A NEW FAMILY OF OPTICALLY CONTROLLED LOGIC GATES USING NAPHTHOPYRAN MOLECULE

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ABSTRACT

Microelectronics is predicted to reach its limit in another five to six years. As an alternative substitute, molecular electronics is analysed as an option, owing to its low power consumption and also very less area occupied by it(typically nm2). Conventional molecular electronic structures for molecular computational structures have been presented in the past. Naphthopyran in one potential candidate in creating optically controllable switches due to its bi-stability. It switches between the open ring and closed ring structures effectively when illuminated with light. In this paper, we will theoretically present a family of logic gates which are controlled optically, using Naphthopyran and associated architectures for basic structures such as AND, OR, XOR, Controlled NOT, Half adder and full adders, which are controlled optically. We see this as a step towards achieving the integration of molecular electronics and photonics, and thus, fabrication of IC like circuits employing the above.

KEYWORDS

Naphthopyran, Azobenzene, Self assembled Monolayers(SAM), Photo-isomerisation, Molecular electronic logic gates(MELG).

1. INTRODUCTION AND BACKGROUND STUDY

Molecular electronics has been investigated as a potential candidate for achieving bottom up fabrication and low power electronics. The attractive feature of this type of materials is that they can self assemble on a substrate. As we go deeper into the subject of molecular electronics, we see a very wide difference from conventional inorganic materials based electronics that is being used in present day electronics. The transport properties are totally governed by quantum mechanics.

The conduction in the molecules takes place due to the transfer of electrons through the pi orbitals. Some candidates have been proposed in the form of long chain polyphenylene for molecular wires. These wires are called Tour-Reed wires[1]. Using these wires, p-n diode like structures were formed, by using electron acceptor and donor groups like $-NO_2$, -CN, -CHO etc. and $–NH_2$, -OH, $-CH_2CH_3$ etc. respectively. This diode was used in preparing various logic circuits. The molecules at the end of the wires which provide the connection are thiol groups, surface adsorbed on gold.

Analogous to energy levels in the semiconductors namely Valence and conduction bands, in molecules, Lowest Unoccupied molecular orbital(LUMO) and Highest occupied molecular orbitals are present. The equivalent electrochemical potential between the two levels at equilibrium is called E_F. The conduction through the molecules is attributed to the movement of electrons through the polarons or the solitons[2]. Since the length of the molecule is very less,

the conduction takes place only through tunnelling. For a detailed study on the various types of tunnelling [3] and [4] can be studied.

Using the above conduction phenomenon, various architectures for molecular diodes have been proposed(six different architectures)[6]. All these diodes have been manufactured using a single molecule. In [1], architectures for molecular logic circuits using the diodes made of Tour-Reed wires was proposed. Circuits were designed using this diode architecture. Even though the architecture covered an area of only about a few nanometers, the circuit's complexity was high, and the defect tolerance of the molecular computer is still under question. Transistors have also been built using the doped molecular wires[7]. The I-V characteristics have also been analysed. The architecture presented was similar to a BJT, where an one electron donor forms the N regions and a one electron acceptor forms the P region. The P can be sandwiched using the two N regions or vice versa.

In organic molecules, photoisomerisation is an important phenomenon. The various organic structures and their photoisomers are studied in depth by various research groups of late due to the fact that they can be used in optical data storage devices of very high densities[5]. The concept for the above application is based on the fact that different photoisomer of the same compound exists at a stable state and also shows a varied conduction property.

The photoconduction phenomenon in conventional electronic devices arises from the fact that carriers are generated by incident radiation. The carriers are generated by incident radiation when the energy of the incident radiation is greater than that of the band gap energy of the semiconductor material [3]. In molecules, photochromic switching occurs because of the change in the absorption spectra of the organic molecule's isomers[6].

The four primary molecules which are investigated for photochromic applications are Azobenzenes(AZ), Spiropyrans(SP), diarylethenes and Rotaxanes and catenanes.

Rotaxanes and catenanes have already found a wide acceptance in molecular motors, due to their rotary switch like character[8].

