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2st Periodic Report SINGLE

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Picture: SINGLE partners, Engelberg, March. 2009.

Coupling charge transport to internal degrees of freedom at the single molecular level - “SINGLE“

The idea underlying the project is to mimic electronic functions as **transistor**, **diode**, **switch**, or **memory** using a single molecule prepared by chemical synthesis.

The scientific objective is to:

- Understand transmolecular conductance of single organic molecules connected to electrodes
- Exploit its relation to **internal degrees of freedom** in the molecules. These include: vibrations, conformational changes (nanomechanics), electronic levels, electron correlations and spin
- Interconnect a few molecules in simple circuits by new patterning and **assembly** methods

We will demonstrate new types of single molecule **switches**, **memory** devices, **diodes** and **transistors** that are radically different from classical semi conducting devices where crystallinity dominates the functionality of the material in the device. The concept underlying 'SINGLE' is hence to exchange the rigid “hard” crystalline semi-conductors with the “soft” and structurally diverse organic molecules that are much more responsive to external stimuli.

In this summary the progress during the first two years of work towards these objectives is presented. The summary is divided into subsection describing some of the main results.

Contact to molecules

One of the greatest challenges in single molecular electronics is to make a well defined contact to the molecule [1]. Thiol endgroups of the molecular wires have so far been preferred, connecting the electrodes with a sulfur-gold bond. However it has been shown that the sulfur atom is capable of binding in multiple ways to the electrodes, each with a different conductance profile.

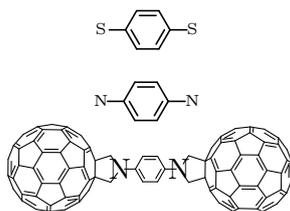


Figure 1: Molecular wires with S, N and “buckyballs“ as end groups.

To overcome this problem we synthesised a molecular wire with “buckyballs”/ C_{60} at the ends mediating the contact to the electrodes (see Figure 1). Due to the large size of C_{60} it binds with multiple bonds to the electrode, averaging out the individual difference in binding sites. The mechanically controllable break junction technique (MCBJ) is used to measure the transconductance of these single molecules.

Our work indicates that the coupling to the contact through C_{60} is high, and that the molecular junction is more stable than using other anchoring groups [2]. To examine this in more depth we have continued the synthesis of C_{60} containing molecules. Using systematic variations of the central part of the molecular wire (length and conjugation) we are seeking a deeper understanding of this new anchoring group. Physicochemical characterization shows the electrical coupling between C_{60} and the central molecule is very small, although quenching of C_{60} emission by charge transfer (tunneling of an electron from the phenylene diamine to C_{60}) is observed. Quantum chemical calculations gives a small transmission through the C_{60} capped wire supporting this observation.

Internal degrees of freedom

Internal degrees of freedom in the molecule are able to assist or scatter the electron transport. We have shown how vibrations affect the electron transport. Conductance channels matching with vibrational energy for the molecule in solution are visible, however not all of the vibrational modes are visible in the conductance and some of the vibrations line of the conductance does not fit with an vibrational mode in solution. With the aid of computational calculation we have been able to make selections rules for the individual vibrational lines. New lines arising in conductance originate from vibrational modes of the entire molecule, e.g. rotation of the molecule or motion of the centre of mass (see figure 2)

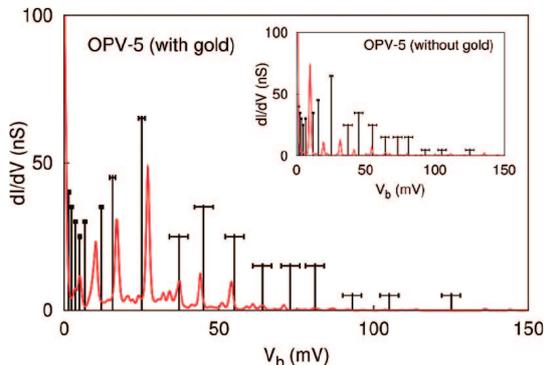


Figure 2: Calculated dI/dV trace of the diamond edge of the neutral charge state in Figure 5b, taking three vibrational quanta into account. The inset shows the same calculations, but with the gold atoms omitted. All measured excitations in this energy range (see Figure 5a) are shown. The uncertainties in the measured energies are indicated by the horizontal bars.

