Molecular QCA embedding in microporous materials
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We propose a new environment for information encoding and transmission via a novel type of molecular Quantum Dot Cellular Automata (QCA) wire, composed of a single row of head-to-tail interacting 2-dots molecular switches. While most of the research in the field refers to dots-bearing molecules bound on some type of surface, forming a bidimensional array of square cells capable of performing QCA typical functions, we propose here to embed the information bearing elements within the channels of a microporous matrix. In this way molecules would self-assemble in a row as a consequence of adsorption inside the pores of the material, forming an encased wire, with the crystalline environment giving stability and protection to the structure. DFT calculations on a diferrocenyl carborane, previously proposed and synthesized by Christie et al.1 were performed both in vacuum and inside the channels of zeolite ITQ-51, indicating that information encoding and transmission is possible within the nanoconfined environment.

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I. INTRODUCTION

Quantum Dot Cellular Automata (QCA) constitute a class of computing devices with very interesting and unique features, first proposed and subsequently mainly investigated, by C. S. Lent and coworkers.2–4 In the classic definition given by these authors the basic building block of a QCA, the cell, is an array of four quantum dots, here generically intended as charge confinement sites, arranged as the corners of a square. Each cell hosts two charges of the same sign, which can occupy any of the four dots, and can switch between them, usually via quantum tunneling. However, due to coulombic repulsion, the only stable configurations of the cell are the ones in which the charges are on opposite corners of the square, as shown in Fig. 1. If there is a sufficiently high barrier between states 0 and 1, as defined in Fig. 1-a, it is clear that each cell is capable of encoding and retaining one bit of information. In a typical QCA, cells are arranged as to form interacting neighborhoods where the state of each cell is dependent on the state of neighboring ones via inter-cell coulombic interactions. A slightly different and better model of cell contains extra sites capable of hosting the charges, resulting in a symmetric null cell state. This is interesting in view of devising an efficient QCA clocking scheme, in order for the information to flow in the system only in a user defined direction.

A linear arrangement of QCA cells like the one in fig. 1-b is called a wire, and is capable of transmitting information between its ends, as its cells switch to the minimum energy state according to the state of neighbors.

While we are going to elaborate mainly on this type of monodimensional QCA, more complex architectures are also possible where information is not only stored and transmitted, but also elaborated via QCA logic gates, allowing these systems to perform all forms of calculation, opening in principle the way to the creation of QCA computers. The first QCA practically built were based on Si/SiO2 interfaces or aluminium dots,6 with aluminium oxide tunnel junctions having a diameter of several tens of nanometers, and were only able to work at cryogenic temperatures. However ionic or zwitterionic molecular switches showing strong charge confinement, could act as cells in a molecular QCA capable of working at room temperature, besides allowing for an unprecedented step in circuit miniaturization and in the minimization of energy loss in information transmission and elaboration.

A number of theoretical investigations led to the recog-
FIG. 2. Schemes of various kinds of molecular QCA cells and wires. a) Complete cells as obtained from (1) a single 4-dots molecule, possibly with a central site, whose occupation results in the null state; (2) two paired 2-dots molecules; (3) two paired 3-dots molecules, resulting in a 6-dots cell, capable of assuming the null state (4). b) A classical wire of molecular QCA cells with molecules assuming side-by-side orientation. c) A wire consisting of head-to-tail oriented molecules, as proposed by Wang et al.17 d) An encased wire consisting of a single row of head-to-tail oriented molecules as the one investigated in this paper. In all cases, white circles represent quantum dots and orange circles represent the moving charges, while cyan circles in d) represent the countercharge for a zwitterionic molecule.

nition of some classes of promising candidate molecules for the implementation of molecular QCA8–11. Among these are a number of dinuclear mixed-valence metal complexes12 mainly involving Fe and Ru, such as Creutz-Taube complexes13, and various larger molecules containing typically four metallic centers in a square, planar arrangement, forming a complete molecular QCA cell14,15. Dinuclear species on the other hand constitute only half of a typical QCA cell, and can be arranged side by side on a surface in order to obtain a complete one16.

The QCA machinery requires the metallic centers to be in different oxidation states with a 1:1 ratio, so that half of the metallorganic groups bear an extra charge, and the molecule (or pair of molecules) to be able to switch between two degenerate, or almost degenerate ground states as to minimize coulombic repulsion between charged groups. By immobilizing such molecules on a suitable surface in such a way that they form a pattern of dots like those shown in Fig. 2, and assuming that it is feasible to interact with them on the molecular scale for input output purposes, one can in principle create a computing QCA device, and modern techniques of electron beam lithography and tunnel electron microscopy seem to bring this goal at hand.