Azobenzenes are another class of switches which is being investigated by molecular electronics engineers all over the world due to their simple structure and superfast switching. Azobenzene molecule contains a double bonded nitrogen bridge between the two benzene molecules. The molecule shows a switching from *trans* to *cis* and vice-versa when exposed to visible and UV light respectively. But for constructing a circuit out of Azobenzene, we need to use metal contacts at the either ends of the molecules. This sometimes results in very unstable structures and zero switching based on the metal used for contact. Tetra-tert-butyl-azobenzene is an intermediate sized azobenzene derivative. The switching is very efficient at Au(111). But it requires as laser illumination as opposed to photo-diode illumination. The carriers in the substrate are also exited at all wavelengths, which makes it tuning the switching impossible. At Ag(111), Cu(111) or Au(100), the molecule does not switch at all[9]. Also, the reverse switching of some molecules due to a temperature rise also makes azobenzene a poor switch.

Diarylethenes have been shown to switch effectively in ordered metal molecule metal devices. Diarylethenes switch to two states, one is the off state in which the ring is closed, and thus the switch is on. When illuminated using *visible* light, the ring opens, and thus the switch is in off state. But, the molecule becomes an irreversible switch when adsorbed to gold. This can be avoided by using spacer groups, but this induces an extra tunnel barrier[10].

Naphthopyrans are characterised by having a pyran ring to a naphthoquinone which showed reversible switching when illuminated with UV/Vis radiation. These switches showed a good stability, photochromicity, and large changes in absorption wavelengths between the isomers. Naphthopyrans were synthesised on a poly-methyl-meth-acrylate(PMMA) with electron donating and electron accepting groups. The compounds showed open-ring isomerisation when illuminated with UV and showed ring closing isomerisation when kept in darkness. Fatigue testing also showed no significant changes in optical density[11].

In [12], a theoretical study of the Naphthopyrans were studied using the Non Equilibrium Green's Function formalism, combined with *ab-initio* studies. The on-off ratio was found to be nearly 90 at a voltage of 1.4V. We will use this molecular switch in the paper to build various logic gates, that are optoelectronic.

2. PHOTONIC LOGIC GATES:

Bottom up approach requires us to come up with new architectures for molecular logic gates with applications in future information technologies. In a molecular photonic gate, the main signal is a light signal. The light signal is the input, as well as the output. This requires the elements to have atleast two bistable states. It also must possess distinguishable properties, such that we can use any of these properties to change between the two or more states. Various such gates are studied in [13]. The logic gates proposed are AND, NAND, OR, XOR, INH(inhibit). Compounds with more switching states can also be used to realise ternary logic gates.

3. OPTICALLY CONTROLLED NAPHTHOPYRAN LOGIC GATES:

For usage of Naphthopyran as a switch, it is adsorbed on gold. The figure of the Naphthopyran switch adapted from [12] is shown below. The conductivity happens when the HUMO and the LUMO of the molecule come within a few k_bT of the Fermi level of the metal.

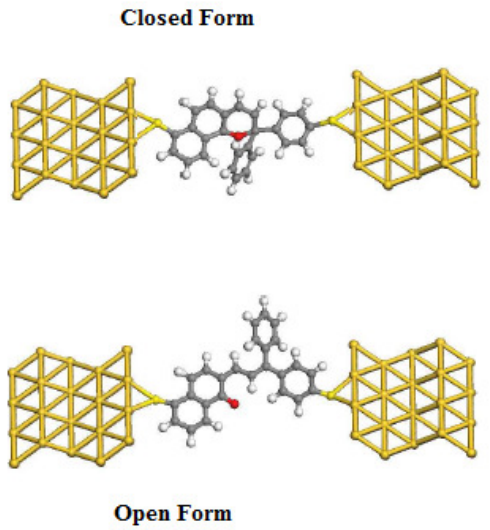

Fig 1. 'Off' and 'On' configurations of Naphthopyrans

The switching can be made from open to closed by using UV and closed to open by using Visible radiation. So, based on the characteristic switching wavelengths, we shall fix visible radiation to be 1(logical) and UV radiation to be 0. Also from [12] we can fix logic 1 as 1.4V, and 0V as logic zero. The reason for this is that, maximum on-off ratio is obtained at 1.4V.

3.1 AND GATE

The construction of an AND gate is quite easy compared to the other logic gates that are optically controlled. The AND gate's output is high only when both the inputs are high. The AND gate structure is shown in figure 2.

