Modeling flip-flops based on molecular diode structures

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Modeling flip-flops based on molecular diode structures

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Abstract

Conventional semiconductor components can be used for modeling and simulating molecular structures, so the progress in molecular electronics can be accelerated by creating a link between molecular electronics and semiconductor technology. Little work has been done so far on molecular electronic modeling. The present work attempts to focus on molecular electronic modeling by proposing a typical model and discussing its theory. Moreover, the circuit components used for modeling the molecules are introduced. An asymmetric oligo phenylene ethynylene (OPE) molecular diode and a four-benzene molecular diode are designed using the presented typical model. Furthermore, using LTspice software, the currents are obtained from the model and molecules for both OPE molecular diode and four-benzene molecular diode to confirm their appropriate performance. Then transmission spectrum, potential drop profile, and rectification ratio are obtained and analyzed for the four-benzene molecular diode using Atomistix ToolKit (ATK) software. Finally, various molecular gates and molecular memory logic circuits including NOT, NAND, NOR, SR Flip Flop, and D flip-flop are designed using the four-benzene molecular diode model.

Keywords: molecular diode, molecular electronics, modeling, flip flop, ATK, LTspice

I. Introduction

Molecular diode was introduced by Ratner and Aviram as the first single-molecular device in the field of molecular electronics [1]. Molecular diodes consist of three parts including the donor groups (-NH2, -OH, -CH3, -CH2CH3), acceptor groups (-NO2, -CN, -CHO), and insulators (-CH2-, -CH2CH2-). The first and second parts have the properties of p-type and n-type semiconductors, while the third part can be a saturated aliphatic group [2, 3]. Several studies have focused on designing molecular logic gates. For example, in [4], a benzene molecule was used to create OR and XOR gates. In [5], a NAND logic gate was constructed using a three-leg molecule. In [6], NOT, AND, and OR logic gates were designed using a benzene ring. The idea behind this work was that in some configurations of molecules, the molecular junctions exhibit anti-resonance states at certain energies. These anti-resonance states play a key role in the function of the gates designed in this work. In [7], a molecule composed of proton-switchable pyrimidine unit and light-switchable azobenzene unit was presented. This molecule normally has a high resistance and in the presence of the ultraviolet (UV) light and acid solution has low resistance. Therefore, this molecule can be as AND logic gate. In [8], the OR and NOR logic gates based on photoswitchable protein were simulated. In [9], a hybrid design was implemented using HSPICE software. In [10], a molecular rectifier with a rectification ratio of greater than 1000 was reported using OPV molecule. In [11], the effect of doping variation on molecular diodes charge transport properties was studied and it is found that the number of donors and acceptors and the rectification ratio are not linearly related. In [12], an adjustable single-molecule rectifier with a rectification ratio of up to 600 has been reported. In [13] a ternary logic gate was designed which has less power consumption than conventional circuits. In [14], molecular AND, NOR, XOR, YES, and NOT gates were presented as four-terminal devices, which consisted of an organic molecule connected to two gold electrodes located between capacitor plates (gate terminals). In [15], a NAND logic gate was implemented in VHDL-AMS software using a molecular FET. In [16], using OPV5 molecules, three types of ternary inverter gates (NTI, PTI, and STI) were designed along with a full adder. Additionally, some studies have focused on modeling. For instance, different molecular components were modeled in [17] using parallel NMOS transistors, and different molecular diodes were modeled based on these models. In [18], a method was presented for modeling molecular logic structures using the circuit model of OPV molecules. In [19], molecular logic structures were simulated based on the Fermi level variations as a function of back gate voltage. In [20] and [21], molecular structures were designed using the OPV7 molecular model and some special techniques. In [22], molecular devices were modeled using three-leg molecules.

The rest of the paper is organized as follows. In Section II, the theory of a typical model is explained, and the circuit components used for modeling the molecules are introduced. The results are presented in Section III in which an asymmetric oligo phenylene

ethynylene (OPE) molecular diode and a four-benzene molecular diode are modeled in LTspice software using the typical model presented in this study. Then, the currents are obtained from the model and molecules for both OPE molecular diode and four-benzene molecular diode to confirm their appropriate performance. Moreover, the transmission spectrum, potential drop profile, and rectification ratio of the four-benzene molecular diode are obtained and then analyzed using Atomistix ToolKit (ATK) software. In Section IV, various molecular gates and molecular memory logic circuits, including NOT, NAND, NOR, SR flip-flop, and D flip-flop are modeled using four-benzene molecular diode model and the method presented in [20]. Finally, the work is concluded in Section V.

II. Typical model theory

When a benzene ring is doped with, for example, a boron atom, it tends to accept electrons, whereas when it is doped with a nitrogen atom, it tends to donate electrons. On the contrary, an undoped benzene ring acts like a wire, which is neither an electron donor nor an electron acceptor. In the proposed model, a benzene ring is considered as two parallel diodes in opposite directions. The ideality factor of the diodes in the benzene ring is considered to be 1.8, while the ideality factors of the diodes in other circuit components change with the type of doping of the benzene ring and the coupling state between the molecular components. Figure 1 shows the circuit components used in the model. It should be noted that the ideality factor is inversely proportional to the threshold voltage and diode current. As a result, when the ideality factor decreases, the threshold voltage and diode current increase. In other words, the current passing through a diode or its threshold voltage can be controlled by the diode ideality factor. In the present study, the ideality factor of diodes are set in the range of 1-2 and the other parameters of the diodes have the default values of the LTspice software [23]. In the following, the circuit components used for the molecular model in this study are introduced. The circuit component in Fig. 1a represents a benzene ring doped with boron atoms for a four-benzene molecular diode. Since the benzene doped with boron atoms tends to accept electrons, the ideality factor of MYdiode21 has to be less than that of MYdiode14, and it has a value of one. Therefore, this component has more tendency to pass the current to the left than to the right, meaning that it tends to accept electrons.

The circuit component in Fig. 1b represents a benzene molecule in which the molecular orbitals are evenly distributed throughout the molecule to help electrons move smoothly along the molecule. In this manner, the currents passing through the benzene (to the right or left) do not exceed each other. Therefore, the benzene molecule is modeled with two MYdiode14 diodes with the same ideality factor. The ideality factor of both diodes is 1.8, leading to a low threshold voltage. The circuit component in Fig. 1c

represents a benzene ring connected to the source electrode through a C2H4 molecule in an asymmetric OPE molecular diode. In this model, the C2H4 molecule weakens the coupling between the benzene and the source electrode, so the threshold voltage of MYdiode17 increases. This increase in threshold voltage reduces the ideality factor from 1.8 to 1.7. The component in Fig. 1d is a benzene ring, which is not connected to the electrode in the asymmetric OPE molecular diode. In this model, both the drain and source electrodes are implemented, and the lack of connection between benzene and drain electrode is considered as a weak coupling between them. This weak coupling is applied to the model by increasing the threshold voltage (i.e., by reducing the ideality factor of MYdiode16 from 1.8 to 1.15). Finally, the circuit component in Fig. 1e represents a nitrogen-doped benzene for the four-benzene molecular diode. Since the nitrogen-doped benzene tends to attract holes, MYdiode20 should have an ideality factor higher than that of MYdiode14, and it has a value of 2. Consequently, the mentioned circuit component has more tendency to pass the current to the left side than to the right side, implying the greater tendency to attract holes.

