	NANOMOL **IST–1999-12603** Manufacturing and Modelling of Nano-Scale Molecular Electronic Devices

Final Report

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Executive summary

The overall goal of the NANOMOL project has been to develop tools and techniques for the fabrication of electronic devices with critical dimensions below 5 nm and integration of such structures to form logic elements and memory cells.

The NANOMOL project has emphasised fundamental investigations using concepts and techniques originating from organic chemistry and supramolecular engineering, combined with surface patterning and nano-manipulation techniques. The major lines of NANOMOL research have involved:

- Definition and realisation of a family of suitable conjugated molecules and investigation of their self-assembling properties
- Investigation of self-assembly of nanoclusters, with molecular bridging between the clusters.
- Fabrication of nanoscale structures for electrical transport measurements on molecules and clusters
- Self-assembled three terminal devices with metallic clusters and conjugated molecules.

At the beginning of the NANOMOL project, the milestones were:

- A family of conjugated molecules synthesised and characterised.
- Models for conductance in molecular wires verified by charge transport measurements.
- Analysis of self-assembly processes. Control of a single nanocluster's position between two electrodes.
- Modelling and synthesis of molecules optimised for a three-terminal device.
- Fabrication and characterisation of 3-terminal devices made by self-assembly of nanoobjects.
- Architecture and implementation plan for information processing devices.

As is evident from the Final Review report, the NANOMOL project has passed these milestones cum laude. The delivered three-terminal devices represent state of the art, and together with the cluster-molecular networks and mazes, they define very important directions of research during the next five years to integrate such structures to form logic elements and memory cells.

Originally, the NANOMOL project was divided into two phases, with a second phase directed toward making small scale integration and demonstration of devices for information processing, such as logic gates and memory cells. In reality, these goals were somewhat too ambitious, and the second phase has so far only been addressed via theoretical considerations and state-of -the-art surveys: the practical implementation remains a great challenge already the near future. It should be noted that this is a challenge for the entire field of Moleclar electronics and will be a major theme in the sixth framwork programmes dealing with nano and information technology.

1. Introduction

The purpose of the NANOMOL project has been to develop nanoelectronic devices involving metal wires and quantum dots connected by molecules as basic elements in switching networks for post-CMOS information processing.

NANOMOL has primaily dealt with fundamental aspects and technology of self-assembly of molecular-scale systems, investigation of electron transport processes, and development of three-teminal devices. Emphasis has been on fundamental investigations using concepts and techniques originating from organic chemistry and supramolecular engineering, combined with surface patterning and nano-manipulation techniques.

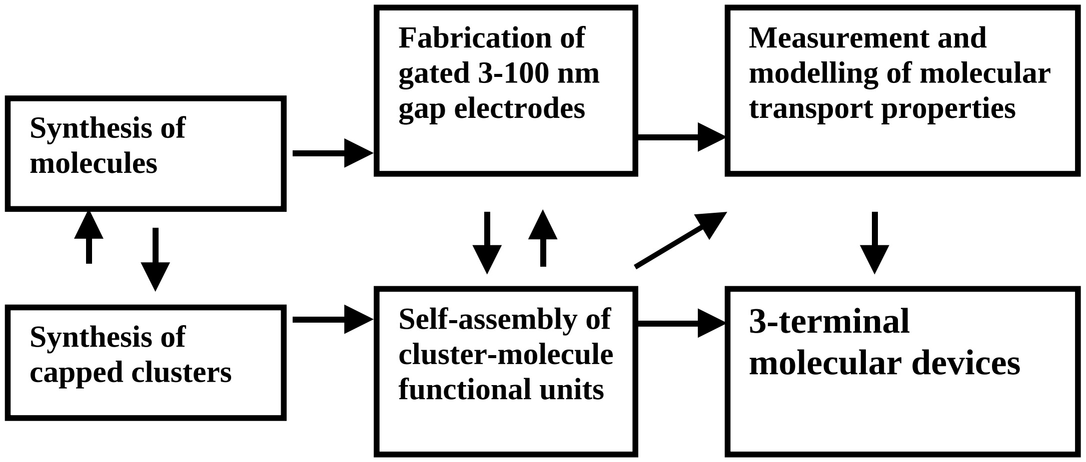
The NANOMOL research has lead to two possible routes for molecular electronics: 1) lithographically defined patterns with self-assembly of molecules or clusters to form circuitry with molecular transistors, and 2) self-assembled cluster-molecule networks contacted by electrode arrays. The delivered three-terminal devices represent state of the art, and togther with the cluster-molecular networks and mazes, they define very important directions of research during the next five years, to investigate integration of such structures to form logic elements and memory cells.

Our conclusion from this study is that a number of roads towards molecular electronics are wide open, and that the work of NANOMOL is highly relevant for exploring all of them, since NANOMOL is sucessfully addressing a number of core issues: lithography and self-assembly, hybrid structures, 2- and 3-terminal devices, and random and organised molecule-cluster networks.

These results have allowed the consortium to contribute significantly to establishing the state of the art in Molecular Electronics based on synthetic molecules, capped clusters, nanogap fabrication and deposition techniques.

2. Structure of the project

- Synthesis of molecular wires
- Synthesis of molecule capped metallic clusters
- Fabrication of gated 3-100 nm gap electrodes
- Self-assembly of cluster-molecule functional units
- Measurement of molecular transport properties
- Fabrication and testing of 3-terminal molecular devices



2.1. Synthesis of molecular wires

The general purpose of this task was to prepare conjugated molecules fitted with reactive groups at the ends that make them suitable for self-assembly onto metallic surfaces (electrodes or clusters).

The strategy has been to prepare molecules that differ either by the nature of the conjugated part (thiophene based in BSFMOL and oligophenylene-vinylene in RFMOL) or by their reactive end (sulfur, selenium in BSFMOL, sulfur or thiomethylene in NFMOL).

A large effort has also been devoted to the synthesis of i) a molecule that should show an increased sensitivity to the electrostatic field applied by a gate (CFMOL) and ii) to synthesize a family of molecules based on a polytolane backbone and fitted with an electroactive ruthenium complex on one side and a thiol on the other side (ETMOL) (for electrochemical measurements).

2.2. Synthesis of molecule capped metallic clusters

This task has been concerned with well-controlled functionalisation of clusters with the aim to develop protocols for cluster attachment to each other or to specific sites on surfaces or devices. In particular, the task involved the preparation of ligand-stabilised gold clusters (gold clusters capped with oligo(phenylenevinylenes)(OPVs)), which will serve along with, or instead of molecules, as functional units of the self-assembled devices.

The general problem of how to achieve the inter-connectivity of clusters has been addressed by preparing clusters with various functional groups in the ligand shell, i.e.

BSFMOL, NFMOL and CFMOL, that can facilitate the interconnectivity problem and at the same time introduce electronically interesting moieties. A number of different approaches towards this aim have been attempted, including the use of complementary DNA strands to link clusters to each other in a controlled fashion.

These tasks have also involved the development of preparative methods for monolayers and networks of clusters on various substrates that may or may not be covered with electrodes for transport measurements. This also dealt with problem of controlling the interconnectivity between the clusters in networks.

2.3. Fabrication of gated 3-100 nm gap electrodes

The task has been to develop new nanofabrication techniques allowing the realisation of *reproducibl*e sub-5nm gaps between electrodes and prepare planar multi-electrode configurations suitable for the complex architecture. Basically, two techniques have been successfully developed and used to fabricate electrodes with gated 3 nm gaps or smaller, namely (1) angle evaporation through masks, and (2) electrical breaking of nanowires using current pulses. In addition, lithographic methods have been used for the more conventional electrodes and larger gap sizes. Also, during the early stages of the project, break junctions were used, and electrodeposition techniques were investigated..

2.4. Self-assembly of cluster-molecule functional units

This part of the project involved the development of preparative methods for monolayers and networks of clusters on various substrates that may or may not be covered with electrodes for transport measurements.

The tasks have been to investigate deposition methods for molecules (OPVs) in order to find suitable conditions for these molecules to adsorb on the electrodes surfaces as individual objects, (i.e., without electronic interactions with their neighbours), in a controlled geometry (typically with the long axis of the molecule perpendicular to the surface), to investigate the positioning of the molecules in the gap between the electrodes, and to prepare networks of clusters control the interconnectivity between the clusters in networks, through place exchange of ligands (bifunctional molecules) in deposited cluster arrays, or via the mobility of the ligands in the capping shell of clusters. A cluster can be capped differently in various direction of space. This is crucial for directing self-assembly and for potential developement in the field of neuromorphic architectures.

2.5. Measurement and modelling of molecular transport properties

This central task has addressed the problems of the electronic transport properties of the nanoobjects synthesized, organized and contacted with the electrodes prepared in the project. The task integrates the basic building blocks to achieve the main objectives:

- To reproduce and demonstrate unambiguously the operation of the single molecule three terminal device.
- To study of the arrays of interconnect nanoparticles
- To investigate complex structures like Metal-capped cluster-Metal junctions

The purpose of theoretical modelling is to help interpreting the experimental results by applying existing theories and developing new theoretical tools. Its role is also to suggest new methods to control the conductance of a molecular or cluster-based device with a third electrode. It is also the place for reflexion on the architectural aspects of molecular electronics based on single molecules and clusters.

2.6. Fabrication and testing of 3-terminal molecular devices

This is the focal point of the entire NANOMOL project. The goal has been to fabricate 3-terminal device demonstrators with single molecules and clusters for the purpose of demonstrating electrostatic gate modulation of the source-drain transport current.
The specific goal has been to fabricate molecular and cluster Single Electron Transistors (SET) showing reproducible characteristics and generic architectures in order to allow interconnection of a few devices to accomplish some simple logic function.

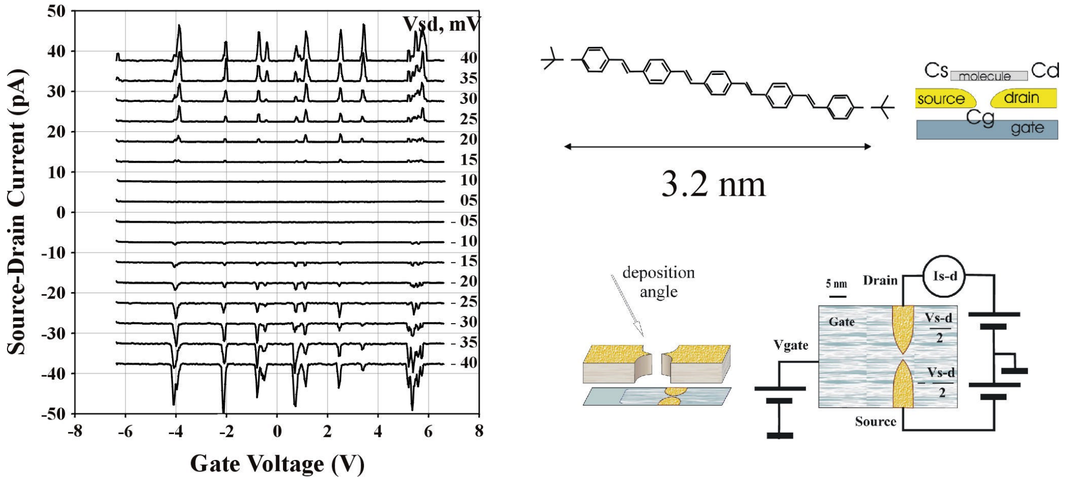
3. Main achievments: device demonstrators

3.1. Three terminal single molecular device (SET transport) [25]

The major result is the demonstration of a single-molecule single electron transistor (SET) in which the electronic transport is determined by the electronic levels of a single pi-conjugated molecule (OPV5) in nine distinct charge states. The OPV5 molecule was connected by high-resistive tunneling barriers to two source and drain gold electrodes and coupled capacitively to a gate electrode to form the single-molecule Single Electron Transistor (SET). Electron transport through this device involves sequential tunneling through the molecule.

Three devices of this kind have been prepared and characterized. They demonstrate for the first time a sequence of open states as the gate potential is varied, allowing to deduce the redox potentials (charge states) of molecular ions in the electrostatic environment of the SET, consistent for all three devices. Simulations of charge-image interaction of molecular ions in the vicinity of the metal surfaces in the SET device predict new values of redox potentials which are in reasonable quantitative agreement with the SET measurements and reproduce their main qualitative characteristics. These can be attributed to modifications in molecular spectra due to image potentials induced in the Source and Drain electrodes.

The oligo-*p*-phenylenevinylene molecule (OPV5) molecule has five benzene rings connected through four double bonds (see Fig. 3.1). It was synthesized by a new method developed in our laboratories which allows thiol end-capping. The terminal thiols were protected with a *tert*-butyl group which prevents chemical binding of the sulfur to the gold electrode thus leading to a poor van der Waals contact between the molecule and both the source and drain electrodes.



OPV5 - ((*E,E)*-1,4-bis{4-{(E)-4-(*tert*-butylthio)styryl}}benzene)

Figure 3.1 Right top: OPV5 and a schematic picture of the junction. Right bottom: the angle evaporation mask and a schematic picture of the actual junction electrodes. Left: traces of the sorce-drain current as function of gate voltage for fixed source-drain voltage.

A planar gate electrode made of oxidized aluminum on top of aluminum metal was prepared on a chip of oxidized silicon (Fig.3.1). A shadow mask used to deposit the gold lead electrodes was defined on top of the gate by standard electron-beam lithography. First, two gold electrodes were deposited through a shadow mask by condensing gold vapor on the substrate held at 4.2K. By using an oblique evaporation angle (Fig.3.1) together with *in situ* conductance measurements, we were able to fine tune the tunneling gap between the gold electrodes to a few nanometers. In this way we fabricated two self-aligned and self-sharpened gold electrodes with a few Mega Ohm tunneling gap in between. By annealing the sample up to 100 K, we increased the gap resistance to a few Giga Ohms, which corresponds to a tunneling gap width of roughly 2 nm. Annealed samples did not show any gate dependence of the tunneling conductance nor any peculiarities in the I(V) curves. At this stage, a sub-monolayer of organic molecules was deposited on the electrodes by quench condensation. The sample was annealed at low temperatures (below 70 K), allowing thermally-activated motion of the organic molecules, while monitoring the nano gap conductance at a source-drain bias of 400 mV. When the conductance changed stepwise, indicating the trapping of a single molecule in the nano gap, the device was cooled down to a temperature of 4.2 K where all transport measurements were taken.

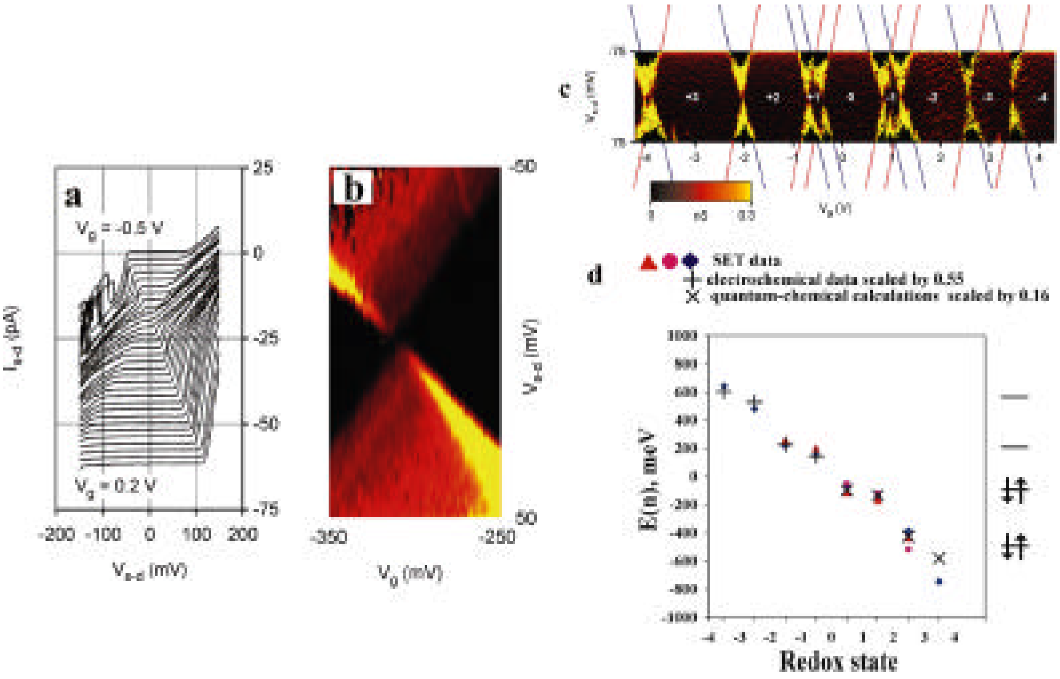


Figure 3.2. (a, b). A set of current-voltage characteristics and corresponding colour derivative plot for one of the open states of molecular transistor. (c). Colour-coded measurements of the device differential conductance as a function of source-drain and gate voltages. (d). Extracted energies of the charge(redox) states (from the capacitance model) together with data from electrochemistry and theoretical estimates.