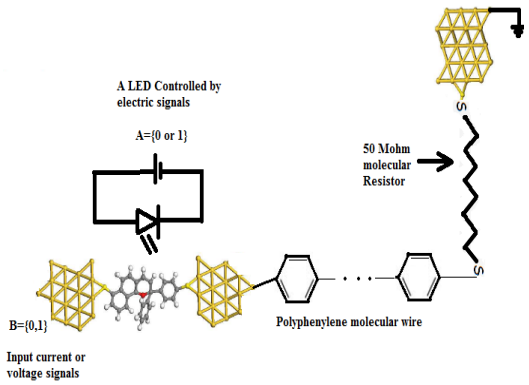

Fig 2. Naphthopyran AND Gate.

The molecule's terminals are adsorbed to the surface of gold with the help of thiol end groups, that acts as alligator clips. The polyphenylene molecular wire is attached to the other side of the surface of gold. This will be discussed in much detail in the 'Discussions' section. The decane molecule is used as a 50 M-ohm load resistor.

The truth table compatible with molecular photonics is shown in table 1.

Table 1. Truth Table of an Optically Controlled Molecular AND Gate

S.No.	A(Light input)	B(Electrical input)	Output
1	0	0	0
2	0	1	0
3	1	0	0
4	1	1	0

In this table, the light input A acts as the control input, and B is the electrical input. In a logic circuit, it can be modified as an AND gate, by giving one of the electrical inputs to A and another one to B. The *voltage* signal A, will drive the LED, to give the *Light* signal A. from the

figure, it can be seen that the molecule is in the closed form, or in the OFF state. For switching it ON, Visible radiation is emitted from the LED, that is controlled by the signal B. The polyphenylene is the molecular wire. The conduction can be enhanced by using triple bonds between the phenyl groups. This is because, in triple bond, the pi bonds are more delocalised.

When the light signal and the electrical signal are off, the output stays at low. In the second case, when the input is high, but the controlling light signal is low, the output still stays low. In the third case, when the input electrical signal B is low, but the control light signal A is high, the output is still low. In the final case, the output is at high, as both controlling signal and the electrical signal both are high. This gives us a brief idea about how to construct gates with a greater number naphthopyran switches. We can manipulate the and gate further to build OR, XOR and Controlled NOT gates. when using this family of optically controlled gates, we are able to build the other gates only by extrapolating the AND architecture. Thus we fix the AND Gate as the mother gate of this family, at a cost of 3, as it has only one switching element, and 2 inputs, one as control and one as the electrical signal input.

3.2 OR-GATE:

A conventional OR gate performs union operation. It gives a high output, when either of the inputs are high. The architecture of an OR gate is shown in figure 3.

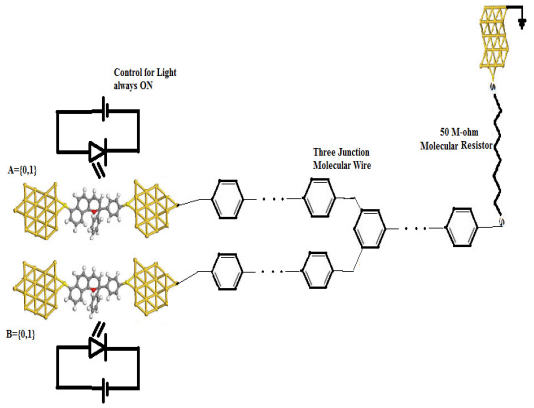

Fig 3. Naphthopyran OR Gate.

From the figure it can be seen that two switches are being used to construct the OR Gate. The High and Low conventions for the optical and the electrical signals remain the same as that mentioned above. The two switches along with the control signals acts as the AND gate, and OR is formed by connecting the two AND gates in parallel, fixing an input to High always.

Let A and B be the electrical inputs, L_1 and L_2 be the control inputs for switch 1 and two respectively.

The Switch one's output is: $L_1.A$; the Switch two's Output is L_2B. The net output will be the output of Switch one added with the output of the Switch 2:

$L_1.A+L_2.B = O$

In this, if we fix $L_1=L_2=1$, then, the output becomes A+B.

Thus, we showed that when the control signals are fixed to 1, the above architecture acts as an OR Gate. The truth table is shown below in table 2.

