

**NATIONAL CENTER FOR SCIENTIFIC  
RESEARCH "DEMOKRITOS"**

**INSTITUTE OF PHYSICAL CHEMISTRY**  
<http://ipc.chem.demokritos.gr/>

**Scientific Report 2008**

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## Introduction

The primary objective of the Institute of Physical Chemistry (IPC) of the National Center for Scientific Research "Demokritos" (NCSR "D") is the fundamental research in physical chemistry which is pursued by both experimental and theoretical methods. Current research activities focus on nanomaterials, functional molecular and supramolecular materials, biomolecules and natural products, but also on equilibrium, transport, catalytic and photoinduced processes as well as environmental technologies and renewable energy issues. The Institute also provides specialized services to the private sector and public organizations, particularly in relation to environmental pollutants analyses, materials characterization, water quality assessment, and glassblowing work.

The year 2008 was characterized by the intensification of the Institute's effort to achieve a series of research and technological objectives, via the implementation of a research and growth policy based on concrete strategy and clearly determined goals.

The main axes of the Institutes research policy aim at establishing it as a National, but also a European, Center of Excellence in the field of physical chemistry and consist of:

- Implementation of high level competitive research
- Converging research activities focusing on topical subjects of both fundamental interest and technological applications in the field of Physical Chemistry
- Attraction of new high-quality research staff, including post-doctoral fellows and PhD students
- Establishment of long term scientific collaboration with research centers and universities (in Greece and abroad)
- Increase the Institute's income from competitive projects
- Improvement of research infrastructure (including research facilities and buildings)

The performance of IPC research groups for 2008 (papers in international journals and conference proceedings, citations, patents, PhD theses and external funding) is remarkable. More specifically, about 120 articles were published in international refereed journals of high impact factor, the research work of the Institute received more from 1900 citations (excluding self-citations), 6 patents were submitted and 3 international conferences were organized. Additionally, IPC presented intense educational activity as indicated by the organization of 3 summer schools, the coordination of postgraduate courses (COSA network) as well as the completion of 6 PhD, 4 Master and 5 diploma theses.

IPC has attracted significant external funding. Currently, 8 European projects are under implementation in the frame of FP6, 2 of them being Networks of Excellence ([NoE]) (one coordinated by IPC). The Institute has also put substantial effort to actively participate in new research projects. The initial participation in FP7 was particularly successful, as already 6 new proposals have been approved and the corresponding projects are either running or under negotiation. The first results are very positive and greater success is expected in the near future, from both European and Greek financing sources.

Particular emphasis was given in the preparation of the Institute for the imminent evaluation of Research Centres (organized by the General Secretariat of Research

and Technology, GSRT). In this respect, restructuring of the Institute's Research Programs is currently underway. This is coupled with the establishment of a modern and functional organogramme that is anticipated to highlight the Institute's uniqueness, but also to strengthen the collaboration between the different IPC research groups and thus allow for optimal exploitation of its research potential.

Considerable effort and capital was also invested in the development of the Institute's infrastructure. A completely new research facility for the assessment of nanomaterials' hydrogen storage capacity (unique in Greece) was established. New and modern systems (including SEM, new AFM, Electrochemical Impedance, Intensity Modulated Photocurrent and Photovoltage Spectroscopies) were acquired. The laboratory of Characterization of Molecular and Supramolecular Systems infrastructure was upgraded with the integration of a Raman Spectrometer and the improved of the old AFM microscope (Nanoscope III of Digital Instruments). The accreditation of the Laboratory of Environmental Analyses for "Determination of polyaromatic hydrocarbons in potable and surface waters" (the only accredited analytic unit in Greece) was completed.

The detailed activity report that follows underlines the ascendant course of IPC . The data presented confirm the production of important research results, awarding the hard effort of the personnel, despite the fact that this work is many times carried out under objectively difficult conditions.

February 2009,

Dr. Polycarpos FALARAS, Director

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## **Scientific Programmes**

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1. Structural and Supramolecular Chemistry
2. Nanomaterials of Organized Supramolecular Structure
3. Molecular Thermodynamics and Modeling of Materials
4. Luminescence Laboratory – Development of Novel Functionalized Materials for Analytical and Bioanalytical Applications
5. Transport Phenomena in Polymers
6. Statistical Mechanics and Non-Linear Dynamics
7. Molecular Computational Chemistry

### **2<sup>nd</sup> Scientific Programme: Nanochemistry, Environmental Friendly Technologies – Energy**.....30

1. Materials & Membranes for Environmental Separations
2. Photoredox Conversion and Storage of Solar Energy – Development of Innovative Functional Materials for Energy and Environmental Applications
3. Catalytic-Photocatalytic Processes (Solar Energy-Environment)
4. Electronic Spectroscopy: Application to Supramolecules and Nanostructures
5. Isotope Hydrology

### **3<sup>rd</sup> Scientific Programme: Chemical Biology**.....49

1. Natural Products Synthesis and Bioorganic Chemistry
2. Chemical Biology of Natural Products and Designed Molecules

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1. Environmental Analysis
2. Isotopic Analysis, Radiocarbon Dating, and Radon Measurements
3. Other Service Laboratories NMR, Macromolecular Crystallography Lab (X-RAY), Elemental Analyzer, AFM, FT-IR, Thermal analysis lab, Micro raman

### **Education Activities**.....63

## **Institute of Physical Chemistry 2008 Performance Indicators**

<b>Publications (International Journals)</b>	<b>85+39*</b>
<b>Conference Proceedings/ Abstracts</b>	<b>84</b>
<b>Citations</b>	<b>1905</b>
<b>Technical Reports</b>	<b>4</b>
<b>Invited Lectures</b>	<b>16</b>
<b>Patents</b>	<b>3</b>
<b>PhD Dissertations</b>	<b>8</b>
<b>Master's Theses</b>	<b>5</b>

**\* in press**

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# **1<sup>st</sup> Scientific Programme**

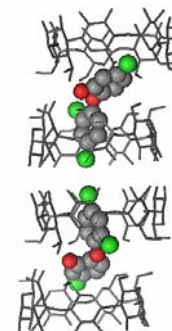
## **Molecular & Supramolecular Nanofunctional Materials**

# STRUCTURAL AND SUPRAMOLECULAR CHEMISTRY

## Research Objectives/Activities

The activities of the laboratory involve the structure determination and the intermolecular interactions of supramolecular systems comprising cyclodextrins (CDs), proteins, nucleic acids and bioactive compounds. Specifically, the areas of research are:

1. *Host-guest systems.* We study the inclusion of biologically active molecules and model compounds in the CD cavity and determine the structure and detailed interactions using NMR in aqueous solutions and/or X-ray crystallography in the crystalline state. Thus, we gain insight in host-guest recognition, non-bonding interactions, self-assembly, chiral discrimination and dynamics (when possible). Besides the fundamental understanding, applications such as controlled release, specific binding and drug formulations are of interest.

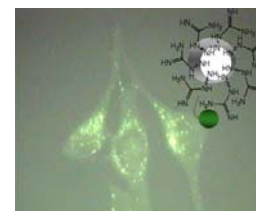


*Structure of  $\beta$ -Cyclodextrin-triclosan complex*

2. *Synthesis of novel, functional cyclodextrin derivatives for biomedical applications.* The derivatives: (a) Complex with small bio-active molecules, e.g. nucleotides. (b) Interact with biological macromolecules, such as DNA, RNA, proteins. (c) Penetrate cell membranes. (d) Complex with metal ions i.e. Gd(III) (new contrast agents for imaging). (e) Bind to each other non-covalently and form biomimetic structures.

3. *Synthesis of novel, functional cyclodextrin derivatives for nanotechnology applications.* The derivatives: (a) Attach onto surfaces (i.e. on Au). (b) When deposited on Si/SiO<sub>2</sub> surfaces form nanostructures in 2D or (c) become the substrate for 2D nanostructures for the electron or energy transfer at specific directions.

4. *Macromolecular Crystallography.* (a) Structure determination of natural and mutated members of the new family of 2[4Fe4S] ferredoxins from selected pathogenic bacteria. (b) Structure determination of complexes of DNA and RNA with modified cyclodextrins. (c) Structure determination of muscle proteins and proteins that synthesize or degrade silica.



*Fluorescent cyclodextrins penetrate cell membranes*

## Publications

- 1.N. Mourtzis, M. Paravatou, I. M. Mavridis, M. L. Roberts, K. Yannakopoulou, "Synthesis, characterisation, and remarkable biological properties of cyclodextrins bearing guanidino-alkylamino and aminoalkylamino groups on their primary side", *Chem. Eur. J.* **2008**, *14*, 4188-4200.
- 2.A. Paulidou, D. Maffeo, K. Yannakopoulou, I. M. Mavridis, "Crystal structure of the inclusion complex of the antibacterial agent Triclosan in  $\beta$ -cyclodextrin and NMR study of its molecular encapsulation in positively and negatively charged cyclodextrins", *Carbohydr. Res.* **2008**, *343*, 2634-2640.
- 3.D. Velessiotis, D. Maffeo, E. Makarona, C. Viswanathan, K. Yannakopoulou, I. Mavridis, Z. Pikramenou, and N. Glezos, Glezos, "Molecular Nanodevices based on Functionalized Cyclodextrins", *Physica Status Solidi A*, **2008**, *205*, (11), 2532-2535.
- 4.I. Mourtzinou, D. P. Makris, K. Yannakopoulou, N. Kalogeropoulos, I. Michali V. T. Karathanos "Thermal stability of *Hibiscus sabdariffa* L. anthocyanins in the presence of  $\beta$ -cyclodextrin " *J. Agric. Food Chem.* **2008**, *56*, 10303-10310.
5. N. E. Chayen, E. Saridakis "Protein crystallization: from purified protein to diffraction-quality crystal", *Nature Methods* **2008**, *5*, 147-153.
- 6.E. Saridakis, N. E. Chayen, "Towards a 'universal' nucleant for protein crystallization" *Trends Biotechnol. in print, available online* **2008**. [Invited review](#)



7. E. Hadjoudis, S. D. Chatziefthimiou, I. M. Mavridis, "Anils: Photochromism by H-transfer" *Current Org. Chem.* **2009**, 13, issue 3, in press. [Invited review](#)
8. C. Aggelidou, I. M. Mavridis, K. Yannakopoulou, "Binding of nucleotides and nucleosides to per(6-guanidino-6-deoxy)cyclodextrins in solution», *Eur. J. Org. Chem.*, in press.
9. E. Saridakis, P. Giastas, G. Efthymiou, V. Thoma, J.-M. Moulis, P. Kyritsis, I. M. Mavridis "Insight into the protein and solvent contributions to the reduction potentials of [4Fe-4S]<sup>2+/+</sup> clusters: Crystal structures of the *Allochromatium vinosum* ferredoxin variants C57A and V13G and the homologous *Escherichia coli* ferredoxin" *J. Biol. Inorg. Chem.*, in press.

## Conferences

1. K. Yannakopoulou, V. Karginov, N. Mourtzis, C. Aggelidou, I. M. Mavridis "Evaluation of modified cyclodextrins as Inhibitors of Anthrax toxins", *4<sup>th</sup> Central European Conference Chemistry towards Biology*, September 8-11, **2008**, Dobogoko, Hungary. *Oral presentation.*
2. S. D. Chatziefthimiou, D. Svergun, I. M. Mavridis, M. Wilmanns, N. Pinotsis "The structure of the 360 Å long C-terminal muscle filament of myomesin, derived from a combined crystallographic and Small-Angle X-ray scattering analysis", *4<sup>th</sup> Conference Hellenic Crystallographic Association*, The National Hellenic Research Foundation, September 26-27 **2008**, Athens, Greece. *Oral presentation.*
3. E. Saridakis, P. Giastas, G. Efthymiou, V. Thoma, P. Kyritsis, J.-M. Moulis, I. M. Mavridis "High resolution X-ray structures of 2[4Fe-4S] ferredoxins: Influence of the protein and solvent environment on the reduction potential of [4Fe-4S] clusters", *4<sup>th</sup> Conference Hellenic Crystallographic Association*, The National Hellenic Research Foundation, September 26-27 **2008**, Athens, Greece. *Oral presentation.*
4. N. E. Chayen, E. Saridakis, R. El-Bahar, S. Stolyarova, Y. Nemirovsky "The application of nanopores for protein crystallization", *International Conference 'Nanoscale Phenomena and Structures in Bulk and Surface Phases'*, Sofia, Bulgaria, 26<sup>th</sup> Feb – 2nd March, **2008**. *Oral presentation.*
5. S. D. Chatziefthimiou, J. A. Zoidberg, D. I. Svergun, I. M. Mavridis, M. Wilmanns, N. Pinotsis, "The structure of the 360 Å long C-terminal muscle filament of myomesin, derived from a combined crystallographic and small-Angle X-ray scattering analysis" XXI Congress of the Int. Union of Crystallography, Osaka, Japan, Aug. 23-31, **2008**. *Poster presentation.*
6. A. Paulidou, K. Yannakopoulou, I. M. Mavridis "Inclusion complexes of β-cyclodextrin with sulfonyl urea hypoglycemic drugs", *4<sup>th</sup> Conference Hellenic Crystallographic Association*, The National Hellenic Research Foundation, September 26-27 **2008**, Athens, Greece. *Poster presentation.*
7. K. Fotiadou, K. Yannakopoulou "Supramolecular assembly of cyclodextrins through carboxylate-guanidinium pairs", *2<sup>nd</sup> European Chemistry Congress*, September 16-20, **2008**, Torino, Italy. *Poster presentation.*
8. M. Lampropoulou, K. Yannakopoulou "Novel sugar-functionalised cyclodextrins and studies on molecular inclusion of model compounds", *2<sup>nd</sup> European Chemistry Congress*, September 16-20, **2008**, Torino, Italy. *Poster presentation.*
9. P. Giastas,<sup>1</sup> G. Efthymiou, P. Kyritsis, J.-M. Moulis, I. M. Mavridis "The merohedrally twin structure of the *Escherichia coli* ferredoxin at 1.65Å", *4<sup>th</sup> Conference Hellenic Crystallographic Association*, The National Hellenic Research Foundation, September 26-27 **2008**, Athens, Greece. *Poster presentation.*
10. N. Kalogeropoulos, I. Mourtzinis, K. Yannakopoulou, A. Gioxari, A. Chiou, V. T. Karathanos "Encapsulation of *Hypericum perforatum* (St John's wort) methanolic extract in beta-cyclodextrin", *Planta Medica* 2008, 74 (9): 1095-1095: *7th Joint Meeting of AFERP, ASP, GA, PSE & SIF*, Athens, Greece, August, 3rd - 8<sup>th</sup>, **2008**. *Poster presentation.*
11. D. Maffeo, M. Woszczyna, D. Velessiotis, V. Chinnuswamy, K. Yannakopoulou, A. Paulidou, I., Mavridis, Th. Gotszalk, J. Mileczarski, E. Mileczarski, N. Glezos "Characterization of surfaces and interactions of self-assembled cyclodextrin monolayers with STM and functionalized AFM probes", *34<sup>th</sup> International Conference on Micro & Nano Engineering*, Athens, Greece, Sept. 15-19, **2008**, *Poster presentation.*

## Funded projects

1. "Development of new pharmaceutical formulations. Molecular inclusion of antibiotics in cyclodextrins for resistant pathogen strains", PENED , 57.5 k€, 1/1/2006 – 30/6/2009.
2. "Tools and Technologies for the Analysis and Synthesis of Nanostructures, STREP: TASNANO, Collaboration with IMEL. Budget of IPC 50 k€, 1/1/2005 – 31/6/2008.
3. "A Network for Bringing NANOTEchnologies TO LIFE, *NANO2LIFE*" "Network of Excellence" Priority 3-NMP 3.4.1.2-1 Nanotechnology, The funding of the collaborating institutes IPC, IMEL and IRRP, varies every year. For 2007: 71.9 k€, 1/2/2004 – 30/9/2008.
4. "Novel tools for crystallisation of macromolecules" *TOPCRYST*, EU People-IAPP (Industry-Academia Partnerships and Pathways) € 241 349, 1/3/2008 – 29/2/2012.
5. "Biom mineralization: Understanding of basic mechanisms for the design of novel strategies in nanobiotechnology" BIOMINTEC, EU People- ITN (Networks for Initial Training), € 184 4081/9/2008 – 31/08/2012.
6. "Autoorganised supramolecular materials with electrical and optical properties" Empirikion Foundation, 12 k€, 2004-.
7. "Optical and electro-active molecular wires organised by aqueous cyclodextrin-assembly of metallounits", COST, Action 31, 2005-2009.
8. "Development of innovative bio-active magnetic nanomaterials for diagnosis and monitoring of pathogenic conditions by magnetic tomography", PEP Attikis, 9.5 k€, 2006-2008.

## International Collaborations

Dr. Zoe Pikramenou, Prof. M. J. Hannon, University of Birmingham, UK; Dr. J.-M Moulis, CEA, Grenoble, France; Dr. V. Karginov, Innovative Biologics, Inc., USA, Dr. M. Wilms, EMBL-Hamburg, Germany Prof. N. E. Chayen, Imperial College, London, UK , Drs. E. Urso and G. Torri, Institute for Chemical and Biochemical Research "*G. Ronzoni*", Milan, Italy.

## Infrastructure

250 and 500 MHz BRUKER NMR instruments (departmental); 4-Cycle diffractometer; Macromolecular data collection system (Rigaku, R-Axis IV); Low temperature for data collection (Oxford cryosystems); Autoclave (Parr); Circular dichroism spectrophotometer (JASCO), Microscope (Olympus).

## Personnel

I. M. Mavridis: research director/group leader (Researcher A); K. Yannakopoulou (Researcher A); E. Saridakis (researcher D); A. Paulidou (post doctoral associate, funding by NCSR "D"); M-D. Manouilidou (PhD student, funding by NCSR "D"); M. Lambropoulou (PhD student, external funding); S. Hadjiefthimiou (PhD student, partial external funding), Ch. Aggelidou (PhD student); K. Fotiadou (MSc student, partial external funding); Dr. E. Hadjoudis (external senior researcher).

