Project II.3 MOLECULAR MATERIALS AS COMPONENTS OF ELECTRONIC DEVICES

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Research orientation:

- To investigate the potential of molecular materials to be used as active components in molecular devices e.g. as switching or memory elements.
- to develop consistent evaluation methods based on the electronic transport properties at the nano- level for the characterization of single layered and few-layered systems.
- to produce physical parameters (film thickness, surface molecular density, contact potential) that could be cross-checked with other surface characterization methods
- To evaluate elements of the class of organic crystals as components of organic FETs
- To develop techniques for thin film deposition and characterization of molecular materials.

MAIN RESULTS IN 2010

The main results obtained in 2010 within the different tasks of the project are given below.

A. Molecular junctions made of tungsten-polyoxometalate self-assembled monolayers

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Polyoxometalates are molecules in which the anion is a complex inorganic oxide of transition metals. The anion is organised in a well-defined, closed-packed form, with a certain number of metal-oxygen polyhedra surrounding one or more heteroatoms. They are highly reactive -yet stable- substances, thus having a plethora of diverse applications. Due to this wealthy chemistry and photochemistry as well as their well-defined dimensions and ability for electron storage and transfer, polyoxometalates have recently attracted attention as candidates for use in molecular electronic and photoelectronic applications .

As our goal is to establish SAM's electrical properties, the fabricated junctions vary so in design as in their dimensions. A group of opposite fingers junctions (Fig 1) with 50, 100, 150 and 200nm electrodes' width are constructed. With opposing electrodes, one can obtain higher values of electric field through limiting of the electrodes' dimensions. At the same time, the observed phenomena are caused by the small number of POMs in between the electrodes. Parallel fingers junctions (Fig 1), with overlaps of 500nm, 1μm and 2μm, are also investigated, in order to obtain the behaviour under lower fields and with a larger number of anions present. For every width (or overlap for parallel electrodes), junctions with different electrodes' distances -varying from 20 to 200nm- are constructed.

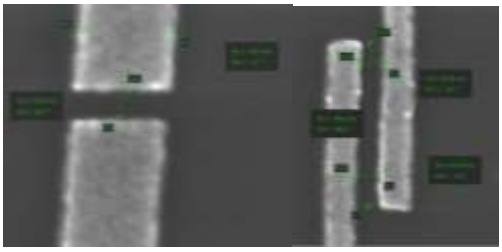


Figure 1: *Scanning Electron Micrographs of the junction's area of 50nm-distant, 200-nm opposite fingers' geometry electrodes (left) and of 50nm-distant, with 500nm overlap, parallel fingers*

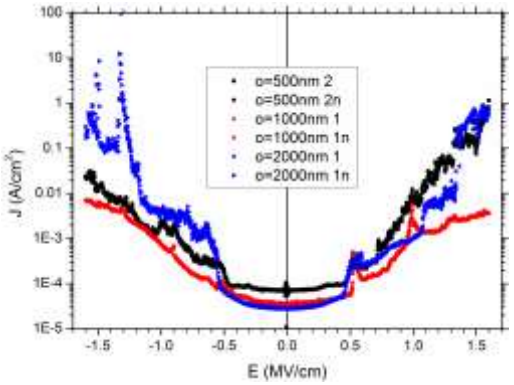


Figure 2: *Current density as a function of the applied electric field for parallel junctions of different electrodes' overlaps and 50nm electrodes' distance. The threshold value for the electric field is about 0.5MV/cm.*

POM anions can be considered as a group of regularly arranged semiconducting islands placed between two electrodes, which can become charged when junction is biased. Conduction in the junction is then governed by percolation, in the case of conductive quantum dots: the islands forms conduction paths that are activated after a certain voltage; the larger the applied voltage, the more the activated conduction paths. At the same time, since anions are not physically connected, the only way the charge can be transported is through tunnelling. Obtained current-voltage characteristics (IVs) verify this behaviour. The IVs (Fig 2) show a low conductance region for low bias, followed -after a certain threshold voltage Vth- by a high conductance region. As IVs general behaviour -along with the field's threshold- is steady for the different overlaps (widths), the observed behaviour is mainly due to the SAM and not a property of the electrodes themselves.

Furthermore, a quantitative analysis of the results is made using the FN representation (ln(I/V2) = f(1/V)) of the IVs. The IVs present a minimum value, which corresponds to the tunnelling mean barrier height φ and divides the IV in the FN and a direct tunnelling region. However, since measurements are performed at room temperature the transition from direct to FN tunnelling is not always abrupt. Fitting by Simmons' tunnelling model is performed for any combination of junction's geometrical features and this way the precise φ values are determined. A linear increase of φ as a function of the electrodes distance is established.

