Project II.3 MOLECULAR MATERIALS AS COMPONENTS OF ELECTRONIC DEVICES

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Funding:

- NMP STREP TASNANO, 1/1/2005-30/7/2008, Contract N^{o} 516865

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 2008

The main results obtained in 2008 within the different tasks of the project are given below.

MAIN RESULTS IN 2008

A. Invastigation of the Transport Properties of *Self-assembled Hybrid Organic/inorganic Monolayers based on Polyoxometalates*

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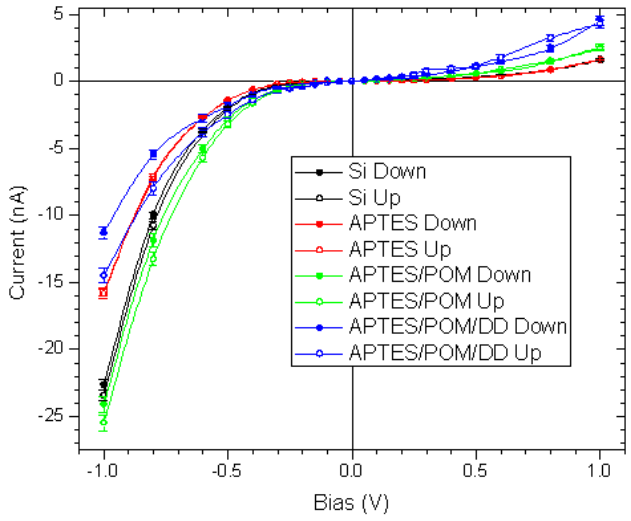
Our aim is to demonstrate the potential of inorganic polyxometalates (POMs) to serve as active layers in molecular electronic devices. So far we have demonstrated the possibility to fabricate organic/inorganic mono- and multi- layers containing polyoxometalates and we are performing electrical measurements with them in various device architectures:

- Vertical capacitor structures with the top electrode evaporated through a mask,
- Planar structures involving nanoelectrodes,
- Vertical capacitor structures fabricated entirely using conventional lithographic patterning techniques, with variable device parameters (capacitor surface, oxide thickness, substrate type),
- Vertical structures using an STM or cAFM tip as the upper electrode.

We have investigated both quantum conductivity effects as well as charging effects. We proceeded along the directions discussed below:

A1. Molecular layer investigation

Silicon n++ samples covered with a) aminosilane (APTES) b) APTES/POM and c) terminated by diamine (DD) APTES/POM/DD were fabricated by NCSR and measured by STM both by NCSR and WRUT. The samples used were fabricated with the layer-by-layer (LBL) method on top of highly doped n+ Si substrates. The obtained IVs were analyzed in two distinctly different ways. Firstly, they were statistically studied so that a “representative” I-V for every sample was constructed. Such an I-V provides us with a general idea of the magnitude of the conductivity for every type of SAM. Secondly, some of the I-Vs were fitted, using the Simmons model for elastic tunnelling in order to estimate the values of the tunneling distance s and the mean energy barrier φ_0 for every sample.



Sample	φ_0 (eV)	s (Å)
Si	0.61	7.5
APTES	0.62	6.7
APTES/POM	0.54	7.7
APTES/POM/DD	0.76	10.59

Fig.1: ‘Representative’ I-Vs for the samples studied. A small hysteresis is evident in the case of APTES/POM/DD sample and negative voltages. The parameters obtained by simulation are also presented in a table. The presence of the terminating diamines (DD) obviously changes the tunnelling mechanism.

A2. Fabrication and characterization of capacitor structures.
We fabricated POM mono- and multi- layers on n-type and p-type substrates with a reference oxide. The fabrication process is CMOS compatible. The devices are packaged and the molecular layers are protected from environmental conditions The objective is to obtain systems capable of being controlled (charging / uncharging) only from one side. This depends on the type of doping, the oxide type and thickness and the covering metal. These parameters were evaluated by I-V and C-V measurements. We defined the conditions for this selective charging by varying the geometry of the substrate. Our conclusion is that these materials are capable for molecular memory node applications.

