

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.

Funding:

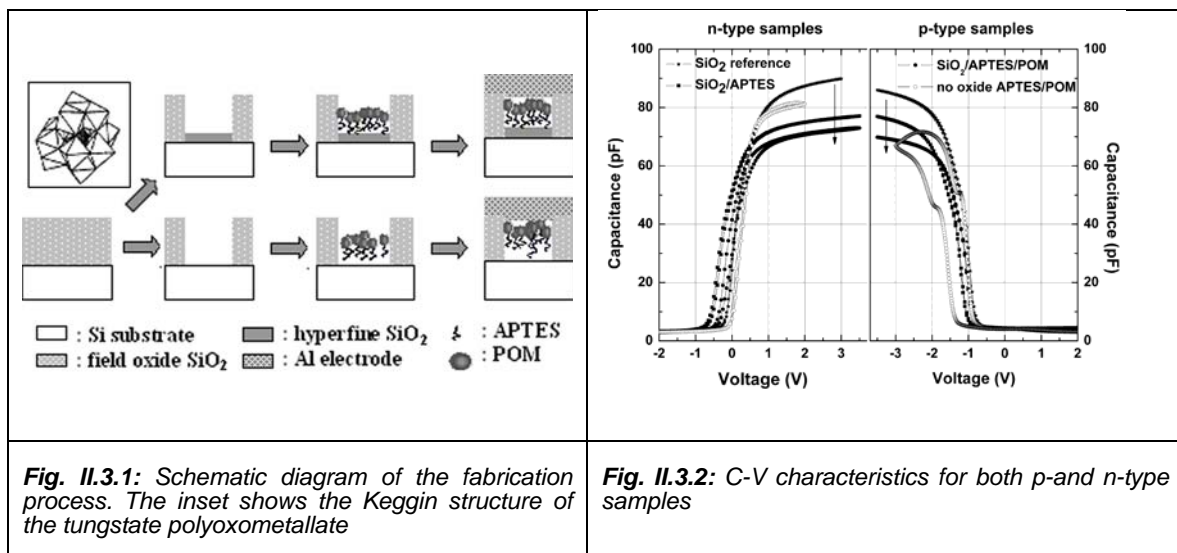
- NMP STREP TASNANO, 1/1/2005-30/7/2008, Contract N° 516865
- EU RTN project Uninanocups, 1/1/2004-31/12/2007, Contract N° MRTN-CT- 2003-7504233

RESEARCH RESULTS

A. Vertical devices of Self-assembled Hybrid Organic/inorganic Monolayers

M. Douvas, E.Makarona, D.Velessiotis, E.Kapetanakis, N.Glezos, P.Argitis, P.Normand

We worked on a new approach to fabricate capacitor-like metal-insulator-semiconductor (MIS) devices the functional part of which is made of hybrid organic/inorganic self-assembled monolayers (SAMs) of tungsten polyoxometalates (POMs). This approach consists in the combination of the layer-by-layer (LBL) method for the growth of the molecular layers and a CMOS-compatible process, and results in functional, large active area devices of up to $300 \times 300 \mu\text{m}^2$ with high yield (>95%). The LBL method, which in essence is based on the successive adsorption of oppositely charged molecules from a solution on a surface, was chosen because of its simplicity, effectiveness, and its ability to produce mechanically and chemically stable molecular layers regardless of the chosen substrate. POMs of the Keggin structure were opted as the functional molecules because of their unique combination of properties: they are stable molecules of well-defined structure and fixed size ($\sim 1\text{nm}$), they can accept one or more electrons without significant structural changes, and these electrons can be delocalized over several metal centers of their framework. In other words, POMs can be viewed as zero-dimensional n-type semiconductors with low charging energies (from the Fermi level of Al or Au electrode to their lowest unoccupied molecular orbital, LUMO, level) in the range of 0.1-0.4eV, i.e. with discrete electronic levels at room temperature.