We measured electrical transport at 4 Kelvin through a single OPV5 molecule (Fig.3.1), placed in a gap of about 2 nm between source and drain electrode of a single electron transistor device (SET). By scanning the gate voltage from – 4.3 V to + 4.3 V while continuously measuring the source-drain current-voltage characteristics, we were able to characterize nine different redox states of the molecule (from the tetra anion to the tetra cation). The results of these measurements are shown in Figs. 3.1 and 3.2 together with the results of a model based on the assumption that the molecule has a constant charging energy of 30 meV. The resulting energy levels of the different redox states extracted from this model are also depicted in Fig. 3.2. For the anionic part, these levels are consistent with electrochemical data reported in literature. In particular the almost degenerate energies of the first two charge states (both positive and negative) are caused by a distortion of the

molecule into a quinoide structure upon charging, as established by electrochemical studies. In physics terms this is referred to as bipolaron formation.
The data clearly reveal a *bunching* effect around the gate voltage *V*= 0, which we simply attribute to the double occupancy of the nondegenerate molecular orbitals in OPV5. In a simple one-electron picture, a unit charge increase from *odd to even* (*e.g.* from –1 to –2) leads to the filling of a singly occupied orbital which requires some charging energy; in contrast, a change from *even to odd* (*e.g.* from –2 to –3) involves the occupancy of a new empty orbital and hence requires a charging energy plus an energetic contribution related to the electronic level spacing.

In electrochemical studies, the energies of the charged states are measured by scanning the potential of an electrode relative to an electrolyte solution containing the redox-active molecules. Such an electrochemical study has been reported for an OPV5 derivative which was reduced in four successive electron transfer steps from the neutral molecule ($n = 0$) to the tetra-anion ($n = -4$). The energy scale of the EC data has been normalized by a factor of 0.5 to best match the SET data; this renormalization reflects namely the differences in surrounding between the solution-based EC experiments and the solid-state SET device. We obtain parallel evolutions of the EC and SET data, which illustrates for the first time the correspondence between redox electrochemistry of molecules in solution and single electron transfer reactions in the SET.

In order to cover the cationic part of the curve (where electrochemical data are not available), we have estimated, at the quantum-chemical level, the total energies of the oligomer from the ground state to the quadruply charged state. We considered OPV5 surrounded by a dielectric continuum; in the absence of any experimental information, the dielectric constant was chosen equal to 2.5, *i.e.*, close to the value expected in isotropic polyparaphenylenevinylene films. Strikingly, as illustrated in Fig. 3.1, the quantum-chemical results (black diamonds) follow exactly the same evolution as the SET data. We note that the quantum-chemical values have to be scaled by a factor of 0.16 to provide the best match. The need of a scaling factor between the two sets of data is not surprising and underlines the inherent differences between the two approaches: The quantum-chemical values are expected to be larger than the EC and SET data since the compensating effect of counter-ions and gate potential, respectively, are not accounted for in the polarizable dielectric continuum used in the quantum-chemical calculations .

In summary, the remarkable agreement among the independent data sets (Fig. 3.2), unambiguously relate the SET data to the properties of the OPV5 molecule for the single experiment in question. This demonstrates, for the first time, the straightforward relation between redox chemistry of molecules in solution at room temperature and the properties of a single molecule in single electron transistor operating at 4 Kelvin. Indeed this is a clear manifestation of the robustness of the redox properties of molecules which is determined uniquely by the quantum confinement of electrons in the particular molecular structure. In relation to possible applications of SETs it is of paramount importance to be able to make many identical quantum systems and in this regard molecules are very strong candidates compared to e.g. quantum dots, nanoparticles or carbon nanotubes which all face size or structure distribution issues, because it is possible to prepare crystals containing moles of identical molecules by organic synthesis. In addition, molecules of the size reported here are easily manipulated by chemical means allowing interfacing with the wealth of self-assembly methods for example for thiole containing molecules. Future experiments will show how far this avenue may be extended towards integrated devices using single molecules.

The present molecular three-terminal device will be an important tool for studying molecular wires and developing small integrated circuits with molecular transistors.

3.2. Self-assembled nanocluster FET (Chalmers) [36]

The task was to fabricate a capped-cluster-based transistor showing reproducible characteristics and a generic architecture allowing to change the molecules capping the cluster. Originally the expectation was to create a single-cluster single-electron transistor (SET) based on a single capped nanocluster, but it turned out that a variety of devices were produced depending on the chemical treatment.

A first series of experiments were made with clusters capped with alkylthiols, showing SET behaviour [4]. The capping agent was then replaced by bifunctional molecules from the BSFMOL family (bisthiolterthiophen). The transport properties then showed a significant increase in conductance and Coulomb Blockade-like transport was still observed. Hence, the required (NANOMOL) proof of principle of a "generic architecture allowing to change the molecules capping the cluster" was obtained. These experiments were done on samples prepared on a membrane to allow for observation of the clusters by TEM. For that reason, a gate controlling the current could not be connected.

A second series of experiment was then performed with an aluminium gate implemented beneath the sample. Gold clusters capped with octylthiols were then adsorbed on the electrodes initially prepared with a sticking bisthiol layer.

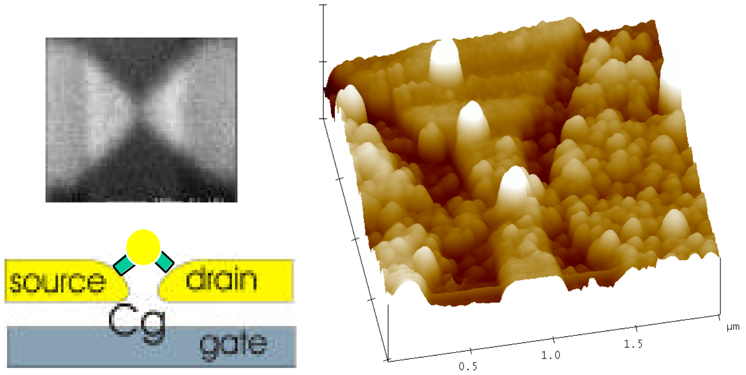
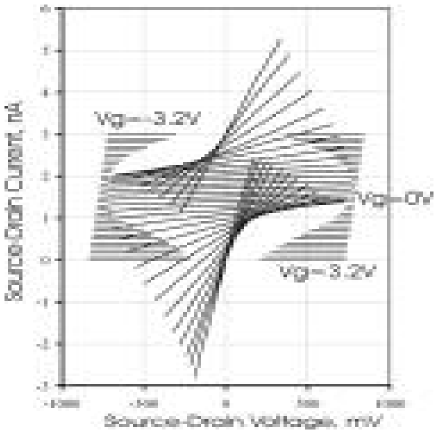


Figure 3.3. SEM picture of a device with nanogap on top of electrostatic gate.



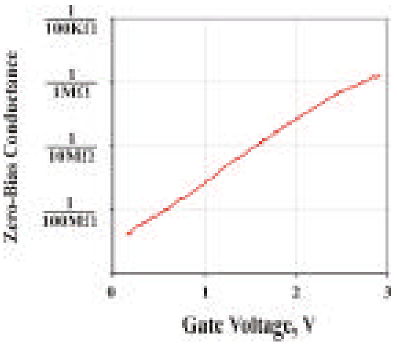


Figure 3.4. I-V characteristic of the FET.

The sample was measured at low temperature and showed a pronounced gate effect, allowing to switch the current on (10MΩ) at 2-3V gate voltage, and off (300MΩ) at zero gate voltage, as shown in Fig.3.4.

Interestingly, the findings show that a simple Coulomb blockade effect cannot account for the transistor effect. We believe [36] that the mechanical stress induced in the molecular tunneling barriers by the electrical polarization of the device is playing a key role. This would explain the fact that the I-V characteristic (Fig.3.4) does not depend on the polarity of the gate voltage.

The original purpose of the experiment was to fabricate a single-electron transistor (SET) based on a single capped nanoparticle. To check the results, these experiments were reproduced on purpose using mastered techniques for step-by step self-assembly of layers of clusters on a gap. It was shown that the experiment involved more than one cluster and definitely cannot be explained by SET operation but rather involves a mechanical action induced by the electrostatic gate field [36].

Using different chemical treatment of similar substrates with the nanogaps and electrostatic gates we were able to prepare devices with *very different transport properties*. Gold clusters (circa 5 or 6 nm) had been deposited onto aluminium oxide covered silicon with a circa 10 nm gap between electrodes. The set of experiments that led to typical Coulomb blockade behaviour started by derivatising the gold contacts with 1,9-nonanedithiol.

After deposition of the first gold particles layer plus a subsequent "protective layer" of dithiol, several devices with typical Coulomb blockade and well-presented gate modulation were observed. Detailed dI/dV patterns revealed that several grains were affecting the electron transport, but a single dominant period of current modulation suggests that transport is due to one dominant grain in the constriction.

We conducted another set of experiments in which we first functionalised the aluminium oxide layer with 3-mercapto-triethoxypropylsilane (boiling for 15 min in 30 ml isopropanol containing only ca. 1 microliter of silane, followed by excessive washing with isopropanol and curing in an oven for 5 min at 100 centigrade) and then immersed the sample in gold sol (1 –3 hours). No thiol layer was applied to these samples.

One gap then demonstrated behavior similar to the one observed a year ago: significant conductance modulation and the absence of Coulomb blockade, with the type of I-V characteristic shown in Fig.3.4.

3.3. Self-assembled nanocluster SET with tailored molecular barriers [35]

The target was in particular to address the problem of the transport in SETs, where conjugated molecules are used to self-assemble the cluster and provide the tunneling barrier at the same time. These investigations are preliminary, but they already proved successful. We observed, in a M-Mol-Cluster-Mol-M junction (M=Au bulk electrode, Cluster=Au cluster, Mol= bisthiolterthiophene molecular capping of the Au cluster) prepared with nanogaps made by electromigration [28], that the transport is SET-like with probable signature of the molecules in the details of the conductance plot (Fig. 3.5). The sharp features of the conductance plot smear out when the temperature is raised from 4K to 150K, whereas the SET still operates. At room temperature (300K) the SET does not show gate modulation any more, as expected with the "large clusters" (5nm) used. We did not yet reach a complete understanding of these results and continue our investigations.

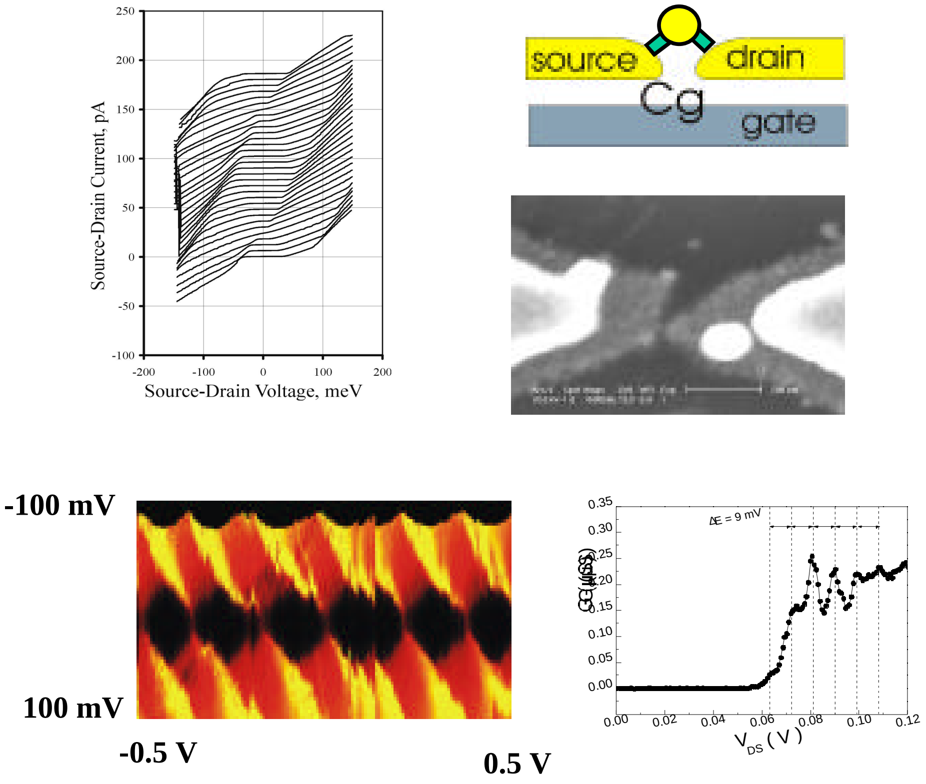


Figure 3.5. Single-capped-cluster SET (CEA)To our knowledge, it is the first time that such an experiment is realized. It opens a new route to understanding the transport through molecules and how interfacing molecules and clusters could allow to develop neuromorphic architecture by controlling the connectivity between clusters for example.

Note that this sub-project has the same target as the one in Sect.3.2. The major difference is that the nanogaps are fabricated in different ways (angle evaporation vs. electromigration) and that the cluster cappings are different.

4. Main achievments: Innovative experimental tools

A large variety of experimental tools have been developed during hte NANOMOL project. The main headings below emphasize points that deserve special attention. However, it must be noted that there is strong overlap. Most of the experimental tools involve a broad range of concepts, and especially the concept of self-assembly is omnipresent.

4.1. New synthetic routes for four complete families of molecules
4.2. New facile and versatile synthesis of capped clusters
4.3. Three types of sub-5 nm gaps developped with local gate
4.4. Mastered deposition of 0D, 1D, 2D clusters assemblies
4.5. Post processing of the assemblies and ligand mobility in the assemblies
4.6. New self-assembly techniques
4.7. Transport measurements

4.1. New synthetic routes for four complete families of molecules

The oligophenylene vinylene backbone was chosen for this family of molecule at the beginning of the project, to be used as molecular wires in three-terminal devices, as cappings on metal clusters, and as linkers between metal clusters. The molecules corresponding to the RFMOL, NFMOL and CFMOL families are presented in the figures below.

RFMOL [17,27] (Fig. 4.1a) has tert-butyl thiol protecting groups that cannot be removed or replaced (left part of the figure), as well as other type of protecting groups that can be removed (right part of the figure).

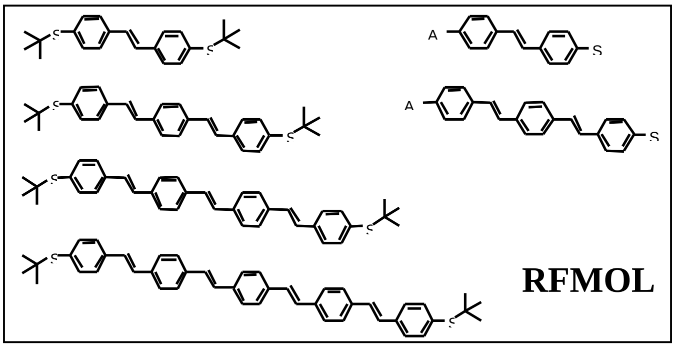


Figure 4.1a RFMOL

NFMOL [17,27] (Fig.4.1b): Based on the first year findings - precipitation of the clusters when capped with bifunctional molecules, and poor ability of the RFMOL molecules to pack up in organized layers - it was decided to prepare three molecules that could solve those problems. First, two oligophenylene vinylene oligomers with two and three repeat units and thioacetyl group at only one end were prepared so that clusters could be prepared that do not precipitate. Second an oligophenylene vinylene oligomer with two repeat units was synthesized with two thioacetyl groups at both ends bound to the phenyl groups through a methylene spacer. One advantage is a better ability to form organised layers. Another advantage is that the methylene spacer may electronically "decouple" the thiol-connecting group from the conjugated backbone compared to direct coupling of the thiol to the aromatic core. Hence, this molecule will allow to investigate (by comparison) the influence of the coupling of the molecule to the electrodes on the transport properties.

