Pico-Inside Report

Computing inside a single molecule using atomic scale technologies

Coordinators

Correia, Antonio (Phantoms Foundation, Spain)
Joachim, **Christian** (CEMES-CNRS, France)

Design and layout

Chacón, Carmen (Phantoms Foundation, Spain)
Fernández, Maite (Phantoms Foundation, Spain)
Narros, Concepción (Phantoms Foundation, Spain)
Serrano, Soraya (Phantoms Foundation, Spain)

Authors

Alemani, Micol (Frei Universitat Berlin, Germany)
Amijs, Catelijne H. M. (Institute of Chemical Research of Catalonia, Spain)
Ample, Francisco (CEMES-CNRS, France)
Baratoff, Alexis (Universitaet Basel, Switzerland)
Barattin, Regis (CEMES-CNRS, France)
Bechstein, Ralf (Universität Osnabrûck, Germany)
Bellec, Amandine (LPM-CNRS / Université Paris-Sud, France)
Benjalal, Youness (CEMES-CNRS, France / Univ. Hassan II-Mohammédia, Morocco)
Bennewitz, Ronald (McGill University, Canada)
Besenbacher, Flemming (University of Aarhus, Denmark)
Bettac, Andreas (Omicron Nanotechnology GmbH, Germany)
Bombis, Christian (Freie Universität Berlin, Germany)
Bouju, Xavier (CEMES-CNRS, France)
Budzioch, Janusz (Jagiellonian University, Poland)
Chiaravalloti, Franco (LPM-CNRS / Université Paris-Sud, France)
De Mendoza, Paula (Institute of Chemical Research of Catalonia, Spain)
Dujardin, Gerald (LPM-CNRS, France)
Echavarren, Antonio M. (Institute of Chemical Research of Catalonia, Spain)
Feltz, Albrecht (Omicron Nanotechnology GmbH, Germany)
Gauthier, Sébastien (CEMES-CNRS, France)
Glatzel, Thilo (Universitaet Basel, Switzerland)
Gnecco, Enrico (Universitaet Basel, Switzerland)
Godlewski, Szymon (Jagiellonian University, Poland)
Goryl, Grzegorz (Jagiellonian University, Poland)
Goryl, Maria (Jagiellonian University, Poland)
Gourdon, André (CEMES-CNRS, France)
Grill, Leonhard (Frei Universitat Berlin, Germany)
Hecht, Stefan (Humboldt-Universität zu Berlin, Germany)
Hirth, Sabine (Universität Osnabrûck, Germany)
Hliwa, Mohamed (CEMES-CNRS, France / Univ. Hassan II-Mohammédia, Morocco)
Joachim, Christian (CEMES-CNRS, France)
Kantorovich, Lev (University College London, United Kingdom)
Kawai, Shigeki (Universitaet Basel, Switzerland)
Köble, Jürgen (Omicron Nanotechnology GmbH, Germany)
Kolodziej, Jacek J. (Jagiellonian University, Poland)

Krok, Franciszek (Jagiellonian University, Poland)
Kühnle, Angelika (Universität Osnabrûck, Germany)
Lægsgaard, Erik (University of Aarhus, Denmark)
Lafferentz, **Leif** (Freie Universität Berlin, Germany)
Linderoth, Trolle R. (University of Aarhus, Denmark)
Maier, Markus (Omicron Nanotechnology GmbH, Germany)
Maier, Sabine (Universitaet Basel, Switzerland)
Mannsberger, Michael (Freie Universität Berlin, Germany)
Martrou, David (GNS/CEMES-CNRS, France)
Meyer, Ernst (Universitaet Basel, Switzerland)
Mielke, Johannes (Freie Universität Berlin, Germany)
Moresco, Francesca (Frei Universitat Berlin, Germany)
Mosseri, Rémy (LPTMC-CNRS, France)
Nimmrich, Markus (Universität Osnabrûck, Germany)
Nony, **Laurent** (Université Paul Cézanne Aix-Marseille III, France)
Ostendorf, Frank (Universität Osnabrûck, Germany)
Peters, Maike V. (Humboldt-Universität zu Berlin, Germany)
Pfeiffer, Oliver (Universitaet Basel, Switzerland)
Piatkowski, Piotr (Jagiellonian University, Poland)
Prauzner-Bechcicki, Jakub S. (Jagiellonian University, Poland)
Rahe, Philipp (Universität Osnabrûck, Germany)
Reichling, Michael (Universität Osnabrûck, Germany)
Renaud, Nicolas (CEMES, France)
Riedel, Damien (LPM-CNRS / Université Paris-Sud, France)
Rieder, Karl-Heinz (Frei Universitat Berlin, Germany)
Schütte, **Jens** (Universität Osnabrûck, Germany)
Shluger, Alexander (University College London, United Kingdom)
Socoliuc, Anisoara (Universitaet Basel, Switzerland)
Solinas, Paolo (LPTMC-CNRS et UPMC, France)
Stara, Irena G. (Institute of Organic Chemistry and Biochemistry, Czech Republic)
Stensgaard, Ivan (University of Aarhus, Denmark)
Stojkovic, Sladjana (CEMES-CNRS, France)
Such, Bartosz (Jagiellonian University, Poland)
Sushko, Maria L. (University College London, United Kingdom)
Szymonski, Marek (Jagiellonian University, Poland)
Tekiel, Antoni (Jagiellonian University, Poland)
Trevethan, Thomas (University College London, United Kingdom)
Villagomez Ojeda, Carlos Javier (CEMES-CNRS, France)
Watkins, Matthew (University College London, United Kingdom)
Xu, Wei (University of Aarhus, Denmark)
Yu, Miao (University of Aarhus, Denmark)
Zambelli, Tomaso (ETH Zurich, Switzerland)
Zimmerli, Lars (Universitaet Basel, Switzerland)