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Web site: <http://lssc.chem.demokritos.gr/>

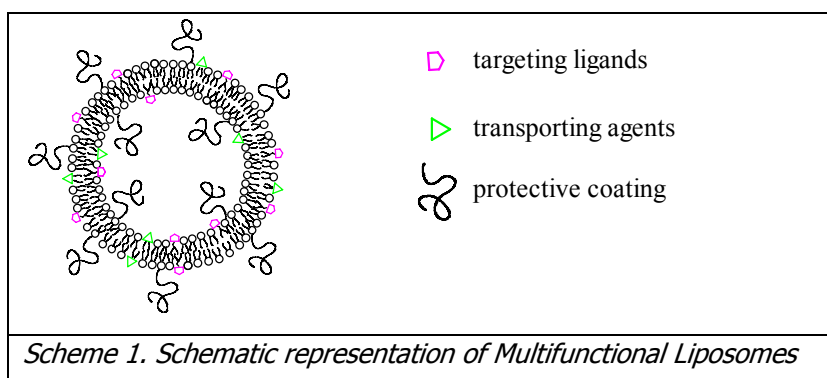
## NANOMATERIALS OF ORGANIZED SUPRAMOLECULAR STRUCTURE

### Research Objectives / Activities

The research activities are mainly focused on the synthesis and physicochemical characterization of functional nanomaterials, namely liposomes and dendritic polymers, giving emphasis on their applications as drug and gene delivery systems as well as, on the use of dendritic polymers for the removal of organic contaminants from water. Specifically, the scientific work is centered on:

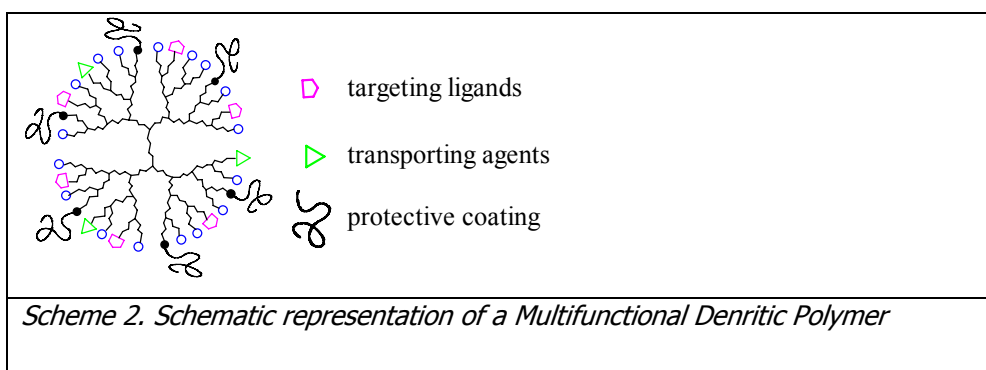
#### 1. Multifunctional Liposomes as Drug Delivery Systems.

Liposomes bearing recognizable groups are employed in molecular recognition experiments with complementary liposomes or simple molecules in an attempt to simulate the behaviour of cells. The external surface of liposomes is modified with appropriate moieties for conducting molecular recognition experiments with the final however objective to develop efficient drug delivery systems, with applications in photodynamic therapy, combining stability, targeting and transporting properties, Scheme 1.



#### 2. Multifunctional Dendrimeric and Hyperbranched Polymers as Drug and Gene Delivery Systems.

Multifunctionalization of dendrimeric and hyperbranched polymers (dendritic polymers) is conducted aiming at developing drug and gene delivery systems exhibiting targeting, stability and transport properties through cell membranes, Scheme 2. Active drug ingredients are incorporated in the nanocavities of dendritic polymers. On the other hand suitably designed positively charged dendritic polymers are also employed for the formation of complexes with DNA and studied either physicochemically or in *in vitro* experiments employing a variety of cell lines.



### 3. Dendritic Polymers with Application in the Production of Ultrapure Water.

Alkylated dendritic polymers have the property of acting as "nanosponges", in the cavities of which hydrophobic water impurities are encapsulated. Ultrapure water is produced, in which the remaining impurities are at the ppb level. Furthermore, cross-linked hydrophobic dendrimeric and hyperbranched polymers have been developed for water purification. Work has also been performed for the preparation of organosilicon dendrimers which were applied at the surface of ceramic filters for the production of ultrapure water.

#### Publications 2008

1. Theodossiou, T.A., Pantos, A., Tsogas, I., Paleos, C.M. "Guanidinylated Dendritic Molecular Transporters: Prospective Drug Delivery Systems and Application in Cell Transfection" *ChemMedChem* **2008**, *3*, 1635-1643.
2. Pantos, A., Tsogas, I., Paleos, C.M. "Guanidinium group: A versatile moiety inducing transport and multicompartimentalization in complementary membranes" *Biochim. Biophys. Acta – Biomembr.* **2008**, *1778*, 811-823.
3. Theodossiou, T.A., Papakyriakou, A., Hothersall, J.S. "Molecular modeling and experimental evidence for hypericin as a substrate for mitochondrial complex III; mitochondrial photodamage as demonstrated using specific inhibitors" *Free Radical Biol. Med.* **2008**, *45*, 1581–1590.
4. Kontoyianni, C., Sideratou, Z., Theodossiou, T.A., Tziveleka, L.-A., Tsiourvas, D., Paleos, C.M. "A novel micellar PEGylated hyperbranched polyester as prospective drug delivery system for paclitaxel" *Macromol. Biosci.* **2008**, *8*, 871-881.
5. Paleos, C.M., Tsiourvas, D., Sideratou, Z., Tziveleka, L.-A. "Multifunctional Dendritic Drug Delivery Systems: Design, Synthesis, Controlled and Triggered Release" *Curr. Top. Med. Chem.* **2008**, *8*, 1204-1224.
6. Galanou, M.C., Theodossiou, T.A., Tsiourvas, D., Sideratou, Z., Paleos, C.M. "Interactive Transport, Subcellular Relocation and Enhanced Phototoxicity of Hypericin Encapsulated in Guanidinylated Liposomes via Molecular Recognition", *Photochem. Photobiol.* **2008**, *84*, 1073-1083.
7. Vinceković, M., Bujan, M., Šmit, I., Tušek-Božić, Lj., Tsiourvas, D., Dutour Sikirić, M. "Influence of Dodecylammonium Chloride on the Properties of Carrageenan Gels" *J. Dispersion Sci. Technol.* **2008**, *29*, 966 – 974.
8. Tziveleka, L.-A., Psarra, A.-M.G., Tsiourvas, D., Paleos, C.M. "Synthesis and evaluation of functional hyperbranched polyether polyols as prospected gene carriers" *Int. J. Pharm.* **2008**, *356*, 314–324.
9. Tsetsekou, A., Arkas, M., Kritikaki, A., Simonetis, S., Tsiourvas, D. "Optimization of hybrid hyperbranched polymer/ceramic filters for the efficient absorption of polyaromatic hydrocarbons from water" *J. Membr. Sci.* **2008**, *311*, 128-135.
10. Paleos, C.M., Tsiourvas, D. "Non-Covalent Interactions of Liposomes", in "Bottom-up nanofabrication: Supramolecules, self-assemblies and organized films", American Scientific Publishers (in press).
11. Paleos, C.M., Tziveleka, L.-A., Sideratou, Z., Tsiourvas, D. "Gene Delivery Using Functional Dendritic Polymers" *Expert Opin. Drug Delivery*, (in press).

#### Conferences

1. Sideratou, Z. "Functional hyperbranched dendritic polymers as drug delivery systems", ESF Exploratory Workshop on "Hyperbranched polymers as novel materials for nanoscale applications: insight from experiment, theory and simulations (HYPER-NANO), Fodele, Grete, Greece, May 25-28, 2008 (Invited lecture).
2. C. M. Paleos, D. Tsiourvas, Z. Sideratou, L.A. Tziveleka, "Targeted and Multifunctional Dendritic Polymers: Magic Bullets for Drug and Gene Delivery", Ehrlich II, 2<sup>nd</sup> World Conference on Magic Bullets, Nuernberg, Germany, October 3-5, 2008.
3. D. Tsiourvas, "Dendrimers and hyperbranched polymers as gene transfection agents", Workshop "Nikos Oikonomakos", Marie Curie TOK programme "SUPRAGENE", Athens, 7 – 8 October 2008.

4. Sideratou, Z., Theodossiou, T., Tsiourvas, D., Fardis, M., Paleos, C.M. "Multifunctional hyperbranched polymers with protective coating and targeting character as MRI contrast agents", ESF Exploratory Workshop on "Hyperbranched polymers as novel materials for nanoscale applications: insight from experiment, theory and simulations (HYPER-NANO)", Fodele, Grete, Greece, May 25-28, 2008.

### **Patents**

D. Tsiourvas, M. Arkas, "The use of metal and/or metalloid oxide nanoparticles produced through an environmentally safe process for the removal of pollutants from water, solvents or fluids", Application Number: 20080100395; Filling Date: 09/06/2008.

### **Funded projects**

1. "Development of a novel anticancer technique: Bioluminescence activated destruction of cancer cells employing targeted gene carriers based on liposomes and dendritic polymers", ENTEP 04EP 61 project, 78 K€, 2006-2008.
2. "Nanoscale Functionalities for Targeted Delivery of Biopharmaceutics", 'NMP' INTEGRATED PROJECT, Contract No NMP4-CT-2006-026723, 537 K€, 2006-2010.
3. "Development of innovative bio-active magnetic nanomaterials for diagnosis and monitoring of pathogenic conditions by magnetic tomography", PEP Attikis, 9.5 k€, 2006-2008.

### **Infrastructure**

Optical and fluorescence microscopy with imaging facilities, Thermal analysis (DSC, TGA), Spectroscopic methods (NMR, FT-IR, UV-Vis, Fluorescence), Dynamic Light Scattering, Multi-angle static light scattering, Zeta-potential.

### **Personel**

Dr Dimitris Tsiourvas Research Director, Dr Zili Sideratou Researcher, Dr. Michael Arkas, Assisting Scientific personel, Collaborating Scientists: Dr Constantinos M. Paleos, Dr Leto-Aikaterini Tziveleka, Dr Theodosis Theodossiou, MSc. Nikoletta Sterioti, Graduate Students

### **Collaborations**

Psarra, A-M.G. (Foundation for Biomedical Research of the Academy of Athens, gene transfection), Allabashi, R. (Institute for Sanitary Engineering and Water Pollution Control, Austria, studies on water pollutants), Tsetsekou, A. (NTUA, ceramic membranes), Nounesis, G. (Institute of Radioisotopes & Radiodiagnostic Products, NCSR "Demokritos", microcalorimetry).

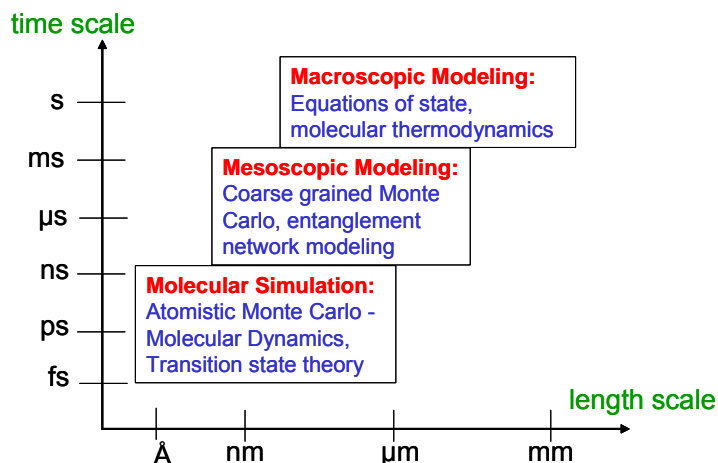
### **Contact**

Dr D. Tsiourvas ([tsiourvas@chem.demokritos.gr](mailto:tsiourvas@chem.demokritos.gr)), Tel. +30 210 6503616, Fax. +30 210 6511766)

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# MOLECULAR THERMODYNAMICS AND MODELING OF MATERIALS

## Research Objectives /Activities



Research work in the Molecular Thermodynamics and Modeling of Materials Laboratory (MTMML) focuses on the development and implementation of novel hierarchical methods and algorithms for the computer modelling and calculation of advanced material properties at the molecular, mesoscopic and macroscopic levels. Through this work, quantitative links are established between chemical constitution, processing conditions, and physical (thermal, mechanical, rheological, transport, interfacial, optical, dielectric) properties, which are critical for the optimal design of industrial processes and also govern the end-use performance of commercial products. In parallel, the molecular mechanisms underlying structure - property - processing - performance relations are elucidated with the objective of designing new, tailor-made materials.

The hierarchical approaches developed and implemented at MTMML start with atomistic simulations addressing length scales on the order of tens of nanometers and time scales on the order of tens of nanoseconds (e.g., Monte Carlo, molecular dynamics, transition-state theory analysis of infrequent events) and proceed with mesoscopic methods (e.g., entanglement network modelling, kinetic Monte Carlo simulation, self-consistent field theory of inhomogeneous systems) to address longer time- and length scale phenomena. Finally, for the efficient design of novel processes mainly for the chemical, polymer and pharmaceutical industry, accurate macroscopic models, mostly in the form of equations of state (eos), are developed for phase equilibria and other thermodynamic properties of multicomponent mixtures. These eos are rooted to statistical mechanics and can be safely extrapolated to conditions where limited or no experimental data exist.

Research work in 2008 focused on:

- Molecular simulation of elastomeric and glassy polymers,
- Polymer solutions and blends,
- Sorption and diffusion of small molecules in silicon-containing polymers,
- Molecular simulation of polar homo- and co-polymers,
- Mesoscopic simulation of polydisperse colloids,
- Thermodynamic properties of polar fluids in pure and in mixture,
- Ionic liquids in pure and in mixture with supercritical carbon dioxide or water,
- Development of a new EoS based on lattice theory for pharmaceutical solutions (new activity initiated in 2008),

- (i) Development of a new molecular model for the prediction of solubility of pharmaceuticals in water and other solvents (new activity initiated in 2008).

In order to strengthen the collaboration with industry, a new project dedicated to research services was formed entitled *Molecular Simulation and Thermodynamics of Fluids and Advanced Materials* co-ordinated by Dr. I. Economou. Within less than a year, the project has signed three research contracts with industry with a total budget of € 53,700.

More information about MTMML can be found at: [www.mtmml.gr](http://www.mtmml.gr).

## Personnel

Dr. Ioannis G. Economou, Research Director, Dr. Niki Vergadou Research Scientist, Dr. Nikolas Zacharopoulos Collaborating Researcher (faculty under contract, University of the Aegean), Dr. Theodora Spyriouni Post-doctoral scientist in project (EU-STREP), Dr. Stelios Karanikas Post-doctoral scientist in project (GSRT – ENTER), PhD students: Zoi Makrodimitri (GSRT – PENED), Marianna Yiannourakou, Eleni Androulaki (Demokritos PhD fellow) Vassilios Niotis (School of Chemical Engineering, NTUA), Senior undergraduate students: Dr. Stanislav Burov Visiting researcher (Department of Chemistry, State University of Saint Petersburg, Russia), Nuno M.F. Garrido (1 / 9 – 20 / 12 / 2008, PhD student, Department of Chemical Engineering, University of Porto, Portugal), Professor Doros N. Theodorou, Collaborator, School of Chemical Engineering, NTUA.

## Publications in peer-reviewed journals

1. Z. Kechagia, C. Kiparissides and I.G. Economou, "Determination of Liquid – Gas Partition Coefficients of BuA and MMA by Headspace-Gas Chromatography Utilizing the Phase Ratio Variation Method", *Fluid Phase Equil.*, **266**, 21 – 30 (2008).
2. I.G. Economou, E.K. Karakatsani, G.-E. Logotheti, J. Ramos and A. Vanin, "Multi-scale Modeling of Structure, Dynamic and Thermodynamic Properties of Imidazolium-Based Ionic Liquids: *Ab initio* DFT Calculations, Molecular Simulation and Equation of State Predictions", *Oil & Gas Sci. Tech.*, **63**(3), 283 – 293 (2008).
3. A. Grenner, I. Tsvintzelis, G.M. Kontogeorgis, I.G. Economou and C. Panayiotou, "Evaluation of the Non-Random Hydrogen Bonding (NRHB) Theory and the simplified Perturbed Chain-Statistical Associating Fluid Theory (sPC-SAFT). I. Vapor – Liquid Equilibria", *Ind. Eng. Chem. Res.*, **47**(15), 5636 – 5650 (2008).
4. I. Tsvintzelis, A. Grenner, I.G. Economou and G.M. Kontogeorgis, "Evaluation of the Non-Random Hydrogen Bonding (NRHB) Theory and the simplified Perturbed Chain-Statistical Associating Fluid Theory (sPC-SAFT). II. Liquid – Liquid Equilibria and Prediction of Monomer Fraction in Hydrogen Bonding Systems", *Ind. Eng. Chem. Res.*, **47**(15), 5651 – 5659 (2008).
5. Z.A. Makrodimitri and I.G. Economou, "Atomistic Simulation of Poly(dimethylsiloxane) Permeability Properties to Gases and *n*-Alkanes", *Macromolecules*, **41**(15), 5899 – 5907 (2008).
6. G. Tsolou, V.G. Mavrantzas, Z.A. Makrodimitri, I.G. Economou and R. Gani, "Atomistic Simulation of the Sorption of Small Gas Molecules in Polyisobutylene", *Macromolecules*, **41**(16), 6228 – 6238 (2008).
7. E.K. Karakatsani, I.G. Economou, M.C. Kroon, M.D. Bermejo, C.J. Peters and G.-J. Witkamp, "Equation of State Modeling of the Phase Equilibria of Ionic Liquid Mixtures at Low and High Pressure", *Phys. Chem. Chem. Phys.*, **10**(40), 6160 – 6168 (2008).
8. T. Spyriouni, G.C. Boulougouris and D.N. Theodorou, "Prediction of Sorption of CO<sub>2</sub> in Glassy Atactic Polystyrene at Elevated Pressures Through a New Computational Scheme", *Macromolecules*, in press (2008)
9. I. Tsvintzelis, I.G. Economou and G.M. Kontogeorgis, "Modeling the Solid – Liquid Equilibrium in Pharmaceutical – Solvent Mixtures: Systems with Complex Hydrogen Bonding Behavior", *AIChE J.*, in press (2008).

10. I. Tsivintzelis, I.G. Economou and G.M. Kontogeorgis, "Modeling the Phase Behavior in Mixtures of Pharmaceuticals with Liquid or Supercritical Solvents", *J. Phys. Chem. B*, in press (2008).
11. G.E. Logotheti, J. Ramos, I.G. Economou, "Molecular Modeling of Imidazolium-Based [Tf<sub>2</sub>N] Ionic Liquids: Microscopic Structure, Thermodynamic Properties and Segmental Dynamics", *J. Phys. Chem. B*, in press (2008).
12. M. Yannourakou, I.G. Economou and I.A. Bitsanis, "Phase Equilibrium of Colloidal Suspensions with Particle Size Dispersity: A Monte Carlo Study", *J. Chem. Phys.*, in press (2008).
13. P. Ahlström, K. Aim, R. Dohrn, J.R. Elliott, G. Jackson, J.-N. Jaubert, M.E.R.A. Macedo, J.-P. Pokki, K. Reczey, A. Victorov, L. Fele Žilnik, and I.G. Economou, "A Survey of the Role of Thermodynamics and Transport Properties in Chemical Engineering University Education in Europe and the USA", *Chem. Eng. Ed.*, in press (2008).
14. H. Leontiadou, I.G. Economou, "Microscopic Structure and Thermodynamic Properties of Aqueous Glycol Mixtures", *Molec. Simul.*, in press (2008).