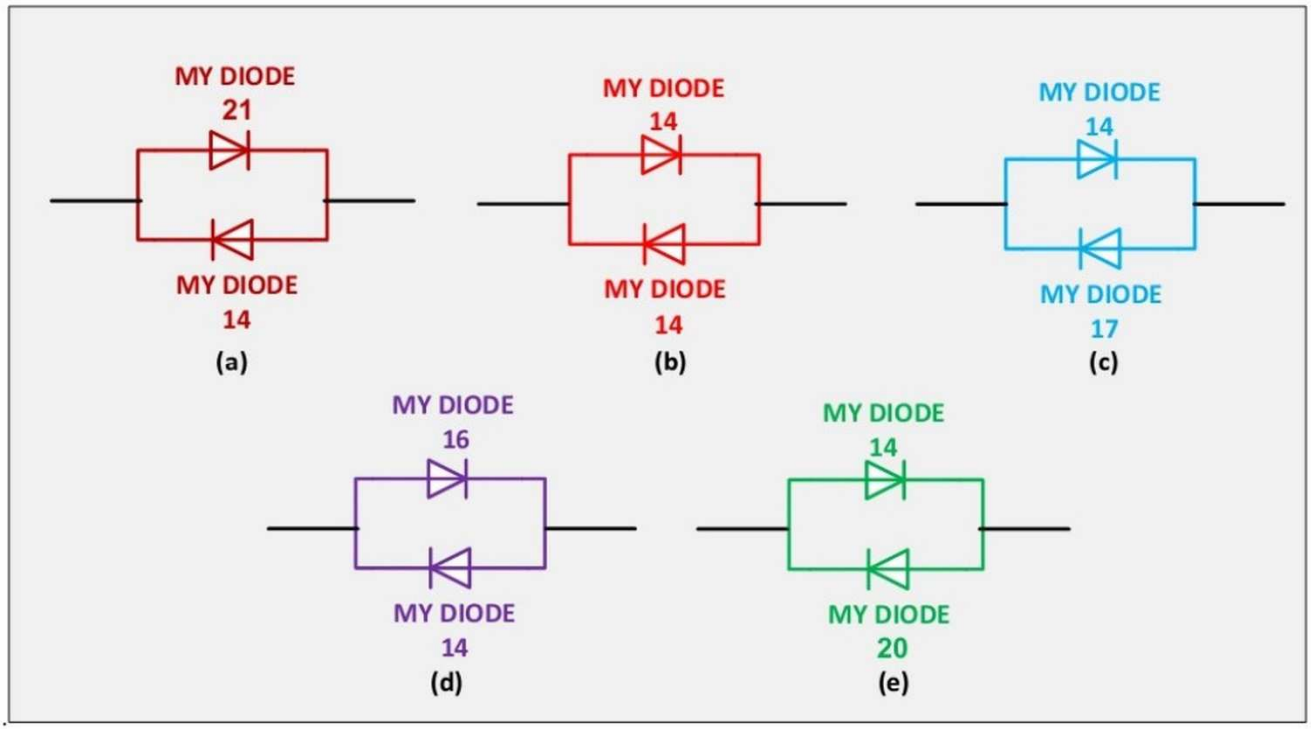


Fig. 1. Circuit components used in modeling molecules

III. Results of proposed model

In the following, different molecular diodes are modeled using the described typical circuit model. It should be noted that the asymmetric OPE molecular diode has been taken from [17] to better demonstrate the correct performance of the presented typical model.

A-Modeling of Asymmetric OPE Molecular Diode

In Fig. 2, a molecular diode consisting of three benzene rings is presented. This molecule is connected to a gold electrode through a thiol group, while on the other side, it has no connection with the gold electrode. In Fig. 3a, the model of this molecule, which uses the components presented in Fig. 1, is shown. According to this figure, the diode pair D3-D4 represents the right benzene ring, the pair D1-D6 represents the middle benzene ring, and the pair D2-D5 represents the left benzene ring. Figure 3b shows the current curves from the atomic simulation of the molecule presented in [17] and the circuit model. A good agreement can be seen between the current curves from the proposed circuit model and the atomic simulation.

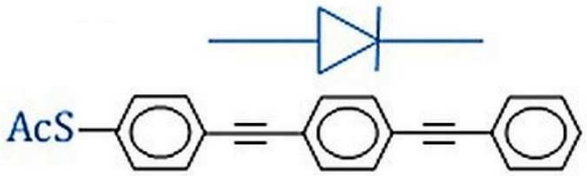
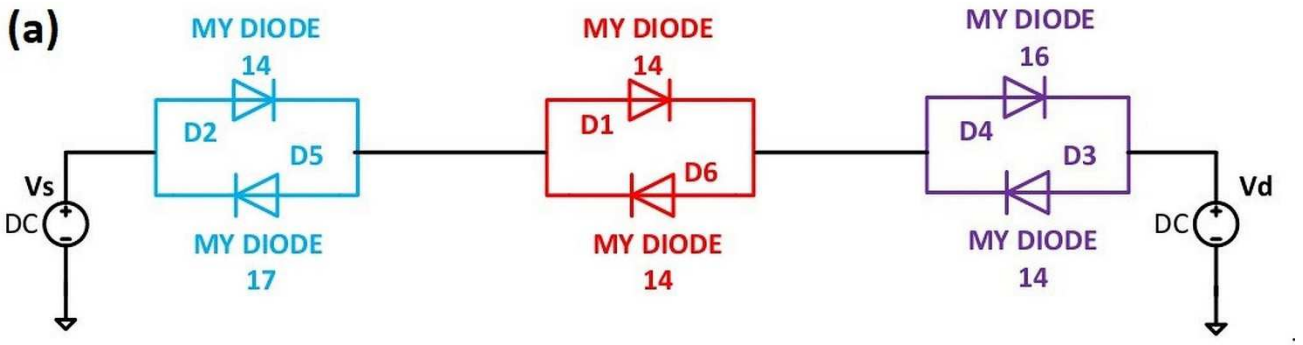


Fig. 2. Asymmetric OPE molecular diode [17, 24].