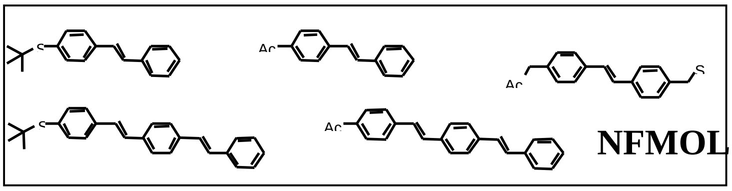


Figure 4.1b NFMOL

CFMOL [30] (Fig.4.1c): The structure of the molecule is shown in the figure below. The molecule with the nitro moiety is expected to show up an increased sensitivity to the electrostatic gating field, while the three terminal molecule is expected to allow the formation of assemblies of three clusters, with potential application in gold particle trimers.

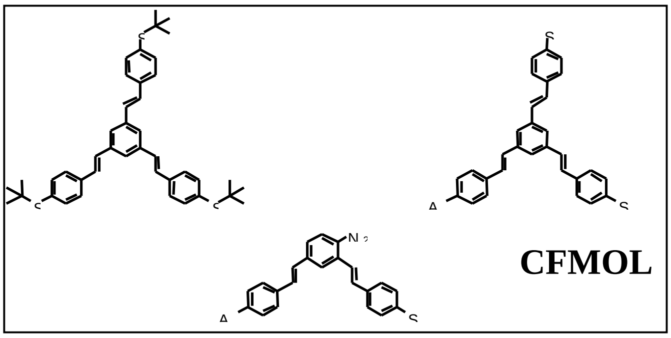


Figure 4.1c CFMOL

ETMOL [18] (Fig.4.1c): A general synthetic scheme was developed, based on the use of a new redox centre, a cyclometallated ruthenium complex **1** $[Ru(bpy)_2(pp)]^+$ (bpy : 2,2'-bipyridine; pp : 2-phenylpyridine [18]. Easily functionalised, moderately oxidisable and highly soluble in various polar solvents, this complex provides a convenient building block to begin the synthesis of usually poorly soluble molecules. Thus the amino derivative of **1** is smoothly converted into a fat ω-bromoalkylamide, precursor of a saturated wire. The ethynyl derivative of **1** is a good substrate for Sonogashira arylation/ethynylation sequence, thus leading to wire of oligophenylene ethynylene backbone, and of various size. Molecules were all terminated by a sulfur atom (thiol or thiophenol) to bind to gold. The solubilizing properties of the complex, acting as a “phase tag”, allow a fast screening of molecular structures that could be performed in a combinatorial way (see Sect.4.7.4).

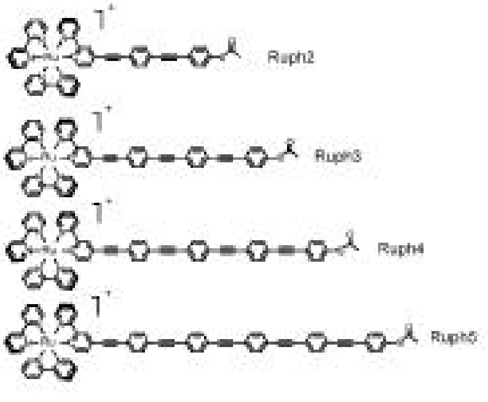


Figure 4.1d ETMOL:
Conjugated polytolane (oligophenylene ethynylene) molecular wires attached to an electroactive Ru-complex (left) via an amide group at one (left) end and an SH thiol group at the other (right) end. (CNRS)

4.2. New facile and versatile synthesis of capped clusters

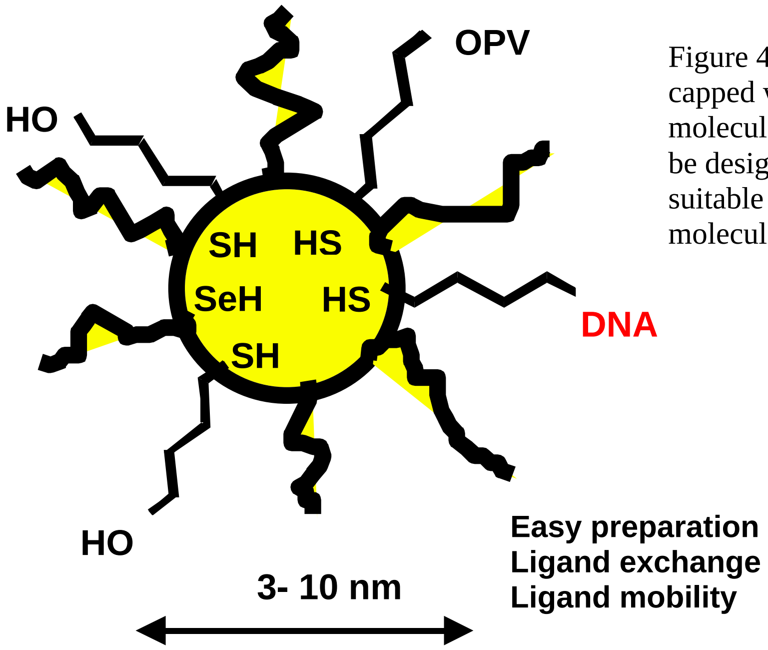


Figure 4.2 Gold cluster capped with a variety of molecules. The free ends can be designed for attaching to suitable substrates, or to other molecules.

New routes for the preparation of functionalised nanoparticles have been developed. It is evident that there is a need for research on well-controlled functionalisation of clusters with the aim to develop protocols for cluster attachment to each other or to specific sites on surfaces or devices. This problem has been addressed by replacing our usual thiolate-capped gold clusters with thioether-capped clusters of ca. 3 nm diameter, as recently reported in literature. We have found that these clusters readily take up thiol ligands and represent a promising new starting material for controlled functionalisation. We have also found that thioether-capped clusters are a good model system to study mechanistic aspects of the attachment of thiol molecules to clean gold surfaces, for the first time by NMR spectroscopy. It was found that "intact" thiols can adsorb, i.e. without losing the sulfur-bound hydrogen. This was shown by the release of “intact” thiols upon replacement of the ligand shell with disulfides. This is an important finding of great interest for the large community working on self-assembled monolayers (SAMs) of thiols on gold. We have further demonstrated the possibility of introducing a range of different ligands including phenanthrolines, bipyridines and oligo(phenylene-vinylene) monothioester (OPV).

We conclude that the use of thioether-capped clusters is a major advantage and will soon lead to completely new opportunities for the preparation of functionalised clusters and their spectroscopic characterisation. Thioether-capped clusters are readily prepared with a narrow size distribution and are reasonably stable when stored as solids under ethanol or dissolved in THF. In contrast to the behaviour of thiolate-capped clusters, even weaker ligands such as bipyridyl and thioesters are quantitatively taken up by the clusters and lead to interesting new adducts. There is no doubt that the ligand addition reactions introduced here will be of importance for the wider community of nanoparticle chemists and represent a significant step forward in this area of research [12].

These tasks also involve the development of preparative methods for monolayers and networks of clusters on various substrates that may or may not be covered with electrodes for transport measurements. This also deals with problem of controlling the interconnectivity between the clusters in networks.

The Liverpool group has investigated further the properties and ligand shell dynamics of thioether-capped gold clusters clusters [12]. It has been found that most of the thioether ligands can be removed from the cluster by repeated precipitation in a non-solvent finally leading to stable gold clusters with as little as one ligand per any 50-60 gold atoms, which corresponds to clusters containing only about 3 % organic material. Solutions of these clusters can be examined by NMR spectroscopy and *represent a nano-scale analogue of clean gold surfaces*. It is thus possible for the first time to study the adsorption of a number of compounds to gold in-situ by NMR spectroscopy. Of particular interest has been the adsorption of amines and the attempt of their subsequent replacement by disulfides and by thiols. Surprisingly, disulfides were unable to replace amines, while the addition of thiols readily led to release of amines from the cluster surface. This indicates that at least a proportion of the amines may adsorb to gold under loss of a hydrogen atom, which would be a highly unexpected behaviour. We are currently trying to corroborate these results by complementary spectroscopic techniques such as FTIR.

The Liverpool group has also developed clusters with *specific recognition function.* This is important to direct the particles to certain surface sites such as the gap between two electrodes. Significant progress has been made in attaching specific DNA sequences to water soluble gold clusters and manipulating their assembly and recognition properties by the use of specific enzymes (restriction endonucleases and ligases). A paper has been published in Angew. Chem. and three more papers are in preparation to be submitted to J. Am. Chem. Soc. Nanoletters and Chem. Comm.

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The importance of water-soluble clusters for such purposes led us to investigate a number of different ligands to render solubility. Of particular use has been a novel thioalkylated oligo (ethylene glycol). These clusters were also delivered to the Toulouse group for dip pen lithography studies [11]. The report describing the preparation of clusters capped by this ligand has been published in Chem. Comm. [14]. We have further discovered extremely stable water-soluble clusters prepared by reduction with either sodium acrylate or polyacrylate. The attachment of DNA to such clusters is currently being investigated. A paper has been published in Langmuir [23].

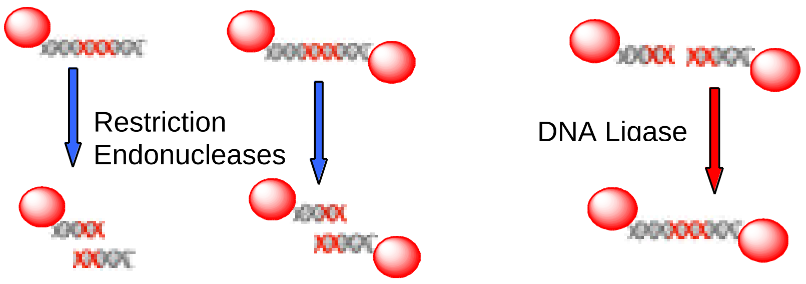


Figure 4.3 Controlling molecular links between gold clusters using DNA recognition

Gold clusters have been linked to each other in a controlled fashion using DNA base-pair recognition as a construction principle. Importantly, DNA processing enzymes have been introduced as new tools for nanostructure assembly. It has been demonstrated that nanostructures obtained in this way can be cut at predetermined sites using restriction enzymes, and linked together in a controlled fashion using ligation enzymes.

4.3. Sub-3 nm gaps with local gate

Sub-3 nm planar nanogaps are central today as tools for probing the transport properties of molecules/clusters and developing molecular electronics devices which may become basic building blocks of circuits for information processing on the long term.

Two techniques have been successfully developed within the consortium (Chalmers and CEA):

- double angle evaporation through a PMMA suspended mask with in situ control of the tunnelling current. This technique has been shown to allow the fabrication of gaps of a size comparable to the size of the molecules synhthesized in the project and used to make a single molecule transistor [25].
- formation of a nanogap by electrically breaking of a gold lithographed wire by a current pulse [35].

Double angle evaporation (Chalmers):

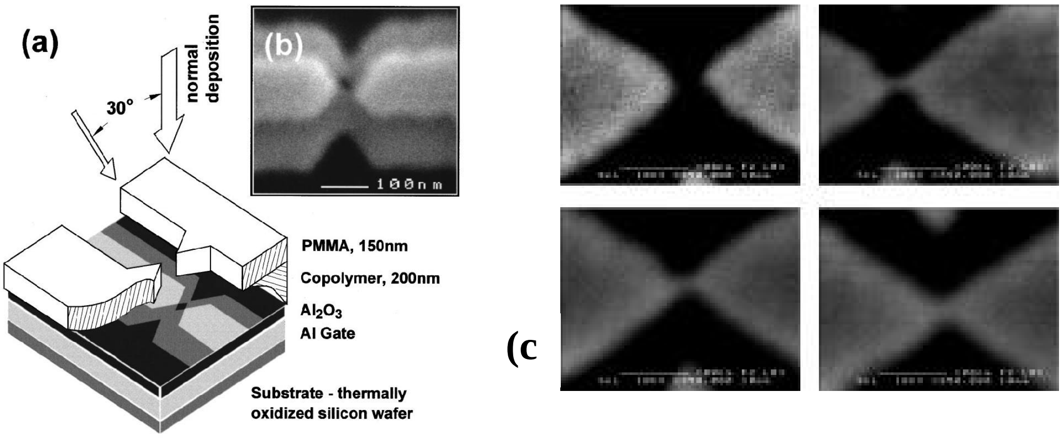


Figure 4.4 Double angle evaporation technique for fabricating nanogap junctions [25].

The electrostatic gate was made of oxidized aluminum. Nanogaps were made by exploiting the thin film deposition through a shadow mask under an angle. we prepared a set of nanogaps with the smoothly reduced separation between electrodes, up to a transition to metallic contact. This was achieved by a gradual increase of the dose during the E-beam exposure of the resist mask. Structures with the doses just below the formation of metallic contact were used. The idea is demonstrated by the four SEM pictures above.

Electrical breaking of a gold lithographed wire (CEA):

A technique has been setup to fabricate a gap at low temperature by driving a current through a 50 nm wide wire until it breaks. The use of the low temperature allowed to improve the reproducibility of the gaps. The mechanism of formation has been elucidated.

An electrical characterisation of the gaps has been developed that allow to know precisely their sizes, which ranges between 1.5 and 3 nm. The gaps have been validated in experiments with adsorbed clusters showing Coulomb blockade

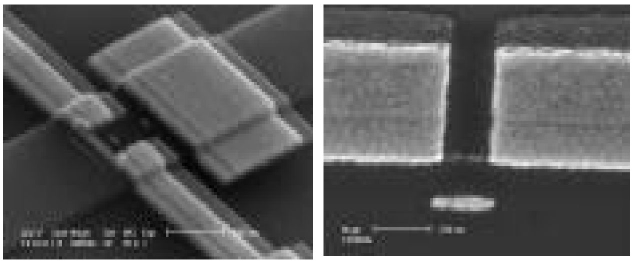


Figure 4.5 Electromigration technique for fabricating nanogap junctions (electrically broken fuse) [35].

4.4. Mastered deposition of 0D, 1D, 2D clusters assemblies

Future application of nanoparticles for information processing requires to master the fabrication of 0D, 1D, 2D or 3D assemblies of nanoparticles. The NANOMOL partners have collaborated to develop solutions for mastering such assemblies.

4.4.1 Zero-dimensional (0D) assemblies
4.4.2 One-dimensional (1D) assemblies
4.4.3 Two-dimensional (2D) assemblies
4.4.3 Three-dimensional (3D) assemblies

4.4.1 Zero-dimensional (0D) assemblies

0D assembly, i.e. single particle deposition, is obtained by appropriate functionalisation of a surface with molecules having a reactive group at the end designed to react and anchor the nanoparticles. Typically, thiol or selenol groups can be used.

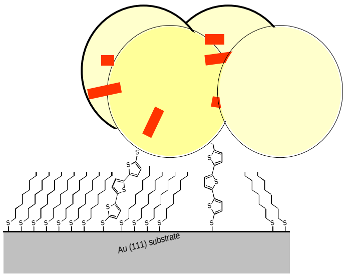


Figure 4.6 The figure illustrates how a Au nanocluster is anchored in a Au substrate by capping molecules sticking at defects or replacing molecules in a SAM.. The figure also illoustrates how this serves to anchor a 2D array of Au clusters connected by (other) capping ligands.

4.4.2 One-dimensional (1D) assemblies

1D assembly, i.e. wires has been obtained in three ways:

1. Depositing nanoparticles on a surface with a local contrast of surface energy: then the nanoparticles have been shown to build up lines at the interface [5,9]:

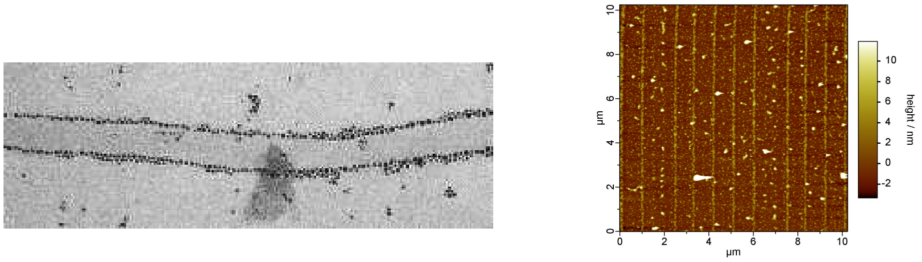


Figure 4.7 Left: gold clusters decorating Teflon tracks. Right: HMDS (Hexa Methyl Di Silazane) line pattern on SiO2 with selective deposition of gold clusters.