### Presentations in international conferences

1. I.G. Economou, "Molecular Design of Rubbery Polymers for Membrane Applications", *International Workshop on Molecular Modeling and Simulation in Applied Material Science*, Frankfurt am Main, Germany (2008). Invited talk.
2. I.G. Economou, "Multi-Scale Modeling of Structure, Dynamic and Thermodynamic Properties of Ionic Liquids: *Ab initio* DFT Calculations, Molecular Simulation and Equation of State Predictions", *11<sup>th</sup> European Meeting on Supercritical Fluids*, Barcelona, Spain (2008). Invited talk.
3. I.G. Economou, "Molecular Simulation of Rubbery Polymer Membranes", *23<sup>rd</sup> European Symposium on Applied Thermodynamics*, Cannes, France (2008). Invited talk.
4. I.G. Economou, "Thermodynamic Properties and Phase Equilibria of Complex Fluid Mixtures: Equation of State Modeling", *Thermodynamic Colloquium*, Erlangen, Germany (2008).
5. I.G. Economou and Z.A. Makrodimitri, "Atomistic Simulation of Poly(dimethylsiloxane) Permeability Properties to Gases and *n*-Alkanes", *7<sup>th</sup> Greek Polymer Conference*, Ioannina, Greece (2008).
6. I.A. Bitsanis, A.N. Rissanou, M. Yannourakou, I.G. Economou and D.Vlassopoulos, "Simulations of Temperature Induced Ageing and Crystallization in Dense Suspensions of Ultrasoft Colloids", *7<sup>th</sup> Greek Polymer Conference*, Ioannina, Greece (2008).
7. G. Tsolou, V.G. Mavrantzas, Z.A. Makrodimitri, I.G. Economou and R. Gani, "Atomistic Simulation of the Sorption of Small Gas Molecules in Poly(isobutylene)", *7<sup>th</sup> Greek Polymer Conference*, Ioannina, Greece (2008). Award for best poster of the conference.
8. I.G. Economou and Z.A. Makrodimitri, "Atomistic Simulation of Poly(dimethyl siloxane): Structure, Thermodynamic and Diffusion Properties to Gases and *n*-Alkanes", *Centennial AIChE Annual Meeting*, Session No 519, Philadelphia, Pennsylvania, USA (2008).
9. I.G. Economou, G.-E. Logotheti, J. Ramos and A. Vanin, "Ab Initio Calculations and Molecular Dynamics Simulations for [Imidazolium][Tf<sub>2</sub>N] Ionic Liquids: Microscopic Structure and Thermodynamic Properties", *Centennial AIChE Annual Meeting*, Session No 182, Philadelphia, Pennsylvania, USA (2008).
10. P. Ahlström, K. Aim, R. Dohrn, R. Elliott, L. Fele-Žilnik, G. Jackson, J.-N. Jaubert, M.E. Rebello de A. Macedo, J. Pekka Pokki, K. Reczey, A. Victorov and I.G. Economou, "A Survey of Thermodynamics and Transport Properties in Chemical Engineering Education in Europe and the USA", *Centennial AIChE Annual Meeting*, Session No 62, Philadelphia, Pennsylvania, USA (2008).



## **Funded Projects**

1. "Computer Aided Molecular Design of Multifunctional Materials with Controlled Permeability Properties" [MULTIMAT], *European Union, STREP FP6, Priority 3, NMP*. Scientific director: Doros N. Theodorou. Total funding for Institute of Physical Chemistry: 173.117 €, funding for MTMML: 86,308 €. Co-funding is provided by GSRT. Duration: March 1, 2005 – February 28, 2008.
2. "Development of New Molecular Simulation Methods and Macroscopic Models for the Calculation of Microscopic Structure and of Thermodynamic Properties of Complex Polymer Systems", *Greek Secretariat of Research and Technology, Program for Research Support (PENED)*. Scientific director: Ioannis G. Economou. Total funding: 57,660 €. Duration: December 1, 2005 – November 30, 2008.
3. "Development of Sustainable Industrial Processes: Experimental, Theoretical and Computational Investigation of Thermodynamic Properties and Phase Equilibria of Ionic Liquid Mixtures", *INTAS*. Scientific director: Ioannis G. Economou. Total funding: 150,000 €. Funding for I.G. Economou: 12,500 €. Duration: September 1, 2006 – May 30, 2009.
4. "Investigation of Structure, Thermodynamic and Transport Properties of Poly(styrene-co-acrylonitrile) in High Temperatures", *Greek Secretariat of Research and Technology, ENTER 2003 Program*. Scientific director: Ioannis G. Economou. Total funding: 78,000 €. Duration: October 1, 2006 – October 30, 2008.
5. "Polymer Surfaces Responsive to Thermal and Chemical Stimuli: Towards the Micro-design of 'Intelligent' Materials", *Greek Secretariat of Research and Technology, Greece – USA Research and Technology Cooperation in Materials Research*. Scientific director: Ioannis G. Economou. Total funding: 50,000 €. Funding for I.G. Economou: 25,000 €. Duration: June 1, 2006 – September 30, 2008.
6. "Implementation of SAFT / PC-SAFT Computer Codes for Polymer and Non-Polymer Systems into MAPS", *Contract Research Services, Scienomics SARL, Paris, France*. Scientific director: Ioannis G. Economou. Total funding: 20,500 €. Duration: March 1 – August 30, 2008.
7. "Implementation of Computer Codes for Physical Properties of Polymer and Non-Polymer Systems into MAPS – Phase II", *Contract Research Services, Scienomics SARL, Paris, France*. Scientific director: Ioannis G. Economou. Total funding: 18,200 €. Duration: September 1, 2008 – February 28, 2009.
8. "Molecular Simulation of Diffusion of Hydrogen, Carbon Monoxide and Water in Heavy *n*-Alkanes at High Temperatures and Pressures", *Contract Research Services, Shell Global Solutions, Amsterdam, The Netherlands*. Scientific director: Ioannis G. Economou. Total funding: 15,000 €. Duration: December 15, 2008 – April 15, 2009.

"Reorganization of the Liaison Office of NCSR "Demokritos"", *Greek Secretariat of Research and Technology, Program for Support of Liaison Offices in Universities and Research Centers*. Scientific director: Ioannis G. Economou. Total funding: 300,000 €. Duration: January 1, 2005 – July 30, 2008.

## **Collaborations**

1. Professor Georgios Kontogeorgis, Department of Chemical Engineering, Technical University of Denmark. Development of thermodynamic models for pharmaceuticals.
2. Dr. Xenophon Krokidis, Scienomics SARL, France. Development of scientific software for prediction of material properties and design of chemical processes.
3. Professor Sofia Lampropoulou, School of Applied Mathematics and Physical Sciences, National Technical University of Athens, Statistical Mechanics Theory
4. Professor Maria Eugénia Rebello de A. Macedo, Department of Chemical Engineering, University of Porto, Portugal. Molecular simulation of the solubility of pharmaceuticals in water.
5. Professor Vlasis Mavrantzas, Department of Chemical Engineering, University of Patras. Molecular simulation of polymers.

6. Dr. Ioannis Bitsanis, Institute of Electronic Structure and Laser, Foundation of Research and Technology, Hellas, Heraklion, Crete, Greece. Mesoscopic simulation of colloids and polymers.
7. Professor Costas Panayiotou. Department of Chemical Engineering, Aristotle University of Thessaloniki, Greece. Development of a lattice equation of state for non-ideal fluids.
8. Professor Cor Peters, Department of Chemical Engineering, Delft University of Technology, The Netherlands. Modeling thermodynamic properties of ionic liquids.
9. Dr. J. Ramos-Díaz, Department of Macromolecular Physics, Instituto de Estructura de la Materia - CSIC, Madrid, Spain. Quantum-mechanics calculations for ionic liquids.

### **Contact**

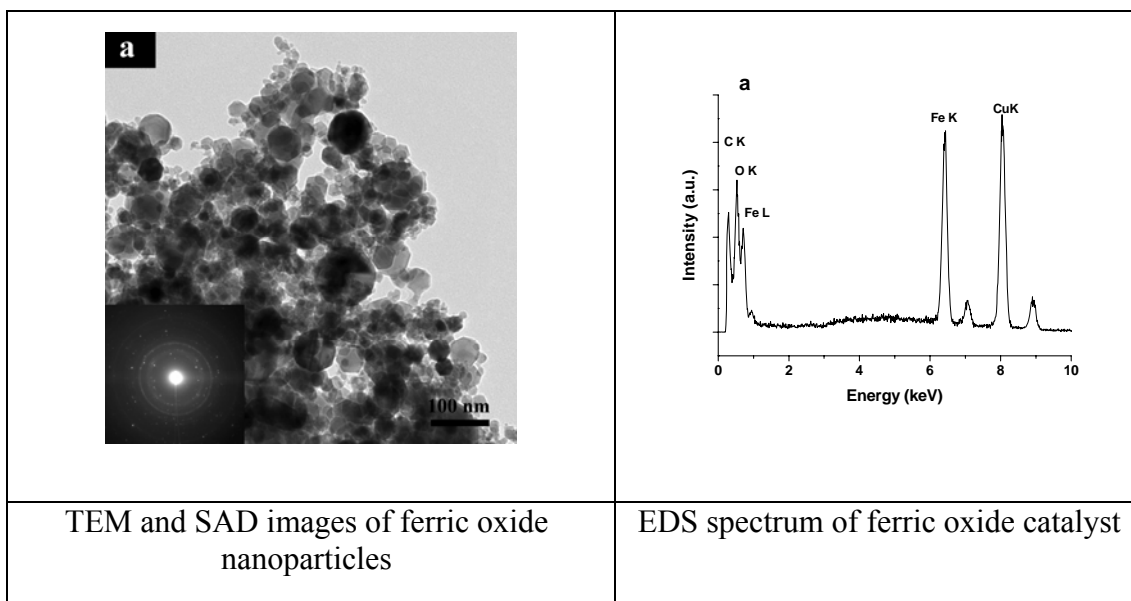
Dr Ioannis G. Economou ([economou@chem.demokritos.gr](mailto:economou@chem.demokritos.gr), Tel. +30 210 6503963, Fax. +30 210 6511766)

Web site: <http://www.mtmml.gr/>

# LUMINESCENCE LABORATORY – DEVELOPMENT OF NOVEL FUNCTIONALIZED MATERIALS FOR ANALYTICAL AND BIOANALYTICAL APPLICATIONS

## Research Objectives/Activities

The main objective of the Laboratory is the development of novel functionalized materials and their application in Analytical and Clinical Chemistry. The most important functionalized materials prepared in our laboratory were (a) biotinylated luminescent materials, (b) paramagnetic europium complexes based on diethylenetriaminopentacetic acid, (c) hybridized organo-inorganic chiral materials and (d) functionalized ferric oxide nanoparticles. The first ones were applied for the quantification of the proteins avidin and streptavidin as well as for the quantification of mouse IgG. The results were published in *Journal Clinica chimica Acta*. The spectroscopic characteristics of paramagnetic europium complexes were found to be similar to those obtained for commercially available MRI agent Magnevist and will be published soon. The novel functional ferric oxide nanoparticles were characterized by TEM, SAD and EDS (Figure) and applied for the chemiluminescent determination of reactive oxygen species (publication No 1). At this point, it should be noted that beside the preparation, characterization and applications of functionalized novel materials, a novel chemiluminescent technique was also developed in our laboratory and used for the estimation of antioxidant activities of important biological materials as well as of natural products, such edible oils or fruit juices. The results were impressive and comparable to those obtained by the internationally established DPPH-method.



## Publications 2008

1. T.M. Triantis, K. Papadopoulos, E. Yannakopoulou, D. Dimotikali, J. Hrbáč, R. Zbořil, Sensitized chemiluminescence of luminol catalyzed by colloidal dispersions of nanometer-sized ferric oxides, *Chem. Eng. J.* 2008, *144*, 483-488.
2. M. Merlani, V. Barbakadze, L. Gogilashvili, L. Amiranashvili, K. Mulkijanyan, E. Yannakopoulou, K. Papadopoulos, D. Christodouleas, 'Synthesis and antioxidant activity of 3-(3,4-dihydroxyphenyl)-glyceric acid. Monomer of a biologically active polyether isolated from *Symphytum asperum* and *S. caucasicum*', *J. Planta Medica* 2008, *74*, 1167-1168.

- G.C. Vougioukalakis, R.H Grubbs, "Synthesis and activity of ruthenium olefin metathesis catalysts coordinated with thiazol-2-ylidene ligands", *J. Am. Chem. Soc.* 2008, *130*, 2234-2245,.
- G.C. Vougioukalakis, R.H Grubbs, , "Ruthenium-based olefin metathesis catalysts coordinated with unsymmetrical *N*-heterocyclic carbene ligands: synthesis, structure and catalytic activity", *Chem. Eur. J.* 2008, *14* , 7545-7556.
- G.C. Vougioukalakis, M.M. Roubelakis, M.N. Alberti, M. Orfanopoulos, "Solvent depended changes in the triazolinedione-alkene ene reaction mechanism", *Chem. Eur. J.* 2008, *14* , 9697-9705.

## Conferences

- K. Papadopoulos, E. Yannakopoulou, T. Triantis, D. Christodouleas T. Yannakopoulou, C. Trapalis, D. Dimotikali, Applications of colloidal nanosized ferric oxides in chemiluminescent reactions, 1<sup>st</sup> IC4N : from Nanoparticles and Nanomaterials to Nanodevices and Nanosystems, June 15-19, 2008, Halkidiki, Greece.
- D. Dimotikali, K. Papadopoulos, E. Yannakopoulou, T. Triantis, D. Christodouleas, J. Hrbáč, R. Zbořil, Evaluation of antioxidant activities of organic compounds using chemiluminescence reactions catalyzed by Ferric Oxide Nanoparticles, 5th International Conference on Nanosciences & Nanotechnologies - NN08, July 14-16, 2008, Thessaloniki-Greece.
- Calokerinos, D. Christodouleas, K. Papadopoulos, Determination of hydrophilic and hydrophobic antioxidants and evaluation of antioxidant activity by chemiluminescence, XIII International Symposium on Luminescence Spectrometry, September 7-11, 2008, Bologna-Italy.
- M. Merlani, Barbakadze, L. Gogilashvili, L. Amiranashvili, K. Mulkijanyan, E. Yannakopoulou, K. Papadopoulos, D. Christodouleas, Synthesis and antioxidant activity of 3-(3,4-dihydroxyphenyl) glyceric acid. Monomer of a biologically active polyether isolated from *Symphytum asperum* and *S. caucasicum*, 7<sup>th</sup> Joint Meeting of AFERP, ASP, GA, PSE, SIF, August 3-8, 2008, Athens-Greece.
- V. Barbakadze, R. Agarwal, G. Deep, K. Mulkijanyan, M. Merlani, K. Papadopoulos, L. Gogilashvili, L. Amiranashvili, E. Shaburishvili, Anticancer effects of poly-3(3,4-dihydroxyphenyl)-glyceric acid isolated from Caucasian species of comfrey and its synthetic monomer, 4<sup>th</sup> International Conference on Oxidative Stress in Skin Biology and Medicine, September 11-14, 2008, Andros-Creece.
- G.C. Vougioukalakis, R.H. Grubbs, Synthesis, structure, and catalytic activity of ruthenium-based metathesis catalysts coordinated with thiazol-2-ylidene and unsymmetrical *N*-heterocyclic carbene ligands. NATO Advanced Study Institute: New smart materials via metal mediated macromolecular engineering; from complex to nano structures, Antalya, Turkey, September 2008.
- G.C. Vougioukalakis, N. Petzetakis, M. Pitsikalis, N. Hadjichristidis, I. Stamatopoulos, P. Kyritsis, A. Terzis, C. Raptopoulou, Vinyl polymerization of norbornene with a novel nickel(II) diphosphinoamine/methylaluminumoxane catalytic system, 7<sup>th</sup> Hellenic Polymer Conference, Ioannina, Greece, September 2008.

## Funded projects

- "Development of innovative bio-active magnetic nanomaterials for diagnosis and monitoring of pathogenic conditions by magnetic tomography", PEP Attikis, 9.5 k€, 2006-2008". The program was completed in March 2008
- Sensitized chemiluminescence using ferric oxide nanoparticles. Bilateral collaboration between Greece and Czech Republic, 12 K€, 2006-2008. The program was completed in March 2008

3. Enhanced chemiluminescence using nanosized catalysts - prospects for analytical applications, internal funding from NCSR Demokritos, "DEMOEREVNA", 14 K€, 2006-2008. The program was completed in June 2008.

### **Infrastructure**

UV-Vis spectrophotometer (Jasco V-560), 2 fluorimeters (Jasco FP-777 and Fluostar Optima BMG), 3 luminometers (Bio-Orbit 1250), complete photolysis system 1000 watt (ORIEL), Elemental Analyzer CHN, Cobalt-60 source (Gamma Chamber 4000A), complete laboratory for the synthesis of organic compounds equipped with rotary evaporators, high vacuum oil pumps, magnetic stirrers, ovens and lines for working in inert atmosphere.

### **Personnel**

K. Papadopoulos (Research director/Group leader, permanent researcher), Dr G. Vougioukalakis (Post – Doctoral), E. Giannakopoulou (technical staff), D. Christodouleas and O. Lanitou (unpaid PhD students).

### **Collaborations Contact**

D. Dimotikali (Chemical Engineering Department, NTUA Athens, Greece), A. Scorilas (Department for Biochemistry and Molecular Biology, University of Athens), M. Maia (Institute of Pharmaceutical Chemistry, University of Tbilisi, Georgia), R. Saicic (Faculty of Chemistry, University of Belgrade, Serbia), J. Hrbac (Faculty of Inorganic Chemistry, University of Olomouc, Czech Republic), A. Meghea (Polytechnique School of Bucharest, Romania).

### **Contact**

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Tel. +30 210 6503647, Fax. +30 210 6511766)

# TRANSPORT PHENOMENA IN POLYMERS

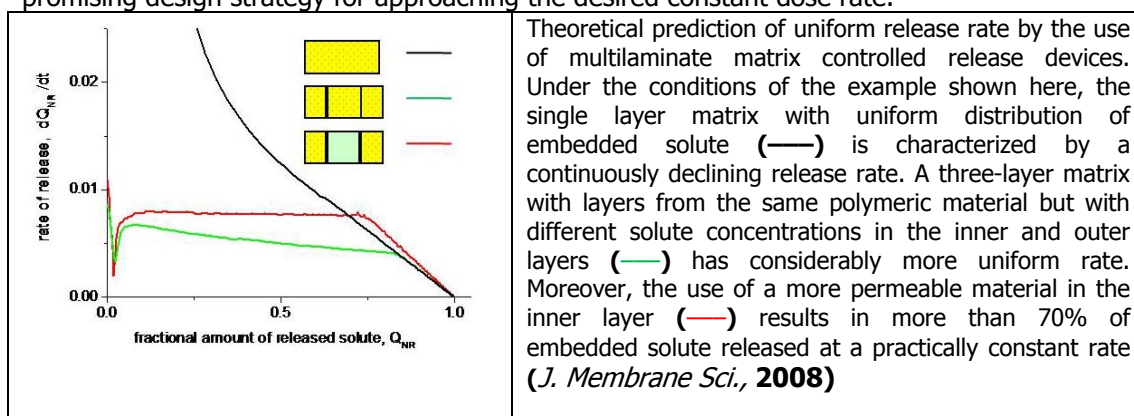
## Research Objectives/Activities

Research focuses on micromolecular sorption and transport in polymeric materials by a combination of theoretical and experimental approaches. The aim of this work is to help create the basic scientific background for the optimization of the design of polymeric materials for important applications (controlled release systems, permselective membranes, packaging, chemical sensors etc).