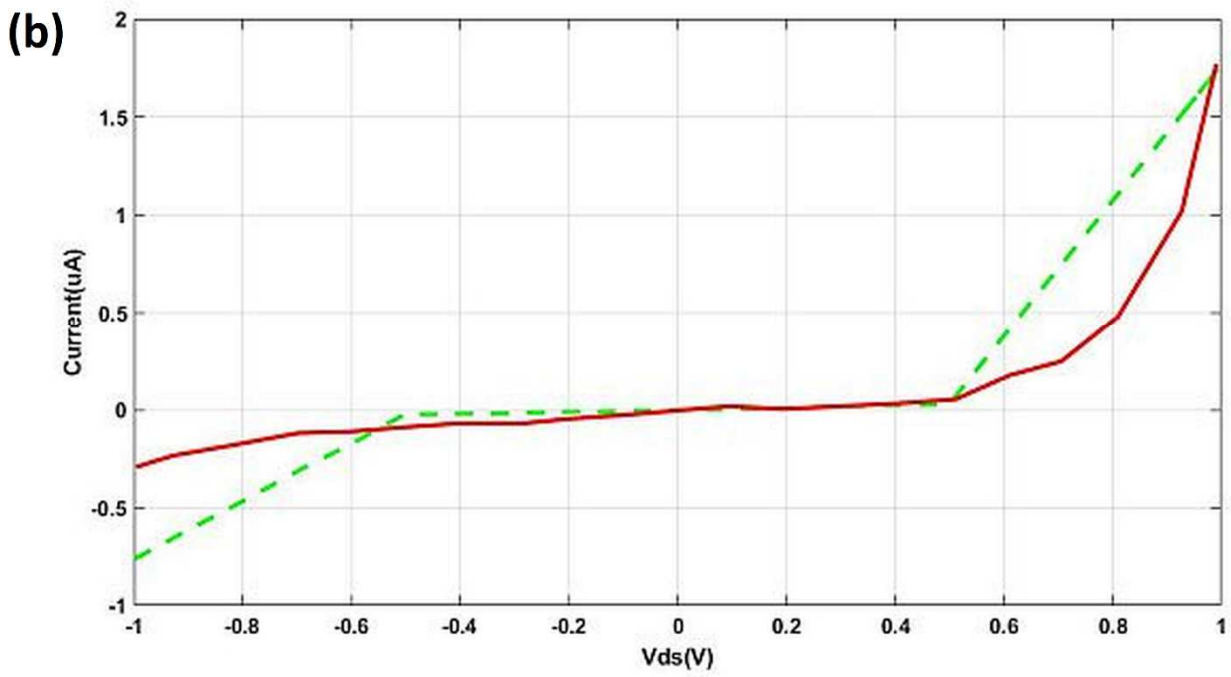


Fig. 3. (a) the circuit model of the asymmetric OPE molecular diode and (b) the current curve resulted from the atomic simulation of molecule in [17] (solid line) and from the circuit model (dashed line).

B-Modeling of Four-Benzene Molecular Diode

Figure 4 shows the molecular diode designed using Atomistix ToolKit (ATK) software [25]. This molecule is composed of four benzene rings doped with nitrogen and boron atoms, which allow the benzene rings to act as acceptors and donors. This molecule is connected to the gold electrodes with thiol groups on both sides. Table I, shows the characteristics of the four-benzene molecular diode. Figure 5 shows the potential drop profile along the four-benzene molecule at biases of -1V and 1V. This molecule is implemented in Fig. 6a using the components presented in Fig. 1. In Fig. 6a, the diode pairs D3-D4 and D7-D8 represent the benzene molecules doped with boron atoms, whereas the diode pairs D2-D5 and D1-D6 represent the benzene molecules doped with nitrogen atoms. Moreover, Fig. 6b shows the current curves from the circuit model and atomic simulation of the four-benzene molecule. As can be seen, there is a good agreement between the two curves. In Fig. 6c, the transmission spectrum of this molecule is shown. The intervals between the electrochemical potentials of the electrodes are shown in blue. The peaks of the transmission spectrum at positive drain-source voltages are higher than those at negative drain-source voltages, and this can affect the current passing through the molecule. For the green curve in Fig. 6b, the current level at positive drain-source voltages is higher than that at negative

drain-source voltages. In Fig. 6d, the rectification ratio of the four-benzene molecule is shown as a function of drain-source voltage. In this figure, the rectification ratio increases up to 0.6, and decreases beyond 0.6.

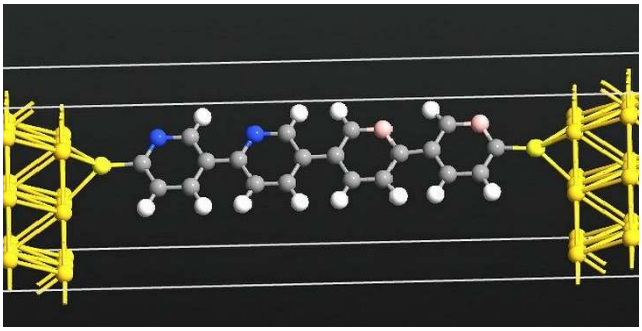


Fig. 4. Four-benzene molecular diode

Table I. Characteristics of four-benzene molecular diode

Length of single-molecule diode (distance between two sulfur linkers)	18.85 Angstrom
k-point sampling	3*3*50
Mesh cutoff energy	75 Hartree
Left electrode temperature	300 K
Right electrode temperature	300 K

