# **Pico-Inside Report**

Computing inside a single molecule using atomic scale technologies

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# **Hybrid and Mono Molecular Electronics**

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The 1974 seminal Aviram-Ratner paper had created a bridge between electronic circuits for computers and molecules. Ten years before, the relation between cybernetic and biomacromolecules was used by J. Monod in explaining the genetic machinery. The bridge between conducting materials and macromolecules was indicated by StGyorgi 30 years before. We have to appreciate the insight of A. Aviram and M. Ratner in their way to obtain a rectifier with a minimum number of atoms and 2 electrodes. Molecular Electronics was born from the idea that a single molecule will perform the same way a solid state device does with the advantage of its size. 30 years later, Molecular Electronics matures because of the invention of new tools to access electronically a single molecule (and always the same) during the measurement. This had created an explosion of sub-fields in Molecular Electronics from plastic electronics to quantum computing in a single molecule.



**Figure 1:** At the origin of molecular electronics: Ari Aviram and its molecular rectifier in the 70's

Following up the development of each Molecular Electronics sub-field, the initial concept of A. Aviram and M. Ratner can be pushed at the limits by asking a simple question: What is the minimum number of atoms required to embody a computer? Of the same question arises course, for mechanics machines, for transducer devices and also for communication machineries. But we will limit our analysis to computers. This question calls for a new approach designated by "monumentalization" and opposed to the miniaturization approach of the microelectronics industry. With miniaturization, the game is clearly to keep an industry growing

with production plan and products. Physics, material sciences and technologies will follow. With monumentalization, the game is first to built up epistemological machines at the nanoscale not for sale but for the sake of understanding where are the physical, chemistry and technological limits of a machine like a computer. This is an up limit and not a down limit.

There are many possibilities to embody a computer with molecule(s). (1) to take benefit of the quantum response of a single molecule prepared in a non-stationary state to perform a computation. (2) to force a molecule to have the shape of an electrical circuit. (3) to attribute a particular electronic function to a single molecule and interconnect each function (each molecule) with metallic nanowires. (4) to attribute a particular electronic function, to fabricate a small film or crystal of such molecules and interconnect each device made of those molecular materials to shape the electronic circuit. (6) to create a crystal or a plastic and print the electronic circuit on this material as an equivalent to solid state micro-electronics.





All those possibilities have their advantages in term of technology, material science and performances. We will restrict our description to (1), (2) and (3) which are in direct lineage with the Aviram-Ratner molecular rectifier. Macromolecular electronics (4) with for example carbon nanotubes or semi-conductor nanowires are leading to fantastic devices. But they are too close to the actual solid-state nano-electronics transistor technology to be a valid candidate for exploring monumentalization. The integrated project NODE of the European Commission was selected to explore this branch of technology. The 2005 Pico-Inside integrated project launched in parallel to NODE under the Emerging Nanoelectronics priority of the IST-FET program started from (1) and www.node-project.com). has (www.PicoInside.org It explored how monumentalization can lead not only to a simple uni-molecular device embarked on a molecule but to a possible large complex computing machine embodies in a single molecule.

#### An atomic scale technology

At the laboratory scale and common to (1), (2) and (3), there was an urgent technological problem to be solved by Pico-Inside before asking for complexes architectures and production of molecular chips: how to interconnect a molecule to metallic electrodes in a planar technology? A related problem is the cleanness and precision of the connections. The rush in fabricating cometallic electrodes with a planar separation below 10 nm starts in the early 90′s culminating with the nanofabrication of 2 nm junctions 10



**Figure 2:** At the origin of the alligator clip in molecular electronics: the artistic view of the interconnection problem painted by C. Coudret from CEMES-CNRS in the 90's

years later in the BUN IST-FET project of the fifth framework program. This was obtained by pushing e-beam nanolithography to the limit while in the mid 90's alternative solutions like the breaking of a metallic wire or the electro-migration techniques started to be explored.



**Figure 3:** Interconnecting a molecular wire supported by 4 legs to a mono-atomic step edge on Cu(111). Left, LT UHV-STM image of the molecule at contact. Right: determined conformation of this Lander molecule from the experimental left image. (ref: F. Moresco et al., Phys. Rev. Lett., 91, 036601 (2003)).