The neutral, mixed valence diferrocenyl-carborane 7-Fc⁺-8-Fc-7,8-nido-[C₂B₁₀H₁₀], Fig. 3, on which we focus in this paper, was synthesized and characterized, along with some closely related species, by Christie et al.1 They found convincing evidence of its zwitterionic nature, as the average Fe-C bond lengths, measured by X-ray diffraction, differ between the two ferrocenyl groups, suggesting that the carborane is able to oxidize one of the ferrocene groups to ferrocenium. The result of this self-doping18 mechanism is a zwitterion with a formal +1 charge on one of the ferrocenyl groups and a -1 on the central carborane group, which could in principle act as an half six-dots QCA cell.

Dealing with a zwitterion is a great advantage, as counterions accompanying other switches proposed in literature, most of which are charged radicals, must be taken care of both in calculations and in devising ipothetical applications. A further advantage of this species lies in its excited, symmetric, non-zwitterionic form, resulting from the electron transfer between the negatively charged carborane cage and ferrocenium. Christie et al. recognize this reversion of self-doping as responsible for a band around 11000 cm⁻¹ they observed in the UV-Vis spectrum of the molecule. As we show below the symmetric form, which can be termed the null-state for our species, is easily obtained by application of a suitable electric field, allowing in principle for efficient clocking. The practical realization of all molecular QCA schemes proposed to date depend on the development of suitable techniques capable of arranging and binding molecules on a surface according to the desired geometry. However, while various promising development in this sense are re-
ported in the literature, a truly effective technique is still missing. In this work we propose a different scheme resulting in the molecules assuming their functional position without external intervention, as they are adsorbed in the channels of zeolite ITQ-51. The framework of this microporous material shows large parallel channels, with an elliptical cross section of $\sim 13 \times 9$ Å. This particular geometry fits quite tightly around diferrocenyl molecules, so that they are forced to move inside channels in a single row, resulting in what is termed single-file diffusion, with their Fe-Fe axis roughly parallel to the channel axis, as depicted in fig. 4.

Under this conditions they cannot overtake each other, nor fully rotate around any of their axis, and basically can only move back and forth between their first neighbours. In this way the system offers itself as a promising candidate for a QCA wire implementation: if, as our calculations demonstrate, the head-to-tail interaction between host diferrocenyl carborane molecules is capable of efficiently orienting the ground state of neighbours, one can easily envision a way of transmitting information along the loaded channel, resulting in a new kind of QCA wire, which consists of a single row of head-to-tail oriented 2-dots molecules. Such a wire model has not yet been studied, the only similar model being the one proposed by Wang et al., with head-to-tail interactions in a double row of fluorinated fullerene, resulting in a wire of tilted 4-dots QCA cells. While the classical 4-dots scheme allows for more complex operations as noted above, it has no particular advantage when dealing with the kind of wire proposed here.

There is however a point which deserves attention in devising a suitable clocking scheme for our system. With reference to Fig. 4, the clocking field should lie roughly along the vertical direction in order to push the excess electron on carborane towards the ferrocenium group. However there are two symmetric orientation available to each molecule within the channels, with respect to this direction, and a simple sweep of the clock would not be effective unless one finds a way of orienting all molecules in the same way. If the molecule in fig. 4 had its carborane group pointing in the opposite direction, the negative charge would further stabilize a state of the molecule with excess positive charge on its side, instead of triggering a switch to the null-state. So if molecules are randomly oriented with respect to the vertical direction, some of them will retain their state, thus interfering with, and possibly stopping, any information propagation. Although such specific problems are not of the kind we are primarily concerned with in this paper, we point out that there should be ways of circumventing it: namely by orienting host molecules during adsorption with the application of a strong electric field, or by implementing more sophisticated clocking schemes which alternates opposite field orientations. Alternatively one could also resort to other means of switching, not yet investigated to date, e.g. light absorption which, according to the aforementioned spectroscopic results of Christie et al., is able to transiently excite the diferrocenyl-carborane to the null-state.