2. Realizing Langmuir-Blodgett (LB) films of a phospholipids - capped clusters mixture which gives rise to a phase segregation resulting in the formation of single clusters lines. Importantly, in both cases, the lines of cluster can be sintered in nanowires less than 10nm wide [8,31,33,40].

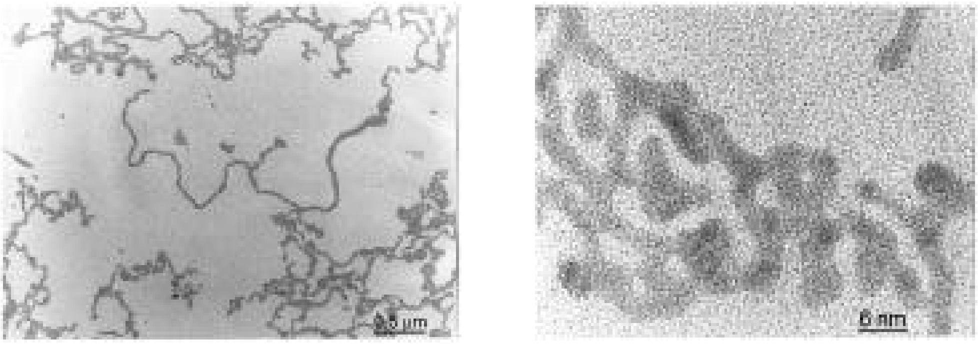
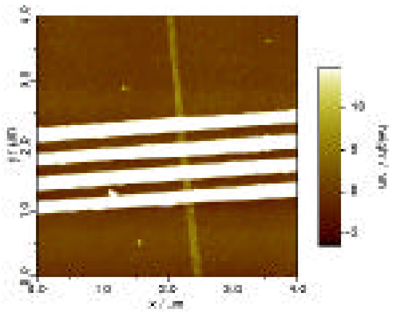


Figure 4.8: TEM images of hydrophobic gold clusters in the surfactant DPPC (left figureis a zoom-in picture) [8].

3. Electron beam lithography on Langmuir-Blodgett films of alkanethiol-capped gold nanoparticles: direct e-beam patterning of contactable sub-30nm lines of clusters, which cross-link under irradiation, and lifting off the non-irradiated parts [9].



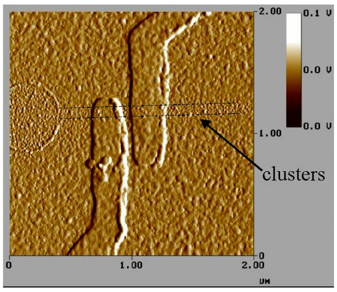


Figure 4.9: e-beam patterned reactive lines with aligned gold particles: Left: Four probe electrodes fabricated on top of a monolayer thick, 100 nm wide AuC12 line [9] (CEA). Right: Gold nanoparticles aligned between electrodes spaced by 30-60 nm [2] (Chalmers)

We have shown [9] that electron beam lithography on Langmuir-Blodgett films of alkanethiol capped gold nanoparticles is a viable strategy to define nanometer scale structures of such particles. Sub-30 nm wide "nanowires", the thickness of which is controlled at the single particle level, are created with e-beam doses in the mC/cm^2 range. It is shown that the patterns are formed by radiation-induced cross-linking of the alkyl chains and that they can be contacted (see Figure above) and studied electrically. Moreover, It was shown that place exchange reactions may be possible in the lines but also that these lines withstand the action of harsh solvent which is not the case of simple arrays and lines of particles.

4.4.3 Two-dimensional (2D) assemblies

2D assemblies have been prepared by either LB or layer by layer deposition from a solution [8,31,33,40].

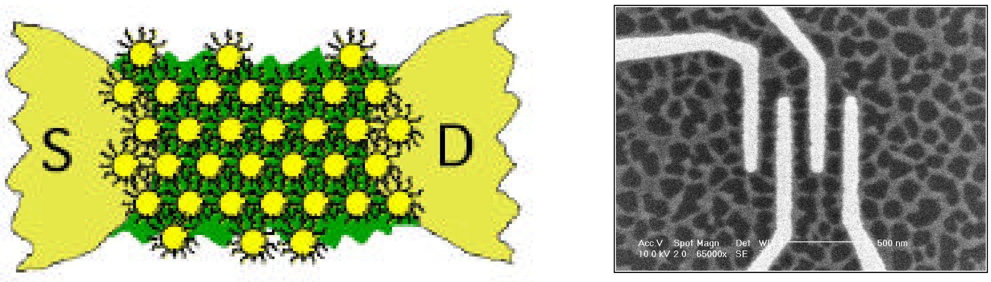


Figure 4.10: Left: schematic picture of cluster-molecule array. Right: Honeycomb cluster-molecule network on top of measuring electrodes for 4-point measurement [31].

Investigation of the ability to make self-assembled structures by the LB technique has been made starting from clusters with a mixed alkylthiol-NFMOL molecules capping shell.

4.4.4 Three-dimensional (3D) assemblies

3D assembly means, within the NANOMOL context, to use 2D cluster monolayers as substrates -"templates" - for building self-assembling functional structures. An example could be to bridge template wires by a cluster or a molecule to produce a local non-linear element (Fig.4.14), or to build molecular wire networks on top of the cluster substrate, as illustrated in Fig. 4.18.

A note on zero-dimensional (0D) assemblies-Nanoprinting of clusters in gaps (CNRS): We have developed an instrument which allows the deposition of small islands of gold nanoclusters with a nanometric precision at a predefined place of a surface such as the material from the tip to the surface by mechanical contact [11]. We showed that this technique can be applied for a direct printing of islands of 2 to 5 nm nanoclusters on the surface. The islands are monolayers with a diameter in the 50-100 nm range. A major improvement of our technique is that it allows printing at a predefined point of the surface. This is achieved by using two tips which can be positioned independently: one for printing (controlled by a nanopositioning table incorporated in a commercial AFM), and one for imaging (controlled by the AFM head). We have shown that this set-up allows, in two steps, to deposit in the gap between the two electrodes of a nanojunction a small island of about 80 nanoclusters.

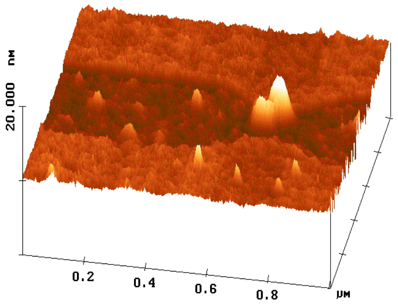


Figure 4.11: Nanoprinting of clusters in gaps [11].

It is very important to get a precise insight of the printing mechanism. With that aim we studied how the length of the stabilizing chains, the nature of the solvent and the chemistry of the surface influence the inking of the tip and then the transfer of the clusters from the tip apex to the surface. This was done using gold clusters of different types with well controlled shapes and composition. We have shown that a crucial parameter is the length of the chains capping the clusters.For example, clusters with different sizes but identical chains behave the same way giving monolayer islands on the surface. On the contrary, clusters with the same size but with shorter chains behaves completely differently and can not be printed using the same conditions. The reason is that a the printing process requires an ink with a liquid-like behaviour. This is the case with long chains that can trap the solvent between the clusters. With short chains this liquid behaviour is obtained only using less volatile solvent as mesitylene. Another evidence of the fact that the ink is liquid appears when changing the chemistry of the surface. On hydrophobic surface the deposit has a spherical shape completely different from the monolayer obtained when the surface is hydrophilic. This probably results from different spreading behaviours on these surfaces.

4.5. Post processing of the assemblies and ligand mobility in the assemblies

Molecular interconnection in assemblies of clusters is important because it controls both the stability and electrical properties of the assemblies. These assemblies may find application as building blocks for future molecular electronics applications.

Within NANOMOL, we have developed techniques for controlling the interconnections within the cluster assemblies *during* formation, and for modifying the interconnections *after* formation.

The former technique (UniLiverpool) is based on DNA capped particles and makes use of the self-assembling properties of DNA and takes advantage of the enzymatic toolbox for modifying the DNA.

The latter technique (CEA, UKBH) principle is based on place exchange reaction of the capping ligands by bifunctional molecules able to interconnect two clusters. As an example, we used rigid rod molecules with thiol or selenol groups at both ends to replace the alkylthiol capping the clusters and shown that the exchange is stoechiometrically accompanied by the modification of the electrical properties of the assemblies.

These studies have been pursued in collaboration between Copenhagen and Saclay. The following studies were made. First, a comparison was made of the kinetics of exchange for BSFMOL (bisthiol and bisselenol molecules) as probed by UV-Visible spectroscopy and conductivity measurements [3,26].

Second, the exchange of alkylthiols capping the clusters by molecules from the CFMOL family were made to evaluate the effect of the modification of the central ring of the oligophenylene vinylene. In the course of these studies we observed quite systematically the formation of honeycomb structure corresponding to the restructuring of the monolayers of clusters. We investigated this phenomenon in detail and found that it was related to the surface pressure at which the LB film was compressed. Finally, exchanges were attempted in networks of clusters with various spacings between the clusters to understand if matching of the size of the molecules has to be comparable to that of the gap to successfully improve the conduction properties. These attempts were made in arrays and in the maze type structures discussed below [8,31,44].

Finally, it was also shown by UKBH that the molecules of the capping shell of clusters (hence their interconnection) were mobile within the shell and could be gathered spatially by chemical type on one side of the clusters using the air-water interface as template [32].

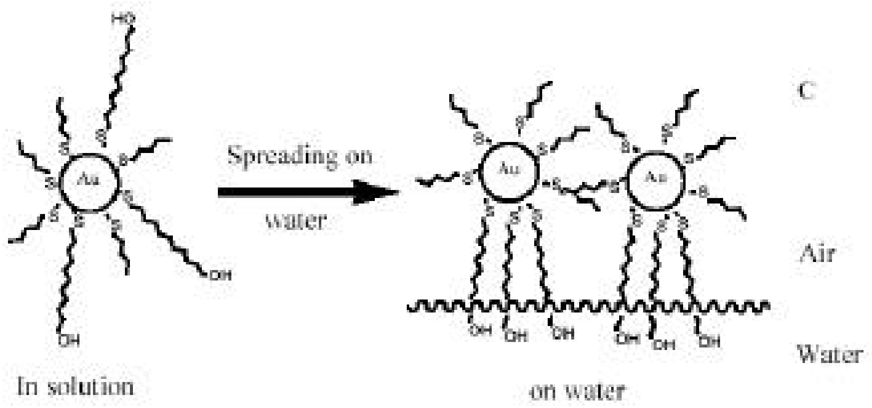


Fig.4.12 Mobile cluster capping molecules: the ligands are highly mobile and that this can be used to spatially differentiate ligands of different nature in the shell, thus opening new perspective of directed self-assembly.

4.6. New self-assembly techniques

Molecular electronics developement is likely conditioned by the developement of efficient methods for fabrication of the devices and circuits by self-assembling nanoobjects. Within the NANOMOL project we have developed and investigated a number of techniques for directing the assembly processes:

- Localized reactive patterns for directing self-assembly of nano-objects
- Template formation of cluster-molecule networks
- Self-assembly from micelles

4.6.1. Localized reactive patterns for directing self-assembly of nano-objects

Teflon scratches (UniLiverpool):
Hydrophobic nanoscale features on glass and silicon surfaces have been created by friction transfer of PTFE (Teflon) lines [5]. These features were shown to serve as a template for the assembly of linear (1D) structures of hydrophobic gold nanoparticles. The lines also served as templates for the fabrication of nano-corrugated carbon substrates. These substrates were found to be excellent for self-assembly of linear structures due to local differences in surface energy (wetting).

To rule out the possible explananation of entropically driven crystallisation as driving force for localized self-assembly onto structured substrates, we produced substrates that did not have any height differences, but only differences in surface energy, by evaporating HMDS onto clean SiO_2 through a lithographically patterned film of PMMA [9]. Figure 4.7 shows that 5 nm AuC12 nanoparticles do line up spontaneously from toluene solution along the borders of areas with high (SiO_2) and low (HMDS) surface energy.

Reactive templates (CEA):
A method has been developed [1] to direct the deposition of nanoobjects (nanotubes and nanoparticles) by first forming a reactive pattern of an amino-terminated silane by e-beam lithography and then exposing that pattern to a solution of the nano-objects that are naturally or artificially prepared to deposit selectively onto the pattern (Fig.4.13). The pattern dimensions are limited by the resolution of e-beam lithography. Application has been made to selective deposition of nanotubes in a controlled geometry (crossings for example) and to the localized deposition of nanoparticles.

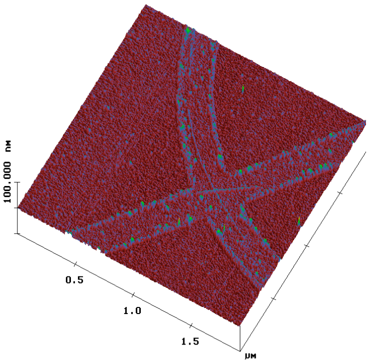


Figure 4.13: Au colloid particles adsorbed on e-beam patterned silane lines [1].

4.6.2 Template formation of cluster-molecule networks (UKBH, UniLiverpool)

We have discovered alternative possibilities for the self-assembly of cluster networks at the water/air interface, based on molecular templating effects in compressed Langmuir-Blodgett films of surfactant/gold cluster mixtures (see Fig.4.14 below). This approach may prove interesting for device fabrication using self-assembly.

The structures described in this sub-section are clearly different from well-defined network structures obtained by controlled multistep deposition of individual clusters. These novel structures contain continuous metal lines of varying length, and the precise directionality of these nano-wires cannot be controlled. It is nevertheless remarkable that in these systems a certain indirect control of structure formation is achieved on both the meso- and the nano-scale. The mesoscale structure is determined by the phase behaviour of the surfactant film, with gold clusters decorating phase boundaries, while the nano-structure depends on the action of a molecular template, ensuring that the metallic line structures grown with single particle width. A strong influence of the hydrophillicity of the clusters (which can be controlled to some extent by ligand exchange) on the formation of such structures has been observed [33]. Work in progress at UKBH includes control of the phase boundary structure of the surfactant by using additives such as cholesterol.

This line of research is clearly in its infancy and holds great promise for future bottom-up fabrication of devices. From the point of view of the NANOMOL project structures like those prepared here represent alternative architectures of great interest. The gaps between the wires within the maze structure are of molecular dimensions and can thus be bridged by the plethora of BSFMOL, NFMOL and CFMOL materials (e.g. OPV dithiols and oligothiophenes) prepared within the NANOMOL project (see Fig. 4.14). Such work combined with transport measurement is in progress at UKBH. Further work will also address the general problem of wiring up such structures to the outside world. For this purpose it is anticipated to create nucleation sites for the quasi 1-D growth of structures by carefully “floating” surface immobilised clusters into the Langmuir film.

