

## **PROJECT II.3**

### **MOLECULAR MATERIALS AS COMPONENTS OF ELECTRONIC DEVICES**

**Project Leader:** N.Glezos

**Permanent Researchers:** P.Argitis, P.Normand

**Permanent Scientific Staff:** A. Douvas

**Post Doctorals Scientists:** D.Velessiotis

**PhD Students:** A.Balliou

**External Collaborators:** Jiri Pflieger, Stan .Nespourek, Samrana Kazim, David Rais (Czech Academy of Sciences), Ulf Soderval, Bengt Nilsson (Chalmers University)

### **OBJECTIVES**

Our research field focuses mainly on the investigation of functional molecules as core components of hybrid molecular-semiconductor and molecular-metal devices. Dealing with molecular electronic devices requires understanding of the electrical properties from atomistic to mesoscopic scale, precise control of the morphology of the molecular structures and the involved interfaces, as well as stability and device variability reduction. Hybrid devices on semiconducting and/or metal surfaces are a test bed for molecular layers, while they can be directly exploited for fast switching, diode and memory applications as well as for chemical or bio-sensors. By selecting the device topology it is possible to highlight electronic and electrical properties of the molecular components, realize devices (exploiting self-assembly and bottom-up fabrication techniques) that will function as non-volatile memories, switches or electrically gated q-bit devices and realize more complex structures such as hybrid networks that could function via bootstrapping heuristics. Specific objectives are:

- 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 molecular few layered systems as part of hybrid devices.
- to produce physical parameters (film thickness, surface molecular density, contact potential) that could be cross-checked with other surface characterization methods
- To develop techniques for thin film deposition and characterization of molecular materials.

### **FUNDING**

- Greek-Czech Cooperation Project, 2011-2013
- Greek-Sloval Cooperation Project, 2012-2014

### **MAIN RESULTS in 2012**

The main results obtained in 2012 within the different tasks of the project are given below.

# 1. Study of conduction mechanisms in molecular junctions made of tungsten-polyoxometalate self-assembled monolayers and bilayers

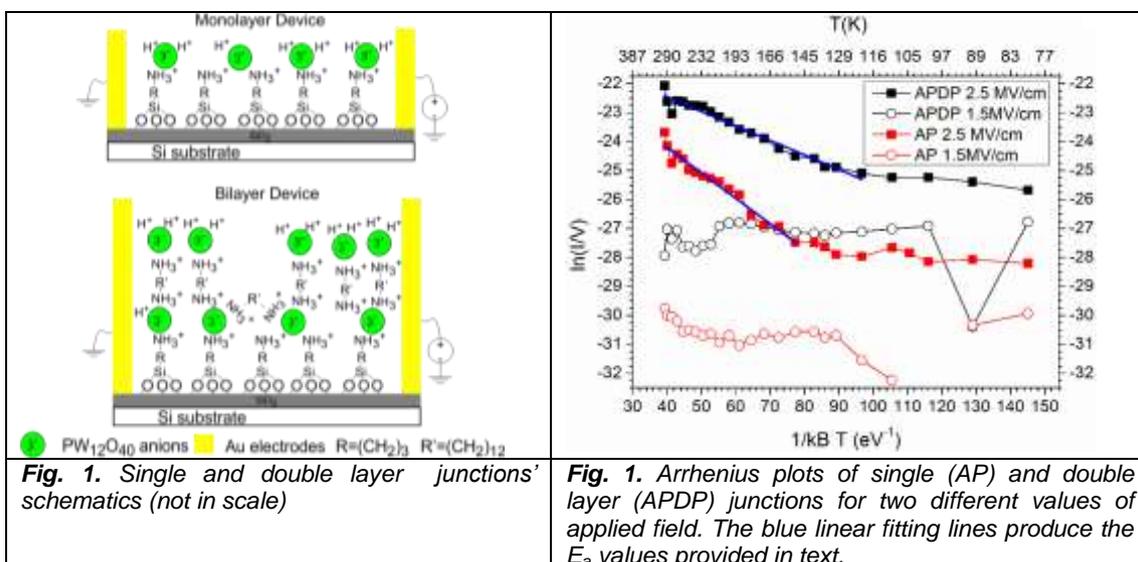
D. Velessiotis, A.M. Douvas, P. Dimitrakis, P. Argitis, N. Glezos