But connecting a molecule to N = 2 or more metallic electrodes means creating an electronic interaction between well determined parts of the molecule and the end surface of the metal electrodes. Therefore, from a surface science point of view, any





change of the detail atomic ordering at the surface-end of the electrodes or any change in the adsorption site of the molecule in interaction with the metal will modify the orbital mixing between the metal surface and the molecule. Then, the conductance of the device will change. This is the explanation of so many different results published in the 90's and at the beginning of this century on planar metal-molecule-metal junctions and why, in the best case, statistical analysis of such experiments are needed. Cleary, the solutions for molecular interconnects explored in the 90's were not adapted to the ultra clean demand of the beginning of this century. In the mid 90's, this point of view was enforced by the first use of UHV-STM to image and contact a single atom and a single molecule in a very reproducible way. As a consequence both the atomic organization of the electrodes and the adsorption site must be mastered with a precision better than 0.05 nm. There is no technology ready yet to achieve such a precision. In PICO-INSIDE, one goal was to explore the possible developments of a new technology called "Atom based technology" for laboratory electrical experiments on a single molecule in a fully planar technology. Ingredients of such a technology are known.

First, the atomic structure and ordering of the surface end of the contact metallic wire must be known. This forbid the use of any resist lithography technique and even of the break junction technology for N = 2. For this "pico to nano" interconnection step, an atomic scale technology does not exist in the actual clean rooms and the new nanostencil technique is not clean enough in this prospect. In Pico-Inside, one solution was the growth of mesa ultra flat metallic nano-cluster. Furthermore, certain well designed molecules can manipulate surface metallic atoms by themselves and will be used to assemble very short atomic wires.

Second, an imaging technique is required to determine the atomic ordering at the interconnections. Scanning tunnelling microscope in the UHV (UHV-STM) is very capable of such a characterization for semi-conductor surface and the non-contact Atomic force microscope for plain insulator. An intermediate step is the use of an ultra thin insulating layer on a metal surface. The ultra low feedback loop tunneling current set-up of certain low temperature UHV-STM will help in understanding surface science at the atomic scale on insulating surface with a mixture of metallic cluster and organic molecules adsorbates.

Third, after this first step of atomic scale fabrication, the wiring fabrication technique for the "nano to meso" interconnection step must also be ultra clean. Again, this forbids the use of resist-like nanolithography. This point out the nanostencil technique where a mastering of the lateral diffusion through the stencil is necessary to limit the spreading of metal atom around.

Fourth, similar to the millipede technology, the "meso to micron scale" interconnection step may be deported on a second surface independent of the active atomic scale precision one. This second floor of interconnect opens the possibility to use standard nano and microlithography technique and to ultra-clean the device before performing the interconnection step. The relative positioning between the "ground" atomic floor and micro-technology floor is a very interesting technology which really needs to be developed

#### **Digital logic in a molecule without circuits**

Integrating a full electronic circuit inside a single conjugated molecule with the goal to reduce the fabrication costs and increase reliability was first proposed by F.L. Carter in





the 80's. Similarly to the "tyrannies of numbers" met in the 50's by those attempting to wire thousand of electronic devices together, F.L. Carter foresees at the end of the seventies that it will not be possible to wire together millions of discrete molecular devices to assemble a molecular circuit. Then, he proposed to shape the conjugate molecule itself like an electronic circuit. In our days, there are at least 2 possibilities to embody a logic function inside a molecule: (1) the use of intramolecular quantum time-dependent processes occurring when a molecule is prepared in a non-stationary state (with or without a structuration of the molecule in qubits) and (2) to force the molecule to have the shape of a standard electronic circuit as proposed by F. L. Carter.



Figure 4: Going away from Hybrid molecular electronics: F. L. Carter in the 80's and its mono-molecular analogue to a Nand gate