From the 1MHz C-Vs of both n- and p-type devices it can be established that, as expected, the capacitance of the devices decreased with the addition of each SAM. The values of the effective thickness of the layers were estimated both through the C-Vs and the corresponding Maserjian plots, and were in good agreement with the actual sizes of the molecules. Fits showed that the APTES layer acts as a dielectric of an effective constant $\epsilon \sim 3.57 \times 10^{-11} \text{ F/m}$ (a value close to the dielectric constant of SiO_2) assuming that the length of the molecules is $\sim 1\text{nm}$. Furthermore, the dielectric behavior of the APTES SAM was further substantiated by the I-Vs under forward bias, where a drop in conductivity was observed after the deposition of the APTES SAM atop the SiO_2 . Hysteresis phenomena appeared for the devices deprived of the gate dielectric, and they were especially pronounced for the p-type samples. In detail, the insertion of the POM SAM resulted in the injection of charge (electrons) from the substrate and their storage in the available states of the POMs.

STM measurements were also performed on n-type substrates to further investigate the transport mechanisms. The samples were structurally similar to the devices so that a direct qualitative comparison would be feasible. Specifically, n-type Si wafers with Al back gate were subjected to the LBL method in order to obtain either the APTES or the APTES/POM layer on

top of them. Current Spectroscopy measurements were then performed, using a NT-MDT Solver Pro® Scanning Probe Microscope (SPM) equipped with a PtIr tip in STM mode. The resulting I-V curves showed increased conductivity upon the addition of POMs -a similar behavior to the devices'- supporting that the transport mechanisms remain the same both on microscopic and on the device level, and advocating to the fact that these mechanisms are dictated by the POM's properties.

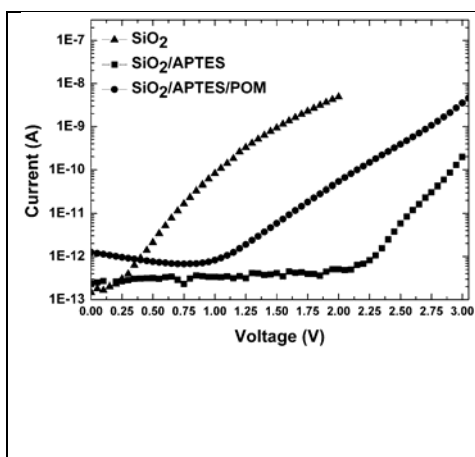


Fig. II.3.3: I-V characteristics for n-type devices. The increase in conductivity for the n-type device including POMs is obvious.

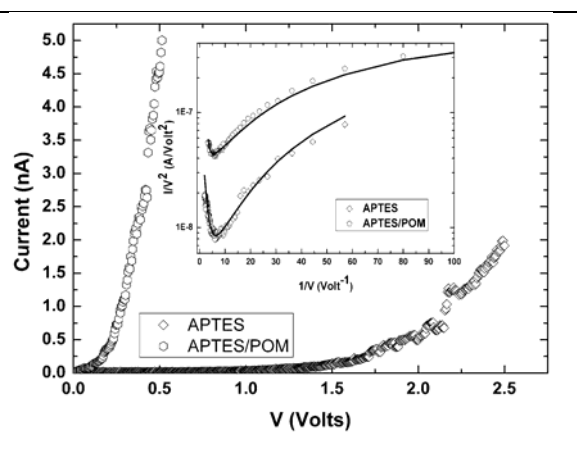


Fig. II.3.4: STM curves for a SAM of APTES (diamonds) and APTES/POM (hexagons) on n-type Si. There is a clear increase of the conductivity with the insertion of POMs. Inset: F-N representation of the I-V curves. Solid lines are theoretical fits according to Simmons's model.