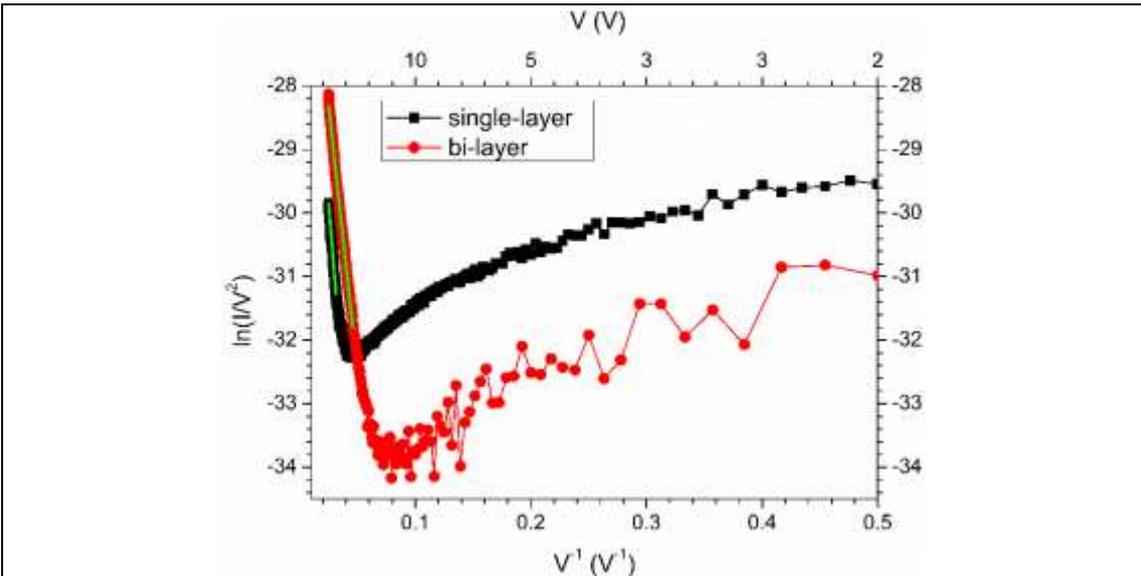
Polyoxometalates are inorganic salts or acids in which the anion is a complex oxide of transition metals. The anion is organized in a well-defined, closed-pack form, with a certain number of metal-oxygen polyhedra surrounding one or more heteroanions. They are highly reactive -yet stable- substances, thus having a plethora of diverse applications. It is exactly this combination of wealthy chemistry/photochemistry, in other words the ability of polyoxometalate anions to exchange electrons with their environment, with their structural stability and well-defined dimensions that has led the research community to consider polyoxometalates as potential candidates for use in molecular electronic and photoelectronic applications.

The next step with the study of 12-phosphotungstic acid (POM) self-assembled materials, taken by our team in 2012, was the comparison between the 3-Aminopropyl triethoxysilane (APTES)/POM monolayer (1L) material junctions and the APTES/POM/12-diaminododecane (DD)/POM bilayer (2L) material junctions for different temperature conditions (Fig 1). In general, it was found that the conduction mechanisms which apply for the 1L material junctions, were applying for the 2L material junctions too. This means that for lower applied fields (~1.5MV/cm or less) or below a certain temperature ( $T_t$ ), tunneling was the dominant conduction mechanism, while for higher applied fields and high temperatures a simple (Arrhenius) hopping mechanism was followed by our system (Fig 2).

While qualitatively the two materials behaved in the same way, there were significant differences in the quantitative parameters of the conduction mechanisms concerned. In the hopping regime, the activation energy ( $E_a$ ) of the 1L junctions was confirmed to be in the neighborhood of 80meV, more specifically 85meV for the 50nm-distant and 76meV for the 75nm-distant junctions. The 2L junctions presented much lower values of  $E_a$  in these two distances, namely 55meV and 41meV, respectively. Moreover, the values of  $T_t$  were different for the two materials; more specifically  $T_t$  was 150K for the 1L and 120K for the 2L junctions. In the tunneling regime, the value of the mean tunneling barrier ( $\phi$ ) obtained (by the Fowler-Nordheim representation of the current-voltage characteristics – see Fig. 3), was significantly lower in the case of 2L material (330meV) than that already obtained for the 1L material (500meV – more or less equal to the expected difference between the Au Fermi level and the POM LUMO).

The above results expressed quantitatively the general idea (already presented before) that POM anions can be considered as a group of regularly arranged semiconducting islands that were placed between the two Au electrodes. It is clear that increased presence of POM anions favored conductivity of the studied device; this was clearly revealed in the lower values of  $E_a$ ,  $T_t$  and  $\phi$  obtained in the 2L junctions.