For (1), the goal is to prepare the molecule in a non-stationary state and to optimize the molecular chemical composition in such a way that during the quantum time dependent evolution of this non-stationary state, the quantum trajectory of the molecule in its state space reaches well specified target states according to the initial preparation or to specific conformations of some specific chemical groups distributed along the molecule. This distinction between different initial preparations points out different kind of quantum computing. When the data are defining the initial quantum state, the molecule is structured in gubits and one recovers the initial 1984 proposal of R. P. Feynman. When the data are input on the molecule by changing for example the conformation of some small lateral groups, a quantum Hamiltonian computing is implemented. In both cases, the very difficult part of an experimental implementation is the fast intramolecular decoherence of the initial state because of the numerous quantum states weakly coupled to the ones in charge of performing the computation inside the molecule. On the top of that, intramolecular relaxations occur. In such a situation, one has to be fast enough to measure the result or to refresh the initial nonstationary state a lot of time to stabilize the result. This is the quantum Hamiltonian computing (OHC) scheme which was studied in Pico-Inside following the fifth framework IST project CHIC (Consortium for Hamiltonian Intramolecular Computing). Spontaneously, a tunnel junction is preparing billions of electron transfer events per second between the electrodes. The data are input on the molecule by changing the conformation of well positioned lateral group around a conjugated board. AND, OR, XOR, NAND and half adder molecules have already been optimized and are ready to be tested experimentally according to the above discussion on progresses of an Atom based technology. One advantage of QHC over a gubit like guantum computer





approach is that only one molecule is active and the statistic is provided by the quantum measurement performed natively by the tunnel junction. For an NMR like qubit molecular quantum computer approach, the statistic is dependent on the large number of active molecules present in solution.

For (2), the molecule must have the real shape of an electrical circuit with all the node and meshes required integrated in a single molecule. In this case, specific intramolecular circuit laws are needed because they are different from the standard Kirchhoff node and mesh laws used to describe the behaviour of an electrical circuit. In the past, a few monumental molecules have been proposed integrating mainly molecular rectifiers groups along the intramolecular circuit. None have been designed according to the specific intramolecular circuit laws. Following those laws, ORmolecules and an AND-molecule have been designed in the BUN IST-FET project. The architecture problem in Pico-Inside was the very fast native decay of the electronic transparence of a molecular wire group as soon as it is elongated. Tunnel current intensity of the order of a femto-ampere had been calculated for the AND-molecule interconnected between N = 4 electrodes. This opens a large field of research on how to optimize the architecture of an intramolecular circuit to compensate this secular property. One has to invent chemical groups able to compensate this phenomenon providing some kind of intramolecular gain. At present, all the intramolecular circuits more complicated than the AND-molecule lead to impracticable tunnel current intensity well below the atto-ampere when calculated using the N-ESQC routine developed in BUN.

#### Molecular board and molecular equipements

The molecular boards supporting the logic function are essentially polyaromatic like molecules. For (1), qubits separation can be triggered from inside the molecule. For (1), the OHC approach is requiring a full polyaromaticity to beneficiate from a very fast computation time and to use the different symmetry of n molecular levels to play with intramolecular time interferences. For (2), some saturated bonds are required for circuit design purpose to compensate for the exponential decay of the electron transfer rate with an increase of the length of the wire groups required along the intramolecular circuit. Molecular equipments are the



**Figure 5:** A mono-molecular AND gate integrating 2 Aviram Ratner molecular rectifiers groups and a few molecular wire groups to form and intramolecular circuit. The logic response of the molecule was optimized using the N-ESQC code (Ref: S. Ami et al, Chem. Phys. Lett., 367, 662(2003))

chemical groups required to port the molecular board in a given environment, to protect the digital logic function embarked on the board and to ease the nanocommunication between the user and the molecule. Molecular legs are very popular on a metal surface to separate the conjugated board from the surface. But other separating groups are needed on insulating surfaces and started to be explored in Pico-Inside. Input/output groups can be specific end groups to increase the electronic interaction between a molecular wire and metallic pads or rotating group to define the logic digital input mechanically.





#### **Molecular devices**

Substituting each of the solid state devices integrated on the surface of a semiconductor by a molecule is leading to the hybrid molecular approach (3) mentioned above, in direct lineage with the Aviram-Ratner 1974 seminal paper. Adding one grid electrode to a single molecule properly interconnected between 2 metallic electrodes may lead to a transistor like behavior. There are many possible parameters to be controlled to obtain a molecular device presenting a power gain: the electronic coupling between the molecule and the source-drain electrodes, the homo-lumo gap of the molecule or the position of the energy level of the molecule relative to the electrode Fermi level. Shifting a few molecular levels by a lateral electric field applied via the grid electrode had long been advocated. But the range of electric field where a power gain can show up is not yet accessible experimentally: the electric field required is so large for the molecule design up to now that the breakdown limit of the metalmolecule-metal junction is reached before gain. Of course, a lot of 3 electrodes structure with a molecule in the nanojunction have been proposed and experimented. But their transconductance is so low that no gain will result while loading the device to an external resistor. A variant of this set-up is to perform an electrochemical experiment where the molecular levels are controlled relative to a reference electrode using an electrolyte. Here, the grid is macroscopic and no more on scale with the molecule.