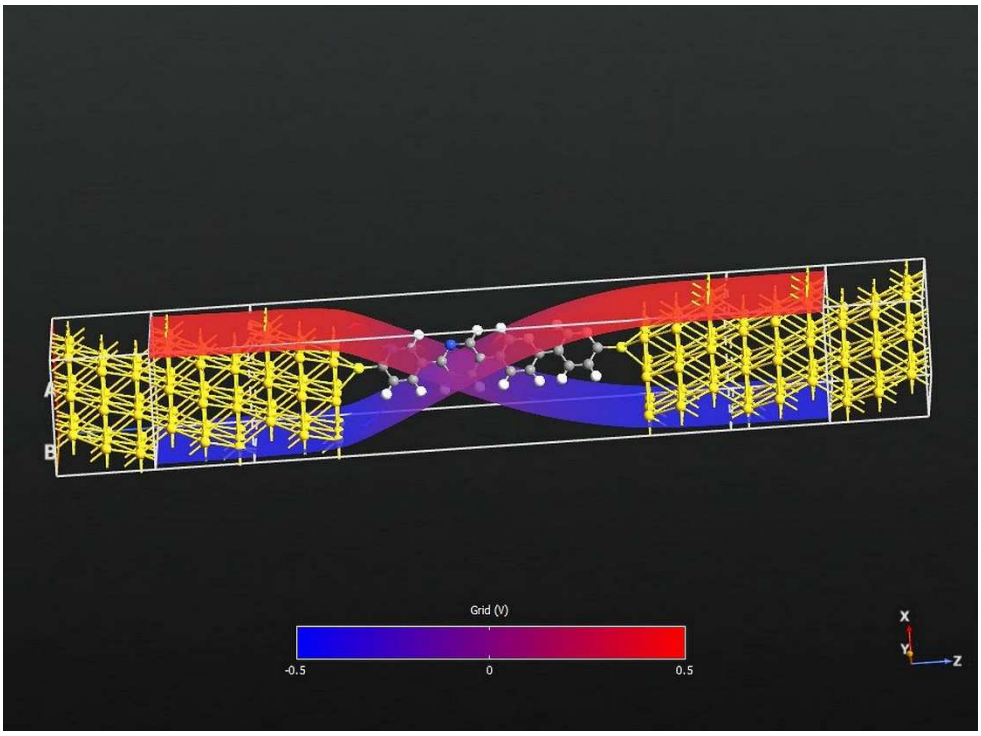
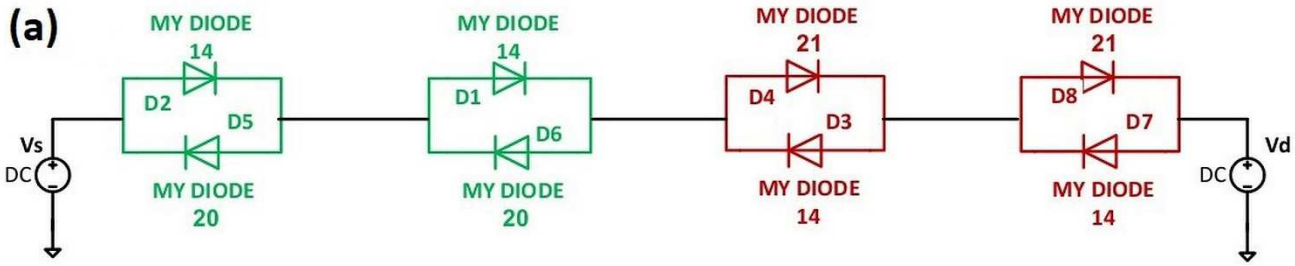
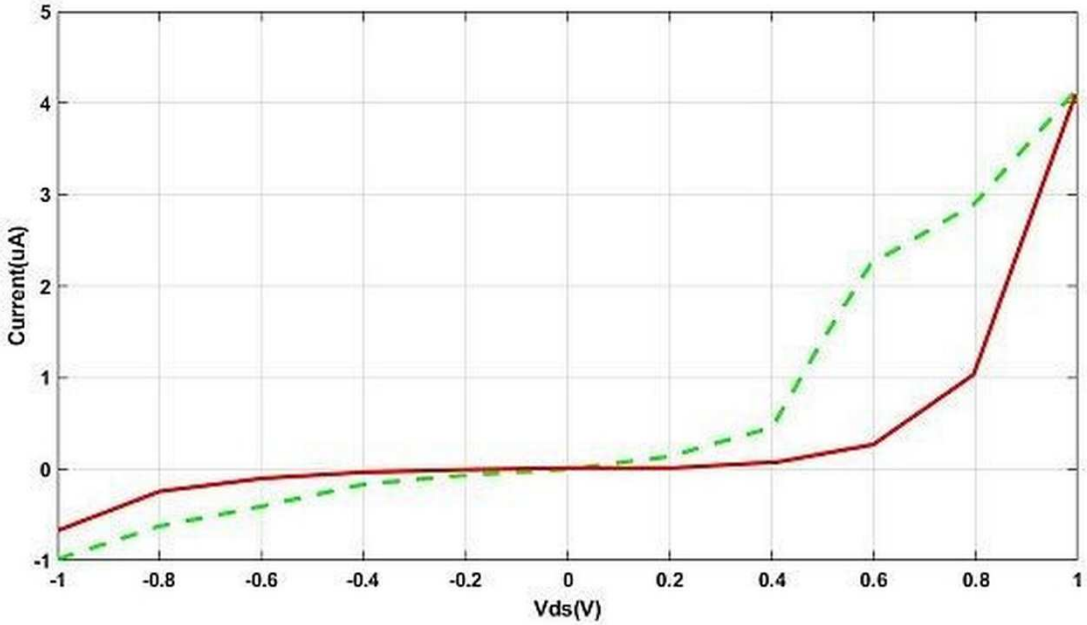


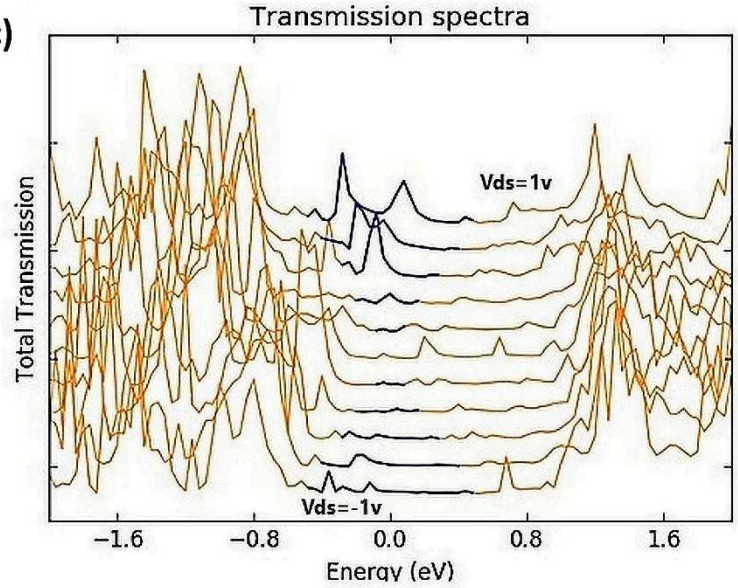
Fig. 5. Potential drop profile along the four-benzene molecule at -1V and 1V.



(b)


Current(uA)
Vds(V)
5
4
3
2
1
0
-1
-1
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
1

(c)


Transmission spectra
Total Transmission
Vds=1v
Vds=-1v
−1.6
−0.8
0.0
0.8
1.6
Energy (eV)