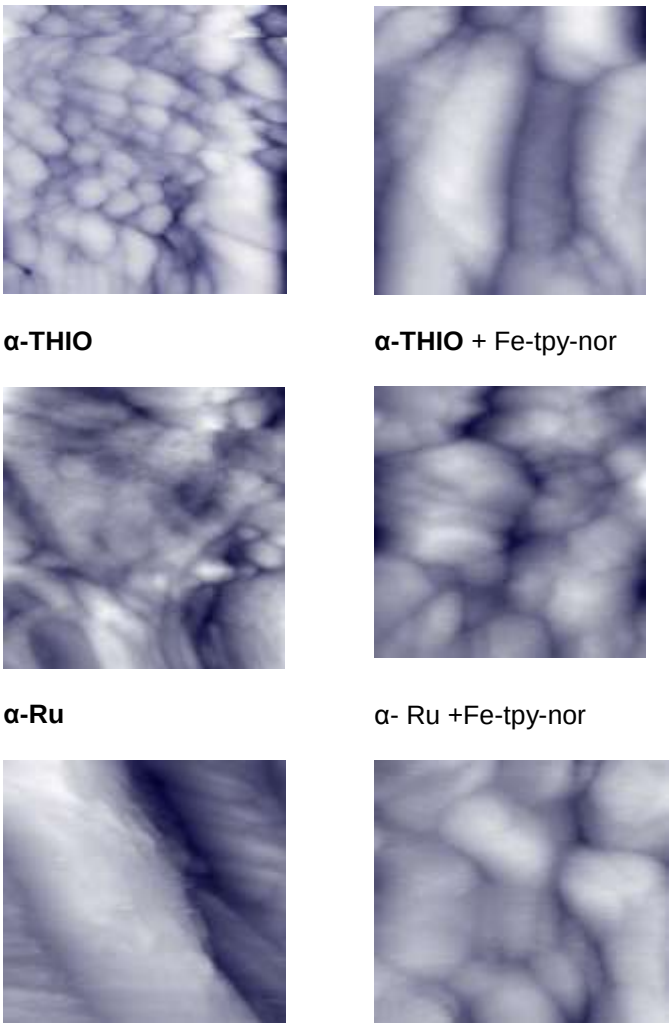
B. Fabrication and electrical characterization of molecular nanowires based on cyclodextrin host-guest systems

Davide Maffeo, Viswanathan Chinuswamy, Konstantinos Anastasiou, Constantinos Milios, Evangelos Kefalas, Maria J.J. Pereira Silva, Zoe Pikramenou, Irene M. Mavridis, Konstantina Yannakopoulou, Nikos Glezos

Using Scanning Tunneling Microscopy (STM) we study the morphology and the electronic transport properties of molecular nanowire systems composed by cyclodextrin hosts (CDs), immobilized on Au surfaces, and suitably-sized metal containing guests. It is shown that the presence of metal complex moieties or units in the structure of guests significantly alters the electronic transport characteristics between Au and STM tip due to the modification of the potential barrier. In one particular case of a Ru(II) containing CD complex and a Fe(II) containing guest, electrostatic effects are present that could be potentially exploitable in future electron storage memory devices.

Morphology was examined by scanning fields as large as 1.5μm x 1.5μm down to 50nm x 50nm. Representative results are shown in Figure 1 for 100nm x 100nm fields. A general conclusion is that the presence of a the metallo- guest induces surface ordering and organization resulting from the evaluation of the RMS roughness values in each case and the mean cluster size. Thus in the case of the presence of the Fe-tpy-nor guest in α-THIO, roughness reduces from 2.4nm to 1.4nm, while 10-15nm clusters are substituted by more extended structures of the order of 50nm. The same is true in the case of DMβ-THIO with the Ir-tpy-bp guest where roughness reduces from 7.0nm to 1.0nm. In the case of the α-Ru and the Fe-tpy-nor guest, the roughness remains practically unchanged (~1nm) however the film

becomes more homogeneous with clusters of the order of 20nm. The small roughness of α-Ru and its complex with the guest can be attributed to results from the orientation of this host molecule, arising by the presence of the planar tpy ligands.



α-THIO **α-THIO** + Fe-tpy-nor

α-Ru α- Ru +Fe-tpy-nor

DMβ-THIO DMβ-THIO + Ir-tpy-bp

Figure 1 Change of surface morphology induced by the presence of a metalloguest.