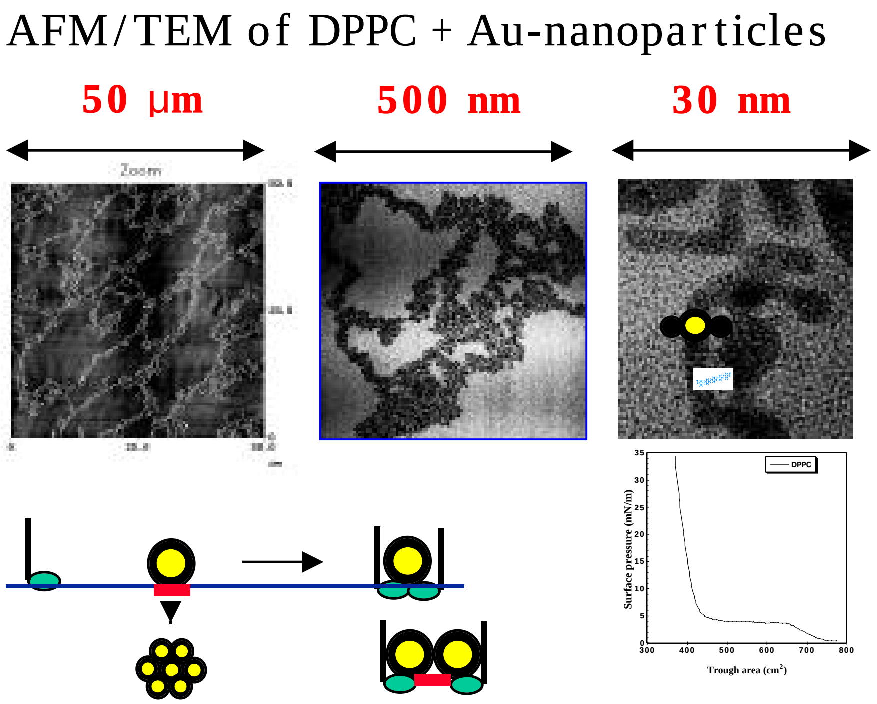


Figure 4.14: Continuous metallic nanostructures of very complex morphology were formed by compressing an LB film of thiol-capped gold clusters in the presence of a surfactant.

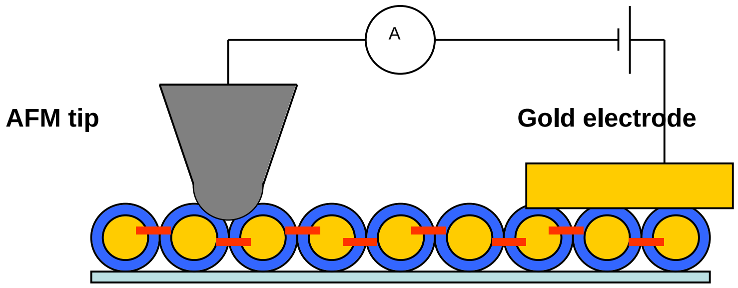


Figure 4.15: Conductive-AFM measurement of network conductivity.

4.6.3 Self-assembly from micelles (CEA)[33]:

An important project has been to investigate Self-Assembly from micellar aqueous solutions of the BSFMOL conjugated molecules T3 and Se3 for which a suitable solvent is often difficult to find.

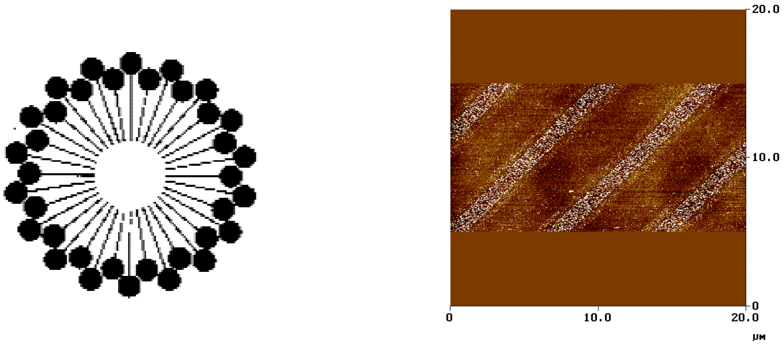


Figure 4.16: Left. Micelle. Right: Local functionalisation of gold by self assembly of dodecanethiol (DT) from micelles through a mask

Micelles are colloidal aggregates (see Fig. 4.16) of amphipathic (surfactant) molecules, which form at a well-defined concentration known as the critical micelle concentration. The typical number of aggregated molecules in a micelle (aggregation number) is 50 to 100. The surfactant (amphiphiles) are chain molecules composed of hydrophobic tails and hydrophilic heads. We aimed at

- checking if the molecules adsorb on a gold surface after being solubilized in the micellar solution
- checking if the SAM ordering was improved with respect to the SAMs made with DT (dodcanethiol) from a thrichloro ethane solvent.
- inserting the conjugated molecules into an alkanethiol SAM from their aqueous micellar solution

We carried out this study on BSFMOL molecules T3 and Se3, and extended it to OPV3. The micelles we used were hexaethylene glycol monododecyl ether ($C_{24}H_{50}O_7$). As a result, we have demonstrated the possibility to prepare an aqueous micellar solution of the conjugated molecules that are under study. From this solution, it is possible to adsorb them onto gold and to insert them inside DT SAMs. This is the first study reported on such molecules for which only chlorinated solvents are efficient. By using water as a solvent, we prevent the alkanethiol SAM from degrading, which is usually the case for long times of dipping into chlorinated solvents. These results are very important regarding their involvement in the preparation and the use of self-assembled molecules.

Recently we have consolidated the results as follows:

- the origin of the reduced permeability of the dodecanethiol self-assembled layers prepared from micelles compared to those prepared from solution has been confirmed to originate from the grain boundaries which are less compact in the latter case.
- The possibility to self-assemble conjugated molecules from micelles has been enlarged to oligophenylene vinylene (OPV) molecules demonstrating the versatility of the technique.
- The demonstration has been made of the local functionalisation of a substrate by self-assembled monolayer prepared through a mask of PMMA by e-beam lithography. A paper is prepared for Advanced Materials on these findings and evaluation of patenting is presently being conducted.

4.7. Transport measurements

4.7.1 Transport properties of T3, Se3 and OPV2 molecules embedded in dodecanethiol.
4.7.2 Metal- molecule/cluster -Metal junctions
4.7.3 Transport in systems of interconnected nanoparticles
  - arrays
  - honecomb structures
  - mazes

4.7.4 Electrochemical transport measurements for quick screening of molecules

Nanoscale control over local conductivities within a thin metal film offers an exciting possibility to design rationally its average and local electrical properties and possibly represents a way to implement neuromorphic network architecture for information processing.

Numerous studies have shown that nanoparticle films can exhibit a broad range of charge transport behavior (e.g. reversible Mott metal–insulator transition; nonactivated, activated and hopping (tunneling) transport; extreme sensitivity of film conductivity to film thickness, etc.). A number of local charge transport mechanisms have been identified in nanostructured systems, but their combined role in determining the average conductivity of the film remains poorly understood. A difficulty is that transport through such films often involves processes that are strongly influenced by local fluctuations, including variations in carriers trapped in the vicinity of particles, particle sizes, and film structure.

Almost all of the NANOMOL work involves thin films of molecules or capped clusters deposited from solution on and between electrode arrangements (the only exception is the low-temperature evaporation of single molecules in the case of the single-molecule SET). In this section we describe a number of transport measurements designed to study fundamental transport mechanisms and basic materials properties, essential for realistic approaches to molecular electronics.

The transistor device-related transport studies are presented in Section 3. The transport experiments discussed in the present section concern studies characterising molecules, clusters and networks, and investigate effects of contacts, interfaces and substitutions.

4.7.1. Transport properties of T3, Se3 and OPV2 molecules embedded in dodecanethiol.

The investigation concerns transport properties of SAMs of pure and matrix-diluted molecules from BSFMOL (T3, Se3) and CFMOL (OPVs). The specific goals are to compare (1) the contact transmission for thiol and selenol "alligator clips", and (2) molecule conductivities for the same contacts

Concerning the molecules from the BSFMOL family, we have focussed our electrical characterisation on the effect of the end-group of the molecule on the tranport properties of these molecules when embedded in a junction. We have also started a series of experiments aimed at comparing the transport properties of two molecules that have the same end-groups and different conjugated bodies.

The electrical investigation of the molecules was done by STM on T3, Se3 and OPV2 molecules embedded in a matrix of dodecanethiol (DT) [10,19].

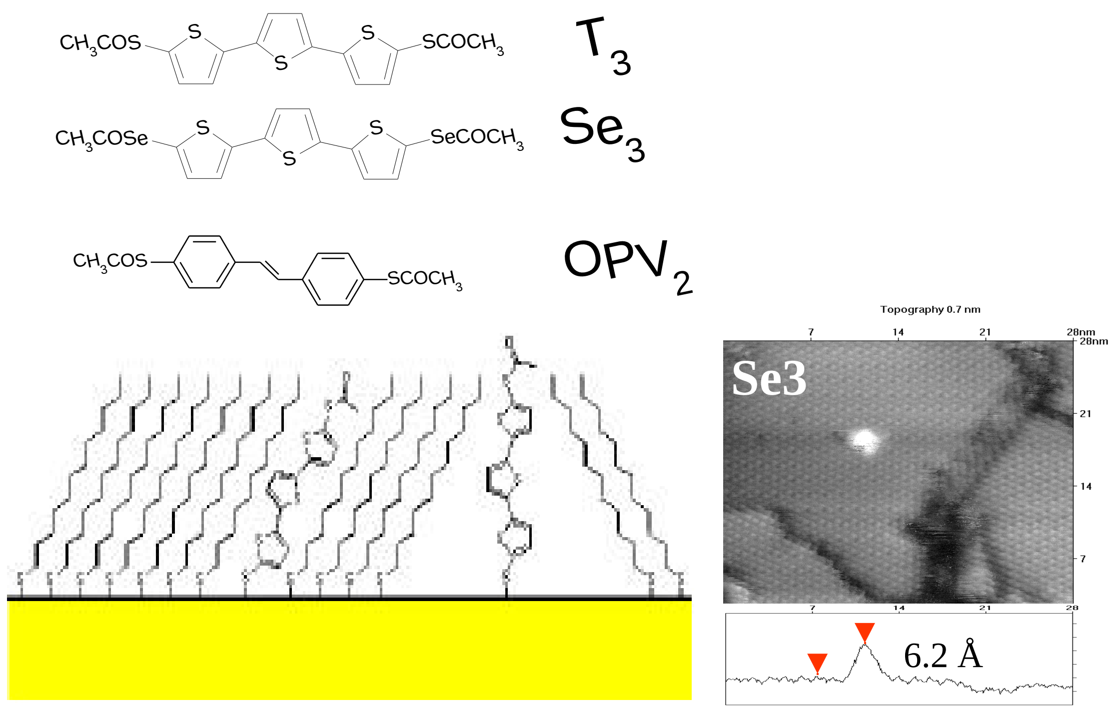


Figure 4.17: Left: Alkane SAMs with Se3, T3 or OPV2 molecules inserted as substitutions or at defects. Right: AFM picture showing a long inserted molecule sticking up above the SAM.

In order to compare the respective ability of the gold- Se3, T3 or OPV2 – tip (AFM) junctions to transport the current, we have used the relative height of the inserted molecules above the DT matrix as a measurement. The following observations have been made.

First of all, and this constitutes the main result of these measurements, the Se3 based are more "conducting" than the T3 junctions, whatever the probe current and bias are: in all the cases, the Se3 molecules appear higher (brighter in the images) than the T3 molecule. The results obtained for two particular sets of It-Vt are gathered in figure 4.17. The height measurements have been presented in a histogram form corresponding to a hundred measurements.

After specific investigation of the energetics of the contact by UPS and appropriate modelling [28] (see 5.1) the origin of the effect was shown to be entirely dominated by the energetics of the contact (HOMO-EF energy difference smaller in the case of Se vs S). This constitues the first experimental confirmation that the contacts can completely dominate the transport prorperties of a device in molecular electronics.

Finally we have also investigated the OPV2 molecules and shown that their apparent height (around 5.5 Å at –0.88V, It=3.5pA) is higher than both T3 and Se3 apparent heights. This observation also gives an input to the theory groups. Given the length of the molecule of 14.9Å, which is shorter than the T3 and Se3 lengths, it seems to indicate that the electronic transport in OPV2 is easier than in T3 and Se3.

We have also studied the conductivities of SAMs of pure and matrix-diluted oligophenylenevinylene(OPV) molecules bearing nitro groups (CFMOL family) on the central ring. This includes the study of the ability to form Langmuir-Blodgett films onto gold substrates with subsequent self-assembly to the gold substrate, and self-assembly in an insulating matrix of dodecanethiol. These studies confirm that these molecules adsorb onto gold even from the thioacetyl protected form. It was not possible to definitely prove that the OPV molecules do stand (instead of lying flat) on the surface but indications have been obtained in that direction from STM experiments. It should be pointed out that these molecules do not form organised close-packed layers.

These molecules do indeed adsorb into alkylthiol layers at the defects sites, like the molecules from the BSFMOL family characterized before. The kinetics of insertion is slower however and clearly depends on the shape (cis vs trans) of the conjugated backbone and on the presence of the nitro group. We have observed as expected that the more the molecules bear side groups, the less facile and robust their adsorption in the insulating matrix is.

4.7.2 Metal- molecule/cluster -Metal junctions

These cases are at the heart of the single-molecule SETs and the capped-cluster FETs and SETs. The measurements are described and discussed in Sect. 3.

4.7.3 Electronic transport in networks of interconnected nanoparticles

Depending on the fabrication method (e.g. multi-step deposition or LB) and the precise conditions, the structure of the films may take a variety of forms which we, somewhat arbitrarily but conveniently, refer to as arrays, honeycomb structures and mazes. In this subsection we will present the essential results of the NANOMOL project in these three categories: arrays, honeycomb structures and mazes.

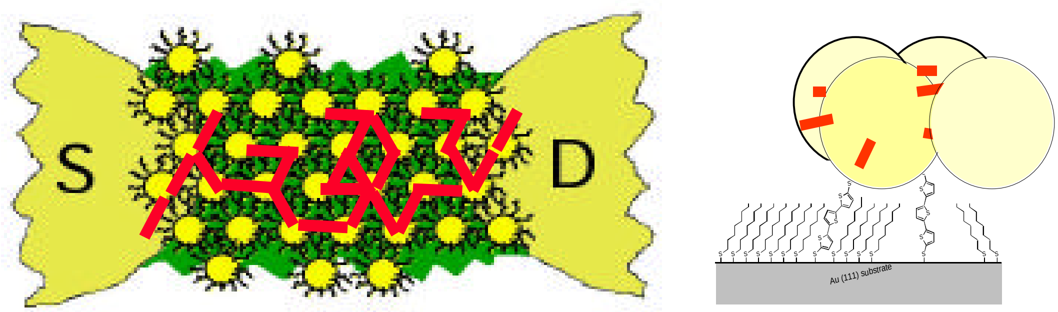


Figure 4.18: Schematic picture of a network of interconnected capped gold clusters connected to gold electrodes. The right part shows a possible vertical structure, emphasizing the vertical linking and anchoring. The left part illustrates the horizontal linking in the 2D monolayer film, and emphasizes the substitutional molecular links, which have the potential to enhance the conductivity of the network. Moleuclar links can in principle also be added on top of the 2D cluster array film, as suggested in the picture.

Electronic transport measurements have been performed on:

- arrays of clusters deposited by the Langmuir-Blodgett technique
- on arrays after exchange of the dodecanethiol capping agent by oligophenylen-vinylene molecules from the CFMOL family showing an enhanced conductivity and a change in the transport regime.

We have pursued four goals:

- understand the nature of transport in cluster-molecule networks
- understand if transport in interconnected arrays is comparable to that in mazes and what the role of the intercluster distance relative to the length of the molecules
- relate the kinetics exchange process to the change of conduction properties
- check in depth if a gate effect could show up at high gate fields.

Electronic transport through T3 and Se3 interconnected arrays

The samples of Se3 and T3-interconnected arrays were prepared by immersing a substrate containing a monolayer of AuC12 on Chalmers s4f2 electrodes into an acetonitrile solution of Se3 resp. T3 for 7h. Upon replacement of the "isolating" dodecanethiol molecules initially separating the gold particles by "molecular wires" T3 and Se3, there is a dramatic increase in the electrical conductivity of the particle array. Due to the small length of the electrodes and the very low conductivity, it is difficult to measure the transport through an unmodified AuC12 layer. On basis of our results we estimate the increase in conductivity to be at least 300-fold upon replacing dodecanethiol by T3, as shown in in Fig.4.19 below.