II. DFT CALCULATIONS AND RESULTS

We investigated the electronic structure of diferrocenyl-carborane by means of Density Functional Theory in the Kohn-Sham formulation, using the ORCA free package. Geometry and orbital optimizations were performed with the test molecule in various environments, in order to test its capabilities as a molecular switch, the nature of the ground state in vacuum and within the confining environment, and the conditions, if any, under which it switches to the null-state. In all cases reported the B3LYP functional was used, with the def2-TZVP basis set and the D3 correction for dispersion interactions. Polarization functions were used in preliminary calculations, resulting in a drastic increase of computational time, while only negligibly affecting the properties of interest, so we
did not use them in production runs. As the molecule investigated is a radical, all calculations were conducted within the open-shell unrestricted Kohn-Sham scheme.

|                | Fe-C(α) | Fe-C(β) | Fe-C(α)* | Fe-C(β)* |
|----------------|---------|---------|----------|----------|
| Single         | 2.1392  | 2.0832  | 2.1386   | 2.0829   |
| Pair(α)        | 2.0878  | 2.1327  | 2.0894   | 2.1297   |
| Pair(β)        | 2.1395  | 2.0831  | 2.1388   | 2.0828   |
| Null           | 2.0870  | 2.0847  | 2.0862   | 2.0839   |

**TABLE I.** Fe-C bond lengths for the two ferrocenyl groups, in Å. The (α) refers to the Fc group or driver being on the side of the asymmetric H atom of carborane, and (β) refers to the opposite side. Data in starred columns refer to the nanoconfined setting.

Quantum calculations under nanoconfinement were performed on the single molecule, with the environment of the ITQ-51 channel, within a radius of 21 Å, simulated by a collection of fixed point charges, namely -0.5 a.u. for O and 1.0 a.u for Si atoms, as obtained in a previous work on ITQ-29, a similar aluminosilicate. The neighboring molecule, acting as driver, was represented by the Loewdin charges previously obtained for the single molecule in vacuum, the distance between the centers of mass of the two molecules being 13 Å in all cases reported. The driver molecule was located on one side of the reference one as depicted in Fig. 5 with the ferrocenium group pointing towards the test molecule. Calculations on all arrangements of the test molecule and driver charges were performed both under confinement and in vacuum, by adding or removing, respectively, the framework of Si and O charges only. Our results confirm

|                | Fc(α) | Fc(β) | C₁₂B₉H₁₆ | Fc(α)* | Fc(β)* | C₁₂B₉H₁₆* |
|----------------|-------|-------|----------|--------|--------|-----------|
| Single         | 0.850 | 0.0733| -0.923   | 0.863  | 0.085  | -0.949    |
| Pair(α)        | 0.854 | 0.868 | -0.923   | 0.861  | 0.886  | -0.947    |
| Pair(β)        | 0.860 | 0.056 | -0.917   | 0.870  | 0.069  | -0.939    |
| Null           | 0.002 | 0.0289| -0.030   | 0.010  | 0.010  | -0.050    |

**TABLE II.** Loewdin cumulative charges on Fc and carborane groups, in a.u. The (α) refers to the Fc group or driver being on the side of the asymmetric H atom of carborane, and (β) refers to the opposite side. Data in starred columns refer to the nanoconfined setting.

that the ground state for the single molecule in vacuum, as well as inside the ITQ-51 channel, is the zwitterionic form, always showing the ferrocenium group on the same side of the asymmetric H atom of carborane, to which we will refer as α-side.

The presence of the second molecule lead to the re-orientation of the dipole moment both in vacuum and under confinement, as to maximize the distance between the two positively charged ferrocenium groups, while no switch is observed when the driver molecule has its ferrocenium group pointing away from the test. The molecule switch is also confirmed by total Loewdin charges on carborane and on the two ferrocenyl groups, as well as by the average Fe-C bond lengths in the latters, as reported in Tab. I. These are consistent with our DFT results for isolated ferrocene and ferrocenium, 2.084 and 2.134 Å respectively, and slightly longer than the experimental values, 2.05 and 2.095 respectively, reported by Lent et al., while the relative difference is almost the same. Another clear signal of the asymmetry between the two groups is given by the free valence, as obtained from Mayer population analysis, for the Fe atoms. This is invariably of ~ 0.9 for Fe(III), and ~ 0 for Fe(II), again

![FIG. 5.](image.png)
in agreement with our DFT results for isolated ferrocene and ferrocenium.

