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A new molecular logic circuit with 4 bit input

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ABSTRACT

In this work, to obtain a new molecular logic circuit with a 4-bit input, boradiazaindacene (BODIPY), spiropyran (SP) and imidazole derivatives were integrated within the same molecular skeleton. Cu^{2+} ions, ethylenediaminetetraacetic acid EDTA, and UV and VIS lights are specified as the 4 inputs. While the SP derivative switches to the merocyanine (ME) form under UV light, VIS light induces the reverse switching of the ME form to the SP form. It is known that the imidazole group is a good probe for Cu^{2+} ions. The fluorescence spectra of the functionalized BODIPY derivative are measured for the 16 possible cases of the 4-bit input. The corresponding truth table is prepared based on the obtained results. The Boolean algebra expressions are then simplified using the Karnaugh map, and finally, a new molecular logic circuit with a 4-bit input is obtained.

1. Introduction

We live in the digital age. Computers are now actively used almost everywhere. Faster computers with much higher performances are required due to the rapid development of technology. The microprocessor is the most important component of the computer. It is the brain of a computer [1] and consists of millions of transistors [1,2]. As the transistors used in microprocessors get smaller, the speed and performance of the microprocessors increase [3]. However, it is thought that the limit to the minimization of transistors is now being gradually approached. According to the currently expected trend, transistors will reach their performance limit in the next two decades. Actually, the existence of this limit was predicted by Moore well in advance [4]. The pioneering study of De Silva in 1993 [5] was an answer to this prediction. It was shown that molecular logic gates might be an alternative to silicon-based circuits, stimulating intense attention and interest in this topic [6] because it does not appear to be possible for the silicon analogues of molecular logic gates to be fabricated in such small sizes.

A molecule used as a single logic gate must change its ground and excited states upon the application of specific chemical, electrical or optical inputs [6]. According to the changes, detectable outputs could be obtained and they are represented with 1 or 0 according to the Boolean formulation, and relevant logic gate operation is extracted following the Karnaugh map simplification [7].

Many studies have been reported in the literature on the three basic logic gate operations [8], i.e., AND, NOT and OR; on the combinational logic functions [9], i.e., NOR, NAND, INHIBIT, and EnOR; and on logic devices that have more complicated functions [10], such as half-adder/subtractor, password protection and encoder/decoder. Molecular logic circuits operating with 4 inputs have not been studied as much as those with one, two or three inputs [11]. This is not due to a lack of interest in research on 4 input molecular logic circuits but rather due to the complexity of the synthesis and application of the required molecules due to the rising complexity of the designed logic circuits with increasing number of inputs.

In this study, a new molecular logic circuit with a 4-bit input was obtained. To achieve this goal, highly fluorescent boradiazaindacene (BODIPY), photochromic spiropyran (SP) and imidazole derivatives were integrated into the same molecular skeleton to obtain a new molecular logic circuit with 4-bit input. Cu^{2+} ions, ethylenediaminetetraacetic acid (EDTA), and ultra-violet (254 nm) and visible (500 nm) light were chosen as the 4 inputs.

2. Experimental

2.1. Materials

All chemical compounds were purchased from Sigma-Aldrich and Alfa-Aesar. These were then used without further purification. Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker instrument at 400 MHz for ^{1}H and 100 MHz for ^{13}C

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NMR. Silica gel (200–400 mesh, Gem Chem) was used for column chromatography. Thin layer chromatography (TLC) was carried out using Merck 0.2 mm silica gel 60 F254 analytical aluminum plates. An Agilent Cary Eclipse spectrophotometer was used to record the fluorescence measurements.

2.2. Synthesis

Compounds **1** and **2** were synthesized according to the procedures described in References [14] and [16]. Additional information about the procedures and a detailed explanation are available in the supporting information.

2.2.1. Synthesis of compound *3*

BODIPY (**1**) (89.6 mg, 0.24 mmol), SP (**2**) (171.6 mg, 0.48 mmol) and DMAP (7.3 mg) were dissolved in 12 mL of CH_2Cl_2 at 0 °C under Argon. DCC (53.55 mg) was added to the solution at 0 °C, the temperature of the mixture was allowed to reach room temperature, and the solution was then stirred at ambient temperature for 36 h. The solvent was then evaporated, and the residue was chromatographed on silica gel EtOAc:Hexane (0.2:0.9 (v/v)) to obtain a dark orange compound **3** (57.3 mg, yield: 34%).