Table 2. Truth Table of an Optically Controlled Molecular OR Gate

L_1	L_2	A(Electrical signal)	B(Electrical Signal)	Output
1	1	0	0	0
1	1	0	1	1
1	1	1	0	1
1	1	1	1	1

The OR gate has two switches, the two light control signals remain high always, hence, the cost can be 1, it has 2 electrical inputs that switch effectively from HIGH to LOW, thus, a cost of 2. Thus, the total cost of the gate is 5.

3.3 EXCLUSIVE OR GATE*:*

The Exclusive OR gate (XOR gate) is often used in digital circuits as a half adder along with an AND gate. Here, in this paper we shall realise the XOR gate as an extension of the OR Gate. The XOR gate will have the same architecture as the OR gate, but the variation lies in the operation of the control signal. But the two control signals are operated simultaneously.

The XOR gate gives a low output when both the inputs are High, but a high output when one input is high, but the other is low. The truth table below the operation of the XOR gate.

Table 3. Truth Table of an Optically Controlled Molecular XOR gate

L_1	L_2	A(Electrical input)	B(Electrical input)	Output
0	0	0	0	0
1	1	0	1	1
1	1	1	0	1
0	0	1	1	0

From the truth table, we can derive the equations for the XOR Gate.

$L_1.A+L_2B=O$ is the basic equation for the OR gate. In this, as per the first and last condition of the truth table, if we fix the L_1 and L_2 control signals as zero, the output is also zero. But, if we fix L_1 and L_2 as 1, and if either of the electrical input is zero, then, according to the OR gate's equation, the output becomes High.

For the XOR Gate, there are 2 switches, two control inputs, which switch twice on the whole, but at the same time, so, the cost for this is 2. The 2 electrical signals cost 2. Thus the total cost of the XOR gate is 6.

The Controlled Not(C-NOT) Gate can be implemented as a special case of the XOR gate. In the conventional C-NOT gate, one of the input signal is fixed as high, then the other input is inverted. In our XOR Gate, for the second condition or the third condition, if we fix A=1 or B=1, we can see that the other input the other input is inverted automatically. For our optically controlled logical gates, we fix the light signals $L_1=L_2=1$, and also the input A=1, then we end up with a C-NOT Gate. The truth table is below.

Table 4. Truth table of an Optically Controlled Molecular C-NOT gate

L_1	L_2	A(Electrical Control Signal)	B(Electrical Signal)	Output
1	**1**	**1**	**0**	**1**
1	**1**	**1**	**1**	**0**
1	**1**	**0**	**X**	**0**

We can see from the truth table that the optical signals remain High throughout the operation of the Gate. If the electrical control signal A is high, then the input B is inverted. But, if the control input is low, irrespective of the input B, then the output remains low always. For this Gate, the cost can be calculated by taking into account the 2 optical control and the electrical control signal, and 2 switches. The total cost is thus 4.

4 SYSTEM DESIGN USING OPTICALLY CONTROLLED MOLECULAR GATES: HALF AND FULL ADDERS

If we pay attention to the switches, we can see the operation is analogous to an optically controlled molecular Relay. In this section, we will design molecular Adders using the control and the input signals as mentioned in the previous sections.

4.1 HALF ADDER

A half adder circuit, takes two inputs, and gives two outputs as carry and sum. The Half adder circuit is implemented using the XOR gate and the AND gate.

For implementing the half adder using the molecular switch, we will be using A as a Electrical as well as an optical switch. The electrical signal A, will be given as an input to the XOR gate,

simultaneously, it will be used to control the AND gate, which will have B as an input to find the carry. The half adder is shown in the next page in the figure 4.

The molecular wire is used to split the signals A and B to give it to the AND gate. For this, the polyphenylene wires must be in out of plane in order to pass the input to the AND gates[1].

The half adder uses an XOR gate, whose cost is 6, and an AND gate, whose cost is 3. The gate has a total cost of 7, because the AND gates are also given the same inputs as the XOR gate, and the AND gate is controlled directly by the signal, A.

Table 5. Truth Table of an Optically Controlled Molecular Half Adder

L_1	L_2	A	B	S	C
1	**1**	**0**	**0**	**0**	**0**
1	**1**	**0**	**1**	**1**	**0**
1	**1**	**1**	**0**	**1**	**0**
0	**0**	**1**	**1**	**0**	**1**

The full adder design will automatically follow the half adder design.