The transport characteristics were investigated by examining groups of I-V curves over different locations of the samples. The curves were compared to the Au sample reference for the shape and the values of the parameters. Each curve was analyzed using existing models for tunneling effects. We used a combination of the low tunneling regime with the Fowler – Nordheim high voltage tunneling as described by Simmons. The parameters that can be evaluated with this method are the potential step and the effective tunneling distance i.e. the width of the region in which the electron feels the presence of the electrical barrier and whose its upper limit is the physical distance between electrodes. The values of the tunneling parameters reflect on the shape of the I-V curves. All the measurements were performed in voltage cycles sweeping from negative values to positive and then back. In the case of the Au substrate reference there are no hysteresis effects related to charge trapping. In the case of α-THIO, DMβ-THIO and their guests, these trapping effects are also non existent or casual (not shown). However the I-V curves of α-Ru with and without its Fe-tpy-nor guest have different structural characteristics. These are shown in Figure 2.

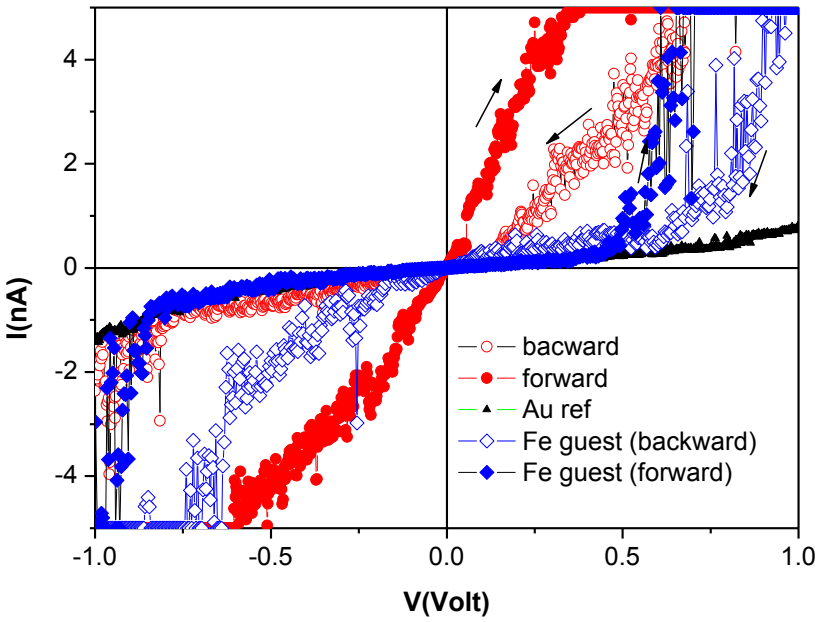


Figure 2 *Hysterisis effects in α-Ru and Fe tpy nor guest. The sweeping of the voltage bias is form negative values to positive and then back.*

The voltage increase in the case of α-Ru results in a normal tunneling procedure that is limited mostly to the low voltage tunneling region. This is consistent with the low value of φ=0.25 averaged over several curves. However voltage biasing also results in storing electrons on the layer which have the effect of reducing the current when the voltage is decreased. As seen in figure 4 the voltage has to reach a value of V= -0.8V before these electrons are released. This is more dramatic in the presence of the Fe-tpy-nor guest. In this case an onset for high conductance exists for the electron path in both directions consistent with the higher value of φ observed. This means that such complex systems have potentially the possibility to be used in future molecular memory applications.

PROJECT OUTPUT IN 2010

Conference Presentations

1. "Inorganic polyoxometalates as components of molecular electronic devices", P.Argitis, N.Glezos, Oral presentation, POM Worshop, NSF Meeting, Newcastle August 2010
2. "Molecular junctions made of tungsten-polyoxometalate self-assembled monolayers: Towards polyoxometalate-based molecular electronics devices", D. Velessiotis, A.M. Douvas, S. Athanasiou, B. Nilsson, G. Petersson, U. Södervall, G. Alestig, P. Argitis, N. Glezos, MNE Conference, September, Genova
3. Scanning Tunnelling Spectroscopy and Topography Recovery of a Polyoxometalate-based Self-Assembled Monolayer, D. Velessiotis, S.Athanasiou, A. Douvas, P. Argitis and N. Glezos, NN Conference, Chalkidiki, July 2010
4. Fabrication and electrical characterization of molecular nanowires based on cyclodextrin host-guest systems, Davide Maffeo, Viswanathan Chinuswamy , Zoe Pikramenou , Irene M. Mavridis, Konstantina Yannakopoulou, Nikos Glezos, NN Conference, Chalkidiki, July 2010