One solution to this problem was to control the closure of the homo-lumo gap of a molecule positioned between the source and the drain of a tunnel junction by a mechanical deformation. The original experiment was performed in 1997 on a single C60 molecule trapped in the tunnelling junction of an STM. A small deformation of the C60 cage provides a large variation of the metal-C60-metal junction conductance leading to power gain. This was a proof of concept that a single molecule-device can provide gain by using the intrinsic electronic property of a single molecule. For C60, the 5 fold degeneracy of its Homo and 3-fold of its lumo are creating a nice destructive interference effect whose matching is cancelled by a compression of the molecule cage by the tip of the STM. This is a perfect example of a pure intramolecular electron transfer quantum phenomenon converted in a measurable tunnel current by the interaction of the molecule with the electrodes. A full planar version of this device had been proposed and its performance simulated in BUN. A full electrical circuit was established and included in a SPICE circuit simulator to evaluate the performances of a complete ALU up to 1000 C60 transistors. Aside from the real difficulties to find a





technology to fabricate such a molecular circuit, the gain in miniaturization is not exceptional since each C60 transistor need a minimum separation distance of a few ten of nanometer for the Kirchhoff electrical circuit node and mesh laws to be applicable. In comparison to the gigantic progress of solid state nanoelectronics, the future progress margin of hybrid molecular electronics is not very clear. This is the explanation why Pico-Inside was organized to intentionnaly remain away from this Hybrid approach.

## Starting Pico-Inside

Pico-Inside was a 3.5 years FP6-IST-FET integrated project whose partnership is explained in the E-nano Newsletter nº 2 (2005):

www.phantomsnet.net/Foundation/Enano\_newsletter02.php

This project decided to explore the monumentalization of a calculating unit up to the limits imposed by physics, chemistry and technology. Atomic scale technology is a very challenging path to be explored. But architecture, surface science (both experimental and theoretical) and chemistry were also included on the agenda. Pico-Inside challenge was to determine if a single unique molecule can compute and communicate its results to the macroscopic level.

#### **Further reading**

- BUN IST-FET final Report: www.phantomsnet.net/Enano/euprojectreports.php
- CHIC IST-FET Project: <u>www.cemes.fr/chic/</u>
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## **Pico-Inside: Summary and Objectives**

Computing inside a Single Molecule using Atomic Scale Technologies (Pico-Inside) was one of the Integrated Projects funded within the 6<sup>th</sup> Framework programme IST-FET (Nano proactive initiative: <u>www.cordis.lu/ist/fet/nid.htm</u>).

Below are detailed a summary of the project objectives (more info available at <u>www.picoinside.org</u>).

During the last 4 years, Pico-Inside objetives were to develop:

- (1) The architecture,
- (2) The atomic scale technology and
- (3) The chemistry to explore and quantify intramolecular resources for integrating much more than a single logic gate inside a single molecule.

Five very recent breakthroughs were fully exploited by Pico-Inside partners.

- (1) The theoretical demonstration that intramolecular quantum evolution based on the nonstationary mixing of large molecule quantum states can perform digital operations.
- (2) The new intramolecular mesh and node circuit rules for large molecules whose internal chemical structure is similar to a standard electronic circuit architecture.
- (3) The experimental demonstration that the electronic contact between a single molecular wire and its contacting atomic pad requires 0.05 nm precision.
- (4) The atomic resolution now obtained by a non-contact UHV-AFM on insulating surfaces and by low temperature UHV-STM on insulator on metal systems.
- (5) The progresses of organic chemists to design and synthesise large multifunctional molecules adapted to surface performances at the atomic scale.

Pico-Inside integrated the necessary groups to explore new architecture concepts with Fujitsu Europe. LT-UHV-STM and NC-UHV AFM offered a complete and true access to the atomic scale for interconnects with Omicron. This included nano-stencil contact experiments, the necessary chemistry labs task force and the required theoretical group to support the architecture, the molecular design and the analysis of Pico-Inside nanoscale experiments. This integration was completed by dissemination activities that created and diffused original roadmaps to a large community around Pico-Inside towards mono-molecular computing and atomic scale technologies.