Current research activities include

### 1. Polymer -based controlled release systems

Development of controlled release devices aims at the regulated, prolonged delivery of drugs, agrochemicals or other bioactive agents. Matrix-type controlled release devices consist of a swellable polymer matrix incorporating the requisite bioactive solute and are activated by the ingress of water when placed in an aqueous environment. Research of our group in this area aims at the optimization of the design of these devices, in order to alleviate their main drawback of continuous decline of dose rate. Theoretical work focuses on the development of advanced, realistic models, simulating the release performance of single-layer as well as multilayered devices. Experimental work includes (i) Validation of models against experiment, based on model experimental systems (ii) Effect of chemical or physical treatment on drug release from hydrogels (iii) Effect of osmotic excipients on drug release from hydrophobic matrices (iv) development of multilaminar devices which constitute a promising design strategy for approaching the desired constant dose rate.



### 2. Mechanisms of Micromolecular Non-Fickian Transport Kinetics in Glassy Polymers

Sorption kinetics in glassy polymers systems exhibits a variety of deviations from normal Fickian behaviour, attributable to either (i) slow viscous relaxations of the swelling polymer, or (ii) differential swelling stresses generated by the constraints imposed on local swelling during sorption. Our group develops models based on both mechanisms, capable of simulating all basic features of observed non-Fickian kinetic behaviour, including Case II kinetics. Experimental work includes (i) sorption from the *vapour* phase. Carefully designed experimental sorption protocols, supplemented by measurement of longitudinal swelling kinetics of the polymer film, enable us to study various types of non-Fickian behaviour. On the basis of the models mentioned above, we develop general diagnostic criteria for distinguishing between the underlying mechanisms responsible for the observed experimental behaviour. (ii) sorption from the *liquid* phase. Combination of various optical techniques enables us to study in detail various types of non-Fickian penetration such as stress-dependent diffusion and Case II kinetics.

### 3. Transport in ultrathin supported films

In collaboration with the Institute of Microelectronics in Demokritos, we evaluate the swelling behaviour polymeric materials in the form of thin supported films upon exposure to different vapour environments, for subsequent use as the sensing layer of chemocapacitive chemical

sensors. The activity aims at the development of sensor arrays for specific applications concerning the detection of analytes in complex vapor environments.

## Publications 2008

1. Papadokostaki, K.G.; Stavropoulou, A.; Sanopoulou, M.; Petropoulos, J.H. "An advanced model for composite planar three-layer matrix-controlled release devices. Part I. Devices of uniform material properties and non-uniform solute load" *J. Membrane Sci.* **2008**, *312*, 193-206.
2. Hasimi, A.; Stavropoulou, A.; Papadokostaki, K.G.; Sanopoulou M. "Transport of water in polyvinyl alcohol films: Effect of thermal treatment and chemical crosslinking" *Eur. Polym. J.* **2008**, *44*, 4098-4107
3. Sarantopoulou, E.; Kollia, Z.; Cefalas, A.C.; Manoli, K.; Sanopoulou, M.; Goustouridis, D.; Chatzandroulis, S. "Surface nano/micro functionalization of PMMA thin films by 157 nm irradiation for sensing application" *Appl. Surface Sci.* **2008**, *254*, 1710-1719.
4. Dallas, P.; Bourlinos, A.B.; Petridis, D.; Boukos, N.; Papadokostaki, K.; Niarchos, D.; Guskos, N. "Synthesis and characterization of 2-D and 3-D covalent networks derived from triazine central cores and bridging aromatic diamines" *Polymer* **2008**, *49*, 137-1144.
5. Vlachopoulou, M.E.; Tserepi, A.; Pavli, P.; Argitis, P.; Sanopoulou, M.; Misiakos, K. "A low temperature surface modification assisted method for bonding plastic" *J. Micromech. and Microeng.*, in press
6. Papadokostaki, K.G. "Experimental realization of sustained simple kinetic regimes of release of particulate solutes subject to slow dissolution in the containing matrix" *J. Membrane Sci.*, in press
7. Oikonomou, P.; Manoli, K.; Goustouridis, D.; Raptis, I.; Sanopoulou, M. "Polymer/BaTiO<sub>3</sub> nanocomposites based chemocapacitive sensors", *Microelectronic Eng.*, in press
8. Soulas, D.: Sanopoulou, M.; Papadokostaki, K.G., "A comparative study on the release kinetics of osmotically active solutes from hydrophobic elastomeric matrices, combined with the characterization of the depleted matrices", *J. Appl. Polymer Sci.* in press

## Conferences

1. K. Manoli, P. Oikonomou, D. Goustouridis, E. Karonis, I. Raptis, M. Sanopoulou "Interdigital chemicapacitive sensors based on polymer/BaTiO<sub>3</sub> composites", EuroSensors 2008, Sept.7-10, 2008, Dresden, Germany, Book of Abstracts, p. 388.
2. K. Manoli, E. Karonis, M. Chatzichristidi, D. Goustouridis, S. Chatzandroulis, I. Raptis, M. Sanopoulou "Evaluation of a chemocapacitive sensor array for the detection of vapor analytes and their mixtures" IEEE Sensors 2008, October 26-29, Lecce, Italy, Book of Abstracts, p. 423-426..
3. P. Oikonomou, K. Manoli, D. Goustouridis, I. Raptis, M. Sanopoulou "Polymer/BaTiO<sub>3</sub> nanocomposites based chemocapacitive sensors", Micro & Nano Engineering 2008, Sept. 15-18, 2008, Athens, Greece Book of Abstracts, p. 511.
4. J.H. Petropoulos, "Of men, pores and heterogeneity" 1<sup>st</sup> International Workshop on Nanoporous Materials in Energy and Environment, NAPEN 2008, Chania, Crete, Greece, October 12-15, Book of Abstracts, p. 8 – 13
5. A. Hasimi, K. G. Papadokostaki, M. Sanopoulou, Study of the release kinetics of a drug and an MRI contrast agent from poly (vinyl alcohol) matrices, 7th Hellenic Polymer Conference, Ioannina, September 28-October 1 2008, Book of Abstracts, p. 229-230

## Funded Projects

1. "Computer aided molecular design of multifunctional materials with controlled permeability properties-Multimatdesign", FP6-NMP-STREP, 86 K€, 2005-2008.

2. "Facing pathogenic conditions by combined use of bio-medical methods and nanotechnology" Ypodomes, Metro 4.5, 4.4.1 Action «Consortia of research and technological development in sectors of National priorities», 2050-4/2, 50 k€, 2005-2008.
3. "Development of innovative bio-active magnetic nanomaterials for diagnosis and monitoring of pathogenic conditions by magnetic tomography", PEP Attikis, 9.5 k€, 2006-2008.
4. "Morphological control of polymer blend nanofilms for organic (opto-) electronics" Joint research and technology programmes, Greece -Poland, 11.7 k€ , 2006 – 2008.

### **Infrastructure**

Vacuum apparatuses for sorption and longitudinal dilation kinetic measurements on polymer samples including electronic microbalances (Cahn 2000 and MK2-M5 CI Electronics) or quartz spring balances, Polarizing and interferometric microscopes, Tensile tester in conjunction with optical setup, Thermal analysis instruments (Temperature Modulated DSC), Home-made apparatuses for kinetic release measurements, Abbe refractometer, Dissolution tester equipped with fraction collector and UV-Vis spectrophotometer (Jasco).

### **Personnel**

M. Sanopoulou: research director/group leader, K. Papadokostaki: principal researcher (permanent staff); J.H. Petropoulos (emeritus researcher); D. Soulas (post-doctoral collaborating researcher); A. Hasimi, K. Manoli , M. Konidari (3 PhD students).

### **Collaborations**

Prof. A. Budkowski , M. Smoluchowski (Institute of Physics, Jagellonian University, Krakow, Poland, bilateral program); Dr. I. Raptis, (NCSR "D", Inst. Of Microelectronics, chemical sensors); Dr. P. Argitis (NCSR "D" Inst. of Microelectronics, DSC); Dr. P. Dallas (NCSR "D", Inst. of Materials Science, DSC)

### **Contact**

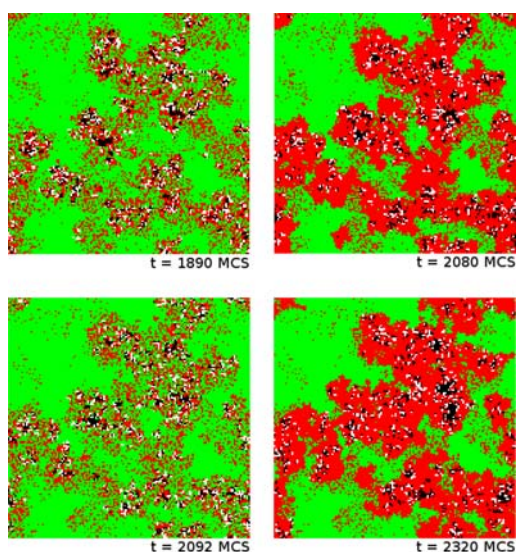
Dr. M. Sanopoulou ([sanopoul@chem.demokritos.gr](mailto:sanopoul@chem.demokritos.gr), Tel. +30 210 6503785, +30 210 6503661; fax. +30 210 6511766)  
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# STATISTICAL MECHANICS AND NON-LINEAR DYNAMICS LABORATORY

## Research Objectives/Activities

The Laboratory of "Statistical Mechanics and Non-linear Dynamics" was formed in 02/2004 as part of the Institute of Physical Chemistry. Its research focuses on the development of Statistical Mechanical and Non-linear Dynamical methods for the study of development of mesoscopic and macroscopic patterns and correlations due to the local interactions between particles at the microscopic level. Such structures include spatiotemporal patterns, aggregates, spiral and stripe formations, helices, fractals etc which can be experimentally observed in material science, physics, chemistry and biology. Our studies in particular include research on fractal pattern formation and correlations near the critical point in phase transitions (eg the gas-liquid phase transition) but also in open systems in constant exchange with the environment, such as in the noncoding DNA. Away from the critical point and in closed, isolated systems (such as in coding DNA), short range correlations and spatiotemporal patterns with well-defined length and time scales are studied (eg. spiral and stripe formations, helices etc.). The study of these structures at the micro-, meso- and macro scale and the interaction between these three levels of description has major technological impact in materials science and physical, chemical and biological processes.



Creation and  
propagation of clusters  
during the CO  
oxidation  
in high pressure  
values  
values  
(MCS=Monte Carlo  
Steps)

For the study of such complex systems in the lab we develop a) statistical methods/tools describing complex morphologies and b) modelling of the dynamics of pattern formation. Statistical methods include thermodynamic approaches, entropic (extensive and non-extensive) approaches, theory of long and short range distributions, and Levi distributions and the theory of random walks. For the study of the mechanisms creating complex patterns, non-linear dynamical systems of hierarchical complexity are used, together with mean-field theories, exact enumeration methods, real space renormalisation theory, theory of stochastic processes and numerical Monte Carlo Methods.

Applications in the lab include, among others, studies of surface phenomena and aggregates with fractal morphology, bioinformatics, statistical analysis and modelling of biological macromolecules, non-linear studies of open and closed catalytic surface reactions as well as the influence of diffusion on low dimensional catalysis.

## Publications 2008

1. Oikonomou, Th.; Provata, A.; Tirnakli, U.; "Nonextensive statistical approach to non-coding human DNA", *Physica A*, 2008, *387* 2653–2659.
2. Noussiou, V.K.; Provata, A.; Kinetic Monte Carlo simulations of the oscillatory CO oxidation at high pressures: the surface oxide model", *Chem. Phys.* 2008, *384*, 11-20.
3. Kouvaris, N.; and Provata, A.; "Trimolecular reactive system with spatial disorder", *Nonlinear Phenomena in Complex Systems*, 2008, *11*, 259-264.
4. Provata, A.; Sokolov, I.; Spagnolo, B.; "Editorial: Ecological Complex Systems", *Europ. Phys. Jour. B*, 2008, *65*, 307-314.
5. Efimov, A.; Shabunin, A.; Provata, A.; "Synchronization of stochastic oscillations due to long-range diffusion", *Phys. Rev. E*, 2008, *78*, 056201.
6. Katsaloulis, P.; Theoharis, Th.; Provata, A.; "Long range clustering of oligonucleotides containing the GC signal" accepted to *J. Theor. Bio.*
7. Katsaloulis, P.; Verganelakis, D.; Provata, A.; "Fractal Dimension and Lacunarity of Tractography Images of the Human Brain", accepted to *Fractals*.
8. Kouvaris, N.; and Provata, A.; "Dissipative oscillations in spatially restricted ecosystems due to long range migration", *Eur. Phys. J. B*, 2008, *66*, 97-106.

## Conferences

1. Kouvaris, N.; Provata, A.; "Diffusion in spatially extended reactive systems", poster at the 21th International Conference and Summer School on "Non Linear Science and Complexity", Athens, Greece, 21 July – 2 August 2008 .
2. Kouvaris, N.; Provata, A.; "Derivation of the Tsallis, Reny and Non-extensive Gaussian Entropy from Deformed Multinomial Coefficients", poster at the International Conference "Sigma-Phi: Statistical Physics", Kolympari, Chania, Crete, Greece, July 14-18 ,2008.
3. Kouvaris, N.; "Diffusion in spatially extended reactive systems", in CHAOTIC MODELING AND SIMULATION International Conference, Chania, Crete, Greece, 3 - 6 June 2008.
4. Provata, A.; "Nonlinear Kinetics on Lattice, with Long Range Diffusion", International Conference "Sigma-Phi: Statistical Physics", Kolympari, Chania, Crete, Greece, July 14-18 ,2008.
5. Provata A.; "Diffusive Mixing Versus Reactive Mixing in Nonlinear Dynamical Systems", Greek-Turkish Conference on "Statistical Mechanics and Dynamical Systems", Rhodos\_Greece, Marmaris-Turkey, September 11, 2008.
6. Provata, A.; "Synchronization of Local Oscillators in a Lattice Model", 21th International Conference and Summer School on Non Linear Science and Complexity", NTUA, Athens, Greece, 24 July 2008.
7. Katsaloulis P.; "Fractal analysis of human brain tractography images", 21th Conference - Summer School. "Nonlinear Science and Complexity". Athens, Greece, 21 July - 2 August 2008.
8. Katsaloulis, P.; "Non-linear analysis of oligonucleotide distribution of evolutionary recent organisms", Greek-Turkish Conference "Statistical Mechanics and Dynamical Systems", Rhodos Greece, Marmaris Turkey, 11-17 September 2008.

## Funded Projects

1. "Development of innovative bio-active magnetic nanomaterials for diagnosis and monitoring of pathogenic conditions by magnetic tomography", PEP Attikis, 9.5 k€, 2006-2008

2. "MOLSIMU: Forging the Missing Link: From Molecular Simulations to Nanoscale Experiments", COST Scientific Network, 10 K€ (from 400 000 € total budget), 2004-2008 .

### **Infrastructure**

2 computers Pentium IV, dual core + dual processor (Linux).  
3 computers Pentium IV (Linux).  
1 personal computer (Windows).

### **Personnel**

A. Provata: research director/group leader (permanent researcher); P. Katsaloulis: (post doctoral fellow, from 06/2008); V. Nousiou, N. Kouvaris: ( PhD students, NCSR "D" fellows), Th. Oikonomou: (PhD student until 07/2008, external funding).

### **Collaborations**

Dr. Y. Almirantis (NCSR "Demokritos", Genome Organisation), Prof. G. Nicolis (Free University of Brussels, Service de Chimie-Physique, Brussels, Belgium, "Entropic Representations of DNA"), Prof. T. Bountis (Univ. of Patras, 'Statistical Properties and Correlations of Genomic Data and Biological Time Series'), Prof. Th. Theoharis (Univ. of Athens, 'Non-linear Dynamics in the Genome of Higher Eucaryotes'), Dr. A. Shabunin (University of Saratov, Russia, 'Non-linear reactive dynamics on low dimensional and fractal lattices'), Profs. A Tsekouras V. Havredaki and A. Koutselos (Univ. of Athens "Chemical Dynamics of Catalytic Reactions"), Prof. D. Kougioumtzis (Univ. of Thessaloniki, "Pattern formation on low dimensional lattices"), Prof. B. Spagnolo (Univ. of Palermo, Dept of Physics, "Ecological Complex Systems), Prof. U. Tirnakli, (Ege University, "Entropic Forms"), Prof. I. Sokolov and Prof. L. Schimansky-Geier (Humboldt Universitaet Berlin, Dept. of Physics, "Reactive Dynamics with Diffusion on Low Dimensional Supports")

### **Contact**

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Web site: <http://limnos.chem.demokritos.gr/>

# MOLECULAR COMPUTATIONAL CHEMISTRY

## Research Objectives/Activities

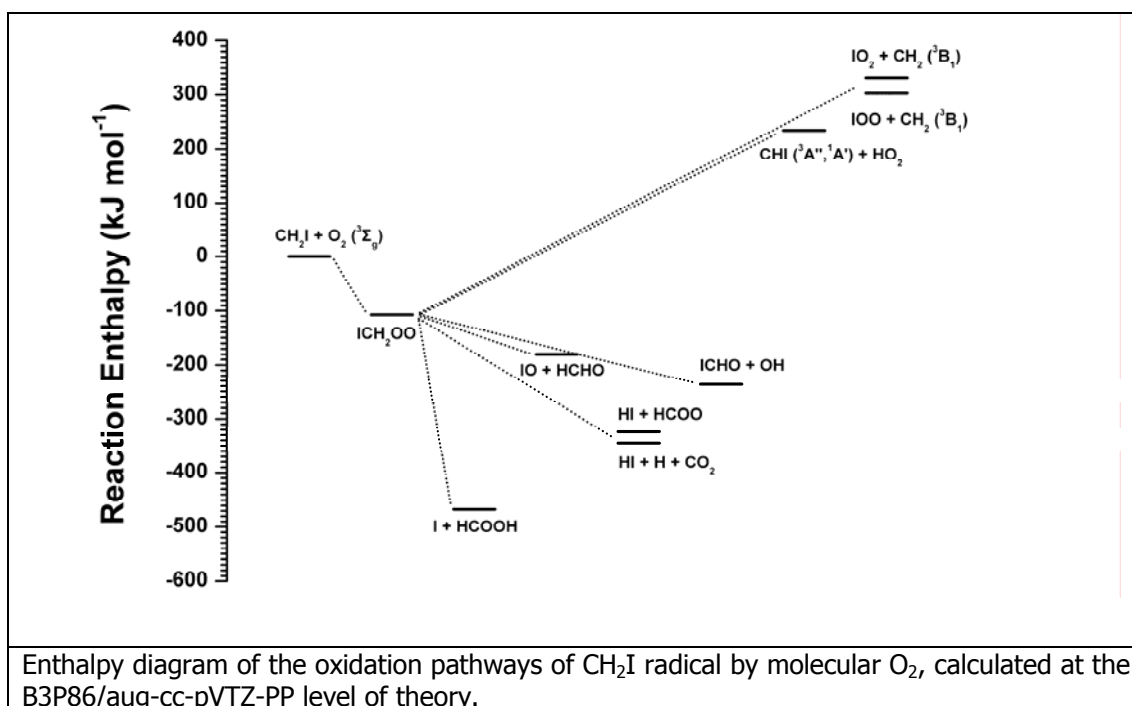
The research activity of Molecular Computational Chemistry Laboratory is focussed on the study of the chemical reactivity and the degradation mechanism of molecules in the atmosphere as well as on the reliable prediction of the properties of molecular materials by using theoretical methods.