The null-state of differrocenyl-carborane was also obtained, by using a single external charge varying in the range from -10 to -3 e, located at ~ 14 Å from the center of mass of differrocene, as illustrated in Fig. 4. This arrangement mimics the effect of a clocking field perpendicular to the channel axis, and results in an electron transfer from carborane to ferrocenium. The transition is made evident by a strong decrease in the magnitude of the dipole moment, and of the cumulative Loewdin charges of the three groups in the molecule, all of which fall to nearly zero. Moreover the Fe-C average bond lengths in the two groups becomes equal, and both Fe atoms assume a null free valence. A comparison of the results for the molecule under confinement and in vacuum, and inspection of the energy values, shows that the ionic form is somehow stabilized under confinement and its charge separation slightly more pronounced. By contrast the effect on the null-state is an almost negligible destabilization and blurring of charge distribution. This implies that a stronger field could be needed in order to clock the system within the zeolite channels.

|                  | Fe(α) | Fe(β) | Fe(α)* | Fe(β)* |
|------------------|-------|-------|--------|--------|
| Single           | 0.9355| 0.9407| 0      | 0      |
| Pair(α)         | 0     | 0.9457| 0      | 0      |
| Pair(β)         | 0.9395| 0     | 0.9434| 0      |
| Null            | 0     | 0     | 0      | 0      |

TABLE III. Free valences according to Mayer for Fe atoms. The (α) refers to the Fe atom or driver being on the side of the asymmetric H atom of carborane, and (β) refers to the opposite side. Data in starred columns refer to the nanoconfined setting.

The (in Debye), and energies (in Hartree). Data in starred columns refer to the nanoconfined setting.

|        | μ   | μ*  | E   | E*  |
|--------|-----|-----|-----|-----|
| Single | 17.53| 17.95| -3605.8544| -3605.8677|
| Pair(α)| 17.41| 18.80| -3605.8604| -3605.8727|
| Pair(β)| 18.29| 18.58| -3605.8569| -3605.8692|
| Null   | 11.70| 11.35| -3605.8819| -3605.8803|

TABLE IV. Modules of the dipole moment μ (in Debye), and energies (in Hartree). Data in starred columns refer to the nanoconfined setting.

III. CONCLUSIONS

We reported DFT calculations results for a differrocenyl carborane which was recently proposed as a promising molecular switch, and found it to be suitable for use in QCA circuitry at the nanometric scale. Our theoretical findings are in agreement with the spectroscopic and crystallographic results previously reported in literature, and support the switchable nature of this species, not only in vacuum or solution, but also in a nanoconfining environment, namely within the channels of zeolite ITQ-51.

The vast class of microporous materials is constantly growing, and synthetic techniques are getting more and more sophisticated, attaining tailored geometries for disparate purposes, while ship-in-a-bottle methods allow complex molecules to be formed inside pores from smaller adsorbed precursors. So if these materials can host molecular switches and act as an embedding matrix for QCA architectures, without hindering their bistability, switchability, and null-state properties, a wealth of interesting opportunities becomes available. We investigated only QCA wires within a framework of straight channels, as this is the simpler and more easily handled system for a preliminary study, as well as for future experimental tests. However nothing prevents in principle future developments towards more complex schemes, perhaps taking advantage of the three dimensional rich structure of microporous materials, which, while posing challenging problems, could result in an exciting enrichment of QCA possible range of implementations. Keeping molecular switches within the channels once they have been adsorbed, and interacting with them for input-output operations, constitute crucial problems in view of any practical application of a zeolite embedded QCA. In this sense we find inspiring the work of Calzaferri and coworkers, who proposed a number of stop-cock molecules capable of binding to the entrance of the zeolite pores and lock inside adsorbate molecules. They could also be very useful in input-output operations, if one succeeds in making a stop-cock which is a molecular switch itself. Moreover as these authors show, it is also possible to link various crystals together, which could be a viable way of assembling longer wires, and ensuring communication between them, as they demonstrate it is possible for electronic excitations. Clearly many aspects still need to be investigated, and in particular the dynamics of the information transfer, both at the level of intramolecular charge migration, and of intermolecular interactions. In this sense, it would be desirable to develop a proper force field for sensible classical Molecular Dynamics simulations, in order to investigate single file diffusion within zeolite channels, and the frequency of encounters between molecules close enough to allow informations transfer. On the other hand more sophisticated methods, such as QMMM calculations, would probably be needed for a quantitative understanding of the switching kinetics in such a complex supramolecular environment.
REFERENCES