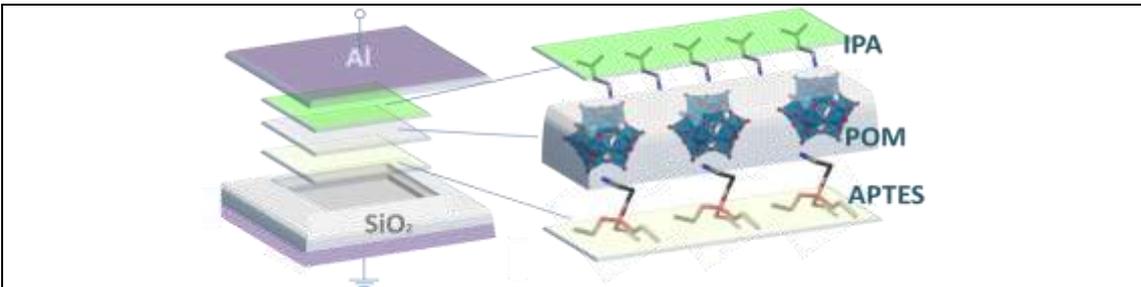


**Fig. 2.** Fowler-Nordheim representation of th100nm-distant junctions for the single and bilayer materials. The solid green fitting lines are used to produce the tunneling barrier values referenced in text

**2. Utilization of tungsten polyoxometalate molecules (POMs) as active nodes for dynamic carrier exchange in hybrid MIS structures**

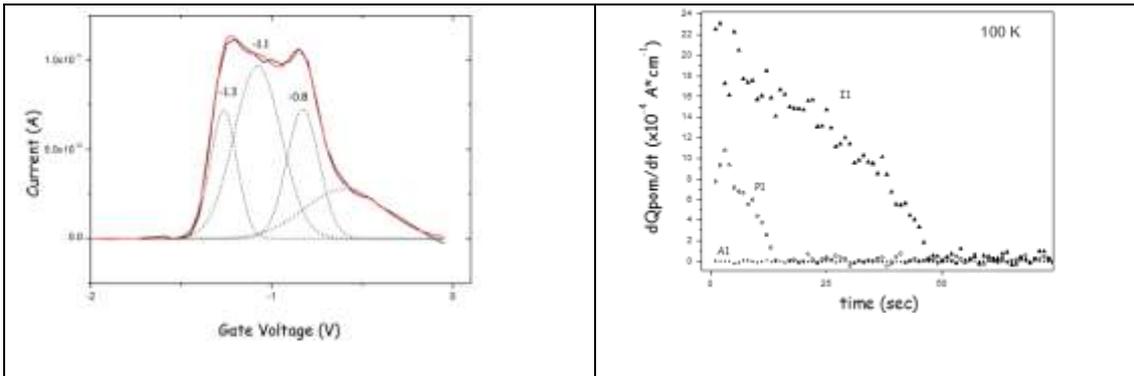
A. Balliou, A. M. Douvas, P. Normand, P. Argitis, N. Glezos

In this work we study the utilization of tungsten-polyoxometalate molecules (POM) as active nodes for potential switching and/or fast writing memory applications. The active molecules are being integrated in hybrid-layer MIS structures, which serve as an investigation/optimization precursor towards the design of more sophisticated devices.



**Fig.4.** Planar MIS structure and incorporated molecular layers in the active region. From bottom to top: APTES (3-aminopropyl triethoxysilane) , forming an ordered molecular template on SiO2, POM anion cage molecules self-arranged on top via electrostatic interactions in aqueous environment and IPA (isopentylamine) oligolayer serving as passivation coating, gate dielectric and oxidation prohibitor from the metal gate.

The charging ability as well as the electronic structure of the molecular layer is probed by means of electrical characterization, namely: capacitance-voltage characteristics, quasi-static and dynamic current-voltage measurements, as well as transient capacitance measurements under step voltage polarization. The measurements are performed in a wide range of temperatures (80K-300K) in order to discriminate between the different transport mechanisms.



**Fig. 5.** Peak analysis of a typical peak of the POM islands' charging current at  $T=240$  K resulting in a state triplet. The measurements were performed in dark faraday cage under ramp rate voltage excitation (dynamic type excitation) and forward sweep. The ramp rate was set at  $0.25$  V/s.

**Fig. 6.** Rate of change of the space-charge region generated charge versus time, for the molecular layer incorporating MIS devices in all fabrication steps in  $T=100$  K. The  $Q_{pom}$  quantity in the y axis is the charge that is being trapped and de-trapped within the molecular epilayers. Curve A1 concerns only APTES functionalization, P1 is the device after POM incorporation and I1 is the final device after passivation of the functional POM layer with the IPA molecular oligolayer.