More specifically, the tropospheric degradation mechanism of diiodomethane,  $\text{CH}_2\text{I}_2$  (an important biogenic source of iodine in nature) was completed by considering its reaction with Cl atoms, as well as the oxidation mechanism of the generated  $\text{CH}_2\text{I}$  and  $\text{CHI}_2$  radicals by molecular  $\text{O}_2$ , using the EI-MS and FT-IR experimental techniques in addition to density functional theory (DFT).

The degradation mechanism of fluorinated unsaturated organic compounds (as promising substitutes for certain categories of freons) effected via their reactions with OH radicals, Cl atoms and molecular  $\text{O}_2$  is theoretically studied using DFT, contributing to the explanation of the corresponding experimental results. In addition, DFT theory is employed in the elucidation of the reaction mechanisms of ozone with organic molecules, in order to understand the processes of their degradation in the environment and the subsequent generation of fine particulate matter (aerosols).

The reaction rates of small organic molecules ( $\text{CH}_4$ ,  $\text{CH}_3\text{F}$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{CHF}_3$  και  $\text{CH}_3\text{OH}$ ) with chlorine atoms and hydroxyl radicals in the presence of water molecules, and the dependence of the kinetic parameters on the structure of the hydrated complexes is computed by *ab-initio* and DFT methods in the framework of Transition State Theory. This study aims at the clarification of the role of clouds and stratospheric ice particles in the atmospheric degradation kinetics of halogenated molecules, directly connected with the stratospheric ozone depletion problem.

The coordination ability of substituted cyclodextrins with lanthanide cations is studied by using semiempirical methods (AM1, PM3), seeking paramagnetic metal complexes with properties permitting their application in magnetic resonance imaging techniques (MRI).



## Publications

1. V.G. Stefanopoulos, V. C. Papadimitriou, Y.G. Lazarou and P. Papagiannakopoulos, "Absolute Rate Coefficient Determination and Reaction Mechanism Investigation for the Reaction of Cl Atoms with CH<sub>2</sub>I<sub>2</sub> and the Oxidation Mechanism of CH<sub>2</sub>I Radicals", *J. Phys. Chem. A* 2008, *112*, 1526 - 1535.
2. I. Morozov, S. Gligorovski, P. Barzaghi, D. Hoffman, Y.G. Lazarou, E. Vasiliev and H. Herrmann, "Hydroxyl Radical Reactions with Halogenated Ethanol in Aqueous Solution: Kinetics and Thermochemistry", *Int. J. Chem. Kinet.* 2008, *40*, 174 - 188.

## Conferences

1. Papadimitriou, V.C., Lazarou, Y.G., Talukdar, R.K., Burkholder, J.B. "Pressure Dependent Rate Coefficients for the Cl + CF<sub>3</sub>CF=CH<sub>2</sub> and (Z)-CF<sub>3</sub>CF=CHF Reactions between 207 - 308 K", 20th International Symposium on Gas Kinetics, Manchester, UK, July 20 - 25, 2008.

## Infrastructure

A cluster of personal computers running Microsoft Windows XP, Linux Redhat and Fedora Core.

## Personnel

Yannis G. Lazarou: group leader (permanent researcher); Christina Tsonaki (PhD student)

## Collaborations

Prof. P. Papagiannakopoulos and Dr. V. C. Papadimitriou (Chemistry Dept., University of Crete, chemical reactions of halogenated molecules, chemical kinetics experiments), Dr. I. Mavridis (Inst. Of Physical Chemistry, NCSR "D", complexes of substituted cyclodextrins), Dr. K. Yannakopoulou (Inst. Of Physical Chemistry, NCSR "D", complexes of substituted cyclodextrins), Dr. J. B. Burkholder (Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado, USA, fluorinated unsaturated organic compounds), Dr. R. Prosmi (Department of Atomic, Molecular and Cluster Physics, Institute of Fundamental Physics 'Blas Cabrera', Spanish National Research Council (CSIC), Madrid, Spain, iodinated compounds), Prof. I. I. Morozov (Russian Academy of Sciences, Moscow, Russia, halogenated ethanol), Dr. Sasho Gligorovski (Universités d'Aix-Marseille, France, reactions of ozone with organic compounds).

## Contact

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# **2<sup>nd</sup> Scientific Programme**

**Nanochemistry,  
Environmental Friendly  
Technologies - Energy**

## **MATERIALS & MEMBRANES FOR ENVIRONMENTAL SEPARATIONS LABORATORY**

### **Research Objectives/Activities**

- Pore Structure Analysis & Characterisation (pore size distribution, specific surface analysis, pore volume, pore connectivity): nitrogen and mercury porosimetry, absolute and relative gas and gas vapours permeability (single and multi phase),
- Microscopy (Scanning Electron-Field Emission, Atomic Force),
- Chromatography
- Spectroscopy (HPLC, GC, MS),
- Development, modification and optimization of membranes, filters and membrane systems: Chemical Vapour Deposition [CVD], Langmuir-Blodgett Deposition, Plasma Treatment, Phase Inversion, Carbonisation – Activation.
- Characterisation, evaluation and performance validation of porous materials (membranes, activated carbon, etc.) under the framework of various environmental and industrial applications (separation of gaseous pollutants, gas-liquid-vapour permeability-selectivity, reverse osmosis, control drug release and transcutaneous dosing systems, other biotechnological applications etc.).
- Mass and heat transfer process simulation in porous media by means of continuous (macroscopic) and discernible numerical modeling (networks) processes.
- Visual reconstruction and representation of flow phenomena through porous media and various pore sizes by means of different techniques.
- Numerical, experimental and visual, realistic representation of oil recovery processes and techniques by means of mathematical models and experimental process reconstruction structures of well-defined geometry and under realistic conditions (realistic high pressure and temperature deposit conditions).
- Reconstruction of porous media with the use of scanning tomography and computer graphic simulations.
- Preparation and characterization of hybrid nanocomposite materials (Polymer/clay nanocomposites).
- Modification and utilisation of natural algal products and processing by-products (i.e. polysaccharides, alginic acids etc.) in environmental applications and pollutant separations (i.e. heavy metal and pesticide removal from water streams, waste and brackish water treatment etc.).
- Development and characterization of single and multi-walled carbon nanotubes.
- Development and characterization of nanostructured materials for hydrogen storage.
- Preparation and characterization of material systems for biotechnological applications and packaging materials of improved barrier properties.
- Synthesis and characterisation of materials for single and multi-layer film and hollow-fibre structures.
- Synthesis and characterisation of zeolitic membranes.
- Synthesis and characterisation of metal nanoparticles.
- National Contact Point, EU FP7, Thematic Priority 6: "Environment, including climate change", Programme Cooperation

### **Publications 2008**

1. Yoo W.C., Kumar S., Wang Z., Ergang N.S., Fan W., Karanikolos G.N., McCormick A.V., Penn R.L., Tsapatsis M., Stein A., "Nanoscale reactor engineering: Hydrothermal synthesis of uniform zeolite particles in massively parallel reaction chambers", *Angew. Chem. Int. Ed.*, 47(47), 9096-9099 (2008). Journal's cover page
2. Karanikolos G.N., García H., Corma A. and Tsapatsis M., "Growth of AlPO<sub>4</sub>-5 and CoAPO-5 Films from Amorphous Seeds", *Microporous Mesoporous Mater.*, 115(1-2), 11-22 (2008).
3. Veziri Ch. M., Pilatos G., Karanikolos G.N., Lambropoulos A., Kordatos K., Rigopoulou-Kaselouri V., Kanellopoulos N.K., "Growth and Optimization of Carbon Nanotubes in

- Activated Carbon by Catalytic Chemical Vapour Deposition", *Microporous Mesoporous Mater.*, **110**(1), 41-50 (2008).
4. Karanikolos G.N., Alexandridis P., and Mountziaris T.J., "Growth of ZnSe and CdSe Nanostructures in Self-Assembled Block Copolymer-Stabilized Templates", *Mater. Sci. Eng. B*, **152**(1-3), 66-71 (2008).
  5. Vermisoglou E. C., Pilatos G., Romanos G. E., Karanikolos G. N., Boukos N., Mertis K., Kakizis N.K., Kanellopoulos N. K., "Synthesis and Characterization of Carbon Nanotube-Modified Anodised Alumina Membranes", *Microporous Mesoporous Mater.*, **110**(1), 25-36 (2008).
  6. Vermisoglou E. C., Romanos G. E., Tzitzios V., Karanikolos G.N, Akylas V., Delimitis A., Pilatos G., Kanellopoulos N. K., "Synthesis of nanocrystalline gold-carbon nanotube composites and evaluation of their sorption and catalytic properties", *Microporous Mesoporous Mater*, in press, 2008
  7. A. Labropoulos, G. E. Romanos, G. I. Pilatos, N. K. Kakizis, E. P. Favvas and N. K. Kanellopoulos, "Investigating the evolution of N<sub>2</sub> transport mechanism during the post treatment of silica membranes by application of a cyclic chemical vapour deposition method", *Microp. Mesop. Mater.*, **110**, 2008, 11 – 24.
  8. Nitodas S. F., Favvas E. P., Romanos G. E., Papadopoulou M. A., Mitropoulos A. Ch. and Kanellopoulos N. K. "Synthesis and Characterization of Hydrogen Selective Silica-based Membranes", *J. of Porous Materials*, **15** (5), 2008, 551 – 557.
  9. Favvas E. P., Kouvelos E. P., Romanos G. E., Pilatos G. I., Mitropoulos A. Ch. and Kanellopoulos N. K. "Characterization of highly selective microporous carbon hollow fibre membranes prepared from a commercial co-polyimide precursor", *J. of Porous Materials*, **15** (6), 2008, 625 – 633.
  10. Favvas E. P. and Mitropoulos A. Ch. "What is spinodal decomposition?", *J. of Engin. Sci. and Tech. Review*, **1**, 2008, 25 – 27.
  11. Romanos G. E., Vangeli O. C., Stefanopoulos K. L., Kouvelos E. P., Papageorgiou S. K., E. P. Favvas and Kanellopoulos N. K. "Methods of evaluating pore morphology in hybrid organic-inorganic porous materials", *Microp. Mesop. Mater.*, in press, 2008, DOI 10.1016/j.micromes
  12. Favvas E. P., Sapalidis A. A., Stefanopoulos K. L., Romanos G. E., Kanellopoulos N. K., Kargiotis E. K. and Mitropoulos A. Ch. "Characterisation of carbonate rocks by combination of scattering, porosimetry and permeability techniques", *Microp. Mesop. Mater.*, in press, 2008, DOI 10.1016/j.micromeso.2008
  13. Lambropoulos A., Romanos G.E., Steriotis Th., Nolan J., Katsaros F., Kouvelos E.P., Kanellopoulos N.K., "Development of an Innovative Mercury intrusion technique to examine defects plugging after CVD treatment of NF composite membranes" *J. Porous Mat.*, **15**, 83-91 (2008)
  14. Papageorgiou S.K., Kouvelos E.P. and Katsaros F.K., "Calcium alginate beads from *Laminaria digitata* for the removal of Cu<sup>+2</sup> and Cd<sup>+2</sup> from dilute aqueous metal solutions" *Desalination*, **224**, 293-306 (2008)
  15. Steriotis Th.A., Stefanopoulos, K.L., Katsaros, F.K., Gläser, R., Hannon, A.C., Ramsay, J.D.F., "In situ neutron diffraction study of adsorbed carbon dioxide in a nanoporous material: Monitoring the adsorption mechanism and the structural characteristics of the confined phase", *Physical Review B - Condensed Matter and Materials Physics*, **78** (11), 115424 (2008). Chosen for the *Virtual Journal of Nanoscale Science & Technology*, October 6, 2008 issue.
  16. Gamari-Seale, H.; Troyanchuk, I.O.; Sazonov, A.P.; Stefanopoulos, K.L.; Toebbens D.M. "Structure and magnetic order in La<sub>0.7</sub>Ca<sub>0.3</sub>Mn<sub>0.5</sub>Co<sub>0.5</sub>O<sub>3</sub> and La<sub>0.8</sub>Sr<sub>0.2</sub>Mn<sub>0.5</sub>Co<sub>0.5</sub>O<sub>3</sub> perovskites", *Physica B*, **2008**, 403, 2924-2929.
  17. Todorova N., Giannakopoulou T., Romanos G., Vaimakis T., Yu J. and Trapalis C.C., "Preparation of fluorine-doped TiO<sub>2</sub> photocatalysts with controlled crystalline structure", *International Journal of Photoenergy* 2008.
  18. Athanasekou C. P., Papageorgiou S.K., Kaselouri V., Katsaros F.K., Kakizis N.K., Sapalidis A.A. and N.K. Kanellopoulos, "Development of hybrid alginate/ceramic membranes for Cd<sup>2+</sup> removal", *Microporous Mesoporous Mater*, in press, 2008.



19. Kakizis N. K., Pilatos G., Andrianopoulos P., Kartel N., Romanos G.E., Grigoriev A. and Kanellopoulos N.K., "Bactericidal and Catalytic Degradation properties of high specific-surface spherical carbon absorbents impregnated with metal salts for medical and packaging applications", *BIOMATERIALS*, in press, 2008.
20. Bourlinos A.; Steriotis Th.; Zboril R.; Georgakilas V.; Stubos A.; "Direct synthesis of carbon nanosheets by the solid-state pyrolysis of betaine", *J. Mater. Sci.* accepted
21. Labropoulos A.I., Romanos G.E., Karanikolos G.N., Katsaros F.K., Kakizis N.K. and Kanellopoulos N.K., "Comparative study of the rate and locality of silica deposition during the CVD treatment of porous membranes with TEOS and TMOS", *Micropor. Mesopor. Mater.* (2008) doi:10.1016/j.micromeso.2008.08.063.
22. Kakizis N.K., Pilatos G., Tsigonias M.K., Andrianopoulos P. and Kanellopoulos N.K., "Printing Process Optimisation of high specific surface carbon adsorbing microspheres in multilayer assemblies of improved gas-barrier properties for environmental and packaging applications", *J. of Imaging Science & Technology*, in press, 2008.
23. M. Konstantakou, Th. Steriotis, E. Kikkinides, A Stubos, "Monte Carlo Simulations of CO<sub>2</sub> sorption in nanoporous Carbons, *J. Porous Media*, in press.
24. C. Zlotea, P. Moretto and Th. Steriotis, "A round robin characterization of the hydrogen sorption properties of a carbon based material", *Int. Journal of Hydrogen Emergency*, in press

## Conferences & Proceedings 2008

- 1) Karanikolos G.N., Vermisoglou E.C., Kanellopoulos N.K., Alexandridis P. and Mountziaris T.J., "Amphiphilic Block Copolymer Nanocontainers for Templated Growth of Nanostructures", 1<sup>st</sup> International Conference from Nanoparticles and Nanomaterials to Nanodevices and Nanosystems, Halkidiki, Greece, June 16, 2008.
- 2) Vermisoglou E.C., Labropoulos A., Romanos G.E., Kouvelos E., Papageorgiou S., Karanikolos G.N., Katsaros F. and Kanellopoulos N.K., "Hydrogen Storage in Polymer-Assisted Pd-Decorated Single Walled Carbon Nanotubes", 1<sup>st</sup> International Conference from Nanoparticles and Nanomaterials to Nanodevices and Nanosystems, Halkidiki, Greece, June 16, 2008.
- 3) Labropoulos A.I., Vermisoglou E.C., Kakizis N.K., Romanos G.E., Pilatos G.I., Karanikolos G.N. and Kanellopoulos N.K., "Controlling the Nanostructure of Nanoporous Solids and the Evaluation of their Performance", 1<sup>st</sup> International Conference from Nanoparticles and Nanomaterials to Nanodevices and Nanosystems, Halkidiki, Greece, June 17, 2008.
- 4) Vermisoglou E.C., Karanikolos G.N., Pilatos G., Romanos G.E., Veziri Ch.M., Likodimos V. and N.K. Kanellopoulos, "Templated Growth of Aligned Carbon Nanotubes on Porous Supports", 1st International Conference from Nanoparticles and Nanomaterials to Nanodevices and Nanosystems, Halkidiki, Greece, June 18, 2008.
- 5) Vermisoglou E.C., Karanikolos G.N., Pilatos G., Romanos G.E. and Kanellopoulos N.K., "Growth and alignment of carbon nanotubes in porous templates", 34th International Conference on Micro & Nano Engineering, Athens, Greece, Sep. 17, 2008.
- 6) Karanikolos G.N., Alexandridis P., Mountziaris T.J., "Self-assembled polymeric templates for confined growth of compound semiconductor nanostructures", 34th International Conference on Micro & Nano Engineering, Athens, Greece, Sep. 17, 2008.
- 7) Karanikolos G.N., Veziri Ch.M., Palomino M. and Kanellopoulos N.K. and Tsapatsis M., "Seeded growth of AlPO<sub>4</sub>-5 and CoAPO-5 films: Control over film morphology and pore orientation", 34th International Conference on Micro & Nano Engineering, Athens, Greece, Sep. 17, 2008.
- 8) Veziri Ch.M., Karanikolos G.N., Kanellopoulos N.K. and Tsapatsis M., "Oriented Microporous Films by Seeded Growth", 1<sup>st</sup> International Workshop of Nanoporous Materials in Energy and Environment, Chania, Greece, Oct. 14, 2008.

- 9) Vermisoglou E.C., Karanikolos G.N., Pilatos G., Romanos G.E., Zafiropoulou I., Kanellopoulos N.K., "Templated Growth Of Aligned Carbon Nanotubes in Anodized Alumina", 1<sup>st</sup> International Workshop of Nanoporous Materials in Energy and Environment, Chania, Greece, Oct. 14, 2008.
- 10) Kakizis N.K., Pilatos G., Tsigonias M.K., Andrianopoulos P. and Kanellopoulos N.K., "Printing of high specific surface carbon adsorbing microspheres in multilayer assemblies of improved gas-barrier properties for environmental and packaging applications", 6th International Conference on Imaging Science and Hardcopy, ICISH'2008, Zhanjiang, China, January 10-13, 2008. (Invited Lecture)
- 11) Kakizis N.K., Tsigonias M.K., Politis A., Nils E., Nomikos S., Kanellopoulou A., Trapalis C. C. and Kanellopoulos N.K. "Development of "micrograna" synthesis methodology for application in e-paper applications, Review of current technologies and Prospects", 6th International Conference on Imaging Science and Hardcopy, ICISH'2008, Zhanjiang, China, January 10-13, 2008.
- 12) Massaras L. V., Mertzanides I. K., Favvas E. P., Mitropoulos A. Ch. and Kargiotis E. K. "Fracture Entry Friction and Fracture Tip Dilatancy: Major Advances on the Design, Placement and Analysis of Propped Hydrofrac Treatments", STIMtech 2008, 3<sup>rd</sup> International Conference and Exhibition, 1–2 February, 2008, Mumbai, India.
- 13) Favvas E. P., Romanos G. E., Papageorgiou S. K., Sapalidis A. A., Katsaros F. K, Mitropoulos A. Ch. and Kanellopoulos N. K. "High pressure gas permeability of carbon hollow fiber membranes", 1<sup>st</sup> International Workshop NAPEN 2008 "NANoPorous materials in ENergy and ENvironment", 12 – 15 October, 2008, Chania – Crete, Greece.
- 14) Nomikos S., Politis A., Renieri D., Tsigonias M. K. and Kakizis N.K., "Printed Technologies for Intelligent Applications, [Market of Printed Electronics]", 6th International Conference on Imaging Science and Hardcopy, ICISH'2008, Zhanjiang, China, January 10-13, 2008. (Invited Lecture).