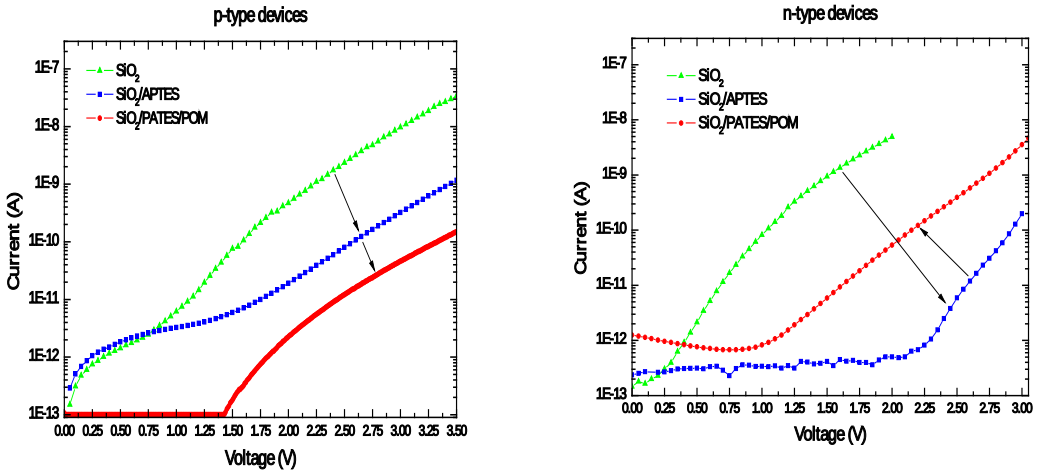
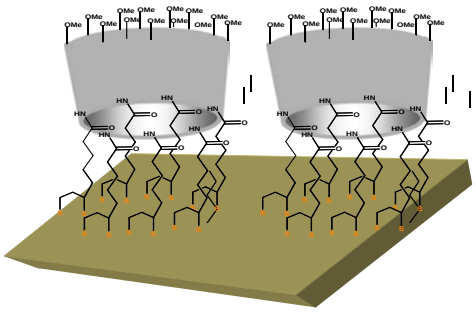


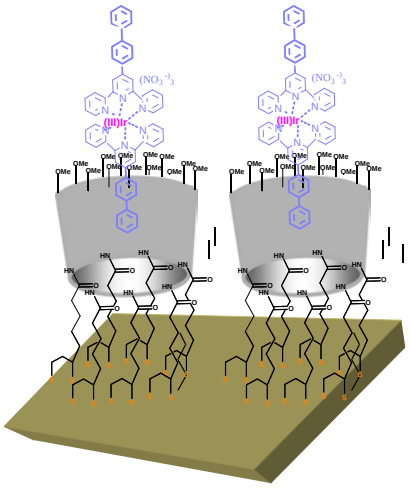
Fig. 2 Depending on the type of the substrate the transport mechanism changes: Electron injection from the top Al electrode(p-type), electron injection from the Si n substrate (n-type)

B. Study of the transport and host – guest properties of cyclodextrin nanowires for molecular devices

D. Maffeo, ,V. Chinnuswamy, D. Velessiotis, N.Glezos, K.Yannakopoulou and I.M.Mavridis

B1. Investigation of electronic transport properties of nanowires.
Molecular nanowires are essential for the development of molecular electronic devices both because of their quantum properties as well as for the possibility of serving as interconnections with other device components. In this work we studied supramolecular wires in the nanoscale based on the non-covalent interactions between metallocyclodextrins and metalloguests. The resulting surfaces were examined as far as morphology and constitution with STM microscopy and other techniques. Furthermore the study of the tunneling current ins an STM setup provided useful information concerning the wire stability, transport properties and the band alignment of the molecules with the Au binding surface. As an example of the whole procedure we examine the case of a hepta-substituted β-CD with (±)-1,2-dithiolane-3-pentanoic acid [(±)-α-lipoic acid] deposited on gold and then incubated with a suitable metallo-guest containing Iridium, thus making up a model molecular wire whose electrical conductivity was investigated.





