**EUPHONON**-Building a European NanoPhononics Community: presentation and goals

- Beyond CMOS: NANO-TEC project recommendations for research in nanoelectronics
- Flatland optics with graphene
- Nanomechanical sensors detect cancer from breath
- Revealing the "Scotch-tape" technique mechanism
- A cool approach to flexible electronics
- Molecular versus Atomic scale circuits for Boolean logic gates (and more) at the atomic scale
- Experimental approach towards molecular circuits
- Surface atomic wires for interconnects and logic gate design
Experimental approach towards molecular circuits

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An essential challenge in the field of molecular electronics is the construction of electronic devices based on the on-surface assembly of single functionalized building blocks. These functional units, supported by a surface, are connected to each other via molecular wires or atomic-scale wires. Such atomic scale circuitry should lead to better performances in terms of power dissipation and operation speed. In order to achieve this goal it is extremely important to gain fundamental understanding how to master the assembly of several atomic/molecular species into predefined architectures, possibly held together by covalently interactions in order to ensure high stability and enable efficient electron transfer between the molecular building blocks.

One strategy is the assembly of semi-classical intermolecular circuits on surfaces. The successful growth of such systems might allow to explore and verify the predicted circuitry laws that these nano-circuits obey. In the tunneling regime, semi-classical intramolecular circuits follow non-standard classical rules, due to the quantum character of electron tunneling [1]. This has been demonstrated theoretically (see Figure 1) [2] and was later used to design a semi-classical molecule OR gate with no molecular rectifier chemical groups [3]. In this regard, a first experimental verification of these laws has been reported recently [1]: Individual intermolecular circuits made of one and two identical paths in parallel have been synthesized ex-situ and their conductance was measured by a statistical break junction technique, confirming the role of interference in the conductance superposition law for an intramolecular circuit (Fig.1d). In AtMol and as a further progress in that direction, we are interested in probing the conductance through semi-classical logic gates circuits comprised of a central molecular node accessible via three branches (wires) as presented in Fig.1c.

Conventional sublimation methods are very limited in the deposition of complex molecular structures (as such a molecular circuitry) onto surfaces since these structures typically have a large molecular weight [4] that results in high sublimation temperatures, potentially above the decomposition temperature. Hence, it is very difficult – if not impossible – to deposit the molecular structures in an intact fashion under ultrahigh vacuum conditions. In this regard, we approached the surface assembly of molecular heterostructures by means of the on-surface polymerization technique [5].

The synthesis of covalently-linked molecular structures on a surface comprises the incorporation of specific, comparably weak intramolecular bonds in the monomer building blocks and the subsequent creation of reactive sites at these positions. This has been realized by the use of halogen–carbon bonds at specific sites of the molecules with lower
bond energies than the organic framework. The halogen atoms are dissociated by providing specific thermal energy, creating reactive sites at their positions in a controlled fashion without breaking other molecular bonds (the so-called activation step) [6]. The activated molecular building blocks subsequently diffuse on the surface and connect with one another by forming new covalent bonds [5]. The direct covalent-connection of aromatic moieties is advantageous to establish π-conjugation for efficient charge transfer [7] and in terms of robustness as well.

**Fig. 1** Simple single molecule circuit diagrams represented with their two contact nanopads metallic interconnects of the different series and parallel association of the molecular wires $M_1$ and $M_2$. The two molecular wires are: (a) bonded in series, (b) connected in parallel on the metallic pads, (c) forming a single molecule with one intramolecular node and (d) forming a single molecule with two intramolecular nodes. /!

In order that this procedure may efficiently work, it is important that the framework of each molecular constituent remains intact during the activation step as well. Furthermore, each individual molecule has to maintain sufficient mobility in order to diffuse sufficiently on the surface to hit other activated molecular species. At the same time chemical reactions between the activated molecular connection points and the surface itself must be avoided in order to preserve the availability of reactive molecular sites.

Incorporating different halogen substituents in the molecular building blocks as activating groups is a highly promising strategy in view of growing molecular architectures according to hierarchical covalent linking. The ability to activate dormant halogen bonds at different and well-defined activation temperatures opens up the possibility to better control the assembly process of molecules as well as the quality and the degree of complexity of multi-component molecular arrangements at surfaces [6]. Additionally, the surface structure
influences molecular diffusion and consequently the covalent linking of the building blocks. It has been shown that the use of stepped surfaces for the on-surface polymerization process does not only give insight into the catalytically active sites of the surface [9], but also can steer the linking reactions. In this way, aligned and parallel polymers as well as a higher polymer quality (in terms of size and defect number) are achieved [6,9].

The assembly of nanocircuits or hetero-nanostructures made of molecular wires and functional building blocks at surfaces is very challenging since the molecular recognition takes clearly place between different molecular species. A functional molecule (for instance a circuit node) must provide reactive side groups for the connection of a certain number of wires. The molecular species has to be designed in a way that the chemical recognition is maximized between the two species in order to efficiently prepare these nanocircuits (in contrast to a segregation process if mixed structures are unlikely formed [6]).

Finally, a way to probe the circuitry laws followed by these nanocircuits is by means of the scanning tunneling microscopy (STM) pulling technique [4]. The STM allows to identify and image specific nanocircuits with submolecular spatial resolution. The circuit conformation within the STM junction as well as the whole environment around the nanostructure can be fully characterized at the atomic scale, unlike typical break junction experiments where the transport information through the single molecule is extracted from a statistical analysis without detailed information about the surroundings [10]. Once an individual nanocircuit is identified, the STM tip will be placed on top of a wire’s end (at disables STM feedback loop) and approached until a robust contact is established. Then, the tip is retracted, the circuit is lifted up and the conductance measured as a function of the vertical tip displacement (I(z) pulling curve) [7]. This shall open the possibility to investigate and isolate the contribution of a single functional groups to the measured conductance by STM imaging of the molecular nanostructure before and after the process. At the same time electron transfer can be explored through simultaneous pathways in the case that a functional unit (e.g. a molecular node) is connected to more than two wires. This should open the possibility of probing expected interference effects when tunneling through a single molecule.

References