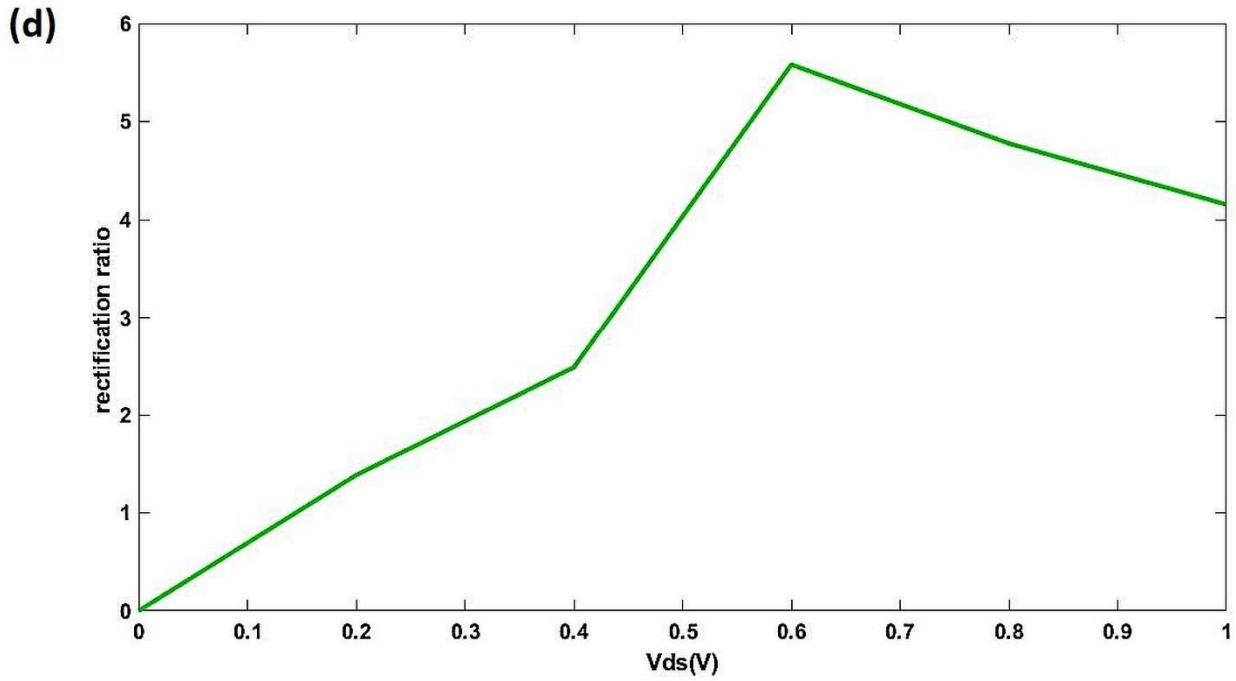


Fig. 6. (a) Circuit model of four-benzene molecular diode, (b) the current curves from circuit model (solid line) and atomic simulation (dashed line), (c) transmission spectrum for different drain-source voltages of the four-benzene molecular diode, and (d) the rectification ratio of the four-benzene molecule.

Table II, compares the results of the study on the OPV7 molecular transistor presented in [20] and the present work, which is based on molecular diode.

Table II. A comparison between the results of Ref. [20] and the present work

Reference	**Number of circuit elements used in model**	**Vds (volt)**	**Ids**	**Power consumption**	**Number of benzene rings used in the molecule**	**Number of used electrodes**	**Switching speed**
[20] (molecular transistor model)	14	1.2	663.86 nA	0.7966 µW	seven benzene rings	three electrodes	3 ms
Present study (molecular diode)	10	1	10.5 pA	10.5 pW	four benzene rings	two electrodes	6 ps

IV- Modeling of Molecular Gates using Four-Benzene Molecular Diode

Using the Four-Benzene molecular diode model, various molecular gates and memory logic circuits, such as NOT, NAND, NOR, SR flip-flop, and D flip-flop are modeled in this section.

A- Modeling of molecular NOT gate

A molecular NOT gate is modeled in this subsection using the four-benzene molecular diode based on the method presented in [20]. In the model presented in Fig.7, first, the current passing through the four-benzene molecular diode is measured using VS. Then, this current, which is induced by source F1, passes through resistor R to form the output of the NOT gate. The results of this model for the input Vin1 are given in Fig. 10.

Table III. NOT gate truth table

Vin	Vout
0	1
1	0

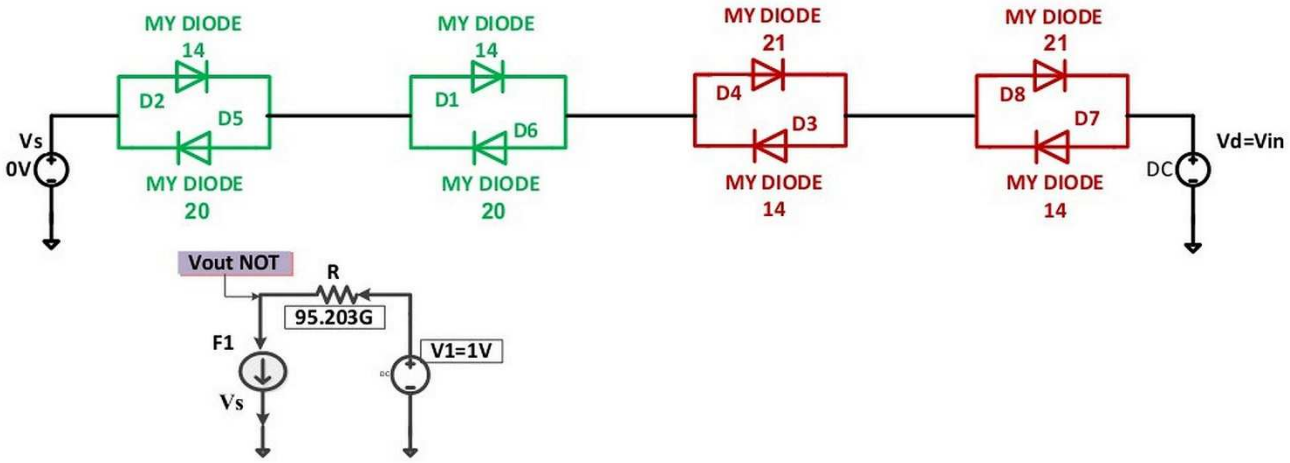


Fig. 7. Molecular NOT gate using the four-benzene molecular diode model

B- Modeling of molecular NOR Gate

In Fig. 8, a molecular NOR gate is modeled using the four-benzene molecular diode. In this model, two molecular diodes are used based on the method presented in [20]. The currents passing through the two molecular diodes are measured using sources Vs

and Vs1, and the maximum of these two currents passes through R to create the output of the NOR gate. The results of this model for inputs Vin1 and Vin2 are given in Fig. 10.

Table IV. NOR gate truth table

Vin1	Vin2	Vout
0	0	1
0	1	0
1	0	0
1	1	0

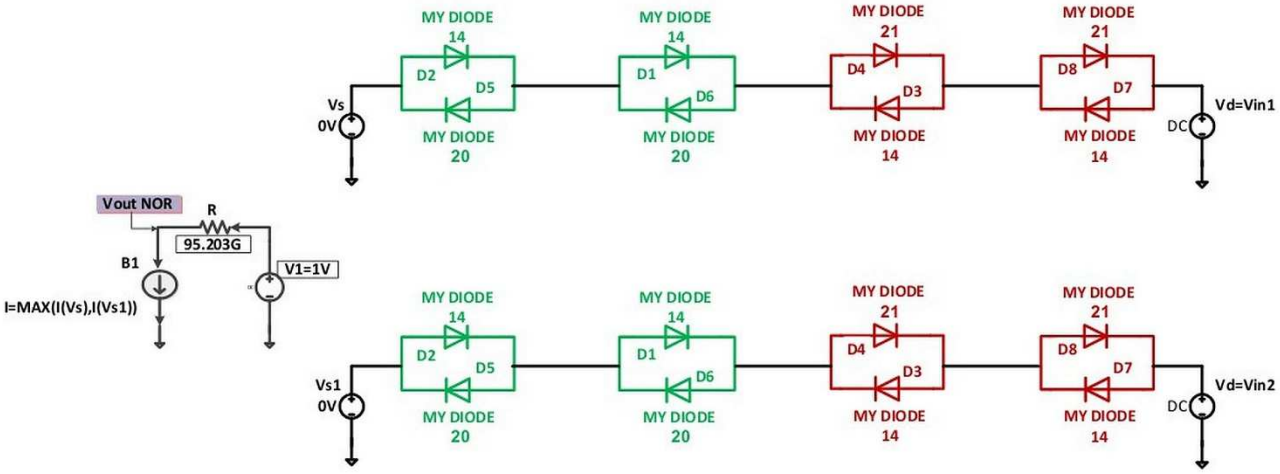


Fig. 8. Molecular NOR gate using four-benzene molecular diode

C- Modeling of molecular NAND Gate

In Fig. 9, a molecular NAND gate is modeled using four-benzene molecular diodes. In this model, two molecular diodes are used based on the method presented in [20]. The currents passing through the two molecular diodes are measured using Vs and Vs1 and the minimum of the currents passes through R to create the output of the NAND gate. It should also be noted that the input voltages of the NAND gate are the same as those of the NOR gate. The results of this model for inputs Vin1 and Vin2 are given in Fig. 10.