Seldenthuis et al. [3]

Conformational changes of the molecule in a junction can also change the conductance. We have examined how bianthrone switches between two conformational states when current passes through. The highest ratio between ON and OFF differential resistances obtained was about 10 and the switching voltages were in the range of 200 - 1500 mV. Theoretical results shows that the conformational change of bianthrone is assisted by interaction with the substrate, which lower the activation barrier.

Other internal degrees of freedom are able to assist the electron transport. The charge of the molecule, proton transfer or the spin of the molecule are examples. Using a high spin molecule, a manganese complex, we have examined the coupling to the spin. As expected a rich Kondo physics is observed, and a model describing the distinct features of the conductance have been developed [4].

Prototype devices

The greatest challenge in single molecular electronic is to fabricate nanosize gaps, and connect molecules to them in a controlled way. We propose to use selfassembly of nanorods and the molecule of interest [5]. Alignment of nanorods by the solvent flow in pre-fabricated trenches, or by control of surface tension and hydrophobic/hydrophilic properties of patterned substrate is two examples of how we address this problem, but also direct growth of few molecular devices from pre-fabricated electrodes, or dielectrophoretic trapping and alignment of dimers in a sub-micrometer sized gaps, or simply to contact the nanorods on a substrate with standard lithographic methods are routes which we are examining.

Impact

As chip structures continue to shrink to the nanometer scale, conventional semiconductor technology will approach fundamental physical limits. Further miniaturization presents ever more complex challenges and appears to be neither technically nor economically feasible. The 2005 International Technology Roadmap of Semiconductors (ITRS) predicts that the industry will reach these limits within 15-20 years time.

In order to increase computing performance beyond CMOS, we need to develop new information and communication technologies and strategies. This includes the use of novel materials and device concepts, innovative device architectures, and smart integration. The overall goal is to project electronic function resembling transistors, diodes, switches or memory onto a single molecule. Therefore, SINGLE addresses the below 2nm range with a time horizon of about 15-20 years.

The knowledge gained is a prerequisite for future use of small ensembles or even individual molecules as functional building blocks in electronic circuitry. Single-molecule devices are possible candidates for future nano-electronics, as they possess the potential for creating high-density devices with low-power consumption in combination with high speed. If molecular devices can take advantage of self-assembly processes, they will also have low manufacturing cost.

Moreover, because of their internal molecular structure, molecules may provide radically new and intrinsic functionality not found in today's conventional semiconductor-based electronics. Our project aims at a detailed understanding and exploitation of the internal molecular mechanisms and processes, which can be used for radically novel approaches in future nanoscale devices. In particular, within SINGLE we study the internal degrees of freedom at a single molecule level. Condensing complex computational processes into a single molecule is the dream this project aims to make the first scientific steps to. Therefore, the scientific accomplishments envisaged by this project are essential for the long-term innovation in the information and communication technology industry.

Furthermore, the development of computational tools for the calculation of the properties of metal-molecule-metal junctions in combination with a variety of experimental measurements is expected to have significant impact on the capability to fundamentally understand and especially to predict the performance of future molecular devices. This is an essential step for the entire field of molecular electronics in order to evolve from a pure scientific discipline towards a viable technology.

Today, the short-term impact of SINGLE is predominantly in the scientific domain, however, in the medium-term the technology development for “beyond CMOS” will be strongly impacted by the results provided by SINGLE. These scientific studies are the groundwork for developing a technology, which could have a tremendous impact on ICT industry and thus Europe’s society. At this stage of research of course, it is difficult to predict when exactly the entry point for molecular electronics as a disruptive technology will occur, however, then it will have a significant impact on the ICT industry.

Conclusion

Using C₆₀ as end groups for molecular wires have become the major point of interest within SINGLE. We have shown that the contact to the electrode is improved compared to thiols and amines. New molecules with C₆₀ as end groups, have been synthesised and more are in the pipeline.

Switching of conductance in biantrhone devices have been observed and described theoretically using DFT. We show that the activation energy of switching is lowered by binding with oxygen to the metal surface.

The first prototype devices build partly by selfassembly techniques have been realized. Multiple strategies using nano gold rods are used to bring this work forward.

References

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