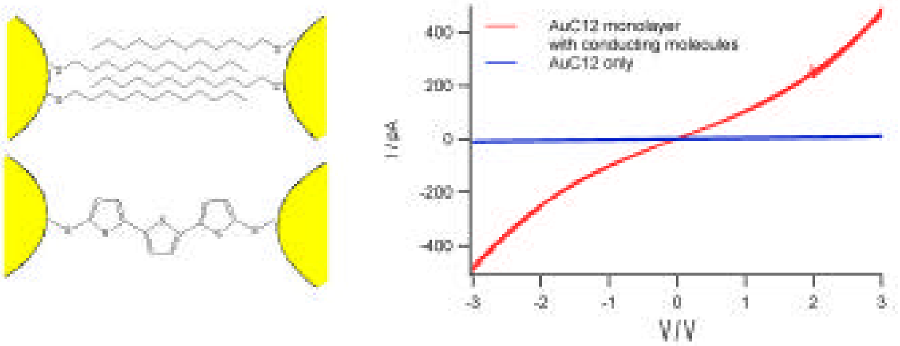


Figure 4.19: Comparison of electrical transport through a bidimensional array of AuC12 particles (like in Fig.4.17) separated by dodecanethiol (dotted line) molecules or inter-connected by T3 (solid line). The left picture illustrates substitution among the gold cluster inteconnections in Fig. 4.18.

The present work is very specific for at least two reasons: it involves a monolayer of clusters and it shows a large increase of the conductivity of the array of cluster with exchange of the capping molecules. This is quite unique since (i) there are a very few experiments having dealt with exchange of molecules for interconnecting the clusters of an array, (ii) even much less in monolayers and (iii) none having shown an increase of conductivity in monolayers.

The electrical conductivity of networks of clusters (grains) can be classified as follows:

1) *Electron hopping* in which the electron tunnels from one cluster core to the next, the electron transfer rate being a combination of thermally activated electron transfer to create charged cores and of distance dependent tunneling. In the hopping model, the temperature dependence of the conductivity scales with $\sigma\ \alpha\ e^{-Ea/kT}$ and the current with $I\ \alpha\ e^{-Ea/kT} \sinh(BV/kT)$ where B is a constant function of the core-core distance or with $\sigma\ \alpha\ e^{-Ea/kT}$ with $Ea = Ec - DV^{1/2}$ where Ec is the charging energy of a cluster and D is a constant. The latter term accounts for the lowering of the barrier in between clusters under a high field.
2) *Activated transport* at high temperatures, switching over to *variable range hopping (VHR)* at low temperatures, below a temperature To which is function of the disorder in the film. The conductivity then scales like $\sigma\ \alpha\ e^{-Ea/kT}$ above To and $\sigma\ \alpha\ \exp(-(To/T)^{1/2})$ below To..
3) *Coulomb blockade* driven transport in arrays of particles. In that case, the current scales with $(V-V_T)^{\alpha}$ with α an exponent that depends on the disorder in the array, and on the size of the particles. α has been predicted theoretically to fall in the range 1 to 5/3 for 1D and 2D arrays but was observed experimentally to be as large as 4. The original model of Middelton and Wingreen, Phys. Rev. Lett. **71**, 3198 (1993) predicts a very weak temperature dependence of the conductivity. However, experimental observations range from absence of temperature dependence to activated dependence with an activation energy being equal to 4 times the charging energy of a single cluster (which is equal to $e^2/8\pi\varepsilon\varepsilon_0 r$). In the present work, these observations have been substantiated by refining the description of the tunneling barriers involving a field dependence, used in the calculation of the transport in the array.

We have analysed the data recorded on monolayers of AuC12 clusters after exchange with T3 and Se3. The resulting I-V characteristics are shown in Fig.4.20:

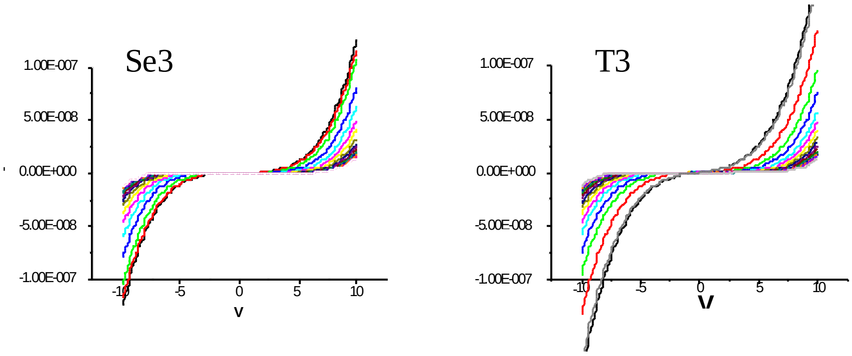


Figure 4.20: Typical I(V) curves for monolayers of AuC12 clusters after exchange with T3 and Se3.

Both sets of curves in Fig.4.20 show that the transport is highly non-linear. Moreover the current varies with temperature. We have found that the transport in these interconnected arrays cannot simply be described as activated at high temperature and almost temperature independent tunneling at low temperature. Nor does it seem to be explained by variable-range hopping at low temperature. Moreover, the behavior markedly differs between different bias values and between T3 and Se3, the latter showing less variation with temperature at large bias compared to the former. Undoubtedly, the electric field bias significantly influences the energies of clusters and molecules at high bias voltages. At high temperature we measured activation energies ranging between 40 and 150 meV depending on the applied bias.

We have scaled the I-V data to test the different transport models. The results tend to rule out the first two models. However, we find that in a log-log representation of the high bias behavior of the higher field part of the transport current is linear, which points toward a power law dependence $I=A(V-V_T)^{\alpha}$. We have extracted the α exponent and V_T threshold values for the two interconnected arrays.

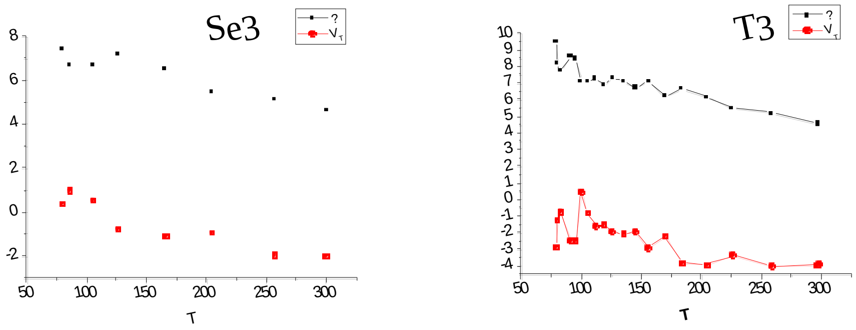


Figure 4.21: Exponent (α) and threshold (V_T) values for the two interconnected arrays.

We therefore arrive at a model in terms of Coulomb blockade driven transport in our arrays of particles combined with temperature dependence probably due to activated transport.

We note that the values obtained for α (>6) are extremely high compared to the model of Middelton and Wingreen and to the highest value reported by Ancona et al., Phys. Rev. B. **64**, 033408 (2001). As observed by these authors, the threshold voltage goes negative which is probably the signature of transport over a barrier. Contrary to their observation, we observe also that the exponent varies with the temperature.

Attempts at measuring gate effects.

Since it was proven that the transport in the films after exchange is largely influenced by the interconnecting molecules, we tried to apply a gate field using the substrate as a backgate. Applying up to 50V to the 200 nm thick silicon dioxyde did not result in any change in the transport properties of arrays interconnected with Se3 or T3. Though it is likely that the transport properties of these interconnected arrays is dominated by disorder averaging of the local transport properties, this is a strong indication that it will be extremely difficult to electrostatically influence the transport in a metal --bifunctional-conjugated-molecule --metal junction when the bifunctional molecule is bonded to both metallic electrodes and when the transport can be considered as coherent. These observations corroborate the calculations made within NANOMOL (CNRS; see Sect. 5) showing that a field about 4 times larger than the field we could apply is necessary to observe an effect.

Electronic transport through the 'honeycomb structure'

The principle of the exchange experiments consists in dipping a cluster array prepared by the LB technique in a solution of bifunctional molecules (from the various families of molecules of the project). AuC12 monolayers sometimes transform into honeycomb-like network structures upon exposure to solvents such as acetonitrile, acetone and ethanol, in which the particles themselves are not soluble. We have investigated this phenomenon in greater detail by changing several process parameters (wetting/dewetting conditions,

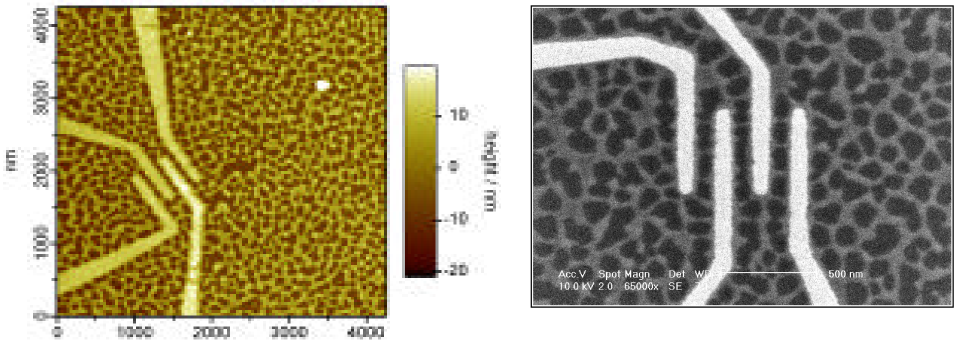


Figure 4.22: 2D film of AuC12 clusters with honeycomb structure on top of electrodes for transport measurements [31,33].

rinsing, temperature, LB films conditions). Finally, we have found that honeycomb formation only occurs in films that have been only feebly compressed (1 mN/m). Well-compressed films (8…12 mN/m) are stable towards solvent exposure.

The "honeycomb" structure of T3-connected AuC12 clusters, which is most likely the result of capillary forces (surface pressure) on the crosslinked LB film during dewetting, can be viewed as a maze of "nanowires". Indeed, this structure is highly conductive (Fig.4.23), compared to a flat film of T3-linked AuC12 clusters. Moreover, different electrode combinations have different conductance, since they are connected by a different numbers of "wires".

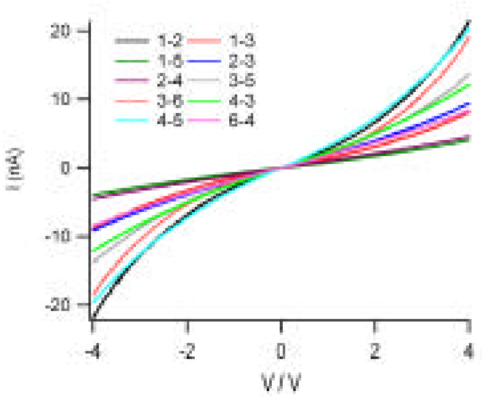


Figure 4.23: "Honeycomb" structure of T3-linked AuC12 clusters: the variation of I-V characteristics between different pairs of electrodes

It is tempting to try and find a correlation between the measured conductivity and the number of "wires" connecting the different electrodes, since this may yield the conductance of a single wire. However, it was not possible to find such a correlation, because the sample geometry allows the current to flow through many different paths. Altogether, the transport properties of the honeycomb structures were very similar to those measured on monolayers of clusters.

Transport in 'mazes' of interconnected nanoparticles:

We used a conductive AFM tip to probe the distance dependence of the conductance of gold nanowire mazes cross linked with various thiol end capped molecules (RFMOL etc) connected to a macroscopic electrode (Fig. 4.24) (CEA, UKBH).

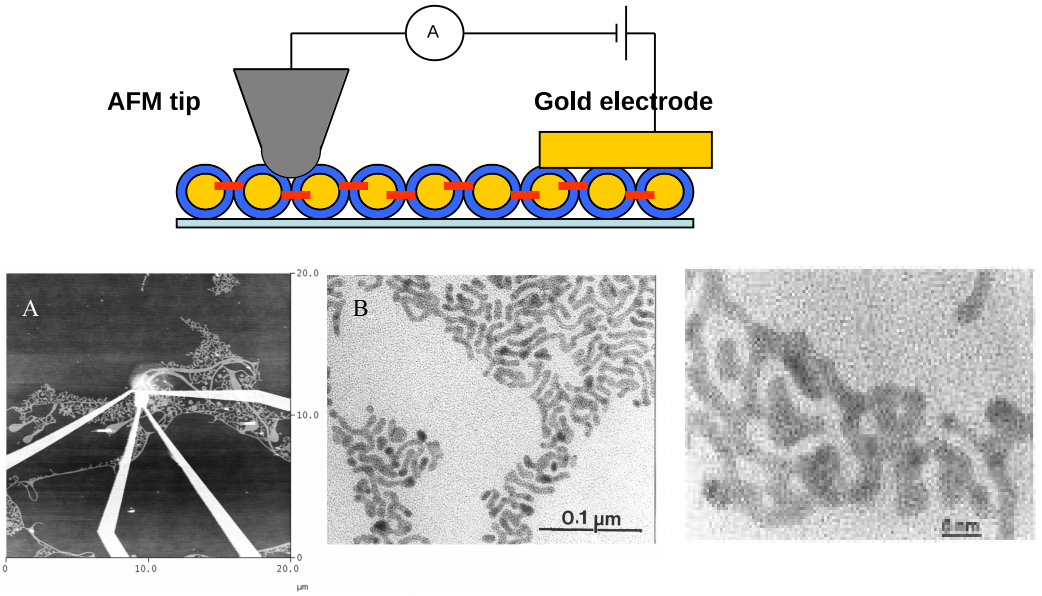


Figure 4.24: Top: Conducting-AFM measurement: schematic picture of measurement setup. Bottom left: An AFM topography map of a goldmaze of Au-S-C12 clusters in a matrix of DPPC covering an electrode system that is connected to external wiring. The height of the gold maze is about 4 nm corresponding well to the height of one cluster. Middle: a TEM zoom-in on a similar gold cluster maze showing the internal structure of the wires in the maze. The sintering of gold clusters into small single-cluster-wide segments is clearly observed in this image. Right: A higher resolution zoom-in on a part of the middle AFM picture.

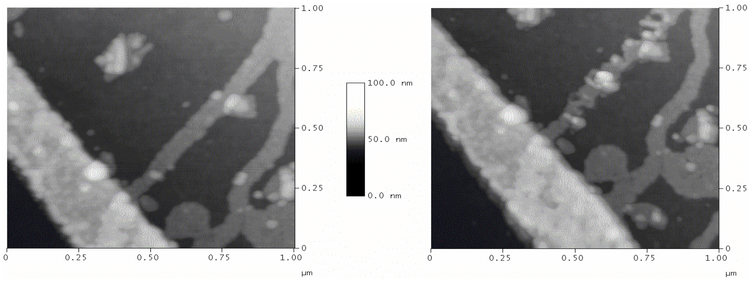


Figure 4.25: Left: An AFM topography map of goldwire crossing an electrode that has been connected to external wiring, the image was obtained before measuring the transport through the wire but after self assembling of OPV-3 into it. Right: The same wire after making the electronic transport measurement using the AFM tip as one electrode and the gold electrode in the lower left of the image as the other electrode. The destruction of the wire due to these measurements is clearly seen.

Using this technique, various type of clusters have been measured, yielding the following results (some of them correspond to a small statistics which is currently being improved):

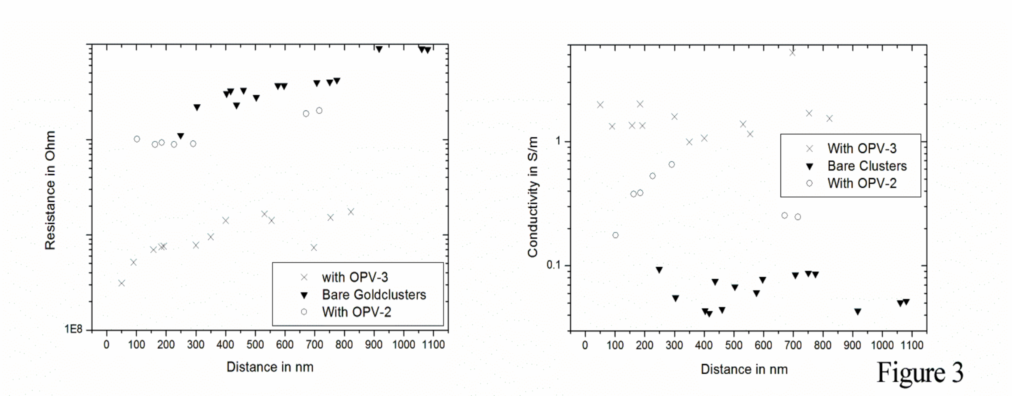


Figure 4.26 The results from the transport measurements: Left: The resistance of similar goldwires with or without OPV on different samples versus the direct distance from the static electrode on the substrate surface. Right: The corresponding conductivity at each point calculated from the geometric shape of the wire, and corrected for an average contact resistance which has been derived from the intercept between the Y-axis a fitted line to the data (on the left). Each point in the datasets represents the resistance derived from datasets of 3-8 IV-curves each with 100 points.