Table V. NOR gate truth table

Vin1	Vin2	Vout
0	0	1
0	1	1
1	0	1
1	1	0

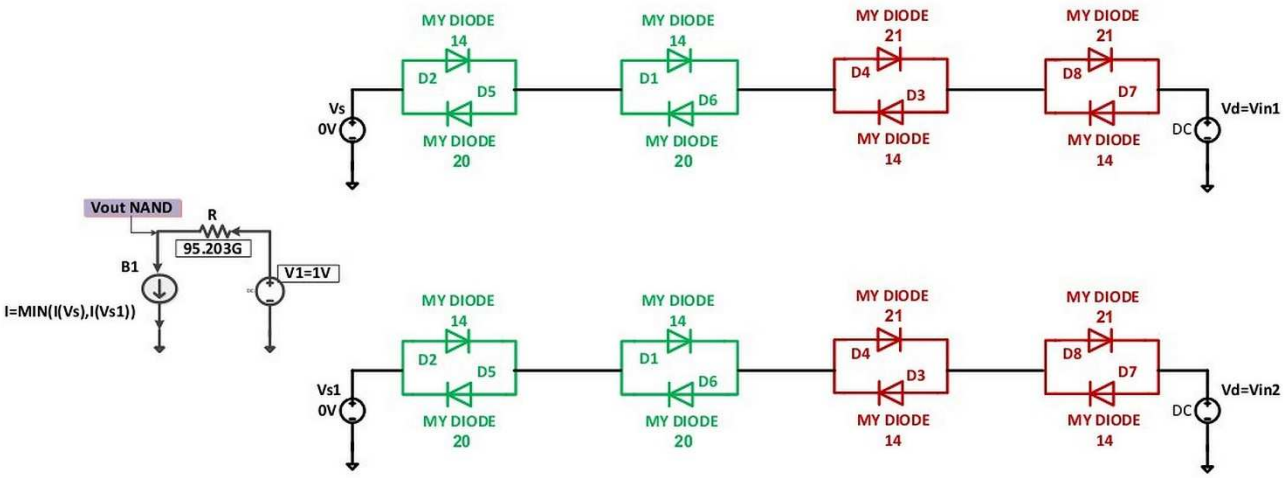


Fig. 9. Molecular NAND gate using four-benzene molecular diode

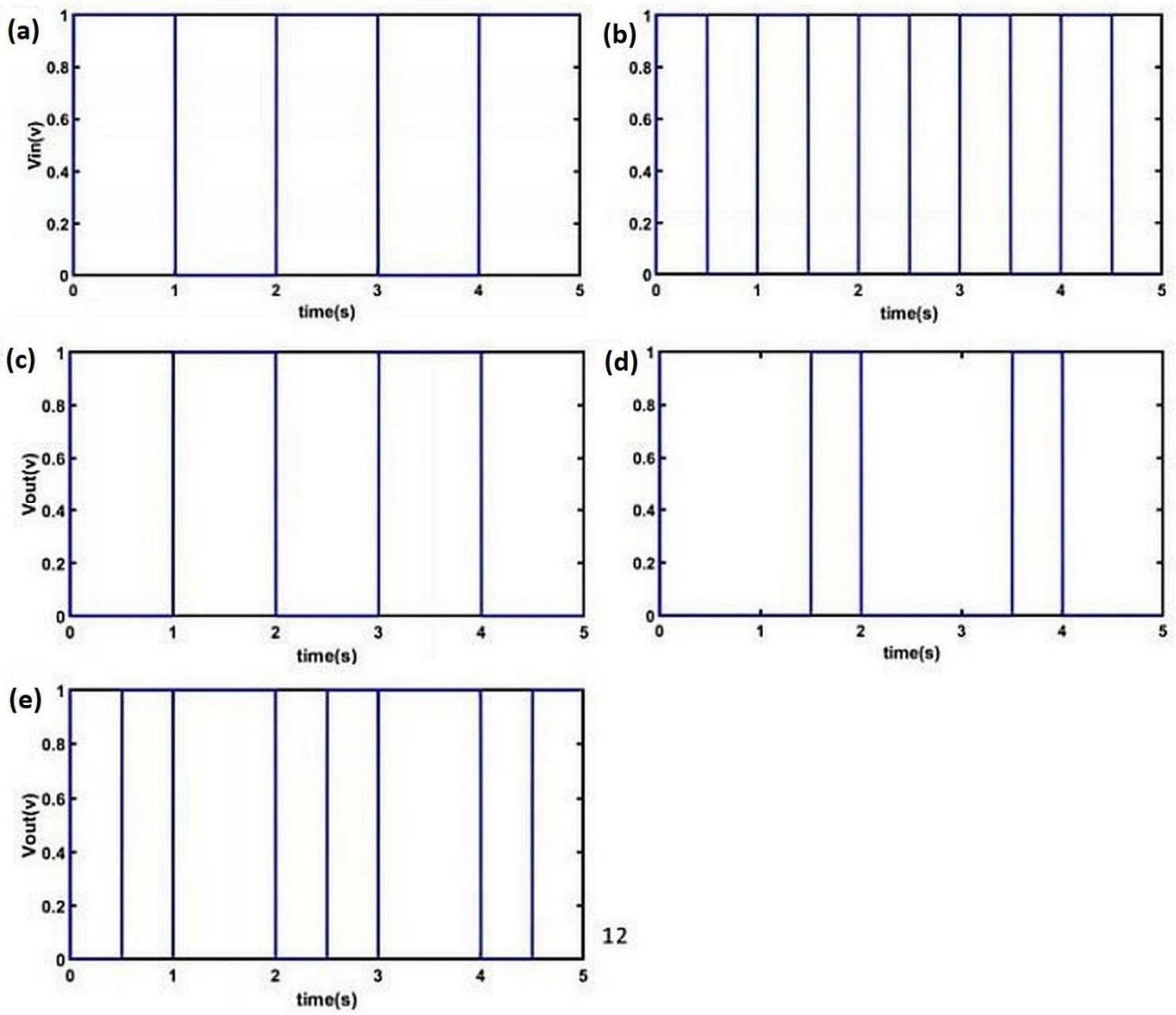


Fig. 10. (a) input Vin1 (b) input Vin2, (c) output of molecular NOT gate, (d) output of molecular NOR gate, and (e) output of molecular NAND gate.