B. Study of the transport and charge storage properties of cyclodextrin nanowires for molecular devices

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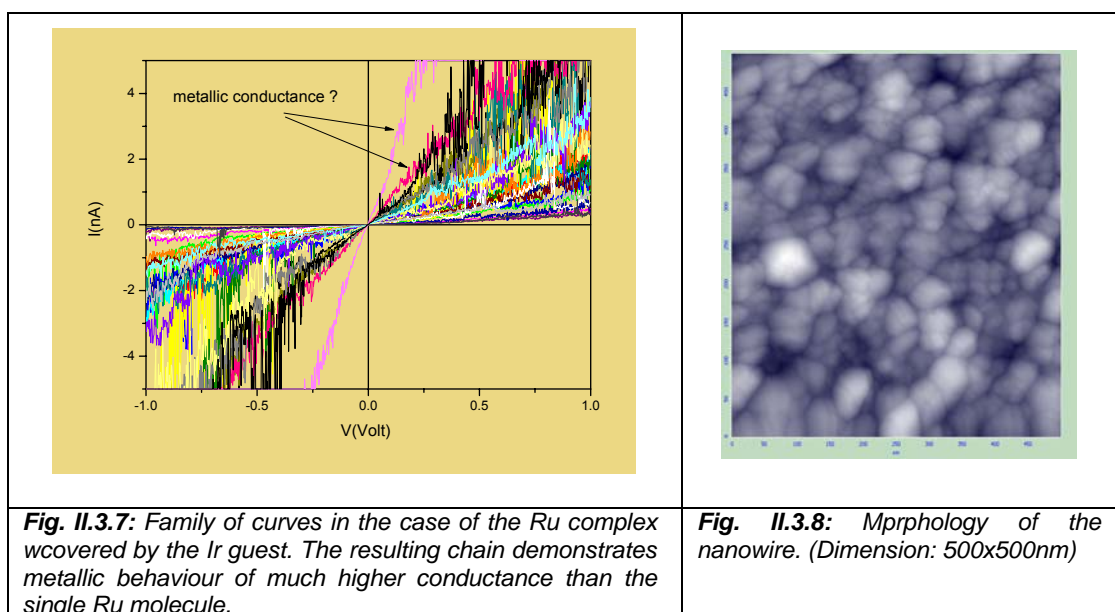
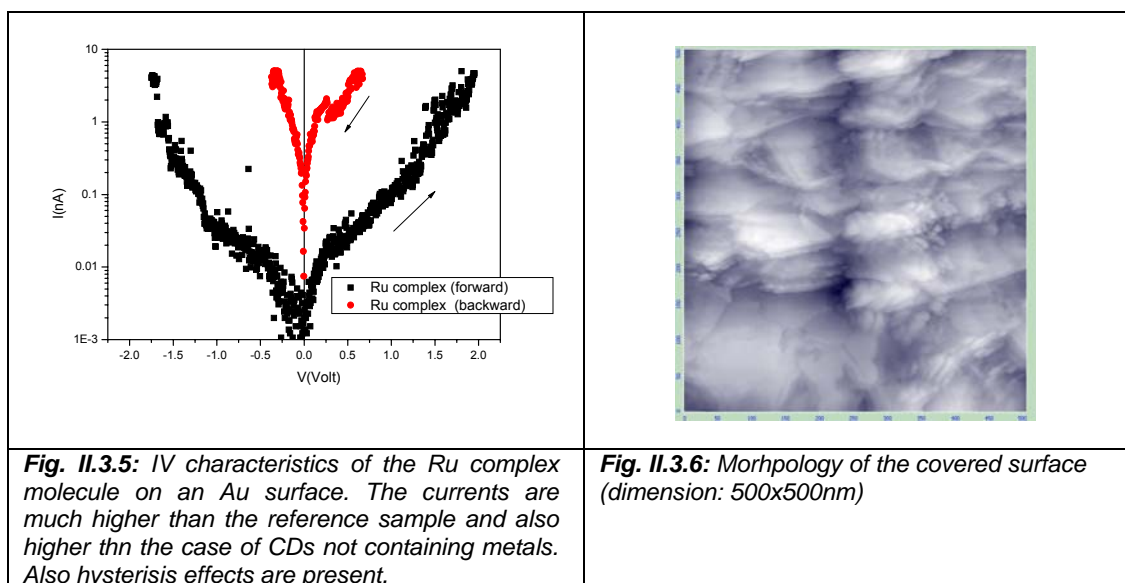
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²Marie Curie Post Doc (Dec 2006- Dec 2007)