It is argued that the transient current peaks observed are manifestations of dynamic carrier exchange between the gate and the POM nano-islands, while the transient  $C(t)$  curves under conditions of molecular charging can supply information, via a modified Zerst equation, for the rate of change of the charge that is being trapped and de-trapped within the molecular epilayer.

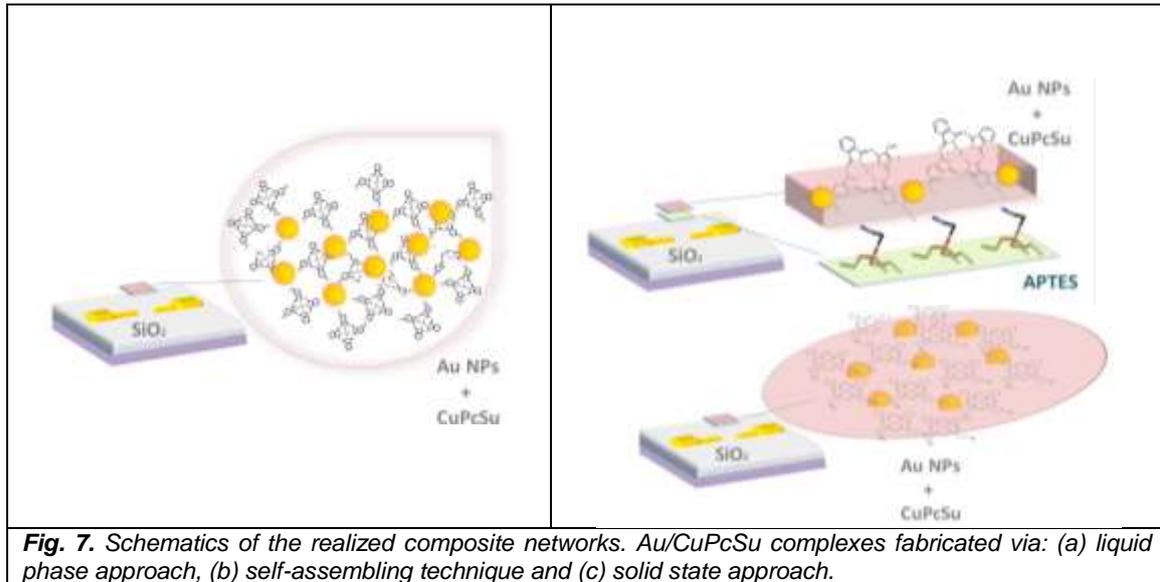
The presence of the charged POM epilayer is expected to reduce the minority-carrier lifetime ( $\tau_{geff}$ ) due to the net increase of the recombination rate that is introduced from the POM-controlled displacement current. This effect can be advantageous in high-speed applications when a short lifetime to achieve fast charge storage time is a desirable feature.

Structural characterization via surface and cross sectional SEM topographies as well as AFM, SE, UV and FTIR spectroscopies facilitate the extraction of accurate electronic structure characteristics and open the path for the design of new devices with on-demand- tuning of their interfacial properties via controlled modification of the POM layer.

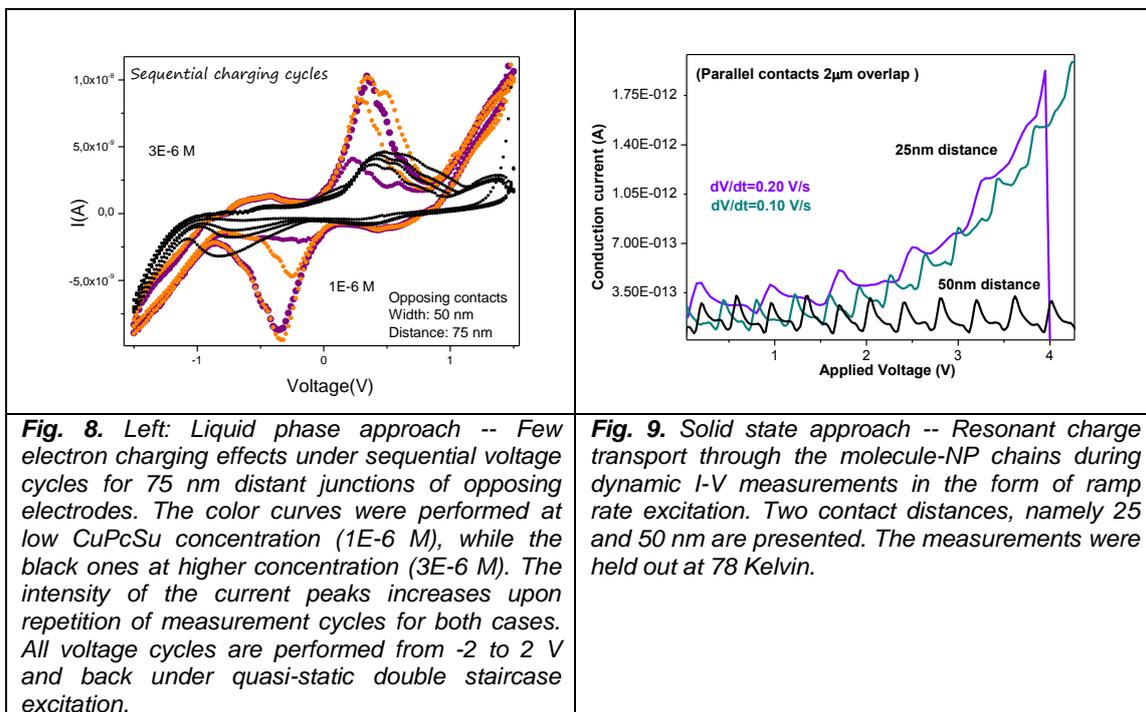
### 3. Formation of Au nano-particle/CuPcSu ligands complex networks