results in a linear metallic behaviour in the voltage region investigated (green line). In this case the molecular layer facilitates electronic transport.
The tunneling regimes in the first two cases are analyzed using the relation :

$$I = C_1 \exp(-a)V + C_2 V^2 \exp(-b/V) \qquad (1)$$

Where C_1 and C_2 are constants, $a = 2s\sqrt{2m\varphi}/(3e\hbar)$, $b = \frac{2}{3}a\varphi$, φ is the potential barrier and s is the effective barrier length . The first term stand for low voltage tunneling and the second term represents situation where the barrier is modified to a triangular form thus resulting in increased currents (Fowler – Nordheim tunneling). The analysis is better visualized in a Fowler-Nordheim plot (figure 5b). In the case of the Au substrate the fitting according to relation (1) results in φ=0.87eV and s=0.72nm. The presence of the **DMBLIP** layer modifies these values to φ=0.22eV and s=1.44nm. Thus the presence of the insulating layer results in lower and broader barrier for the electrons. The presence of a metal containing guest (Iridium) results in metallic behaviour of the contact despite the tunneling effect. This is promising if these systems will be used as metallic self-assembled conductors in a molecular scale.

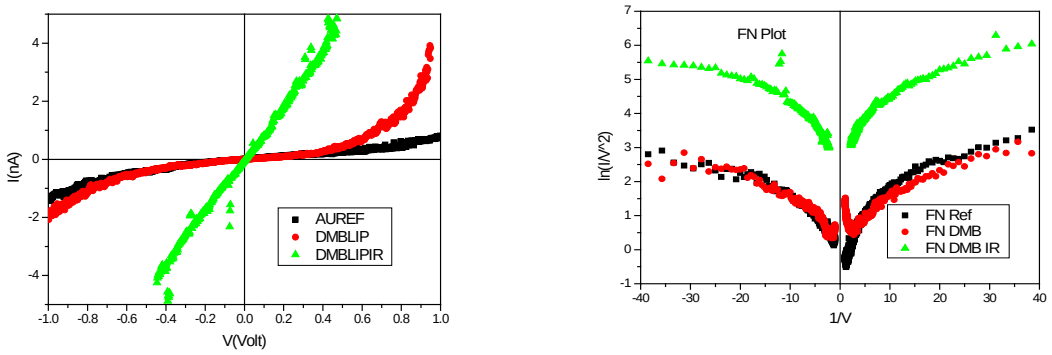


Fig. 5. Electronic transport properties in STM configuration. The I-V characteristics are averaged over different points on the surface. Au reference: black; **DMBLIP** on Au, red line; **IrGuest/DMBLIP** on Au, green line.

B2. Surface Characterization with AFM functionalized probes

The aim of this task is to exploit the potential of cyclodextrins to act as hosts to other molecules. Specifically modified cyclodextrin hosts can bind via weak intermolecular forces with suitable guest molecules, bound also via –SH bonds to AFM tips, in a manner that manifests molecular recognition.