1. J. A. Christie, R. P. Forrest, S. A. Corcelli, N. A. Wasio, R. C. Quardokus, R. Brown, S. A. Kandel, Y. Lu, C. S. Lent, and K. W. Henderson, Angew. Chem. Int. Ed. 54, 15448 (2015).
2. C. S. Lent, W. P. P. D. Tougaw, and G. H. Bernstein, Nanotechnology 4, 49 (1993).
3. C. S. Lent and P. D. Tougaw, Proc. IEEE 85, 541 (1997).
4. T. Cole and J. C. Lusth, Prog. Quant. Electron. 25, 165 (2001).
5. E. P. Blair and C. S. Lent, in International Conference on Simulation of Semiconductor Processes and Devices, 2003. SISPAD 2003. (2003) p. 14.
6. A. O. Orlov, I. Amlani, G. H. Bernstein, C. S. Lent, and G. L. Snider, Science 277, 928 (1997).
7. A. Bianchi, E. Delgado-Pinar, E. Garcia-Espana, and F. Pina, Compr. Inorg. Chem. 12, 969 (2013).
8. Y. Lu and C. S. Lent, J. Comput. Electron. 4, 115 (2005).
9. Y. Lu and C. S. Lent, Chem. Phys. Lett. 582, 86 (2013).
10. X. Wang, L. Yu, V. S. S. Inakollu, X. Pan, J. Ma, and H. Yu, J. Phys. Chem. C 122, 2454 (2018).
11. C. S. Lent, B. Isaksen, and M. Lieberman, J. Am. Chem. Soc. 125, 1056 (2003).
12. S. B. Braun-Sand and O. Wiest, J. Phys. Chem. B 107, 9624 (2003).
13. K. Tokunaga, Phys. Chem. Chem. Phys. 11, 1474 (2009).
14. T. Groizard, S. Kahlal, and J. Halet, J. Organomet. Chem. 844, 35 (2017).
15. J. Jiao, G. J. Long, L. Rebbouh, F. Grandjean, A. M. Beatty, and T. P. Fehlner, J. Am. Chem. Soc. 127, 17819 (2005).
16. V. Arima, M. Iurlo, L. Zoli, S. Kumar, M. Piacenza, F. D. Scala, F. Matino, G. Maruccio, R. Rinaldi, F. Paolucci, M. Marcaccio, P. G. Cozzi, and A. P. Bramanti, Nanoscale 4, 813 (2012).
17. X. Wang and J. Ma, Phys. Chem. Chem. Phys. 13, 16134 (2011).
18. Y. Lu and C. S. Lent, Phys. Chem. Chem. Phys. 13, 14928 (2011).
19. W. Humphrey, A. Dalke, and K. Schulten, J. Molec. Graphics 14, 33 (1996).
20. R. Martinez-Franco, M. Moliner, Y. Yun, J. Sun, W. Wan, X. Zou, and A. Corma, PNAS 110, 3749 (2013).
21. J. Karger, “Single-file diffusion in zeolites,” in Molecular Sieves. Adsorption and Diffusion, Vol. 7, edited by H. G. Karge and J. Weitkamp (Springer Berlin Heidelberg, 2008) p. 329.
22. X. Wang, S. Chen, J. Wen, and J. Ma, J. Phys. Chem. C 117, 1308 (2013).
23. F. Neese, WIREs Comput. Mol. Sci. 2, 73 (2012).
24. A. D. Becke, J. Chem. Phys. 98, 5648 (1993).
25. F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys. 7, 3297 (2005).
26. A. Gabrieli, M. Sant, P. Demontis, and G. B. Sufrittii, J. Chem. Theory Comput. 11, 3829 (2015).
27. I. Mayer, Int. J. Quantum Chem. 39, 73 (1986).
28. A. C. H. Garcia, Eur. J. Inorg. Chem. (2004).
29. H. Maas and G. Calzaferri, Angew. Chem. Int. Ed. 41, 2284 (2002).
30. G. Tabacchi, E. Fois, and G. Calzaferri, Anghew. Chem. Int. Ed. 54, 11112 (2015).
31. I. Lopez-Duarte, L. Dieu, I. Dolomic, M. Martinez-Diaz, T. Torres, G. Calzaferri, and D. Bruhwiler, Chem. Eur. J. 17, 1855 (2011).
32. D. Bruhwiler, G. Calzaferri, T. Torres, J. H. Ramm, N. Gartmann, L. Dieu, I. Lopez-Duarte, and M. V. Martinez-Diaz, J. Mater. Chem. 19, 8040 (2009).
33. E. P. Blair, S. A. Corcelli, and C. S. Lent, J. Chem. Phys. 145, 014307 (2016).
34. Y. Lu, M. Liu, and C. S. Lent, J. Appl. Phys. 102, 034311 (2007).
35. P. D. Tougaw and C. S. Lent, J. Appl. Phys. 80, 4722 (1996).