at 490 nm, 570 nm and emission intensity at 572 nm (Fig. 3 C) as output 1, output 2 and output 3 respectively. In case of output 1, output 2 an absorbance of 0.25 has been taken as a threshold value. At 490 nm absorbance above 0.25 gives output = 1 and below of which gives output = 0. In absence of both the input 1 and input 2 the absorption intensity of solution is below the threshold value. In all other circumstances it remained in ON state. This logic operation resembles with OR (Fig. 3A) logic gate and is represented in (Fig. 3B) as combinatorial logic scheme. The absorption intensity response at 570 nm may be represented by INHIBITOR logic gate. Upon treatment with Fe^{2+} the absorption intensity was more than the threshold value. However upon addition of H^+ the absorptions intensity is in OFF state. However on simultaneous addition of both the inputs it remains in OFF state. This implies INHIBITOR (Fig. 3A) logic operation. The emission intensity at 572 nm was taken as output 3. The Emission intensity