## Funded Projects

1. EE 1195 – INSIDE\_PORES NMP3-CT-2004-500895, "In-Situ Study and Development of Processes Involving Nano-Porous Solids", Network of Excellence in nanotechnology FP6, Priority 3 – NMP, Thematic priority 3.4.1.1. Partners to NCSR "D": Centre Nationale de la Recherche Scientifique (France), Imperial College (United Kingdom), University of Leipzig (Germany), University of Antwerp (Belgium), University of Stuttgart (Germany), Institute of Energy and Technology (Norway), TuDelft (The Netherlands), University of Alicante (Spain), Instituto di Chimica dei Mateiali (Italy), Centre for Research and Technology Hellas (Greece), University of Hannover (Germany), SINTEF(Norway),TNO (The Netherlands). Total Budget: 6.800.000 €, NCSR "D" Budget: 1.844834 €. (October 2004- October 2008).
2. EE 1399 - HYCONES NMP3-CT-2006-032970, "Hydrogen Storage in Carbon Cones", Partners to NCSR "D": Institute for Energy Technology (NO), The University of Nottingham (UK), Institute of Nuclear Physics, Polish Academy of Sciences (PL), Scatec AS (NO) Total Budget 2.564.000 €, NCSR"D" Budget: 577.000 € (November 2006-September 2009).
3. EE 1242 - EPAN-NANOFOOD TP-21, "Development of ceramic membranes for applications in food industries", GREEK NATIONAL OPERATIONAL PROGRAMME "COMPETITIVENESS", AXIS 4 – MEASURE 4.5, CONCERTED PROGRAMME "Food Agriculture", Partners to NCSR "D": Tsantalís S.A., Greek Sugar Industry, Zenon S.A., Technological Educational Institute (T.E..I.) of Athens, EVGA S.A. Total Budget 600.200 €, NCSR"D" Budget: 112.800 € (November 2004-October 2007).
4. EE 1232 - HUNGARY–GREECE JOINT RESEARCH AND TECHNOLOGY PROGRAMMES 2003 – 2006, "Preparation of Highly Selective Carbon for CO<sub>2</sub>/CO Separation", Partners to NCSR "D": Department of Physical Chemistry Budapest University of Technology and Economics (Hungary), SUC Hellas (Greece). NCSR"D" Budget: 23.460 € (January 2005-December 2006)

5. EE 1290- EPAN – O3EΔ181, "Design and development of carbon and silicon nanostructures. Theoretical and experimental investigation of their application in hydrogen, or other gas, mixtures separation and storage processes." GREEK NATIONAL OPERATIONAL PROGRAMME "COMPETITIVENESS", MEASURE 8.3, CONCERTED PROGRAMME "Nanotechnology". Partners to NCSR "D": University of Athens, University of Illinois Chicago, SUC HELLAS Ltd (IPEL). Total Budget: 111.660 €, NCSR "D" Budget: 67.642 € (December 2005 – December 2008).
6. POLAND-GREECE 157-ε, Development and Testing of Ordered Porous Materials for Olefin-Paraffin Gas Separations, JOINT RESEARCH AND TECHNOLOGY PROGRAMMES 2005 – 2007, Partner to NCSR "D": Institute of Chemical Engineering-Polish Academy of Sciences (PO). Budget NCSR "D": 11.740 € (October 2006-March 2008).
7. Development of innovative desalination and waste-water treatment systems utilising bi-layered hollow fibre membranes (AFEP), (GSRT Grant: ATT-68), Budget NCSR "D": 141500€.
8. G.N. Karanikolos, ENTEP 04 – Accession to the Hellenic registry of R&D researchers from abroad, 3<sup>rd</sup> EU support framework – operational programme "Competitiveness, GSRT: "Synthesis of nanoporous molecular sieves through optimisation of the nanostructure", Budget: 78000€, October 2006 – October 2008
9. FUSION "Fundamental Studies of Transport in Inorganic Nanostructures", FP6, Thematic priority 3.4.2.1-2. Partners to NCSR "D": University College Dublin (Ireland), University of Edinburgh (UK), Delft University of Technology (The Netherlands), Warsaw University of Technology (Poland), VTT Technical Research Centre of Finland, EcoCeramics B.V. (The Netherlands). Total budget: 2.137.000 €, NCSR"D" Budget: 180.000 €. (December 2004-November 2007).
10. ERA Pilot MiNa TSI "European Research Area Pilot Action onMicroNano Technology Systems Integration", FP6 Priority. Partners to NCSR "D": VDI/VDE Innovation + Technik GmbH (Germany), Österreichische Forschungsförderungsgesellschaft (Austria), University Of Tartu (Estonia), Ministerio De Educacion Y Ciencia (Spain), Association Eurimus Office (France), Association For Pidea (France), Commissariat A L'Energie Atomique (France), Ente Per Le Nuove Tecnologie, L'Energia E L'Ambiente (Italy), Israeli Industry Centre For Research and Development (Israel), Fondazzjoni Temi Zammit (Malta), Slovenska Technicka Univerzita v Bratislave (Slovakia). Total Budget: 850.000 €. NCSR"D" Budget: 42.366 €. (July 2005-July 2007).
11. "Environment NCPs cooperating to improve their effectiveness", (ENV-NCP-Together-21249), Coordination Support Action, N. Kakizis, Partners to NCSR"D" the Network of the 36 National Contact Point Organisations in Europe, Asia and N. Africa, Budget: 2997000€, NCSR"D" budget: 73.345€, 2008-2013.

## Research Infrastructure & Facilities

Nitrogen Porosimeter with Krypton Upgrade – Quantachrome, Mercury Porosimeter – Quantachrome, Low Pressure Permeability rig , High Pressure permeability rigs (2, up to 70 bars), High pressure selectivity rigs (2, gaseous phase) , Low pressure selectivity rig (gaseous phase) , Gas chromatographers (3) with automated sampling capabilities Gas Chromatographer – Mass Spectrometer – Pfeiffer, Dynamic gas adsorption rig Hybrid fluidised bed – membrane system for the removal of volatile organic compounds High pressure automated gravimetric sorption analyser – HIDEN IGA, Magnetic suspension gravimetric analysers (2) – Rubotherm, Low pressure sorption gravimetric analysers (3) – CI balances, Langmuir-Blodgett (LB) trough for the preparation of thin films, Chemical Vapour Deposition reactors, Grazing incidence infrared GIIR reflection unit, Advanced Imaging Equipment, including a Computerized Video Unit for the Investigation of Flow Phenomena through Porous Systems, Extensive IT and Network infrastructure available including UNIX servers, access to supercomputer clusters for advanced modeling applications, T3 Network Lines etc., Quartz crystal microbalances (2) – Q-sense, ThinkSRS, High vacuum systems High pressure, hydrogen volumetric sorption apparatus for isotherms – (VTI, HPVA 100)

Gas and vapour permeability apparatus for polymers and nano-composites (oxygen permeability – Danseror PBI, AFM –VeeCo, diInnova , FTIR Nicolet 6700, High pressure cell for FT-IR, Ultra pure water production unit, Ion chromatography system – Dionex HPLC – Dionex, Calorimeter Calvet – Setaram, Thermal analysis (TGA) – Setaram, Zero length Chromatography, Field emission scanning electron microscope, (FE-SEM) Jeol –JSM-7401F

## **Personnel**

(Research Director); Dr. Nick Kanellopoulos, Researcher A', ; Dr. Theodore Steriotis, Researcher B', Dr. Kostas Stefanopoulos, Researcher C', Dr. Fotis Katsaros, Researcher C', Dr. George Romanos, Researcher C', 8 Research & Technical Personnel; Dr. Nickolas Kakizis, Dr. Sergios Papageorgiou, Evaggelos Kouvelos, Andreas Sapalides, Evaggelos Favvas, George Pilatos, Chrysa Athanasekou, Anastasios Gontzias, (2 post-doctoral associates, external funding); Dr. George Karanikolos, Dr. John Nolan; (6 PhD Students); Charitomeni Veziri, Eleni Vermisoglou, Anastasios Labropoulos, Victoras Akylas, Marios Tsigonias, Olga Vaggeli (3 MSc Students); Eleni Chatzidaki, Panagiotis Karatzis, Panagiota Tatsiou, (Technical & Administrative Associates, External Funding); Stefanos Christou, Edward Zienger,

## **Collaborations – Invited Visits**

Prof. Michael Tsapatsis (Department of Chemical Engineering and Materials Science, University of Minnesota, Development of Porous Films and Membranes), Prof. Avelino Corma (Instituto de Tecnologia Quimica, CSIC-UPV, Universidad Politecnica de Valencia, Development of oriented Nanotubes), Prof. T.J. Mountziaris (Department of Chemical Engineering and UMass NanoMedicine Institute, University of Massachusetts, Development of Nanoparticles), Prof. P. Alexandridis (Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Amphiphilic Co-Polymers).

## **Contact**

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NCSR - National Center for Scientific Research "Demokritos"  
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Network of Excellence: INSIDE\_PORes - IN-Situ study and DEvelopment of processes involving nano-PORous Solids.

URL: <http://www.inside-pores.gr>"<http://www.inside-pores.gr>

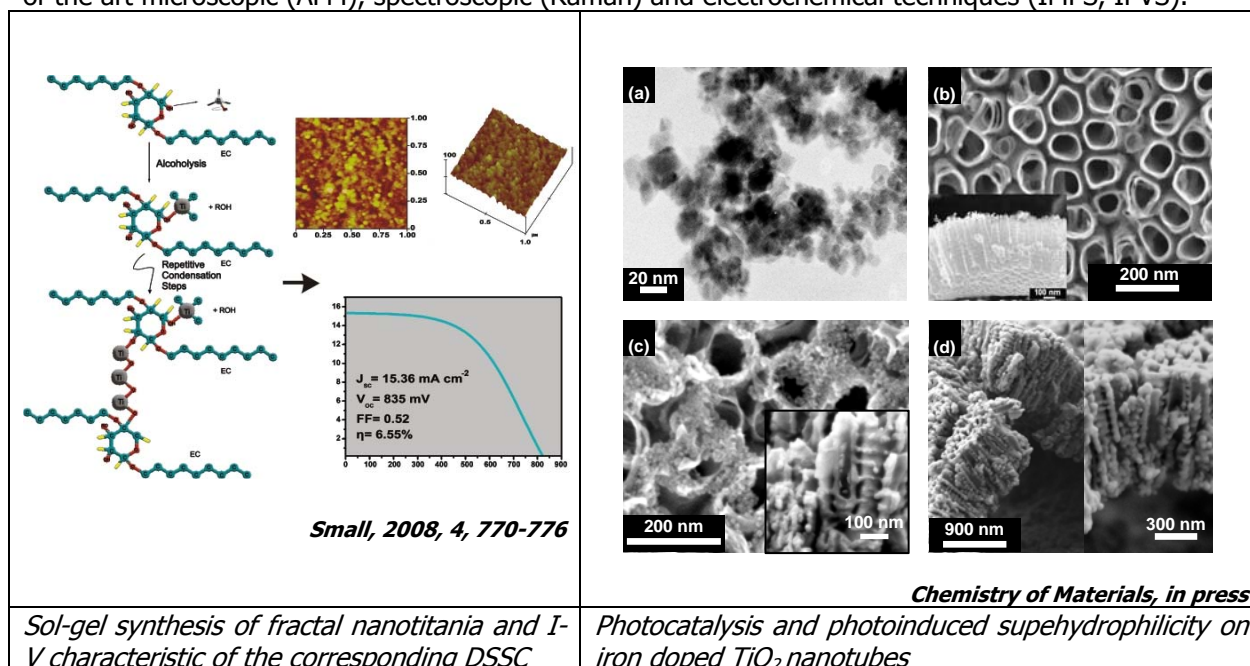
# PHOTOREDOX CONVERSION AND STORAGE OF SOLAR ENERGY DEVELOPMENT OF INNOVATIVE FUNCTIONAL MATERIALS FOR ENERGY AND ENVIRONMENTAL APPLICATIONS

## Research Objectives/Activities

The research activities are mainly centered on the investigation of photoinduced processes and their application to direct conversion of solar energy to electricity as well as to environmental cleaning and health protection. The scientific work is centered on:

### 1. Dye-sensitization of large band-gap semiconductors

The direct conversion of solar energy to electricity is investigated by developing heterojunctions consisting of large band-gap semiconductors sensitized by light harvesting molecular antennas-transition metal complexes. The main objectives concern the investigation, tuning and optimization of photoinduced processes taking place at the semiconductor/dye/electrolyte interface. Essential emphasis is given to the design, synthesis/preparation, characterization, theoretical analysis/modeling and evaluation of performance of multifunctional inorganic photonic compounds [metal oxide thin films (of nanoparticles, nanospheres and nanotubes), transition metal complexes and redox nanocomposite polymer electrolytes as well as their efficient incorporation in the photoelectrochemical device. Intensive research activity aims at controlling the photoelectrode nanostructure using sol-gel templating synthesis and electrochemical self-assembly supported by versatile deposition techniques: screen-printing, doctor-blade, spin-coating, dip-coating, anodic oxidation in corrosive media (aqueous and organic). In addition, the team has intensive research activity, for the development of dye-sensitized solar cells (DSSCs) and their optimization in terms of efficiency, life-time and stability, combining state of the art microscopic (AFM), spectroscopic (Raman) and electrochemical techniques (IMPS, IPVS).



### 2. Innovative nanostructured photocatalysts for environmental cleaning and health protection

Heterogeneous photocatalytic processes and related applications are investigated, involving functional photonic materials in the nanometer scale. The scientific effort aims at improving the efficiency of photocatalytic processes via: a) increase of the photocatalyst effective surface area; b) efficient separation of the photogenerated charge carriers ( $e^-$  and  $h^+$ ); c) photocatalytic sensitization into the Vis light region-shift of the absorption onset; d) judicious balance of photocatalytic and superhydrophilic properties on multi-dynamic surfaces able to photochemically decompose harmful organics, kill bacteria and viruses and being easily self-cleaned; e) increased anticancer and anticoagulant action of titanium dioxide on neoplasm and inflammatory cells. Special emphasis is paid to the combination of advanced oxidation technologies, titania modified nanomaterials and nanotechnology for water treatment.

## Publications

1. Kontos, A.I.; Kontos, A.G.; Tsoukleris, D.S.; Bernard, M.; Spyrellis, N.; Falaras, P. "Nanostructured TiO<sub>2</sub> films for DSSCS prepared by combining doctor blade and sol gel techniques", *J. Mater. Process. Techn.* 2008, *196*, 243-248.
2. Kontos, A.G.; Stergiopoulos, T.; Tsiminis, G.; Raptis, Y.S.; Falaras, P. "In-situ micro- and macro- Raman investigation of the redox couple behavior in dsscs", *Inorg. Chim. Acta*, invited paper, 2008, *361*, 761-768.
3. Katsanaki, A.; Tsoukleris, D.S.; Falaras P.; Karayianni, H.S. "Preparation and characterization of nanocrystalline Pt/TCG counter electrodes for dye-sensitized solar cells", *ASME J. Sol. Energy Engin.* 2008, *130*, 041008 (1-7).
4. Falaras, P.; Stergiopoulos, T.; Tsoukleris, D. "Enhanced efficiency in solid-state dye sensitized solar cells based on fractal nanostructured TiO<sub>2</sub> thin films prepared via sol-gel process in polymer matrix", *Small*, 2008, *4*, 770-776.
5. Kontos, A.I.; Kontos, A.G.; Raptis Y.S.; Falaras P. "Nitrogen modified nanostructured titania: electronic, structural and visible-light photocatalytic properties" *Phys. Stat. Sol. (RRL)*, 2008, *2*, 83-85.
6. Ibhaddon, A.O.; Greenway, G.M.; Yue, Y.; Falaras P.; Tsoukleris, D. "The photocatalytic activity of TiO<sub>2</sub> foam and surface modified binary oxide titania nanoparticles", *Journal of Photochemistry and Photobiology A: Chemistry*, 2008, *197*, 321-328.
7. Stergiopoulos, T.; Ghicov, A.; Likodimos, V.; Tsoukleris, D.; Kunze, J.; Schmuki, P.; Falaras, P. "Dye-sensitized solar cells based on thick highly ordered TiO<sub>2</sub> nanotubes produced by controlled anodic oxidation in non aqueous electrolytic media" *Nanotechnology*, 2008, *19*, 235602 (7pp). *Highly accessed paper, among 10% of articles across all IOP journals. Selected for Nanotechweb (IOP) Journal Highlights Articles: Photoinduced applications of titania nanotubes: Self-assembled anodized titania nanotubes for light-induced environmental cleaning, health protection and solar energy conversion. <http://nanotechweb.org/cws/article/lab/37280>.*
8. Kyrkou, A.; Kontos, A.I.; Papavasileiou G.; Falaras P. "Highly Photoactive Monodisperse Titania Hollow Nanospheres", *J. Adv. Oxid. Technol.* 2008, *11*, 402-410.
9. Likodimos, V.; Stergiopoulos, T.; Falaras, P. "Phase composition, Size, Orientation and Antenna Effects of Self-Assembled Anodized Titania Nanotube Arrays: A Polarized micro-Raman Investigation", *The Journal of Physical Chemistry C*, 2008, *112*, 12687-12696.
10. Ibhaddon, A.O.; Greenway, G.M.; Yue, Y.; Falaras, P.; Tsoukleris, D. "The photocatalytic activity and kinetics of the degradation of an anionic azo-dye in a UV irradiated porous titania foam", *Applied Catalysis B: Environmental*, 2008, *84*, 351-355.
11. Stathopoulos, N.A.; Palilis L.C.; Vasilopoulou, M.; Botsialas, A.; Falaras, P.; Argitis P. "All-organic optocouplers based on polymer light-emitting diodes and photodetectors", *Phys. Stat. Sol. (a)*, 2008, *205*, 2522-2525.
12. V.C. Stergiou, A.G. Kontos and Y.S. Raptis, "Anharmonic Effects and Faust-Henry coefficient of CdTe in the vicinity of the energy gap", *Phys. Rev. B*, 2008, *77*, 235201.
13. Pandiyaraj, K.N.; Selvarajan, V.; Pavese, M.; Falaras, P.; Tsoukleris, D. "Investigation on surface properties of TiO<sub>2</sub> modified by DC glow discharge plasma", *Current Applied Physics*, (in press).
14. Kontos, A.G.; Kontos, A.I.; Tsoukleris, D.; V.Likodimos, V.; Kunze, J.; Schmuki, P.; Falaras, P. "Photo-induced effects on self-organized TiO<sub>2</sub> nanotube arrays: Influence of surface morphology", *Nanotechnology*, (in press).
15. Kontos, A.I.; Likodimos, V.; Stergiopoulos, T.; Tsoukleris, D.S.; Falaras, P.; Rabias, I.; Papavassiliou, G.; Kim, D.; Kunze, J.; Schmuki, P. "Self-Organized Anodic TiO<sub>2</sub> Nanotube Arrays Functionalized by Iron Oxide Nanoparticles", *Chemistry of Materials*, accepted.
16. Pelaez, M.; de la Cruz, A.A.; Stathatos, E.; Falaras P.; Dionysiou D.D.; "Visible Light-activated N-F-codoped TiO<sub>2</sub> Nanoparticles for the Photocatalytic Degradation of Microcystin-LR in Water", *Catalysis Today*, accepted.
- \*17. K. M. Ochsenkuhn, Maria Ochsenkuhn – Petropoulou, Arsenic "Heavy Metals in Airborne Particulate Matter of an Industrial Area in Attika, Greece and Their Possible Sources". 6th Aegean Analytical Chemistry Days, 6-13 October 2008, Turkey Fresenius Environmental Bulletin, PSP volume 17 – No 4. 2008 (p. 1-9)