D- Modeling of Molecular SR flip-flop

Figure 11 shows the circuit of an SR flip-flop. An SR flip-flop consists of two NOR gates. Figure 12 shows the molecular SR flip-flop model, which includes two molecular NOR gate models placed next to each other as shown in Fig. 11. The two molecular NOR gates are linked together based on the method presented in [20]. Figure 13 shows the results for two different inputs.

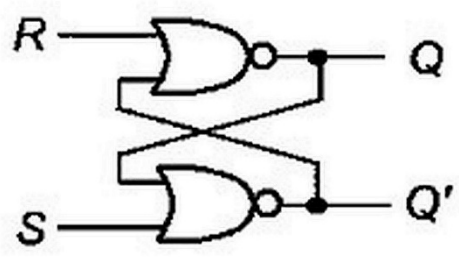


Table VI. SR flip-flop truth table

Set	Reset	Output (Q)	Output (Q')
1	0	1	0
0	0	1	0
0	1	0	1
0	0	0	1
1	1	0	0

Fig. 11. An SR flip-flop

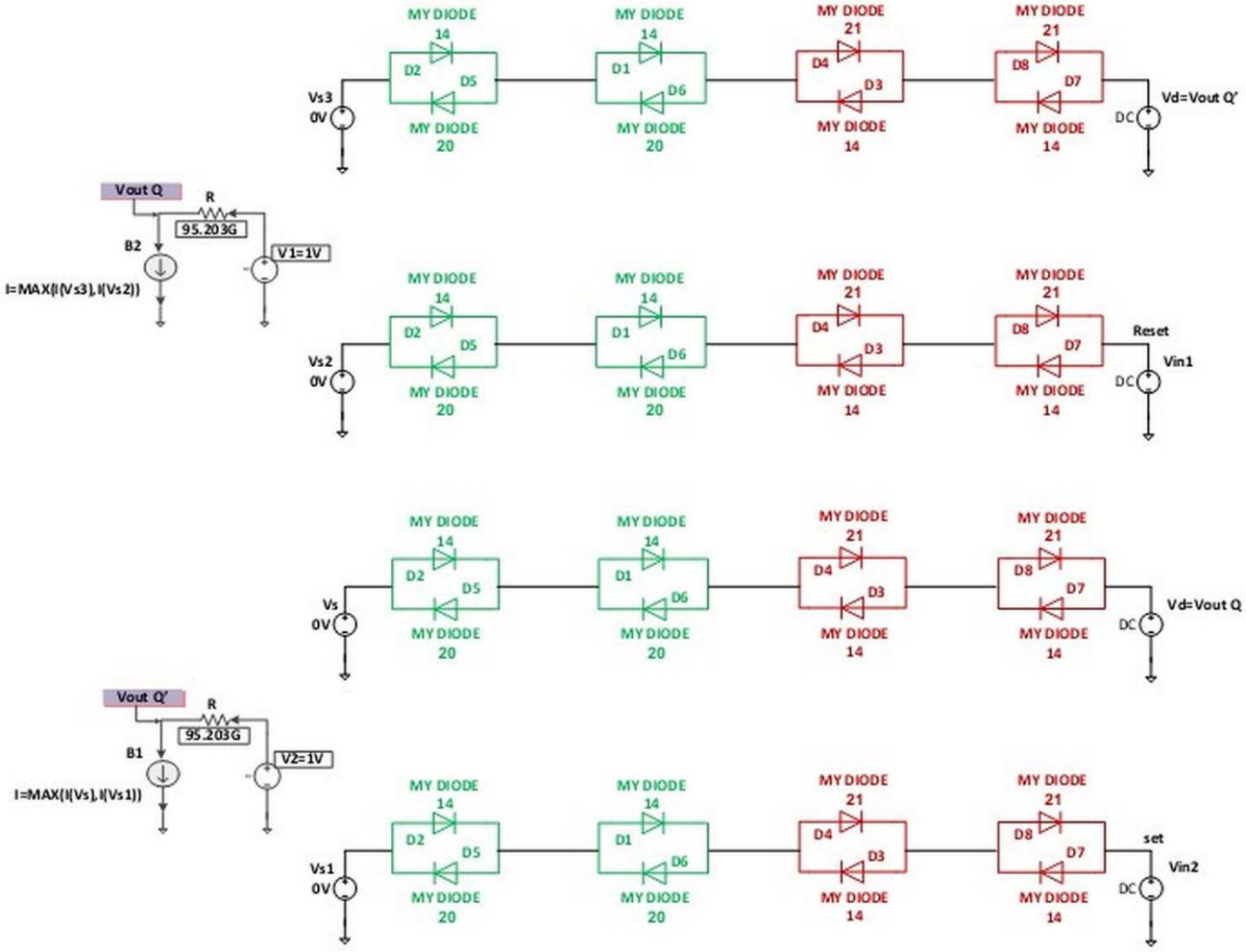


Fig. 12. Molecular SR flip-flop circuit using four-benzene molecular diode

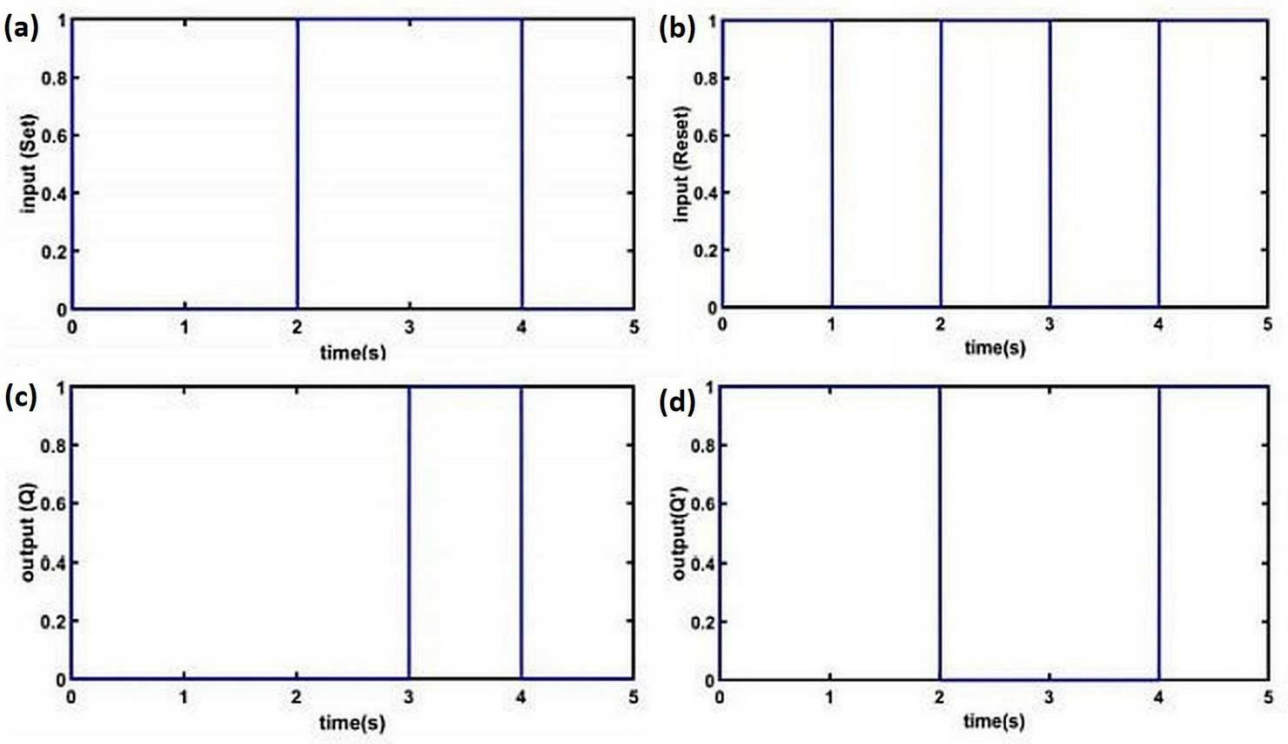


Fig. 13. (a) and (b) inputs; (c) and (d) outputs

E- Modeling of molecular D flip-flop

Figure 14 shows the circuit of a D flip-flop and Table 6 gives its truth table. A D flip-flop consists of two NOR gates, two NAND gates, and a NOT gate. To model a molecular D flip-flop, two molecular NOR gate models, two molecular NAND gate models, and a molecular NOT gate model are put together as shown in Fig. 14. These gates are linked together based on the method presented in [20]. Figure 15 shows the results for two different inputs.

Table VII. D flip-flop truth table

Enable	D	Output (Q)	Output (Q')	Comment
0	X	Q_{prev}	Q'_{prev}	NO change
1	0	1	0	Reset
1	1	0	1	Set

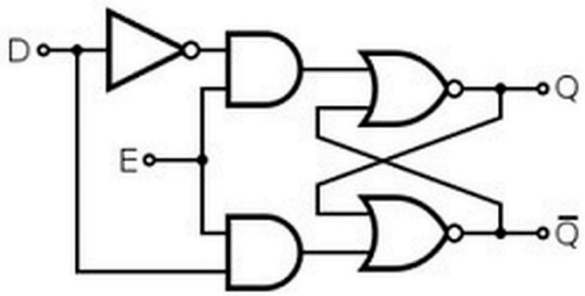


Fig. 14. A D flip-flop