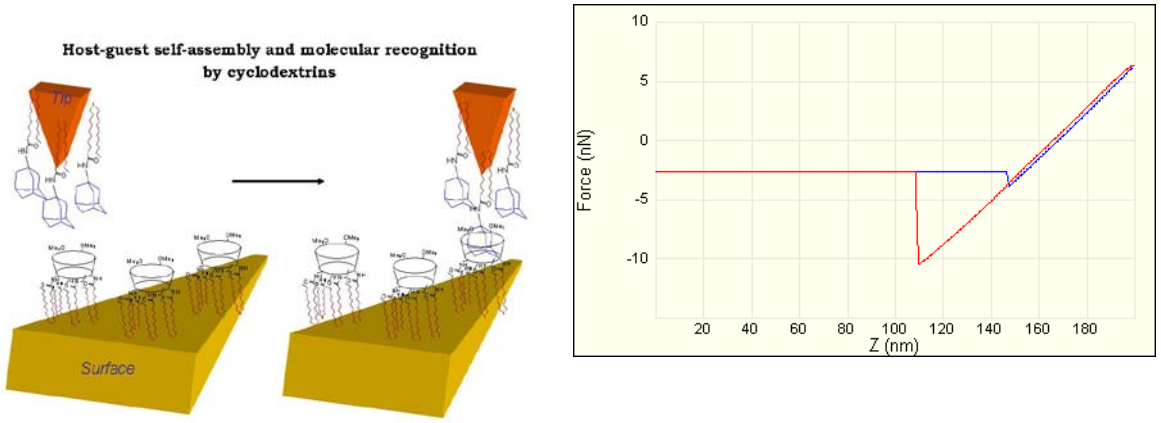


Fig. 6 Arrangement of functionalized tip/ surface for the force measurement.

Fig 7. Example of force measurement. In the case presented F=7.2nN

The functionalization of gold surfaces and cantilevers was carried out using the following compounds :

1) The natural cyclodextrins are molecules of increasing cavity size in the order αCD <βCD<γCD. Three different modified cyclodextrin molecules (**Hosts**) of increasingly larger cavity size (αTHIO <DMβTHIO <γTHIO) specifically prepared, were used to functionalise gold surfaces.
2) An adamantane guest molecule was selected to bind specifically and strongly with a βCD-type cavity and much less with either an α- or a γ-type cavity, ADASH.. This was used to functionalize AFM tips.

Force measurements of the above complementarily functionalized pairs, Guest on-Gold AFM Tip/Host-on-gold surface, were carried out at the University of Wroclaw. The results showed that significant attractive forces were recorded in the pair ADASH/DMβTHIO, as expected, since the adamantyl group-βCD entities constitute an acknowledged pair with strong ands specific binding. On the contrary, the pairs ADASH/αTHIO and ADASH/γTHIO show attractive forces of approximately the same order, showing no specificity in either binding.

The measured results are summarized in the following table:

	αTHIO	**DNβTHIO**	**γTHIO**	**Difference DMβTHIO/αTHIO**	**Difference DMβTHIO/γTHIO**
Plain tip	6.8	9.3	6.2	2.5	3.1
ADASH charged tip	22	27	19	5	8

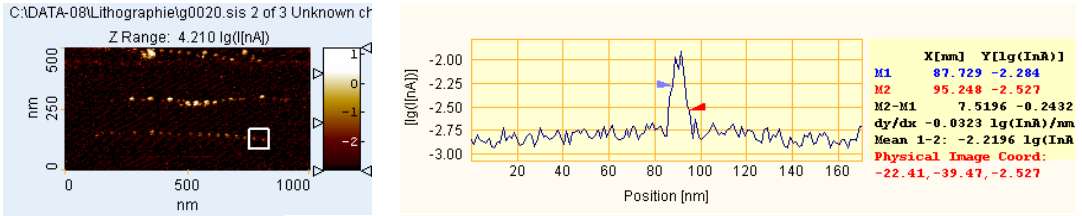
Therefore the specific molecular recognition ordinarily observed in aqueous environment is also demonstrated in the surface/AFM tip interactions.

C. SPM nanopatterning of biotin monolayers

P.Petrou, F. Saurenbach, D.Velessiotis, N.Glezos

Scope of the activity was to define a process based on a biomolecular layer for sub 10nm lithography. A biotin covered surface was prepared according with methods developed at NCSR and patterned by AFM tips at SIS in order to create patterns with dimensions below 10 nm. The pattern has been identified before and after reaction with streptavidin by employing AFM imaging. The streptavidin-biotin system is an ideal demonstrator of pattern recognition due to the high affinity of streptavidin for biotin (affinity constant $K=10^{15}$ L/mol) that makes their binding almost irreversible even under very harsh conditions.
The biotin covered surfaces were sent to SIS for patterning with AFM tips. The pattern created was imaged by AFM both at NCSR and SIS. Two types of patterns were created (a) A line pattern where the minimum dimension achieved was about 15 nm and (b) A dot pattern where the minimum dimension achieved was about 8 nm.