4.2 FULL ADDER

The design of a full adder using Naphthopyran is different from the design that is conventional. This is because of the difference in the working of the optically controlled switch compared to the normal one. The Naphthopyran full adder's operation is quite different from the half adder. For the full adder, we use a three input XOR gate, an OR gate, contrary to the conventional circuit for full adder where we use two AND gates and an OR gate. This is because, since the OR gate implemented using the Naphthopyran switches themselves come from the AND gate, we directly use a two input OR gate to generate the carry term.

The working of the gate is as follows:

The 3 outputs of the XOR gates will be controlled by the optical signal inputs. The output of the first two inputs, will be separated from the main wire to get the term A XOR B(not shown in figure). This term can be separated by using an out of plane connection of the wire. This intermediate input, A XOR B, is given as the control input to the LED of the 2 input OR gate. The other switch in the OR gate, is used conventionally with A as the control and B as the electrical input signal.

The full adder uses 5 switches altogether, it uses three inputs. The control for the and gates are only intermediate outputs of the circuit. So the cost will be only 9.

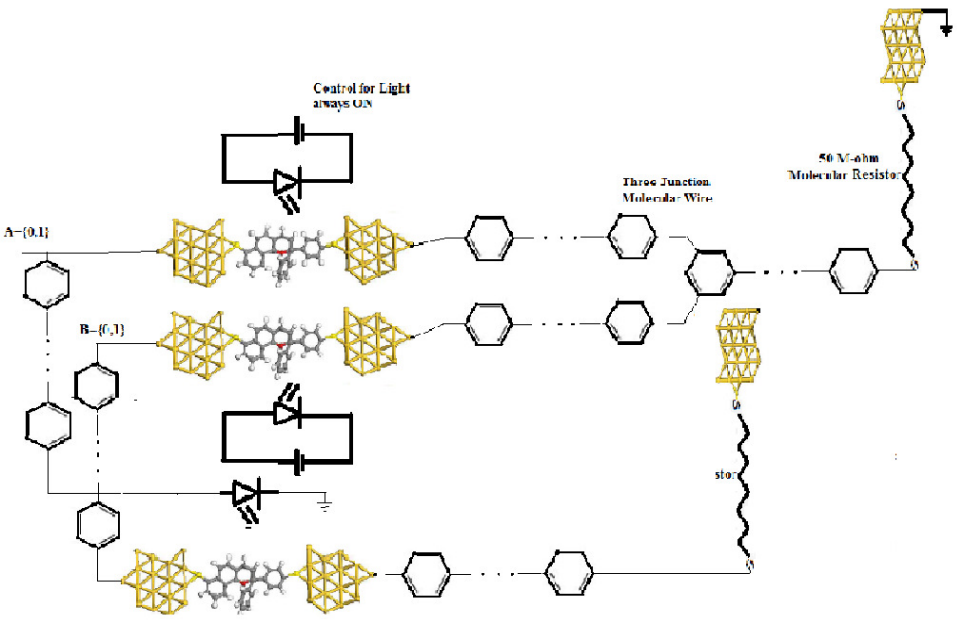

Fig 4. Naphthopyran Half Adder

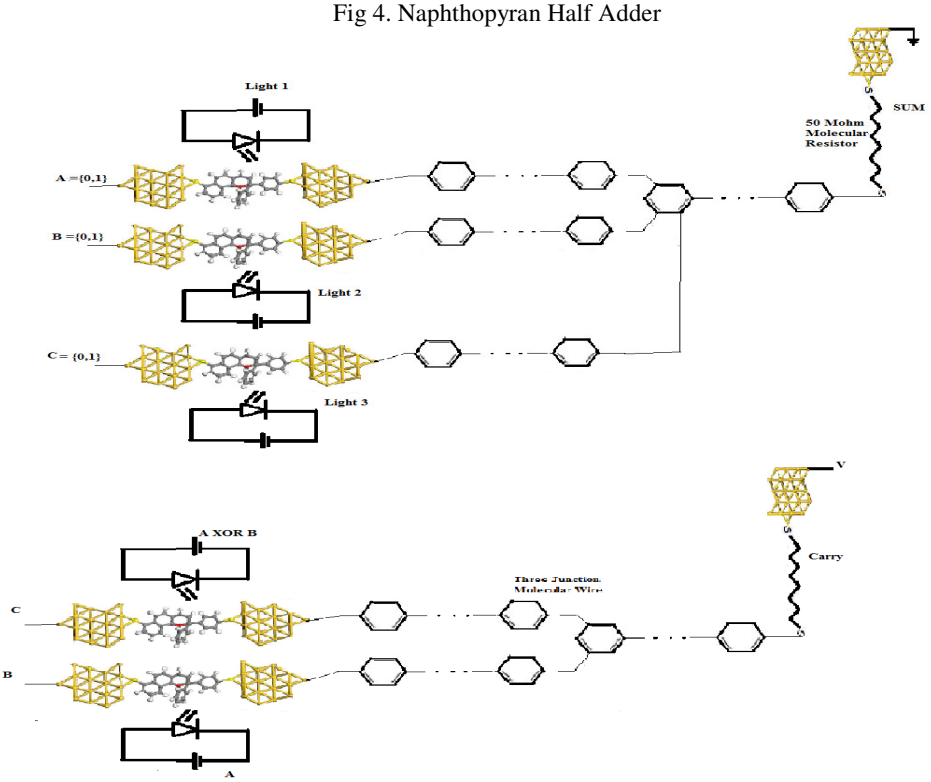

Fig 5. Naphthopyran Full Adder.

5. RESULTS, DISCUSSIONS AND CONCLUSIONS:

In the above four sections we discussed various architectures of logic gates using Naphthopyran switches, that are optically controlled. Even though these switches have some advantages such as lower power consumption, lower areas and larger densities, the methods for manufacture of these switches in a bulk is still unknown. We can safely say that we are still at least half a decade or a full away from bulk manufacturing these switches.

The switches have been manufactured in bulk by using Surface Adsorption or on Langmuir Blodgett films by using chemisorption and other known methods using surface chemistry. These molecules will be many in number, but they are considered as one because only one molecule is effectively in contact with the STM tip. Even though there are presently ways to produce these molecules in large numbers adsorbed to a surface, defect tolerant architectures for the molecular integrated circuits will prove difficult to achieve. This may require a lot of synthetic chemistry in action to guide the growth of the molecule to yield a required architecture.