Some conclusions:

- from the distance dependence we can extract the intrinsic change in conductance due to the presence or absence of OPV molecules because we can subtract the contact resistance from the data (intercept in Fig. 4.26, left)
- by combining the size of the ligand shell with OPV molecules of various length we can clearly distinguish situations where sulfur can bind covalently to both sides of the gaps to those situations where covalent binding only occurs on one side
- we demonstrate clear signatures of percolation behavior in the distance dependence of the conductivity of the un-bridged clusters.

<u>Summary of transport measurements on Arrays, Honeycombs and Mazes</u>:

The main results are that

- the transport is by tunelling at low bias and temperature activated at higher bias and temperature
- no gate effect could be detected whatever the gate field up to 4MV/cm
- the change in conduction properties is absolutely correlated with the kinetics of insertion
- the maze probed by conducting AFM and the arrays seem to behave similarly in terms of modification of transport by place exchange reaction on the cluster shells
- comparable results obtained in Arrays, Honeycomb and Mazes, with increase of conductance up to 10^2 to 10^3 upon place exchange.
- the magnitude of the increase in conductivity after such reaction depends on the molecule tested and large increases seem to be observed only when the size of the gap matches the size of the bifunctional molecule.
- Transport is Coulomb blockade driven with unusual power law dependence of I with V.

4.7.4 Electrochemical transport measurements on polytolanes (CNRS) [18]

The purpose of this study is the q*uick screening of molecular transport properties:* electron transport in molecular wires using electrochemical methods. The molecular wire is attached to an electroactive Ru-complex via an amide group at one end and an SH thiol group at the other.

In the case of the molecules based on polytolanes (ETMOL), a new electrochemical technique has been validated allowing a quick screening of the molecular transport properties. The rate constant of heterogeneous electron transfer of a redox centre grafted to an electrode contains a tunnelling component that characterizes the bridge connecting the redox site to the electrode. Reliable results are obtained for molecules organized in a self assembled monolayer. In order to use this approach to screen molecular backbones, a general synthetic scheme was developed, based on the use of a new redox centre, a cyclometallated ruthenium complex **1** $[Ru(bpy)_2(pp)]^+$ (bpy : 2,2'-bipyridine; pp : 2-phenylpyridine). Easily functionalised, moderately oxidisable and highly soluble in various polar solvents, this complex provides a convenient building block to begin the synthesis of usually poorly soluble molecules. Thus the amino derivative of **1** is smoothly converted into a fat ω-bromoalkylamide, precursor of a saturated wire. The ethynyl derivative of **1** is a good substrate for Sonogashira arylation/ethynylation sequence, thus leading to wire of oligophenylene ethynylene backbone, and of various size. Molecules were all terminated by a sulfur atom (thiol or thiophenol) to bind to gold. The solubilizing properties of the complex, acting as a "phase tag", allow a fast screening of molecular structures that could be performed in a combinatorial way.

We succeeded to measure the electron transfer for a non-conjugated molecule (saturated alkane molecular wire) [13]. The major result is that the electron transfer rate is much bigger ($k=45000s^{-1}$) than its ferrocene analog ($k=1200s^{-1}$). This can be explained by reorganisation energy considerations.

The experiment with conjugated polytolane (oligophenylene ethynylene) molecular wires, the objective of this task, turned out to be very delicate. However, through an investigation in collaboration with R.J. Forster from Dublin using chronoamperometry technique, elecron transfer rates for the polytolanes have been determined. The results are in the process of publication.

5. Main achievments: improved theoretical tools

These efforts led to the successful interpretation of two sets of experiments, the transport measurement in a single OPV5 molecule and the STM experiments on conjugated molecules inserted in a dodecanethiol SAM.

5.1. Semi-empirical method allowing semi-quantitative interpretation and simulation of STM experiments on conjugated molecules in SAM.
5.2. Coulomb-Blockade model for electron transport through single molecules.
5.3 Transverse field and contact effects implemented in coherent transport models
5.4 DFT calculations of bonding sites and energies at metal-molcule interfaces
5.5 DFT calculations of current-voltage characteristics

5.1 Semi-empirical method allowing semi-quantitative interpretation and simulation of STM experiments on conjugated molecules in SAM. (CEA and CNRS) [26].

The present result deals with the investigation of self-assembled monolayers onto gold to realize metal-molecule-metal junctions and a method to compute the transport properties of a molecule in such junctions [28]. First, a SAM of the molecule to study are prepared either as a pure SAM or as a mixed SAM with alkylthiols. The former is studied by Ultraviolet Photoelectron Spectroscopy (UPS), while the latter is studied by STM.

In this work, the methodology for interpreting the STM experiments on the various molecules investigated in the consortium has been refined. The well known ESQC method is based on the semi empirical Extended Hückel Molecular Orbital theory and use the scattering theory of transport to simulate STM images and transport properties of single molecules connected in between two electrodes. However, to interpret the STM measurements on SAM in which different molecules are adsorbed simultaneously on metallic electrode, the relative position of molecular orbital to the Fermi level for each molecule is the most important parameter. For this we have chosen to combine this information obtainable from UPS measurement and the ESQC calculations to probe the real transport properties in M-Mol-M junctions. In this technique, the applied bias could be taken into account, as well as the environment of the molecule. The application of this technique in the case of oligothiophene derivatives has demonstrated its capability to reproduce semi-quantitatively STM measured quantities to distinguish the role of the coupling group in the transport properties [28]. This capability is also verified in the case of OPV family oligomers measured by STM. We believe that this simple procedure can be used to predict the transport differences in families of other molecules.

5.2. Coulomb-Blockade model for electron transport through single molecules. (Chalmers, UKBH, University and the Universities of Louvain) [25].

These work involved the successful interpretation of transport measurements in a single OPV5 molecule [27] (see also Sect. 3.1). A procedure of molecular SET data treatment was developed, converting the spectroscopic data taken for a Single Electron Transistor (SET) with a single OPV5 into the differences of ionization potentials for the corresponding molecular ions. These energies were extracted and compared to electrochemical data and the results of first principle calculations. It was found that the orthodox capacitance model, accounting for electron-electron interaction, is applicable to the system. The development of models mixing coulomb blockade and coherent transport remains to be done.

5.3 Transverse field and contact effects implemented in coherent transport models (CNRS)

Routines for calculation of the effect of the application of a uniform electric field have been implemented in the ESQC program at the EHMO approximation level. The electric field is introduced in the problem by considering only the Stark shifts of the atomic orbitals energies used to build the model. Deformation of the atomic orbitals and charge redistribution effects are neglected in this rather crude approach that is nevertheless expected to give qualitative trends and good orders of magnitude for the effect. Tests on benzene, phenyl-dithiol and phenyl-dithiolate molecules were made. The method was also applied to the electric-field-switchable CFMOL molecules proposed by UKBH. The first results confirm the findings reported by DiVentra et al, in the literature based on a different model. Rather high gate field values of the order of 1V/Å are required for the appearance of a significant effect on transport properties.

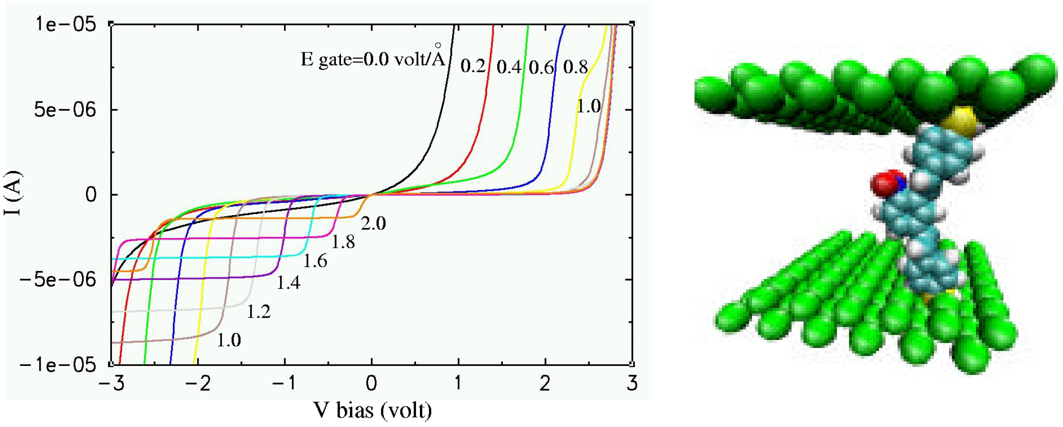


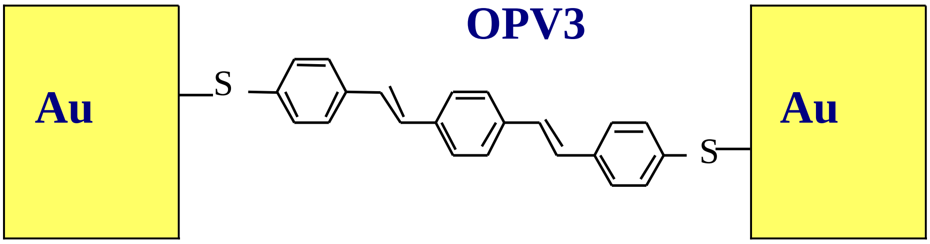
Figure 5.1: Left: I(Vbias) curves versus electric field intensity (Egate) for phenyl-dithiolate dianion. Right: a CFMOL switch2-NO_2 molecule embedded between two Au [100] pads. The electric field is directed along the axis of the molecule, i.e. perpendicular to the surface of the contacting electrodes. (CNRS)

5.4. DFT calculations of bonding sites and energies at metal-molcule interfaces (Chalmers) [21].

Sulfur (S) terminations of molecular chains often serve as molecular "alligator clips" for attaching molecules to gold electrodes. Using ab initio density functional theory (DFT) we have investigated the Au:S and Au:Se systems with respect to the bond geometries, charge density, coverage dependency and phase transitions between the low and high coverage regime respectively. For low coverage we find that the S atom prefers the three-fold in-hollow sites where it forms symmetric bonding states with the metal substrate, while the in-hollow position is energetically degenerate with the bridge position in the case of Se. Investigating the intermediate coverage range (0.5 and 0.75 ML) we find that the topmost atomic layers of the metal become partly depleted of free charge. In the 0.75 ML case this leads to the S (Se) atoms leaving the in-hollow positions and forming S3 (Se3) molecules on top of the gold, which stabilize the system. This phase is also found to be the most stable of all geometries investigated for both S and Se. However, for full ML coverage the chemical bonds with the substrate are completely broken and S(Se) instead forms the electrostatically physisorbed layers situated on top of the Au atoms. Artificially placing one of four S atoms in the surface cell higher than the remaining leads to formation of S3 molecules and expulsion of the fourth atom into the vacuum upon relaxation. Depositing hydrogen on the most stable Au:S system (S3 we find that energyis lost or that the system is energetically degenerate compared with the clean Au:S surface and free H molecules. That is, if there is any H atom/ion close by, the adsorbed H will instead form a free H2 molecule. Hence the S-covered Au(111) system acts as a catalyst in most cases. Only for the intermediate and low concentrations of S on Au(111) considered was hydrogenation found to be energetically favourable. In no other cases did we find a stable geometry for a 1:1 balance between S and H. Exposed to S, the system will go through a phase transition and expel H.

5.5. DFT calculations of current-voltage characteristics (Chalmers) [41].

The TranSIESTA density-functional (DFT) based scattering code is used to calculate current-voltage characteristics (IVC) for OPV3 (three coupled benzene rings) and DTB (dithiolbenzene) between gold contacts. The work is a collaboration between Chalmers and the group of Kurt Stokbro at MIC, DTU, Denmark. The SIESTA code is first used to calculate the electronic structure of the OPV3 and DTB molecules with gold clusters attached to each end, forming the first layers of semi-infinite gold electrodes. This then serves as input to the electron transport calculation of transmission coefficients and currents at different sorce-drain bias voltages. Note that TranSIESTA allows self-consistent inclusion of effects of the finite bias voltage on orbitals and steady-state charge density.



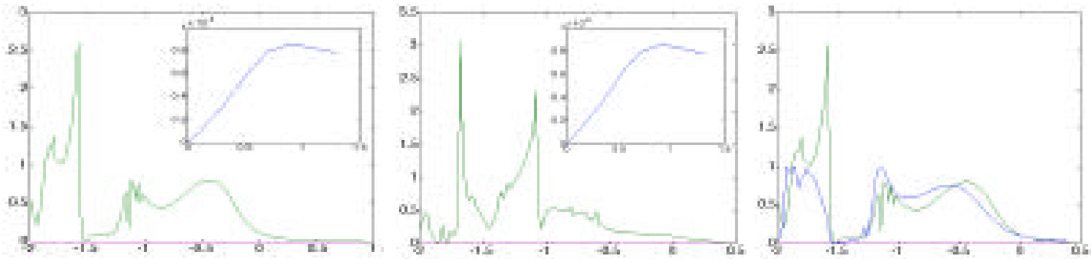


Figure 5.2. Theoretical transmission curves for Au-OPV3-Au (bulk contacts) at source-drain bias V_{SD}=0V (left) and V_{SD}=1 volt (middle). The inset shows the current-voltage characteristics (IVC). OPV3 is adsorbed at the hollow Au site in both electrodes. Transmission (right) for OPV3 at zero bias voltage for the hollow and bridge adsorption sites on the gold electrodes. (Chalmers)

We are presently in the middle of a study [41,45] of how electronic transport through the OPVn (N=3-5) and DTB molecules depends on the metal molecule contacts: binding site, rotation around the surface normal, and perhaps also tilt angle. The first IVC results indicate that the IVCs seem to be rather insensitive to the detailed binding site.

In future the work will be extended to including gate effects, i.e. to study three-teminal behaviour. It will also be necessary to take into account effects of Coulomb interaction, even to the point of Coulomb blockade. The Coulomb blockade limit is not compatible with the coherent transport model of the present study, but has to be treated as incoherent transport involving a number of distinct charge states using a Master equation approach.

5.5 Architectures for complex structures based on molecules or clusters (Chalmers)

The NANOMOL research has lead to two possible routes for molecular electronics:

- Lithographically defined patterns with self-assembly of molecules or clusters to form circuitry with molecular transistors
- Self-assembled cluster-molecule networks contacted by electrode arrays.

The delivered three-terminal devices represent state of the art, and togther with the cluster-molecular networks and mazes, they define very important directions of research during the next five years, to investigate integration of such structures to form logic elements and memory cells. This is indicated in Fig. 5.3a which illustrates a solution with a few molecular transistors combined into logic elements, deriven by elementary CMOS components and embedded into a cell structure.

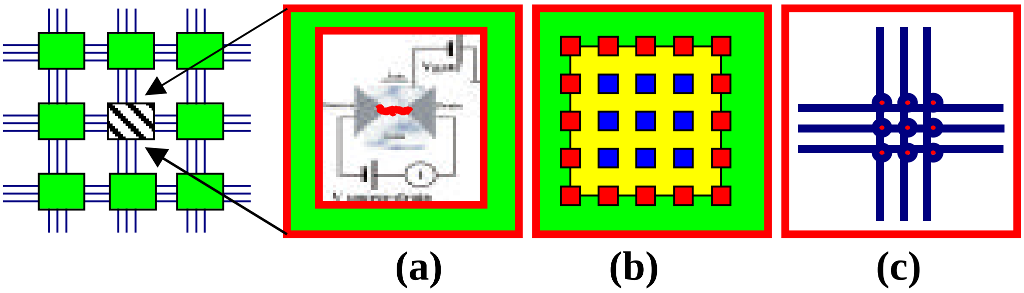


Figure 5.3. "Nano-FPGA" (FPGA = Field-Programmable Gate Array) CMOS structure with specific blocks assigned to transistor-based logic circuits (light grey (greeen)) or single or multi-molecular devices (hatched). The molecular device (hatched square) will contain a central cell of molecular components and a surrounding shell of elementary CMOS driver circuits (e.g. a few transistors). (a) The molecular cell consists of a small number of molecular transistors forming logic functions. (b) The central molecular cell is a cluster-molecule network with distributed gates and edge contacts controlled by the surrounding CMOS logic and driver circuits. (c) The molecular cell is a cross-bar structure with two-terminal bistable molecular switches. The dots represent active (conducting/isolating) two-terminal molecular links.