A



B

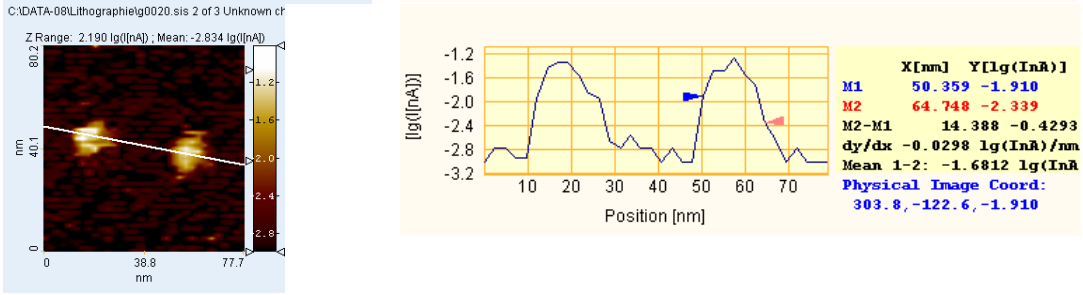


Fig. 8 Example of nanopatterning of biotin / streptavidin monloayers with an STM probe with a tresolution of 8nm.

PROJECT OUTPUT IN 2008

Publications in International Journals

1. “Molecular nanodevices based on functionalized cyclodextrins”, Velessiotis, D. , Maffeo, D. , Millios, C. , Makarona, E. , Viswanathan, C., Yannakopoulou, K. , Mavridis, I. , Pikramenou, Z. , Glezos, N. .(2008) Physica Status Solidi (A) Applications and Materials, 205 (11), pp. 2532-2535, 2008.
2. “Soluble substituted phthalocyanines for OFET applications”, Chaidogiannos, G.a, Petraki, F., Glezos, N., Kennou, S., Nešpurek, S. Materials Science and Engineering B: Solid-State Materials for Advanced Technology, 152 (1-3), pp. 105-108 , 2008
3. “Vertical devices of self-assembled hybrid organic/inorganic monolayers based on tungsten polyoxometalates”, Makarona, E. , Kapetanakis, E. , Velessiotis, D.M. , Douvas, A. , Argitis, P. , Normand, P. , Gotszalk, T. , Woszczyna, M. , Glezos, N., Microelectronic Engineering, 85 (5-6), pp. 1399-1402, 2008.
4. “Polyoxometalate-based layered structures for charge transport control in molecular devices”, Douvas, A.M. , Makarona, E. , Glezos, N. , Argitis, P. , Mielczarski, J.A. , Mielczarski, E. ACS Nano, 2 (4), pp. 733-742, 2008.

Conference Presentations

1. “Characterization of surfaces and interactions of self-assembled cyclodextrin monolayers with STM and functionalized AFM probes”, D. Maffeo, M. Woszczyna, D. Velessiotis, V. Chinnuswamy, K. Yannakopoulou, A. Paulidou, I.Mavridis, Th. Gotszalk, J. Milecszarski, E. Milecszarski, N. Glezos, , MNE 2008 Athens
2. “Molecular proton memory”, E. Kapetanakis, A. M. Douvas, D. Velessiotis, E. Makarona, P. Argitis, N. Glezos, P. Normand, , MNE 2008, Athens
3. “Quantitative force and mass measurements using piezoresistive cantilever with integrated thermal deflection actuator “ M. Woszczyna, P. Zawierucha, M. Świątkowski, T. Gotszalk, P. Grabiec, N. Nikolov, J. Mielczarski,E. Mielczarska, N. Glezos, Tzv. Ivanow, “, MNE 2008, Athens

4. “Characterisation of surfaces and interactions of self-assembled cyclodextrin monolayers with STM and functionalised AFM probes”, D. Maffeo, M. Woszczyna, D. Velessiotis, V. Chinnuswamy, K. Yannakopoulou, A. Paulidou, I. Mavridis, T.Gotszalk, J. Milecszarski, E. Milecszarski, N.Glezos, MNE 2008, Athens