In this paper, we have used a technique in which we assume that the molecular wire is adsorbed to the other side of the gold surface.

We believe that this will not bring much of a change in the conductivity of the molecule as the use of thiol end groups attached to gold has worked fine in existing molecular electronic circuits. Other non-metallic interconnects or contacts in the form of CNTs, Graphene and fullerenes are also being explored by various research groups. But nevertheless, the consequence of such a method of adsorbing the molecule to both sides of the surface has to be studied in detail experimentally to check the effects of the level broadening of energy levels of gold into the HOMO-LUMO of the molecular wire.

It will also be interesting to study contacts at the terminal end of the molecules which are just two to three atoms thick. Because of the thinness of such a barrier there is a good possibility that we may get near ohmic electron transfer through the molecules forming the contact. But there is a possibility that coulomb blockade, Kondo effect and splitting of the broadened levels between the HUMO and the LUMO may occur and may act as a catalyst or poison to the conductance of the molecule. this is also an area of future research.

There is also a need to find a contact surface, that will remain universal for all the molecular electronic components or switches. This is because, a molecule which may show a good conductivity when adsorbed on gold, may show an entirely different behaviour when adsorbed on Copper or silver.

The manufacture of the Naphthopyran gates on a substrate may call for the need for smaller molecular LEDs. Presently, we have OLED materials like conjugated poly-phenyl-vinylene, Rubrene etc., but single molecular light emitters may also help greatly in reducing the space of such a molecular integrated circuit.

The author feels that for successful integration of a molecular integrated circuit, various properties of the molecule such as the fluorescence, adsorption, redox reactivity and transport properties must also be exploited in some way or the other.

All the above factors make molecular electronics challenging. The successful integration of the first molecular electronic integrated circuit adsorbed on a single substrate may still be far away, but once realised, may change the face of electronics once and for all.

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