*b*₁ Study of cyclodextrin nanowires using STM spectroscopy

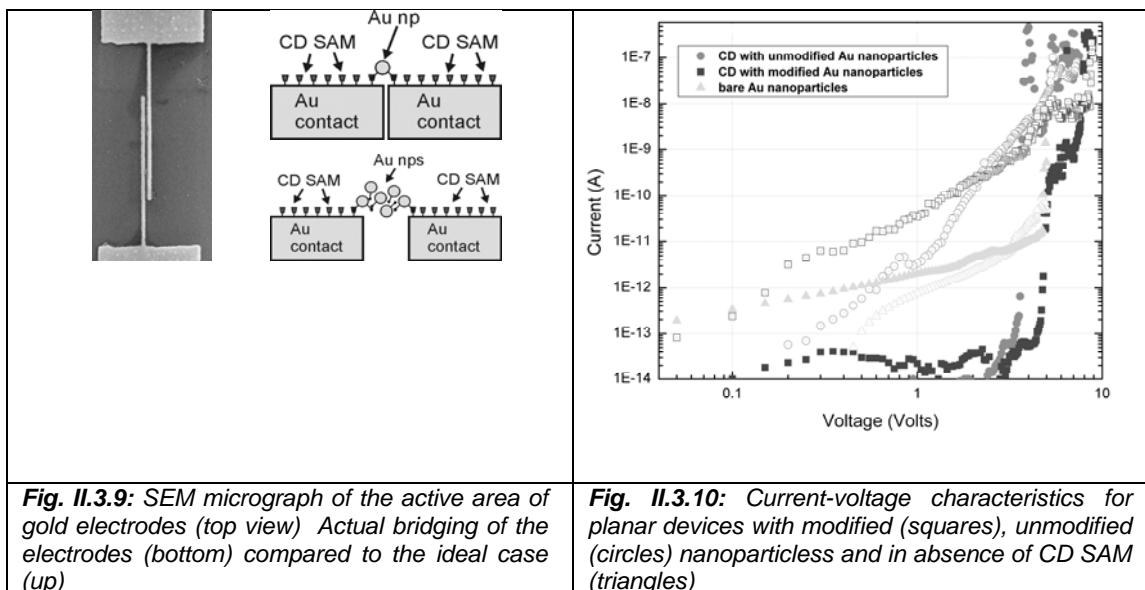
The aim of this work was to evaluate the potential of CD monolayers to be used as active components in nanoelectronic devices. Specially we were interested in the transport properties of molecular nanowires based on CD and guests containing metals. STM measurements were performed in a NT-MDT P47Pro® machine with the purpose of obtaining information about the coverage of gold surface and the electrical behaviour of the SAMs. The work was focused on the transport properties of composite nanowires containing metals. Alpha-THIO, Alpha-Ru, dM-beta-THIO and gamma-THIO were used as hosts while a Fe complex was used as a guest molecule for alpha-CDs and an Ir complex for beta-CDs.

Good coverage of the surface was established, especially in the DMBTHIO case. Current-voltage spectroscopy measurement revealed that only the low voltage tunnelling regime is present in the cases of ATHIO and DMBTHIO, with low hysteresis presented. This hysteresis loop was symmetric for the DMBTHIO case and non-symmetric for ATHIO. In aRuCD samples, a clear hysteresis loop was observed and attributed to the presence of the metallic atom in the molecular structure: electric charge was trapped by the molecule during the first voltage scan (from positive to negative values) and released during the second scan. The presence of a Fowler-Nordheim tunnelling region in this case was also indicative of the presence of Ru atom. The Au reference sample showed no such charging effects.



b₂ Planar nanodevices containing CDs bridged with Au nanoparticles

A first attempt to fabricate and electrically connect CD nanowires was made. The final structures consisted of back-to-back molecular diodes connected to planar gold nanoelectrodes through CD guest-host chemistry. Intermediate functionalised gold nanoparticles served as a bridges for the nanowires. Three different compounds were studied: a thiolated alpha-CD (ATHIO), a thiolated beta-CD (DMBTHIO) and an alpha-CD (aRuCD) that was modified by an organic complex (ending with S), which contained Ru (II). On the other hand, if one wished to construct back-to-back diodes, using SAM and Au nanoparticles, he should keep the **nanoparticles** still in their position. This could be done by modifying the nanoparticles with a suitable group, so that they stick to the SAM. In our case, modification was made by an adamantyl thiol molecule, which is both a CD guest (the adamantyl group) and can also be attached to gold nanoparticles (thiol group).



