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Abstract— **Molecular Quantum Dot Cellular Automata (MQCA) are an emergent beyond CMOS technology that uses molecular systems as elementary nanoelectronic devices with computational purposes. The binary encoding is provided by the charge localization within the molecule, so that no current flows among the cells. We discuss a method to write a logic state in a molecule synthesized ad hoc for this technology. Our idea is to apply specific electric field to move the electrons inside the molecule, forcing a logic state. A combination of ab-initio calculations and molecular dynamics simulations allowed us to fix the working point of our experimental system and to assess the feasibility of this method, as well as to investigate further experimental solutions for the read-out issue.**

Keywords: molecular QCA, molecular computation, nano-gaps.

I. INTRODUCTION

Quantum-dot Cellular Automata (QCA) is a new paradigm for digital computing that, theoretically, is expected to reach very high operating frequencies and significant power consumption reduction [1]. According to the Lent theory [2], a possible implementation of a QCA cell could be physically based on a molecular system with two or more redox-centers, where the charge configuration encodes the binary information (Fig. 1a) and the electrostatic repulsion provides the device-device interaction. As a result, simple logic gates could be implemented, such as a wire or a majority voter (Fig. 1b and 1c). These gates are the building blocks for more complex digital systems [3].

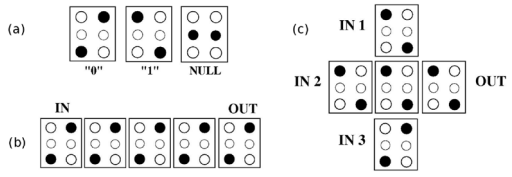

Figure 1. (a) Six dots QCA cell [1]: two free electrons (filled circles) are localized along one of the two diagonals, encoding the "0" or "1" logic value. When the electrons are forced into the central dots (due to an external signal called "clock") the cell is in the NULL state; it erases the previous logic information in order to assume a new one when no clock but an input is forced. QCA basic logic gates: (b) a wire, each cell along the line reorganizes its state according to its neighbor; if an external input is forced on the extreme left cell (IN), then the binary information flows from there to the extreme right cell (OUT) in a domino-like style; (c) a majority voter, the output depends on the state of the majority of the input cells.

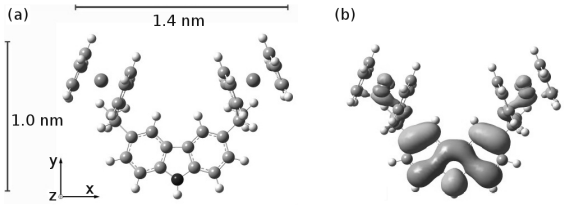

Figure 2. Bis-ferrocene molecule[8]: (a) the two ferrocenes (the molecular site at the top) represent the dots for the binary encoding, while the carbazole is the central bridge that provides the dot isolation and works as third dot for the clock signal application. (b) Ground state HOMO: we perform ab-initio simulations (DFT with B3LYP-LANL2DZ) to calculate the Highest Occupied Molecular Orbital (HOMO) of the bis-ferrocene molecule in its ground state. The HOMO is delocalized along the molecule, no logic state is encoded.

Concerning the physical implementation, in [3 - 5] ideal molecular systems are proposed. In addition, experimental studies have been carried out on a mixed-valence complex [6, 7], even though a molecular QCA prototype is a long way-off.

We present a method to use a bis-ferrocene molecule (Fig. 2) [8] as an half QCA cell and a write-in system (Fig. 3c) based on the application of electrical fields. Results discussed in the following are obtained by means of ab-initio and Molecular Dynamics (MD) simulations.

II. WRITE-IN METHOD SIMULATIONS

A. The Bis-ferrocene Molecule

A new molecule has been synthesized by the authors in [8] (in the frame of a collaboration with ST Microelectronics and with the authors of this paper) ad hoc to implement a QCA device with two redox-centers (Fig. 2a): two ferrocenes are separated by a central carbazole bridge, that provides the isolation between the two dots. Though not conductive, this molecule can be influenced by an external electric field in order to change its internal state (HOMO), encoding thus the "0", "1" and NULL logic values. From an ab-initio analysis, the HOMO of this molecule in its ground state is de-localized along the molecule and mainly on the carbazole (Fig. 2b).