## Conferences (International)

1. Falaras, P.; Stergiopoulos, T. "Advanced Materials with Tailored Properties and Innovative Functionalities for Nano Dye-Sensitized Solar Cells (NDSSCs)", International Symposium TOWARDS ORGANIC PHOTOVOLTAICS in the field of Organic and Dye Sensitized Solar Cells, Linz, Austria, February 6-8 2008, Abstract, p.101.
2. Pefkianakis, E.K.; Tzanetos, N.P.; Stergiopoulos, T.; Falaras P.; and Kallitsis, J.K. "Synthesis and Characterization of Polymeric [Ru<sup>2+</sup>] Complexes and their Application as Dyes in Solar Cells" 1st International Symposium on Flexible Organic Electronics (IS-FOE), 9-11 July 2008, Halkidiki, Greece.
3. Katsiotis M.; Karatasios I.; Kontos A.I.; Likodimos V.; Papavasiliou G.; Falaras P.; Kilikoglou V.; "Study of Lime - TiO<sub>2</sub> Self-cleaning Repair Mortars", Historical Mortars Conference 2008-HMC08: Characterization, Diagnosis, Conservation, Repair and Compatibility, 24-26 September 2008, Lisbon, Portugal.
4. Konti, G.H.; Chatzivasiloglou, E.; Lykodimos, V., Kantonis, G.; Kontos, A.G.; Philippopoulos, A.I.; Falaras, P. "Synthesis and Characterization of Ruthenium (II) Complexes for Dye Sensitized Solar Cells", 5<sup>th</sup> European Meeting on SOLAR CHEMISTRY AND PHOTOCATALYSIS: ENVIRONMENTAL APPLICATIONS - SPEA 5, 4-8 October 2008, Sicilia, Italy, Book of Abstracts, PP 1.13.
5. Tsoukleris, D. S.; Stergiopoulos, T.; Kontos, A. I.; Likodimos, V.; Kim, D.; Ghicov, A.; Kunze, J.; Schmuki, P.; Kompitsas, M.; Falaras, P. "Photocatalytic Activity of Self-organised Anodic TiO<sub>2</sub> Nanotubes Modified by Au Nanoparticles", 5<sup>th</sup> European Meeting on SOLAR CHEMISTRY AND PHOTOCATALYSIS: ENVIRONMENTAL APPLICATIONS - SPEA 5, 4-8 October 2008, Sicilia, Italy, Book of Abstracts, PP 3.56.
6. Spanou, S.; Pavlatou, E.A.; Kontos, A. I.; Falaras, P.; Spyrellis, N. "Development of Ni/nano-TiO<sub>2</sub> composite electrodeposits for innovative photocatalytic applications", East Forum 2008, Trento, Italy, 23-24 October 2008.
- \* 7. K. M. Ochsenkuhn, Fotis Tsopelas, Maria Ochsenkuhn – Petropoulou, "Arsenic Speciation in Aerosol Samples from an Industrial Area in Greece". 6th Aegean Analytical Chemistry Days, 6-13 October 2008, Turkey Book of abstracts, p. 363
- \* 8. M. Ochsenkuhn, P. Razos, L. A. Tsakanika, M. Ochsenkuhn – Petropoulou, "Particulate Matter and Heavy Metals in the Atmospheric Aerosol of an Industrial and an Urban Area in Athens, Greece". Abstract of European Aerosol Conference 24-26 August 2008 Thessaloniki, Greece.

## Funded Projects

1. "Molecular Engineering of Interfaces of Photonic Devices based on Mesoscopic Oxide layers", COST Action D35- "From Molecules to Molecular Devices", 2005-2009.
2. "Ti-nanotubes", FP6-NMP-STREP, 300 K€, 2006-2009.
3. "Facing pathogenic conditions by combined use of bio-medical methods and nanotechnology" Ypodomes, Metro 4.5, 4.4.1 Action «Consortia of research and technological development in sectors of National priorities», 2050-4/2, 300 k€, 2005-2008.
4. "Organic Solar Cells" PENED 03ΕΔ 118 project, Coordinator P. Falaras: 144 k€, 2005-2008.
5. "Development of composite nanostructured titania. Incorporation into photocatalytic construction materials and application in the decomposition of model liquid and gas pollutants", PENED 03ΕΔ 963 project, 51 k€, 2005-2008.
6. "Development of integrated control analytical methods and advanced oxidation processes for the detoxification of natural water and treated wastes", PENED 03ΕΔ 926 project, 2005-2008.
7. "Development of innovative bio-active magnetic nanomaterials for diagnosis and monitoring of pathogenic conditions by magnetic tomography", PEP Attikis, 9.5 k€, 2006-2008.
8. "Developing of a managing system for monitoring the concentration of suspended particles and the estimated population exposure in Attica", PEP Attikis, 30 k€, 2006-2008.
9. "OrgaPVNet – Coordination Action towards stable and low cost organic solar cell technologies and their application", FP6-Energy-CA, 2006-2009.
10. "Clean Water", FP7-ENV-NMP-2008-2 STREP, 580 K€, 2008-2012, Coordination of the project.

## **Infrastructure**

Micro-Raman spectrometer with visible and IR excitation, UV-Vis spectrometer with integrating sphere, cyclic and linear sweep voltametry, Autolab with possibility of electrochemical impedance spectroscopy (EIS), intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy, photoelectrochemistry unit, screen printing and spin coating deposition facilities, photocatalytic reactors, contact angle meter, viscosity meter, autoclave.

## **Personnel**

P. Falaras, research director/group leader (permanent researcher); A.G. Kontos (permanent researcher); T. Stergiopoulos, V. Likodimos: (2 post doctoral associates, external funding); G. Konti: (PhD students, NCSR "D" fellows); A.I.Kontos, G. Kantonis, E.Rozi, N. Alexaki, A. Katsanaki: (5 PhD students, external funding); D.Tsoukleris: (technical staff, external funding), \* Klaus Oxenquen, (external senior researcher, retired).

## **Collaborations**

M. Grätzel (EPFL Lausanne, Switzerland, DSSCs), G. Tulloch (Dyesol, Australia, Light and Thermal Stress on DSSCs.), P. Schmuki/ J. Kunze (Erlangen, Germany, Ti-Nanotubes), G. Thompson (Manchester, UK, Ti-Nanotubes) V. Catalano (Nevada, USA, Ligands for Ru-dyes), P. Potvin (Toronto, Canada, Dyes for DSSCs), Z. Picramenou (Birmingham, UK, Supramolecular Dyes), A. Ibbandon (Hull University, UK, Photoreactors), D.D. Dionysiou (UC, USA, Photocatalytic water treatment), G.A. Moulas (s.a. company, Greece, Photocatalytic applications)

## **Contact**

Dr. P. Falaras ([papi@chem.demokritos.gr](mailto:papi@chem.demokritos.gr), Tel. +30 210 6503644, Fax. +30 210 6511766)

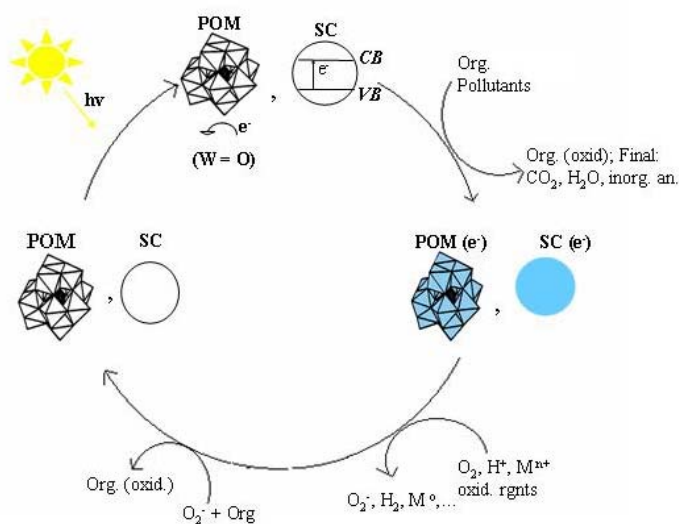


# CATALYTIC-PHOTOCATALYTIC PROCESSES (SOLAR ENERGY-ENVIRONMENT)

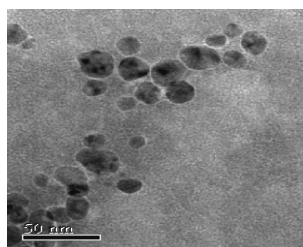
## Research Objectives/Activities

Focus on Catalytic photocatalytic reactions for solar energy utilization, environmental detoxification and environmentally friendly processes. In particular aggregates of metal oxides, mainly  $\text{TiO}_2$ , and polyoxometallates (POM) mainly of W, are used in thermal and photochemical reactions for: (a) Water splitting (hydrogen production), (b) photoelectro-chemical production of electricity, (c) modification of electrodes (photoelectron-chemical reactions), (d) selective oxidation-synthesis of organic chemicals, (e) non-selective oxidation (photodegradation) of organic pollutants to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and inorganic anions, (f) reduction-removal of metallic ions and (g) synthesis of metal nanoparticles

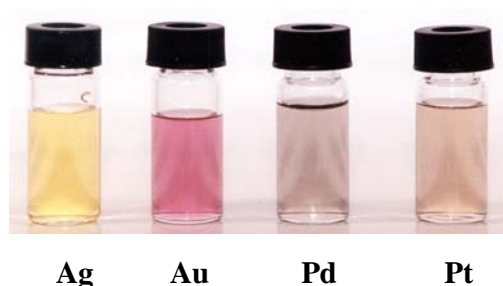
Current research interests: (a) immobilization of photocatalysts in optically active and/or inert substrates, (b) synthesis of nanocomposite films of polymer/POM with layer by layer (LbL) technique, characterization and investigation of their photocatalytic properties (c) photocatalytic synthesis of metallic nanoparticles deposited in nanostructured multilayer films (d) sensitisation of photocatalysts towards the visible light and (e) development of new methods of analysis for trace organic pollutants.



Hiskia et al., Chem. Soc. Rev., 30 (2001), 62



Hiskia et al., Angew. Chem. Int. Ed. 41 (2002) 1911-1914



Ag Au Pd Pt

## Publications 2008

1. T. M. Triantis, A. Troupis, I. Chassiotou, E. Papaconstantinou and A. Hiskia, "Photochromic and Photocatalytic Inorganic-Organic Multilayer Films based on Polyoxometalates and Poly(ethylenimine)" *J. Adv. Oxid. Technol.*, **2008**, *11*, 231-237.
2. Tsimeli, K.; Triantis, T.M.; Dimotikali, D.; Hiskia, A. "Development of a rapid and sensitive method for the simultaneous determination of 1,2-Dibromoethane, 1,4-Dichlorobenzene and Naphthalene residues in honey using HS-SPME coupled with GC-MS." *Anal. Chim. Acta*, **2008**, *617*, 64-71.
3. A. Troupis, T. Triantis, A. Hiskia and E. Papaconstantinou, "Rate-Redox-Controlled Size-Selective Synthesis of Silver Nanoparticles Using Polyoxometalates" *Eur. J. Inorg. Chem.*, **2008**, 5579-5586.
4. T.M. Triantis, K. Papadopoulos, E. Yannakopoulou, D. Dimotikali, J. Hrbáč, R. Zbořil, "Sensitized chemiluminescence of luminol catalyzed by colloidal dispersions of nanometer-sized ferric oxides", *Chem. Eng. J.*, **2008**, *144*, 483-488.

5. A. Troupis, T.M. Triantis, E. Gkika, A. Hiskia and E. Papaconstantinou, "Photocatalytic Reductive-Oxidative Degradation of Acid Orange 7 by Polyoxometalates" *Appl. Catal. B- Environ.*, (in press).
6. T. Triantis, A. Troupis, E. Gkika, G. Alexakos, N. Boukos, E. Papaconstantinou, A. Hiskia, "Photocatalytic Synthesis of Se Nanoparticles using Polyoxometalates", *Catal. Today*, (in press).
7. M. Pelaez, M.G. Antoniou, D.D. Dionysiou, A.A. de la Cruz, K. Tsimeli, T. Triantis, A. Hiskia, T. Kaloudis, C. Williams, M. Aubel, A. Chapman, A. Foss, U. Khan, K.E. O'Shea, J. Westrick, "Sources and Occurrence of Cyanotoxins Worldwide" in D.F. Kassinis, K. Bester, K. Kümmerer (Eds), "Xenobiotics in the Urban Water Cycle", Springer, in press.

## Conferences

1. K. Tsimeli, T. Triantis, T. Kaloudis, A. Hiskia, "Determination of cyanotoxins in surface and drinking water of Athens by LC-MS/MS", 3<sup>rd</sup> International Conference of Water Science and Technology, Integrated Water Resources Management with Emphasis on Climate Change Adaptation, AQUA 2008, Athens Hellas, 16-19 October, 2008.
2. T. Kaloudis, N. Thanasoulis, L. Kousouris, E. Lytras, T. Tzoumerkas, T. Triantis, K. Tsimeli, A. Hiskia, "Laboratory Analysis of Cyanotoxins in Surface and Drinking Waters using ELISA, PPIA, HPLC/PDA AND LC-MS/MS", 3<sup>rd</sup> International Conference of Water Science and Technology, Integrated Water Resources Management with Emphasis on Climate Change Adaptation, AQUA 2008, Athens Hellas, 16-19 October, 2008.
3. E. Gkika, A. Troupis, T. Triantis, E. Papaconstantinou, A. Hiskia, "Photocatalytic Synthesis of Se Nanoparticles using Polyoxometalates", 5<sup>th</sup> European Conference on Solar Chemistry and Photocatalysis: Environmental Applications, Palermo, Italy, 4-8 October, 2008, pg. OP3.8.
4. D. Dimotikali, K. Papadopoulos, E. Yannakopoulou, T. Triantis, D. Christodouleas, J. Hrbac, R. Zboril, "Evaluation of antioxidant activities of organic compounds using chemiluminescence catalyzed by ferric oxide nanoparticles", 5<sup>th</sup> International Conference on Nanosciences & Nanotechnologies, Thessaloniki, Greece, July 14-16, 2008, pg 239.
5. K. Papadopoulos, E. Yannakopoulou, T. Triantis, D. Christodouleas, T. Yannakopoulou, C. Trapalis, D. Dimotikali, "Applications of colloidal solutions of nanosized ferric oxides in chemiluminescence reactions", 1<sup>st</sup> International Conference from Nanoparticles & Nanomaterials to Nanodevices & Nanosystems, Halkidiki, Greece, June 16-18, 2008, pg 263.
6. T. Kaloudis, K. Tsimeli, T. Triantis, N. Thanasoulis, L. Kousouris, E. Lytras, P. Tzoumerkas, A. Hiskia, "Development of an integrated laboratory system for the monitoring of cyanotoxins in surface and drinking waters", 5<sup>th</sup> European Conference on Pesticides and Related Organic Micropollutants in the Environment and 11<sup>th</sup> Symposium on Chemistry and Fate of Modern Pesticides, Marseille, France, 22-25 October, 2008.
7. K. Tsimeli, T. Triantis, T. Kaloudis, A. Hiskia, "Development of a new method for the determination of microcystins and nodularin in surface and drinking water by LC-MS/MS", 5<sup>th</sup> European Conference on Pesticides and Related Organic Micropollutants in the Environment and 11<sup>th</sup> Symposium on Chemistry and Fate of Modern Pesticides, Marseille, France, 22-25 October, 2008.

## Funded Projects

1. "Development of an integrated system for the monitoring of cyanobacteria toxins in surface and processed water by advanced analytical methods", PABET 2005, 27.5 K€, 2006-2008.
2. "Development of innovative bio-active magnetic nanomaterials for diagnosis and monitoring of pathogenic conditions by magnetic tomography", PEP Attikis, 9.5 k€, 2006-2008.
3. "Integrated National Center for Environmental Technology" EPAN, 36 K€, 2006-2008.
4. "Development of a multi-residue method for the determination of pesticides in water by LC-MS/MS. Determination of pesticides and cyanotoxins in drinking and surface water", Research project funded by EYDAP SA, 25 K€, 2008-2009.

## Infrastructure

Photolysis apparatus, Catalytic/ Photocatalytic reactors, Spectrophotometers UV-VIS-near IR, GC equipped with FID, ECD and TCD, HPLC equipped with UV-VIS and FLD, GC/MS, HPLC/MS/MS triple

tetrapole, IC, Polarographic unit, TOC, SPE and SPME apparatus, oven, ultrasound bath, analytical balances, pHmeter, Rotary evaporator, ultrapure water apparatus.

### **Personnel**

A. Hiskia: research director/group leader (permanent researcher); T. Triantis: (post doctoral associates); A. Tsimeli, G. Alexakos: (2 PhD students, NCSR "D" fellows); S. Antonaraki, P. Kormali, I. Dimitracopoulos, S. Anagnostou, S. Zervou: (5 PhD students, without pay); E. Papaconstantinou, T. Caloudis: (adjunct scientists).

### **Collaborations**

Prof. D. Dionysiou (University of Cincinnati, USA, AOP for cyanobacteria toxins destruction), Dr. S. Lacorte (Dep. of Environ. Chem., CID-CSIC, Barcelona, Analytical method development), Dr. T. Caloudis, (EYDAP, trace organic analysis in water)

### **Contact**

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# ELECTRONIC SPECTROSCOPY LABORATORY: APPLICATION TO SUPRAMOLECULES AND NANOSTRUCTURES

## Research Objectives/Activities

- Guest stability and Dynamics in Nanocavities.
- Organized Supramolecular Assemblies: Non-covalently bonded Nanotubes.
- Spectroscopic research of conformers in ground and excited state.
- Photophysics and Dynamics of Linear and Dendronized Photonic Polymers: Applications to Organic Light Emission Diodes (OLEDs) and Optical Lithography

## Publications 2008

1. A. A. Stefopoulos, C. L. Chochos, M. Prato, G. Pistolis, K. Papagelis, F. Petraki, S. Kenou and J. K. Kallitsis, "Novel Hybrid Materials Consisting of Regioregular Poly(3-octylthiophene)s Covalently Attached to Single-Wall Carbon Nanotubes", *Chemistry-A European Journal* 14 (28), 2008, pp. 8715-8724.
2. D. Georgiadou, M. Vasilopoulou, G. Pistolis, D. Dimotikali and P. Argitis, "Energy transfer processes among emitters dispersed in a single polymer layer for colour tuning in OLEDs", *Physica Status Solidi (A) Applications and Materials* 205 (11), 2008, pp. 2526-2531.
3. M. Vasilopoulou, L. C. Palilis, A. Botsialas, D. Georgiadou, P. Bayiati, N. Vourdas, P. S. Petrou, G. Pistolis, N. Stathopoulos, and P. Argitis, «Flexible Organic Light Emitting Diodes (OLEDs) based on blue emitting polymers», *Physica Status Solidi (C) Current Topics in Solid State Physics* 5 (12), 2008, pp. 3658-3662.