Planar gold electrodes of sub-100nm distances were used for the electrical measurements, while pure gold substrates were used for the STM study. The electrode fabrication was achieved by electron-beam lithography and a conventional lift-off process on Si wafer covered by a 200nm SiO₂. CD SAMs were grown on the surface (either pure gold or electrodes) through immersion of the sample to a solution containing the CD molecules. Attachment of gold nanoparticles to the CDs was achieved by a second immersion step.

C. Low voltage operating OFETs based on solution processed metal phthalocyanines

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We investigated the class of sodium salts of sulfonated metal phthalocyanines (MePCsXs) as candidates for p-type channels in organic transistors. These materials are selected because of their enhanced solubility compared to their non-sulfonated counterparts. MePCsXs were either synthesized (Me = Ni, Co, Zn or Al), or purchased by Aldrich Co. (Me = Cu). The comparison among phthalocyanines under study is based on their electric behavior depending on the type of the central metal and the presence of substituents. The objective is to select the type of the material and the film preparation process with the optimal performance of electrical parameters. The semiconducting layers of MePCsX were prepared by spincoating at room temperature. The samples were dried at 50°C for 20 minutes. MePC based OFETs which served as a reference were fabricated by vacuum evaporation of metal phthalocyanine thin films (Me = Ni, purchased by Aldrich Co., or Me = Co, synthesized, see Fig. 1a) in high vacuum onto the substrates.

The sodium salts of sulfonated metal phthalocyanine were all synthesized from the non-substituted ones. The number of substituents produced in the synthesis process depends on the oleum concentration, temperature and duration of the reaction. Mono-, di-, tri- and tetra-sulfonated species may be separated using high pressure liquid chromatography analysis (TLC).

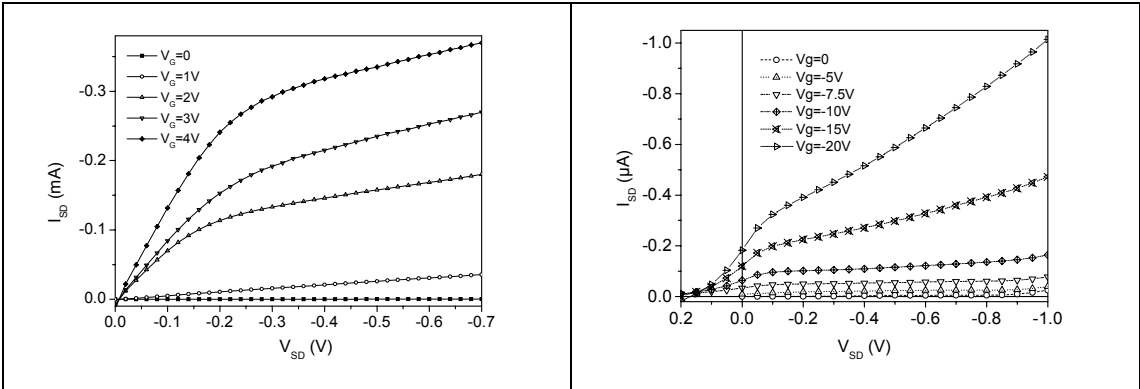


Fig. II.3.11: Dependence of drain current on the drain voltage of an OFET with 50 nm NiPCS_x layer, W/L ratio of 23275 and 42 nm thick SiO₂ oxide dielectric, deposited by spin-coating and annealed at 50°C: (a) NiPCS_{2.4} and (b) NiPCS₄.

The ion movement which results in the formation of an additional field was studied by current vs time measurements for a given gate biasing. This allowed the determination of the total charge shifted to the interface.