^{1}H NMR ($CDCl_3$): 8.06 (d, J = 8 Hz, 2H), 7.98–7.9 (m, 2H), 7.32 (d, J = 8 Hz, 2H), 7.12 (t, J = 8 Hz, 1H), 7.03 (d, J = 8 Hz, 1H), 6.83 (t, J = 8 Hz, 2H), 6.70 (d, J = 8 Hz, 2H), 5.92 (s, 2H), 5.81 (d, J = 8 Hz, 1H), 4.45 (t, J = 8 Hz, 2H), 3.65–3.54 (m, 1H), 3.53–3.43 (m, 1H), 2.49 (s, 6H), 1.26 (s, 6H), 1.22 (s, 3H), 1.18 (s, 3H) **^{13}C NMR($CDCl_3$):** 165.7, 159.3, 156.1, 146.6, 142.7, 141.2, 140.1, 135.7, 130.9, 130.6, 130.4, 128.9, 128.4, 127.8, 126.0, 122.8, 121.9, 121.7, 121.5, 120.1, 118.4, 115.6, 106.8, 106.5, 63.10, 52.8, 42.5, 29.7, 25.9, 19.9, 14.5. **HRMS (EI):** Calcd. for C40H37BF2N4O5 $[M^{\bullet}]^-$ 701.2867; found 701.2510.

2.2.2. Synthesis of the targeted compound *5*

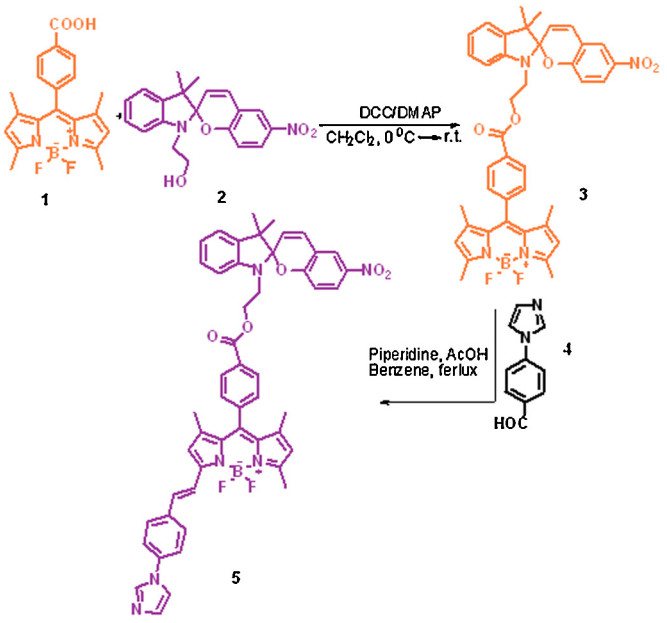
Compound **3** (168.3 mg, 0.24 mmol), 4-(1H-imidazole-1-yl) benzaldehyde (41.44 mg, 0.24 mmol) glacial acetic acid (0.15 mL), and piperidine (0.15 mL) were refluxed in benzene (25 mL). After two hours, the crude product was concentrated under vacuum and purified by silica gel column chromatography EtOAc:$CHCl_3$ (0.1:3, (v/v)). The pink colored fraction was collected and again purified by silica gel column chromatography EtOAc:$CHCl_3$ (0.8:0.3 (v/v)) and the solvent was removed under reduced pressure to obtain a dark purple solid, compound **5** (31.5 mg, yield: 15%). If the reaction time was extended, the yield of the target product **5** was reduced. Therefore, the reaction was repeated using compound **3** recovered by column chromatography.

