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1st Periodic Report SINGLE

(Project number: 213609)

March 5, 2009

Picture: SINGLE partners, Copenhagen Sept. 2008.

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, switche,** 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 year 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. 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.

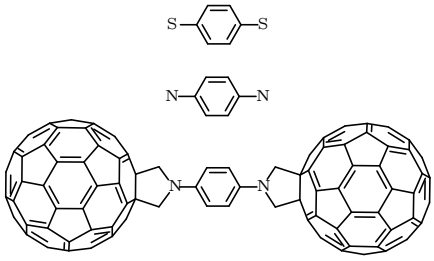

Figure 1: Molecular wires with S, N and "buckyballs" as end groups.

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.

The preliminary 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

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 center of mass (see figure 2)

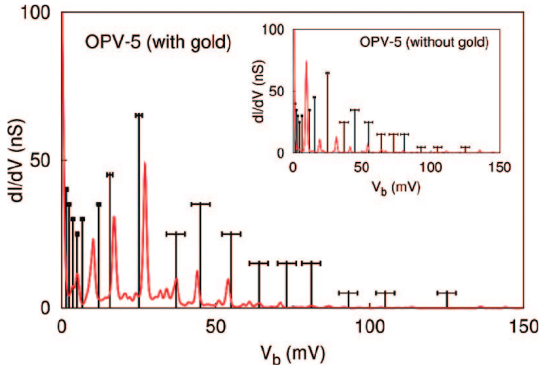

Figure 2: Calculated dI/dV trace of the diamond edge of the neutral charge state in Figure 5b, taking three vibrational quanta into account. The inset shows the same calculations, but with the gold atoms omitted. All measured excitations in this energy range (see Figure 5a) are shown. The uncertainties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

Seldenthuis, J. S. et al., ACS NANO, 2008, 2, 1445-1451

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.

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 is currently being developed (Nature, submitted).

Theoretical investigations provides a powerfull tool to design and examined possible new devices before actual producing them. Systems with intramolecular proton transfer have been explored for the use as a switch controlled by external electric field. It is predicted that the neutral form of this molecule will not swich upond electron transfer. By using a gate it is however possible to reduce the molecule thus making it negatively charged. The reduced molecule have not been investigated theoretically yet, but it is anticipated that this is a better candidate for proton transfer. An electrical field across the molecule will coulple stronger to the molecule, when a charge is localised on it.

Theoretical prediction of other systems includes the connection of a molecule or quantum dot with three or four contacts, or with superconducting contacts. For all systems investigated

predictions have been made, which are able to be tested if devices are fabricated. An interesting possibility of some of the systems is the realization of qubit's, the fundamental units for quantum computations.

Having established the improved contact through the C_{60} -moiety to the electrode in this period, the next period will focus on molecules where the electronic transport couples to internal degrees of freedoms. Especially we will focus on molecules with proton transfer and compunds which can undergo significant conformational changes induced by various stimuli. In addition will we focus on molecules which change the conjugation abruptly due to a change in the overall charge.

The next periode we will start to address the development of prototype devices. One of the greatest challenges, is the up scaling of the number of single molecular devices on a single chip. We believe that self assembly is part of the answar, and will follow that route. Long thin gold nanorods have allready been synthetised withing SINGLE, and is proposed to form a wiring network between molecules. Another method to produce the wiring network would been to use the air/water interface to produce well-ordered 2D gold nanostructures by spreading a mixture of alkanethiol-capped gold nanoparticles and an amphiphilic poly(p-phenylene) and compressing the mixture. This network has also been achieved within the SINGLE project.

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.