Cluster-molecule networks (Fig.5.3b) have interesting properties if the network shows non-linear properties at local sites (e.g. two-state or multi-state behavious). This means for example variable couplings (resistances, capacitances) or variable cluster level structure. Variable couplings can mean either variable strengths of a fixed number of links, or a variable number of links, or both.

The research within NANOMOL has produced a number of interesting cluster-molecule networks built from capped Au clusters, forming a 2-dim network of clusters coupled by molecuar links.

The system is structurally fixed. How can we influence on-site energies and hopping (tunneling) rates? The usual assumption is that such a system will be so dense that individual elements cannot be gated and controlled. Nevertheless, there should be some kind of local control to have easy functionality for computation. It will be first class challenge to introduce nanoscale (or at least mesoscale) gate control through electrical, optical or mechanical means.

One aspect of the type of QD-molecule networks that can be created within NANOMOL is that they are always limited to essentially nearest neighbour coupling, which results in low connectivity, i.e. short range interactions. Information processing with such kinds of random networks has however been simulated in recent work [Tour et al.]. Provided the molecules have discrete internal states, simulations indicate that a random array of such switch states can be influenced to program a nanocell as a useful logical device, even in the absence of local gate control. It seems theoretically possible to obtain high level function from these cells.

6. NANOMOL and the State of the Art

Let us first simply state what we consider to be a number of facts characterising the research of NANOMOL:

<u>NANOMOL groups *defining the state of the art*:</u>

- Single-molecule SET [25]
- Self-assembled nanocluster FET [36]
- Self-assembled nanocluster SET with tailored molecular barriers [35]
- New synthetic routes for several types of moleculelar wires [8,31,33,40]
- New facile and versatile synthesis of capped clusters [12,37,38]
- Reproducible sub-3 nm gaps with local gate [25,28,35,36]
- Post processing of assemblies with ligand exchange [8,31,44]
- Langmuir-Blodgett techniques for self-assembly of 2D cluster-molecule networks [8,31,32,44]
- Micellar deposition technique [34]
- Self-assembly onto locally functionalized surfaces [1,5,9]
- Semi-empirical method allowing semi-quantitative interpretation by simulation of STM experiments on conjugated molecules in SAM [26].
- Single-molecule SET: Single molecule interpretation by Coulomb-Blockade [25]
- Dip-pen lithography for cluster deposition [11].

<u>NANOMOL groups part of the state-of-the-art:</u>

- Density Funcitonal Theory (DFT) study of adsorption sites for sub-monolayers of S and Se on gold surfaces: molecular "alligator clips" [21].
- TranSIESTA DFT transport calculations [41]
- Quantum Chemical calculations; simulation of gate effects on transport in molecular wires

<u>State of the art, further discussion:</u>

Let us first mention the very interesting special issue of “Chemical Physics” (**28** 1(2-3) (2003)) entitled “Processes in Molecular Wires”, which presents an up-to-date general overview of the domain. Noticeably, NANOMOL members were invited to contribute.

During the last year, the tendency toward producing more reliable results has been much pronounced, in particular due to the well known problems related to a number of publications of J.H. Schön et al. Many groups tried to reproduce the results, without any success. In particular, regarding the paper by J. H. Schön, H. Meng and Z. Bao, "Field-Effect Modulation of the Conductance of Single Molecules", Science **294**, 2138 (2001), the group of CEA-Saclay spent much time trying to evaporate gold on SAMs at low temperature. They obtained in a systematic way short circuits because of the unavoidable presence of defects in the SAMs. This was a blocking point in reproducing the structure proposed by Schön et al.

Data produced on many different molecules by the method of Mechanically Controlled Break Junctions (MCBJ) have been shown to exhibit a high degree of dispersion. This dispersion could be related to different molecular adsorption sites, but even criteria for distinguishing what comes from the molecule and what constitutes artefacts are lacking. A recent theoretical paper (D. Krüger, H. Fuchs, R. Rousseau, D. Marx and M. Parrinello: “Pulling Monoatomic Gold Wire with Single Molecules: An Ab Initio Simulation", Phys. Rev. Lett. **89**, 186402 (2002)) suggests that “pulling a single thiolate molecule anchored on a stepped gold surface does not preferentially break the sulfur-gold chemical bond” but “leads to the formation of a monoatomic gold nanowire”. This could explain many features observed on MCBJ experiments.

Nano-gaps produced by the electromigration technique have been used in two papers in ‘Nature’ (the first one by a Cornell-Berkeley collaboration (J. Park et al: ‘Coulomb blockade and the Kondo effect in single-atom transistors’, Nature **417**, 722 (2002)), the second one by a Harvard-Berkeley collaboration W. Liang et al.: ‘Kondo resonance in a single molecule transistor’, Nature **417**, 725 (2002)) to investigate transport in molecules containing magnetic transition metal atoms. A new very interesting finding is that the gate voltage of the ‘transistors ‘ based on these molecules can be used to control not only the charge state of the molecule as in usual Coulomb Blockade devices but also the spin state of the molecule. The molecule is tuned between two states differing by one charge and one spin unit. In one of these states, the electron transport is enhanced by Kondo scattering on the magnetic transition metal atom. These devices do not have any (short term) technological interest due to the very low temperature, but they are certainly very interesting from a fundamental quantum engineering point a view for the understanding of transport in single molecules. In addition, they are among the first (together with the NANOMOL by S. Kubatkin et al. [25]) to demonstrate in a convincing way that the concept of ‘Coulomb Blockade’ is applicable to single molecules sufficiently weakly connected to metallic electrodes.

Theory is making considerable progress and simulations are begining to be realistic, but many basic questions remain unanswered. An important step in this direction is the development of computer codes for *ab initio* self-consistent approaches to non-equilibrium transport (like the non-equilibirium Green's function DFT (density functional theory) package TranSIESTA) (M. Brandbyge, et al.: "Density functional method for nonequilibrium electron transport", Phys. Rev. B **65**, 165401 (2002); K.Stokbro et al.: "Theoretical study of the nonlinear conductance of di-thiol benzene coupled to Au(111) surfaces via thiol and thiolate bonds", Computational Materials Science (2003), in press; Stokbro's discussion of rectification in Tour wires). Related calculations have recently been performed in Karlsruhe by J.Heurich et al., Phys. Rev. Lett. **88**, 256803 (2002) and revied by J.C. Cuevas et al., Nanotechnology **14**, R29 (2003).

There is no doubt that great progress will come from a better theory-experiment interplay, validating theoretical models and approximations, and sorting out experimental problems. This requires setting up simple well controlled experiments. In our opinion, the NANOMOL work on T3 and Se3 inserted in dodecanethiol matrices [26] is a first attempt in this promising direction. In this context one could also mention the NANOMOL DFT investigation [21] of the coverage-dependent adsorption sites of S, Se and SH on Au surfaces, which was selected for the cover page of a forthcoming isuse of the journal "Nanotechnology".

Finally, recently the domain has seen the impressive demonstration by the HP labs of a 64 bit memory (http://www.hp.com/hpinfo/newsroom/press/09sep02a.htm) using bistable molecules. This experiment involving about 1000 molecules for each bit raises a series of questions like the mechanism of transport that is not understood, the stability/ reproducibility and the downscalability. If these questions are answered positively, a technological route to molecular electronics memory will have been unveiled.

7. NANOMOL and the Future

The original plans for NANOMOL included making small scale integration and demonstration of devices for information processing, such as logic gates and memory cells. However, this turned out to be premature. The original milestone "Architecture and implementation plan for information processing devices" was therefore replaced by "Investigation of neuromorphic architectures". In this way, the question of building molecular functional logic circuits has only been addressed via theoretical considerations and state-of -the-art surveys. The practical implementations of circuits remain a great challenge for the future. It should be noted that this is not only a challenge for NANOMOL. It is a challenge for the entire field of Molecular Electronics and will most certainly be a major theme in the sixth framwork programmes dealing with nano and information technology.

An interesting comparison of the state of Molecular Electronics at the beginning and at the end of the NANOMOL project is provided by two popular articles (C. Joachim, J.K. Gimzewski and A. Aviram, “Electronics using hybrid-molecular and mono-molecular devices”, Nature **408**, 541 (2000), and J.R. Heath and M.A. Ratner:"Molecular Electronics", Physics Today, May 2003).

In spite of all visions and beautiful pictures, there have been no dramatic breakthroughs except perhaps for the Hewlett-Packard cross-bar switches and molecular memeory, as mentioned in Sect. 6. On the other hand, there is steady progress on a broad scale with many exciting results. Whether some of these represent breakthroughs is too early to say, and is anyway related to future technologies that have not yet been established.

In this perspective, what is the best way for potential successors of NANOMOL to proceed? There are two distinct ways ahead:

- To follow up the original NANOMOL objective and build elementary logic units with a small number of the discrete molecular transistors of the types fabricated during the NANOMOL project.
- To exploit the discoveries during NANOMOL concerning cluster-molecule networks (quantum dot/or nanocrystal ordered and disordered films) to investigate the functionality of molecular networks, e.g. for unconventional neuromorphic-style computing.

The first approach is straightforward, though diffficult, and will no doubt be pursued by NANOMOL teams and by many other groups. An important aspect is that it will most likely be necessary to create hybrid devices with CMOS drivers and support electronics. Major issues will then be to create interfaces bridging the different scales and electronic characteristics.

The second approach, Molecular Electronics with self-assembled cluster-molecule quantum dot networks, is totally open and implies investigating a number of new fields. Self-assembled cluster networks are so dense that individual elements cannot be gated and controlled, at least not via external leads. A major challenge will be to achieve sufficient local control to have functionality for computation, by some form of local gating, or via control from the edges.

Neuromorphic computing means that one tries to mimic the computing power of biological neuron nets and brains. This can be done by artificial neural nets (ANN) implemented in various forms of software simulation on ordinary processors, or by using special hardware for direct simulation of network structures, e.g. Celllular Automata (CA) and Field Programmable Gate Arrays (FPGA) machines.

The well-known Hopfield model (1982) for coupled biological neurons was originally inspired by the Heisenberg spin hamiltonian of Statistical Physics. It was re-applied already some time ago by Roychowdhury et al. to the problem of arrays of quantum dots [V.P. Roychowdhury, D.B. Janes, S. Bandopadhyay, and X. Wang: "Collective Computational Activity in Self-Assembled Arrays of Quantum Dots: A Novel Neuromorphic Architecture for nanoelectronics", IEEE Trans. El. Devices **43**, 1688 (1996)]. Roychowdhury et al. also discussed how to use such structures for convential logic [V.P. Roychowdhury, D.B. Janes and S. Bandopadhyay: "Nanoelectronic Architecture for Boolean Logic", Proc. IEEE Trans. El. **85**, 574 (1997)].

Moreover, Cohen et al. [M.L. Cohen, S. G. Louie, A. Zettl: "Random Access of Nanodevices", Solid State Commun. **113**, 549 (2000)] recently investigated the multi-terminal characteristics of a "spaghetti" of nanotubes and showed that some logical functions could be achived in some cases.

A likely road toward Nanoelectronics and Molecular Electronics may then be to fabricate lithographcally defined FPGA-style "checker-board" structures of elementary functional units based on CMOS and molecular devices, e.g. discrete molecular/cluster transistors or self-assembled cluster-molecule networks.

Several research programs are currently pursued along these lines. Goldstein and coworkers (CMU) are pursuing a CMOS-molecule hybrid scheme called "Nanofabric" based on regular patterns and two-terminal cross-bar structures on the molecular level [http://www-2.cs.cmu.edu/~phoenix/; S. C. Goldstein and D. Rosewater: "Digital Logic Using Molecular Electronics", to appear in ISSCC 2002; S. C. Goldstein and D. Rosewater: "What Makes a Good Molecular-Scale Computer Device?" (Sept 2002)]. Barhen and coworkers at the Oak Ridge National Laboratory (ORNL) are pursuing a project on "Computing with Arrays of Quantum Dots" [ORNL Review 34, No. 2 (2001); http://www.ornl.gov/ORNLReview/ v34_2_01/arrays.htm] involving regular arrays of molecule-capped gold clusters "gated" by microwave radiation. Moreover, Likharev and coworkers (SUNY, Stony Brook) are developing a general scheme for Nanoelectronics with regular arrangements of nanoscale switches (SETs, molecules) in cross-bar structures [Ö. Türel and K. Likharev: "CrossNets: Possible Neuromorphic Networks based on Nanoscale Components", Int. J. of Circuit Theory and Appl. 31, pp. 37-52 (2003). http://rsfq1.physics.sunysb.edu/~likharev/nano/IJCTA03.pdf].

Finally, Tour et al. (Rice University) [J.M Tour, W.L Van Zandt, C.P Husband, S.M Husband, L.S. Wilson, P.D Franzon and D.P Nackashi: "Nanocell Logic Gates for Molecular Computing", IEEE Transactions on Nanotechnology **1**, 100-109 (2002)] are investigating how to create functional computational units from quantum dot arrays randomly connected by molecules with switching capabilities (the "Nanocell" could be one type elementary logic unit in a general array processor).

In summary, our conclusion from the NANOMOL project is that a number of roads towards molecular electronics are wide open, and that the NANOMOL work is highly relevant for exploring all of them, since NANOMOL is sucessfully addressing a number of core issues: lithography and self-assembly, hybrid structures, 2- and 3-terminal devices, and random and organised molecule-cluster networks.

Appendix 1: Main technical results

No.	Self-descriptive title of the result	Partner(s) owning the result(s)
1	Synthesis of redox actives molecular wires to screen potential molecular wires backbones	CNRS
2	Synthesis of oligophenylenevinylene	UKBH
3	Improvement of gold nanocluster chemistry by exploitation of novel capping strategy	Liverpool
4	Routes for formation of 0D, 1D, 2D, and 3D assemblies of nanoparticles.	CEA, UKBH, Liverpool, CNRS
5	Routes for formation of 1D and 2D assemblies of nanoparticles: deposition onto surfaces with local energy differences.	Liverpool, CEA, UKBH
6	Routes for formation of 1D and 2D assemblies of nanoparticles: Langmuir-Blodgett (LB) films	UKBH, Liverpool, CEA
7	Routes for controlling the interconnection between clusters in 1D, 2D, 3D assemblies: place exchange reactions of the capping ligands	CEA, UKBH, Liverpool
8	Routes for controlling the molecular interconnection between clusters in 1D, 2D or 3D assemblies: linkage with DNA.	Liverpool
9	Routes for controlling the interconnection between clusters in 1D,2D, 3D assemblies: organisation of the ligandshells on water and exchange reactions	UKBH
10	Realisation and use of Self-Assembled Monolayers (SAMs) for probing molecule assembly and electrical properties; developement of a method for probing the electrical transport properties of self-assembled molecules and application to the elucidation of the role of the metal-molecule contact.	CEA, CNRS
11	Localized reactive patterns for directing self-assembly of nanoobjects	CEA, Chalmers
12	Three terminal single-molecule Single Electron Transistor (SET)	Chalmers, UKBH
13	Self-assembled nanocluster Single Electron Transistor	CEA, Liverpool, Chalmers
14	Self-assembled nanocluster Field Effect (FET) and Single Electron (SET) Transistors	Chalmers, Liverpool, CEA
15	Set-up for measuring electron transfer	CNRS
16	Sub 3nm gap fabrication	Chalmers, CEA
17	Nanoprinting of nanoclusters in nanogaps	CNRS
18	A semi-quantitative method for simulating STM experiments on conjugated molecules in SAM	CNRS
19	DFT calculations of current-voltage characteristics	Chalmers
20	Investigation of the effect of a transverse field in coherent transport	CNRS
21	Investigation of neuromorphic architectures	Chalmers

Dissemination of research results

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