**A. Balliou, S. Kazim, N.Glezos, J.Pfleger**

We fabricated planar devices based on nano-dimensional components, namely semiconducting conjugated oligomers and metal nanoparticles (NPs) and studied their electronic transport properties. Spherical gold (Au) NPs were linked by means of copper 3-diethylamino-1-propylsulphonamide sulfonic acid substituted phthalocyanine (CuPcSu) molecules to form a network confined between Au nanodistant electrodes. The fabrication of the network was realized via three different approaches: (a) liquid phase approach: Au NPs (av. diameter  $\sim 17$  nm) prepared as hydrosol via chemical reduction were functionalized with CuPcSu and drop cast on the substrate, (b) self-assembling technique: The  $\text{SiO}_2$  surface was chemically modified with a stable, positively charged template molecule (3-aminopropyl triethoxysilane, APTES) and the CuPcSu surface-functionalized Au NPs were subsequently adsorbed on the surface driven by electrostatic-type forces and (c) solid state approach: Ultra-fine (av. diam.  $\sim 1.5$  nm) Au NPs were prepared by thermal evaporation and inter-particle gaps were filled with CuPcSu ligands in a subsequent step. The above systems were confined between Au nano-electrodes with inter-electrode distances of 25, 50 and 75 nm fabricated on n-Si/ $\text{SiO}_2$  substrate via e-beam lithography.



The conduction mechanisms of these 2D systems were studied using quasi-static and dynamic voltage-current measurements in the 78K-300K temperature range. It was possible to discriminate between various transport mechanisms typical for such structures (i.e. tunnelling and hopping), to evaluate conduction thresholds and to reveal charging effects involving few electrons, at lower temperatures. The interpretation was assisted by AFM, FE-SEM and TEM imaging techniques. The system of evaporated NPs (case c) resulted in formation of closely-packed linked NP networks and yielded the best stability and results' reproducibility.



## **PROJECT OUTPUT in 2012**

### **Conference Presentations**

1. *On the Electrical Behavior of Planar Tungsten Polyoxometalate Self-Assembled Mono- and Bi-Layer Junctions*,  
D. Velessiotis, A. M. Douvas, P. Dimitrakis, P. Argitis, N. Glezos  
Frontiers in Electronic Materials (FEM 2012), June 17 to 20, Aachen, Germany
2. *Charging Effects and Electron Transport Phenomena associated with the redox properties of self-assembled Polyoxometalate Molecules*,  
A.Balliou, A.Douvas , D.Velessiotis, V.Ioannou-Sougleridis, P.Normand, P.Argitis, N.Glezos,  
Frontiers in Electronic Materials (FEM 2012), June 17 to 20, Aachen, Germany
3. *Study of the transport mechanisms and charging effects in nanodevices based on inorganic polyoxometalate molecules*,  
38<sup>th</sup> International Conference on Micro and Nano Engineering (MNE 2012), September 16 to 20, Toulouse, France
4. *Electronic Conduction Mechanisms in Polyoxometalate Seld-Assembled Planar Molecular Junctions*,  
D. Velessiotis, A. M. Douvas, P. Dimitrakis, P. Argitis, N. Glezos  
Materials Today Virtual Conference: Nanotechnology, December 11-13, <http://www.materialstoday.com/virtualconference/materials-today-virtual-conference-nanotechnology>