B. Electric Field Application

Applying an electric field along the x axis, we force a "1" or "0" state (Fig. 3a and 3b, respectively) obtained by the

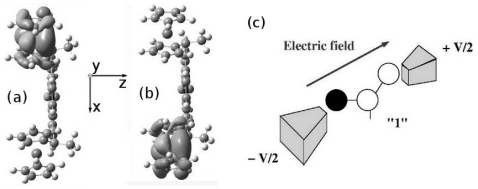

Figure 3. Write-in ab-initio simulation: (a) applying an electric field along the x axis the HOMO localized on one ferrocene and the molecule assumed the logic state "1"; (b) changing the sign of the electric field, the HOMO moved on the second dot and the molecule encoded the "0" state. (c) Write-in system: a bis-ferrocene molecule is bonded between the electrodes of a nanogap; a voltage drop across them produces an electric field that forces the molecule into a logic state, in this case "1". Varying the applied voltage, and so the electric field, it is possible to change the state of the molecule.

HOMO localization around one of the two ferrocenes. An electric field applied along the y axis has the effect of localizing the HOMO on the carbazole, forcing the molecule into a NULL state. We found that an electric field in the same direction but with opposite sign localizes the HOMO around the two ferrocenes, enhancing the molecule sensitivity to assume one of the two logical states in presence of a driver (a neighbour identical molecule). These results are important for what concerns clock issues and information delivering [9].

In order to validate the results expressed by the HOMO, we calculated the dipole moment of the molecule with different values of applied electric field along the x axis. We obtained significant variations only on the x component of the dipole moment and this confirmed the electron localization on one of the two dots. Results are shown in Fig. 4a.

The applied electric field used in simulations was on the order of 1 V/nm. As a consequence, it could be easily obtained with a nanogap of about few nanometers. In Fig. 4 the scheme of the planned write-in system is sketched: a bis-ferrocene molecule is bonded between the nanogap electrodes and a voltage drop across them generates the electric field in the horizontal direction. We generated and tested our nanogaps [10] which are now ready for this experiment.

C. Molecular Dynamics Simulations

Since a molecular system is affected by structural changes in time, related both to intrinsic factors (like thermal vibrations) and to external perturbations (like electrical stimuli), we performed several simulations of the bis-ferrocene molecule when different values of electrical field were applied along the x axis. We analyzed the variations of the molecule structure at several time steps and we found that the main differences were in the distance between the two ferrocenes. In particular, when the electrical field is off, the fluctuations are more remarkable, while increased values of electric field seemed to force the molecule into a more stable configuration. In Fig. 4b we reported the trend of the two dots distances varying the applied electric field, in terms of minimum and maximum values obtained during the simulation time for a specific field. The two curves (Dmin and Dmax) seemed to converge towards a similar values and this pinpointed that the range of variation was more and more reduced. The structure is thus expected to "freeze" to a stable configuration with high electric fields.

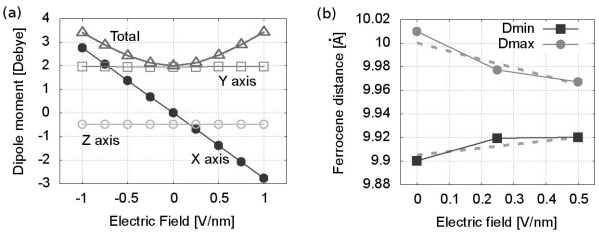

Figure 4. (a) Dipole moment trend as a function of electric field applied along the x axis, shown in terms of Cartesian components, as well as of the total amount. (b) Molecular Dynamics simulations: the avarage fluctuations in time of the maximum and minimum distances between the two ferrocenes are shown as a function of the electric field. For each simulation the total time is of 0.05 ps for any value of applied field, with time steps of 1.00 fs and a total amount of 50 number of steps. Dashed ones are the trend lines.

III. CONCLUSIONS

Molecular QCA are a new emerging technology in the field of nanoelectronics that aims at using a single molecule as an electronic device. We have analyzed and simulated a system in which a real molecule is forced to assume a logic value (1, 0 or NULL) by means of particular electric fields. Results are well in accordance with the theory discussed in literature. Moreover, they pave the way to the design of an experimental system that we are setting up in order to demonstrate the molecule bistability. In particular, the dipole moment variations obtained as a function of the electric field could be a starting point for a capacitance measurement. In addition, molecular dynamics results let us assume that the system is not affected by intrinsic transient state degradations.

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