1. Introduction

Hybrid and Mono Molecular Electronics

IST-FET European Integrated Project
Christian Joachim (Pico-Inside Coordinator)

Nanoscience Group CEMES-CNRS 29, Rue J. Marvig BP94347 31055 Toulouse France

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.

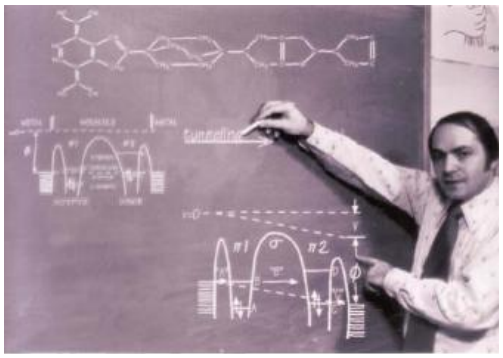

Figure 1: *At the origin of molecular electronics: Ari Aviram and its molecular rectifier in the 70's*

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 course, the same question arises 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 micro-electronics 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 a macromolecule and interconnect them too. (5) instead of one molecule per 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.

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

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, OR-molecules and an AND-molecule have been designed in the BUN IST-FETproject. 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 open 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 QHC approach is requiring a full poly-aromaticity to beneficiate from a very fast computation time and to use the different symmetry of π 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.

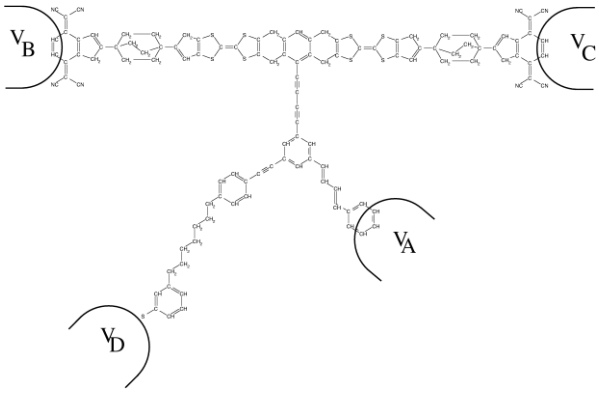

Figure 5: *A mono-molecular AND gate integrating 2 Aviram Ratner molecular rectifiers groups and a few molecular wire groups to form and intramolecular circuit. The logic response of the molecule was optimized using the N-ESQC code (Ref: S. Ami and All, Chem. Phys. Lett., 367, 662(2003))*

Molecular equipments are the 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 nano-communication 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.

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:
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- C. Joachim, J. K. Gimzewski and A. Aviriam, Nature, 408, 541 (2000)
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More Relevant Pico-Inside publications

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N. Renaud, M. Ito, W. Yen, M. Hliwa, M. Seays and C. Joachim
Chem. Phys. Lett., 472, 74 (2009).

Study and manipulation of single functionalized molecules by low temperature STM
L. Grill, M. Alemani, K.-H. Rieder, F. Moresco, G. Rapenne, C. Joachim, M. V. Peters, and S. Hecht,
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Molecular assemblies grown between metallic contacts on insulating surfaces
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Appl. Phys. Lett. 94 (2009) 1

Nanoscale Engineering of Molecular Porphyrin Wires on Insulating Surfaces
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Small, 4, (8), (2008), 1115

Generalised Langevin Equation for solids: II. Stochastic Boundary Conditions for non-equilibrium molecular dynamics simulations
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Phys. Rev. B, v. 78, No. 094305 (2008)

Building blocks for molecular devices: Organic molecules on the MgO (001) surface
T. Trevethan and A. L. Shluger
J. Phys. Chem. C 111 (42), pp.15375-15381 (2007)

Designing molecular architecture to control diffusion and adsorption on insulating surfaces
M. Watkins, T. Trevethan, M. L. Sushko and A. L. Shluger
J. Phys. Chem. C 112 (11), pp. 4226-4231 (2008)

The role of dopant in silicon on the dynamics of a single adsorbed molecule
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Phys. Rev. B 77, 125316 (2008)

STM induced modifications of the trima molecule chemisorbed on Si(100)
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J. Chem. Phys. 129, 1 (2008)

A straightforward route to helically chiral N-Heteroaromatic compounds: Practical synthesis of racemic 1,14-Diaza[5]helicene and optically Pure 1- and 2-Aza[6]helicenes
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