^{1}H NMR (d-DMSO): 8.35 (br.s, 1H), 8.21 (br.s, 1H), 8.1 (d, J = 4 Hz, 2H), 8.00 (d, J = 8 Hz, 1H), 7.84–7.46 (m, 9H), 7.24–7.06 (m, 4H), 6.97 (br.s, 1H), 6.89–6.78 (m, 3H), 6.26 (br.s, 1H), 5.88 (d, J = 8 Hz, 1H), 4.58 (br.s, 1H), 4.43 (br.s, 1H), 3.34 (s, 2H and H_2O of d-DMSO) 2.54 (s, 3H), 1.37 (s, 3H), 1.33 (s, 3H), 1.22 (br.s, 6H). **^{13}C NMR (d-DMSO):** 165.1, 159.0, 155.9, 151.9, 146.4, 142.7, 141.8, 140.6, 139.2, 138.9, 137.1, 135.6, 135.4, 134.5, 131.6, 130.8, 130.3, 130.0, 128.8, 128.63, 128.61, 128.5, 128.2, 127.6, 125.8, 122.8, 122.0, 121.7, 121.4, 120.7, 119.4, 118.7, 118.3, 118.2, 115.5,106.6, 106.2, 62.8, 52.3, 42.0, 25.4, 22.0, 14.2, 14.0, 13.9. **HRMS (EI):** C50H43BF2N6O5 calcd. for $[M^{\bullet}]^-$ 855.3398; found 855.3084.

A detailed description of the synthesis of all compounds is provided in Supporting information.

3. Results and discussion

BODIPY derivative **1** was reacted with the photochromic component SP via Steglich esterification to receive the output obtained under the ultraviolet (UV) and visible (VIS) light illuminations that constitute two of the 4 inputs. After obtaining product **3**, the 3



Scheme 1. Structure and synthesis of target compound **5**.

position of the BODIPY derivative was functionalized with 4-(1-*H*-imidazol-1-yl) benzaldehyde by the Knoevenagel condensation reaction for detecting Cu^{2+} ions, which is one of the 4 inputs (Scheme 1).

It was shown that monostyryl and distyryl-BODIPY derivatives containing imidazole groups were highly selective for Cu^{2+} ions [12]. For a 4 bit binary system, sixteen (2^4) cases exist, which are 0000, 0001, 0010, 0011, 0100, 0101, 0110, 0111, 1000, 1001, 1010, 1011, 1100, 1101, 1110, and 1111. Hence, to obtain a molecular logic circuit with 4 inputs, it was necessary to measure the changes in the emission spectra of target compound **5** in the presence of the sixteen possible input combinations. To accomplish this, solutions with Cu^{2+} ions and EDTA concentrations of 500 μM and 1250 μM, respectively, were prepared in the required cell, while the concentration of the compound **5** was adjusted to 10 μM in each cell. The effect of the 500 μM Cu^{2+} ions can be overcome with the 1250 μM EDTA solution [13]. When it was necessary to use UV light, VIS light or both, the cell was exposed to illumination (by UV, VIS or both) for 30 min. UV, VIS, Cu^{2+} ions and EDTA are denoted as In 1, In 2, In 3 and In 4, respectively. Fig. 1a shows the emission spectra of the compound **5** in the presence of all possible combinations of the 4 inputs with the relative emission intensities of the compound **5** at 578 nm for all possible combinations presented in Fig. 1b. According to the results shown in Fig. 1a and b, the fluorescence intensity of the compound **5** did not meaningfully change in the measurements for case 1 (0000), case 2 (0001), case 4 (0011), case 5 (0100), case 6 (0101), and case 8 (0111). While compound **5** existed in the cell solution for all cases, EDTA was also present in case 2 (0001), Cu^{2+} ions and EDTA were present in case 4 (0011), VIS light in case 5 (0100), VIS light and EDTA in case 6 (0101) and VIS light, Cu^{2+} ions and EDTA in case 8 (0111). EDTA did not interact with any part of compound **5**; thus, no change was seen in the fluorescence intensity in case 2 (0001). When Cu^{2+} ions interacted with the imidazole group, the fluorescence intensity of compound **5** decreased, and compound **5** recovered its fluorescence intensity after the addition of the required amount of EDTA to the solution because it is known that EDTA [14] is a strong metal chelator and has a high binding constant for Cu^{2+} ions. All measurements were made during the daytime and VIS light induced only the switching of the merocyanine (ME) form to the SP form [15] because the SP form existed in compound **5**. Thus, VIS light in case 5 (0100) did not