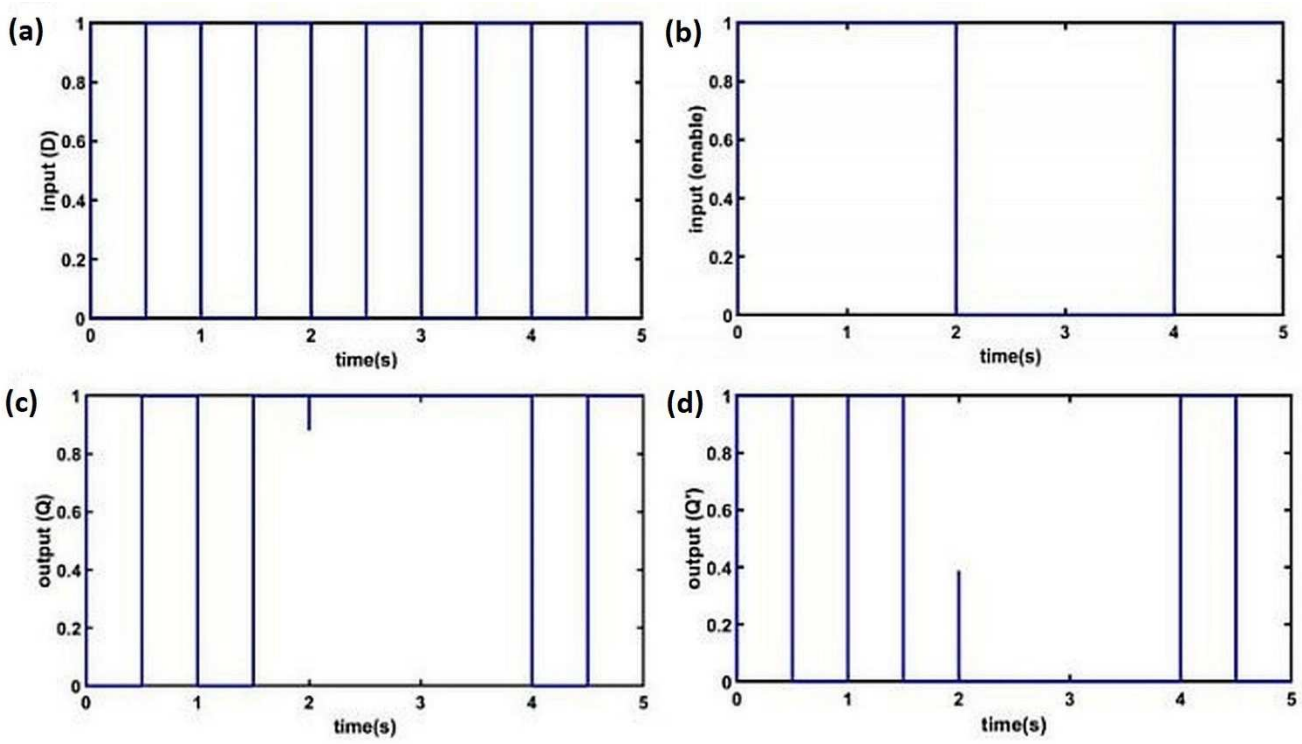


Fig. 15. (a) and (b) inputs; (c) and (d) outputs

V. Conclusion

In this work, a typical molecular model was proposed and its theory was discussed. Furthermore, the circuit components used for designing the molecules were explained. Devices such as asymmetric OPE molecular diode and four-benzene molecular diode were first modeled in LTspice using the presented typical model. Then, the currents were obtained from the model and molecules for

both the asymmetric OPE molecular diode and four-benzene molecular diode to confirm their appropriate performance. Moreover, the transmission spectrum, potential drop profile, and rectification ratio of the four-benzene molecular diode were obtained and analyzed using Atomistix ToolKit (ATK). Finally, various molecular gates and molecular memory logic circuits, including NOT, NAND, NOR, SR flip-flop, and D flip-flop were designed using the four-benzene molecular diode model. The results indicated the correct performance of the presented model.

Declarations

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Conflict of Interest: The authors have no relevant financial or non-financial interests to disclose.

Author Contributions: All authors contributed to the study conception and design. The first draft of the manuscript was written by Saleh Safapour and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Data Availability:

Data will be available on reasonable request.

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