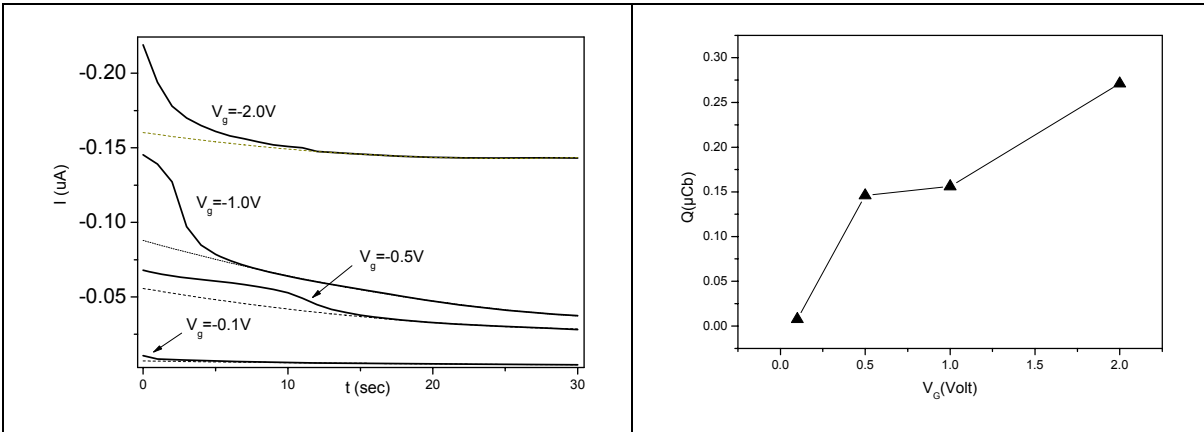


Fig. II.3.12: Determination of the charge transfer in the case of the NiPC. The charge shift is responsible for the low voltage operation of the device.

PROJECT OUTPUT IN 2007

Publications in International Journals and Reviews

1. "Some new nickel 1,2-dichalcogenolene complexes as single-component semiconductors", Papavassiliou, G.C.a , Anyfantis, G.C.a , Steele, B.R.b , Terzis, A.c , Raptopoulou, C.P.c , Tatakis, G.d , Chaidogiannos, G.d , Glezos, N.d , Weng, Y.e , Yoshino, H.e , Murata, K.e, Zeitschrift fur Naturforschung - Section B Journal of Chemical Sciences ,Volume 62, Issue 5, May 2007, Pages 679-684
2. "Soluble Phthalocyanines: Perspective Materials for Electronics", S. Nespurek, G. Chaidogiannos, N.Glezos, G.Wang,S. Bohm, J.Rakusan, M.Karaskova, Mol. Cryst. Liq. Cryst., Vol. 468, pp. 3=[355]-21=[373], 2007

Papers in Conference Proceedings

1. "Evaluation of sulfonated metal phthalocyanines for OTFT applications", G.Chaidogiannos, N.Glezos, K.Yannakopoulou, I.M.Mavridi, S. Kennou, F. Petraki, S. Nespurek, Rakusan, M. Karaskova, ICOE, Eindhoven, June , Oral presentation
2. "Charging Effects in Hybrid Structures Based on Polyoxometalate Layers for Molecular Memory Applications", E. Makarona, A.M. Douvas, E.Kapetanakis, D.Velessiotis, P.Argitis, P.Normand, N.Glezos, J.Mielczarski, E. Mielczarski T.Gotszalk , M. Woszczyna, MRS Boston, November, Oral presentation
3. "Soluble Substituted Phthalocyanines for OFET Applications", G. Chaidogiannos, N. Glezos, S. Nešpůrek, NN Thessaloniki, July, Oral presentation
4. "Molecular Nanodevices based on Functionalized Cyclodextrins", Dimitrios Velessiotis, Davide Maffeo, Eleni Makarona, Viswanathan Chinnuswamy, Constantinos Milios, Konstantina Yannakopoulou, Irene Mavridis, Zoe Pikramenou and Nikos Glezos, MMN Athens, November, Oral presentation
5. "Vertical Devices of Self-assembled Hybrid Organic/inorganic Monolayers based on Tungsten Polyoxometalates: a step towards molecular electronic devices", E.Makarona, E.Kapetanakis, D.Velessiotis, A.Douvas, P.Argitis, P. Normand, T.Gotszalk, M. Woszczyna, N.Glezos, MNE, Copenhagen, September, Oral presentation

Conference Presentations

1. "Applications of water soluble metal containing phthalocyanines in organic transistors", G.Chaidogiannos, F.Petraki, N.Glezos S.Kennou and S.Nespurek, XXIII Panhellenic Conference of Solid State Physics, September 2007, Athens

PhD Thesis

1. "Applications of oligomeric crystal materials in Organic Field Effect Transistors" G.Chaidogiannos, Faculty of Electrical and Computer Engineering NTUA, December 2007