## Conferences 2008

1. L.C.Palilis, M.Vasilopoulou, N.A.Stathopoulos, A.Botsialas, D.G.Georgiadou, G.Pistolis, D.Davazoglou, P.Falaras, P.Argitis, "Air-stable solution-processed polymer optocouplers", *1<sup>st</sup> International Symposium on Flexible Organic Electronics (IS-FOE), Halkidiki, Greece, 2008*
2. M.Vasilopoulou, D.G.Georgiadou, L.C.Palilis, G.Pistolis, P.Argitis, "Photochemical study of organic dyes for color tuning in dye-doped OLEDs", *1<sup>st</sup> International Symposium on Flexible Organic Electronics (IS-FOE), Halkidiki, Greece, 2008.*
3. D.G.Georgiadou, M.Vasilopoulou, L.C.Palilis, G.Pistolis, P.Argitis, "Improved charge injection in OLEDs via onium-salt addition inside polymer matrices", *1<sup>st</sup> International Symposium on Flexible Organic Electronics (IS-FOE), Halkidiki, Greece, 2008.*
4. D.G.Georgiadou, M. Vasilopoulou, L. Palilis, G.Pistolis, P.Argitis, "Photochemically Induced Emission tuning of fluorescent and phosphorescent emitters in full colour, single layer organic light emitting diodes", *IV International Krutyn Summer School, Masurian Lake District, Poland, 2008.*

## Funded Projects

1. "Development of innovative bio-active magnetic nanomaterials for diagnosis and monitoring of pathogenic conditions by magnetic tomography" PEP Attikis

## Infrastructure

A Perkin-Elmer Lambda-16 UV - Visible spectrophotometer, a LS-50B Perkin-Elmer Fluorometer, a time correlated single photon counter FL900 of Edinburgh Instruments.

## **Personnel**

G. Pistolis: research director/group leader (permanent researcher); I. Balomenou, : (PhD student, NCSR "D" fellow), A. Kaloudi-Chantzea: (PhD student).

## **Collaborations**

- J. K. Kallitsis, Professor in Department of Chemistry, University of Patras.
- P. Argitis, Researcher in Institute of Microelectronics, NCSR "Demokritos".

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# Isotope Hydrology Laboratory

## Research Objectives/Activities

The Isotope Hydrology Laboratory has developed Technical and Scientific Methods that can be reproduced with particularly high accuracy and reliability. The contribution of our laboratory focuses on the solution of environmental problems, as well as the study of physical processes, which are difficult to follow and comprehend by using the classical methods.



*Mass Spectrometer*

Isotope Hydrology is a multi-disciplinary scientific field that traces and studies stable and radioactive isotopes in the water cycle, such as  $^{18}\text{O}$ ,  $^2\text{H}$ ,  $^{15}\text{N}$ ,  $^{13}\text{C}$ ,  $^3\text{H}$ ,  $^{14}\text{C}$  and  $^{222}\text{Rn}$ . Stable and Radioactive isotope analyses are applied in research concerning the development and the rational management of water potential, such as:

- Identification of the elevation at which groundwater recharge takes place.
- Flow velocity and residence time of groundwater.
- Percentage of mixing between different aquifers and between surface outflow and ground water.
- Tracing the origin of surface and ground water pollution from various sources (e.g. nitrogen pollutants from agricultural and urban activities).
- Estimation of enthalpy of geothermal fields.
- Estimation of groundwater potential.
- The climate change impact on hydrological systems.
- Relation between salinity and isotopic composition in coastal springs.
- Determination of base flow in hydrogeological catchments.



Synthesis of benzene samples for Radiocarbon dating.

## Other applications of the Techniques and Methods used in Isotope Hydrology

The stable and radioactive isotope analyses have an extensive use in:

- Dating any kind of samples for archaeological and palaeo-environmental research.
- Reconstruction of palaeo-dietary habits.
- Study of sea level changes in the past.
- Palaeo-climatology research
- Radioactive radon measurements in indoor spaces and water supply networks.
- Fraud tracing in alcoholic drinks (spirits).
- Estimation of the percentage of carbon dioxide emissions from petrol combustion (i.e. cars, central heating, industry).
- Studies on the occurrence of radioactivity in the atmosphere as a result of the nuclear tests in the 1960s.

## Infrastructure

SIRA Series II Isotope Mass Spectrometer-VG for the determination of isotopic ratio ( $^{18}\text{O}/^{16}\text{O}$ , D/H,  $^{13}\text{C}/^{12}\text{C}$ ,  $^{15}\text{N}/^{14}\text{N}$ ). Low Radiation counting device, using the technique of liquid scintillation for Radiocarbon measurements (Packard-Tricarb LSA, Model 2560TR/XL). Low Radiation counting device, using the technique of liquid scintillation for Tritium and Radon measurements (Packard-Tricarb LSA, Model 2250 CA). Mobil Radon detector of high accuracy for measuring liquid and air samples (Durrige Radon Detector- Rad 7). Electrolysis device for the enrichment of water samples in Tritium. Two glass tubing devices of high vacuum used for Benzene synthesis from various Radiocarbon dating samples. Glass tubing device of high vacuum, for the preparation of the samples, for  $^{18}\text{O}/^{16}\text{O}$  and  $^{13}\text{C}/^{12}\text{C}$  measurements, for the Mass Spectrometer. Glass tubing device of high vacuum, for the preparation of the samples, for D/H measurements, for the Mass Spectrometer.

## Collaborations

The Director of Isotope Hydrology Laboratory, Dr. Nicholas Zouridakis has established a great number of collaborations with various Research Institutes, University Departments and Public Authorities. Representative collaborating projects include:

Isotopic Research at the Carstic system of Lefka Ori, Crete, Institute of Geological and Mineralogical Exploration of Crete, University of Avignon, 1999-2001. Isotopic Research at Mount Troodos, Cyprus, Hellenic Mineral Society, 2000-2001. Isotopic Research of Nestos and Kosphos rivers, Xanthi. Polytechnic School of Ksanthi, University of Thrace, 2003-2006. Determination of Radon concentrations in water supply networks at Thrace. Polytechnic School of Ksanthi, University of

Thrace, 2005. Isotopic Research at Lake Trichonis. Hellenic Center for Marine Research/ Institute of Inland Waters, 2003-2004. Radiocarbon dating of the Neolithic Cave Diro, 1995-2000. Radiocarbon dating of a turf from Maliako Gulf, Ephorate of Palaeoanthropology and Spylaiology, 1996. Radiocarbon Dating of the Cave Kapsia, Tripoli, 1996. Isotopic Research at Lake Vegoritida. Geodynamiki Ltd, 2002-2003. Determination of Radon concentrations in water supply networks at Chalkidiki and Lake Volvi, Terramentor Ltd, 2001-2003. Isotopic Research at the Mediterranean Temporary Ponds, Life Nature, 2005-2006. Isotopic Research in Central and South Peloponnesus, Institute of Geological and Mineralogical Exploration, 2005-2006. Estimation of radioactivity in the atmosphere in Greece, as a result of the nuclear tests in the 60s, International Atomic Energy Agency, 1997-1998. Contribution of the Isotopic Methods in the determination of the baseflow in hydrological catchments, International Atomic Energy Agency, 2004-2006.

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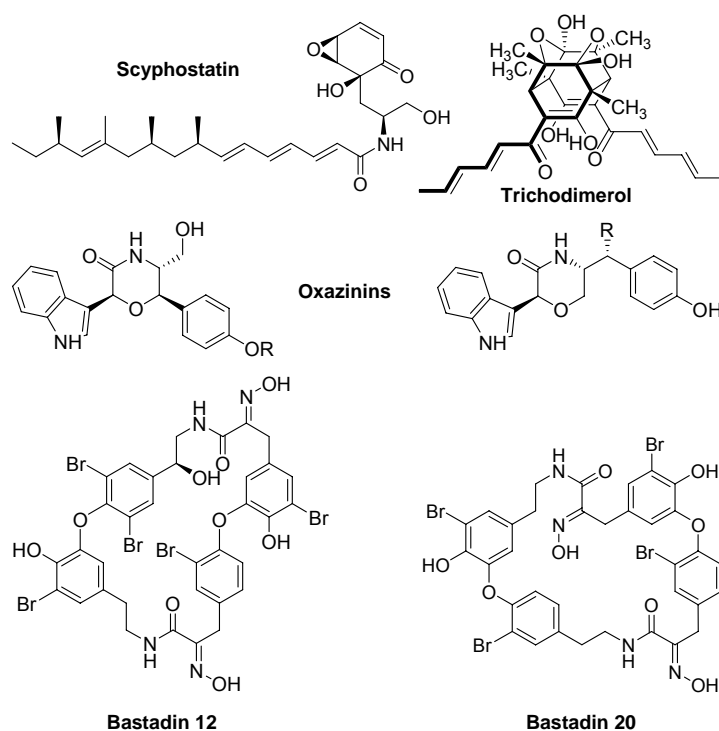
# **3<sup>rd</sup> Scientific Programme**

## **Chemical Biology**

# NATURAL PRODUCTS SYNTHESIS AND BIOORGANIC CHEMISTRY

## Research Objectives/Activities

Our group is involved in the design and synthesis of organic compounds. The targeted molecules are mainly natural products or designed analogues with the aim to prepare and study novel compounds with interesting and/or improved biological activity and possible pharmaceutical applications. The evaluation of their biological activity is performed through collaboration with specialized laboratories. In parallel, the expertise of the team in the design and synthesis of complex organic molecules is exploited for the preparation of organic molecules with possible technological applications (e.g. photoresist etch enhancement additives, linkers for the preparation of polymers) or molecules with interesting supramolecular behavior.



The team has also initiated research in the area of combinatorial chemistry introducing the use of polymorphic scaffolds for the generation of libraries of pharmacophoric structures. Indicative accomplishments of the group are the total synthesis of **Trichodimerol** (TNF- $\alpha$  inhibitor), **Bastadins** (a family of marine natural products that modulate  $\text{Ca}^{2+}$  homeostasis and have antiangiogenic activity), **Oxazinins** (marine toxins related to "red tide" incidents), and the efficient and short synthesis of the pharmacophoric core of **Scyphostatin** (selective inhibitor of Neutral Sphingomyelinase, N-Smase).

## Publications 2008

1. Koulocheri, S.D.; Pitsinos, E.N.; Haroutounian, S.A. "Stereoselective syntheses of 2,6-disubstituted piperidin-3-oles (alkaloid lipids)", *Current Org. Chem.* 2008, *12*, 1454-1467.
2. Zieminska, E.; Lazarewicz, J.W.; Couladouros, E.A.; Moutsos, V.I.; Pitsinos, E.N. "Open-chain half-bastadins mimic the effects of cyclic bastadins on calcium homeostasis in cultured neurons", *Bioorg. Med. Chem. Lett.* 2008, *18*, 5734-5737.
3. Efthimiadou, E.K.; Katsarou, M.E.; Fardis, M.; Zikos, C.; Pitsinos, E.N.; Kazantzis, A.; Leondiadis, L.; Sagnou, M.; Vourloumis, D. "Synthesis and characterization of novel natural product-Gd(III) MRI contrast agent conjugates" *Bioorg. Med. Chem. Lett.* 2008, *18*, 6058-6061.
4. Michaelakis, A.; Mihou, A.P.; Koliopoulos, G.; Couladouros, E.A. "Influence of the microencapsulated pheromone from aged infusion as an oviposition medium of the West Nile virus vector *Culex pipiens*", *Parasitology Res.*, in press (Published on line: 11/2008).

5. Michaelakis, A.; Strongilos, A.T.; Bouzas, E.A.; Koliopoulos, G.; Couladouros, E.A. "Larvicidal activity of naturally occurring naphthoquinones and derivatives against the West Nile virus vector *Culex pipiens*", *Parasitology Res.*, in press (Published on line: 11/2008).
6. Argitis, P.; Niakoula, D.; Douvas, A.M.; Gogolides, E.; Raptis, I.; Vidali, V.P.; Couladouros, E.A. "Materials for lithography in the nanoscale", *Int. J. Nanotechnology*, 6 (1-2), 71-87. in press

## Conferences

1. Couladouros, E.A. "Research at the cutting edge and spin-offs", 9<sup>th</sup> Conference Medicinal Chemistry: Drug Discovery and Design, Patras, 26-28 March 2008, p. 31.
2. Dakanali, M.I.; Vidali, V.P.; Couladouros, E.A. "Synthesis of the bicyclic common core of polycyclic polyprenylated acylphloroglucinols; Synthetic studies towards Hyperforin", 9<sup>th</sup> Conference Medicinal Chemistry: Drug Discovery and Design, Patras, 26-28 March 2008, p. 56.
3. Efthimiadou, E.; Katsarou, M.; Fardis, M.; Zikos, C.; Pitsinos, E.N.; Kazantzis, A.; Leondiadis, L.; Vourloumis, D. "New Contrast Agents for Magnetic Resonance Imaging targeting Cancer Cells", 2nd price Award, 9th Conference Medicinal Chemistry: Drug discovery and design, Patras, 26-28 March 2008, p. 61.
4. Pitsinos, E.N.; Athinaios, N.; Kazantzis, A. "Synthetic studies towards Laurenditerpenol, a novel HIF-1 inhibitor", 9<sup>th</sup> Conference Medicinal Chemistry: Drug Discovery and Design, Patras, 26-28 March 2008, p. 74.
5. Zieminska, E.; Stafiej, A.; Pitsinos, E.N.; Couladouros, E.A.; Moutsos, V.I.; Kozłowska, H.; Toczyłowska, B.; Lazarewicz, J. "Effect of synthetic Bastadins and analogues on the activity of ryanodine receptors in cultured cerebellar granule cells", 7<sup>th</sup> Joint Meeting of AFERP, ASP, GA, PSE & SIF: Natural Products with Pharmaceutical, Nutraceutical, Cosmetic and Agrochemical Interest, Athens, 3-8 August 2008, p. 50.
6. Pitsinos, E.N.; Leondiadis, L.; Giannis, A.; Wacholowski, V. "Novel Scyphostatin analogues: Synthesis and biological evaluation as inhibitors of neutral sphingomyelinase (N-SMase)", 7<sup>th</sup> Joint Meeting of AFERP, ASP, GA, PSE & SIF: Natural Products with Pharmaceutical, Nutraceutical, Cosmetic and Agrochemical Interest, Athens, 3-8 August 2008, p. 51.
7. Ciminiello, P.; Dell'Aversano, C.; Fattorusso, E.; Forino, M.; Grauso, L.; Santelia, F.U.; Tartaglione, L.; Moutsos, V.I.; Pitsinos, E.N.; Couladouros, E.A. "Stereostructural determination of Oxazinins based on a combination of synthetic and NMR studies", 7<sup>th</sup> Joint Meeting of AFERP, ASP, GA, PSE & SIF: Natural Products with Pharmaceutical, Nutraceutical, Cosmetic and Agrochemical Interest, Athens, 3-8 August 2008, p. 51.
8. Pitsinos, E.N.; Athinaios, N.; Kazantzis, A. "Synthetic studies towards Laurenditerpenol, a novel HIF-1 inhibitor", 7<sup>th</sup> Joint Meeting of AFERP, ASP, GA, PSE & SIF: Natural Products with Pharmaceutical, Nutraceutical, Cosmetic and Agrochemical Interest, Athens, 3-8 August 2008, p. 51.
9. Efthimiadou, E.; Katsarou, M.; Fardis, M.; Zikos, C.; Pitsinos, E.N.; Kazantzis, A.; Leondiadis, L.; Vourloumis, D. "New Contrast Agents for Magnetic Resonance Imaging targeting Cancer Cells", 7<sup>th</sup> Joint Meeting of AFERP, ASP, GA, PSE & SIF: Natural Products with Pharmaceutical, Nutraceutical, Cosmetic and Agrochemical Interest, Athens, 3-8 August 2008, p. 52.
10. Efthimiadou, E.; Katsarou, M.; Fardis, M.; Zikos, C.; Pitsinos, E.N.; Kazantzis, A.; Leondiadis, L.; Vourloumis, D. "New Contrast Agents for Magnetic Resonance Imaging targeting Cancer Cells", XX<sup>th</sup> International Symposium on Medicinal Chemistry, Vienna, Austria, August 31 - September 4, 2008. Abstract published in *Drugs of the Future* 2008, 33, Suppl. A, P226.
11. Efthimiadou, E.; Katsarou, M.; Fardis, M.; Zikos, C.; Pitsinos, E.N.; Kazantzis, A.; Leondiadis, L.; Vourloumis, D. "New Contrast Agents for Magnetic Resonance Imaging targeting Cancer Cells", 8th International Conference of Anticancer Research, Kos, Greece, October 17-22, 2008. Abstract published in *Anticancer Research* 2008, 28, 3272-3273.

## Funded Projects

1. "Structure-related pharmacological effects of synthetic bastadins in neurons", Greece-Poland Joint Research and Technology Programmes 2005-2007, 11,74 k€.
2. "Development of innovative bio-active magnetic nanomaterials for diagnosis and monitoring of pathogenic conditions by magnetic tomography", PEP Attikis, 10 k€, 2006-2008

3. "Inhibitors of angiogenesis: design, synthesis and biological exploitation (AngioKem)", COST Action CM0602, 2007-2011.

### **Infrastructure**

Polarimeter, parallel synthesizer, HPLC.

### **Personnel**

E.N. Pitsinos: researcher A level (permanent researcher); V. Vidali: (research fellow NCSR "D");, A. Chiotellis: (post doctoral associate, external funding); N. Athinaios: (PhD student, NCSR "D" fellow); M. Dakanali, C. Mitsopoulou, K. Tsiliouka (3 PhD students, external funding), Prof. El. Couladouros (Collaborating faculty)

### **Collaborations**

Prof. A. Giannis (Universität Leipzig, Fakultät für Chemie und Mineralogie, Institut für Organische Chemie, Leipzig, Germany), Dr. Joe Lewis (Chemical Biology Core Facility, EMBL Heidelberg, Heidelberg, Germany), Prof. J.W. Lazarewicz (Medical Research Centre, Polish Academy of Sciences, Warsaw, Poland), Prof. E.-I. Negishi (Purdue University, Purdue University, West Lafayette, Indiana, USA).

### **Contact**

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# CHEMICAL BIOLOGY OF NATURAL PRODUCTS AND DESIGNED MOLECULES

## Research Objectives/Activities

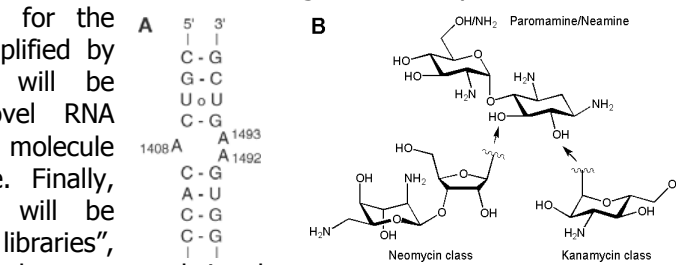
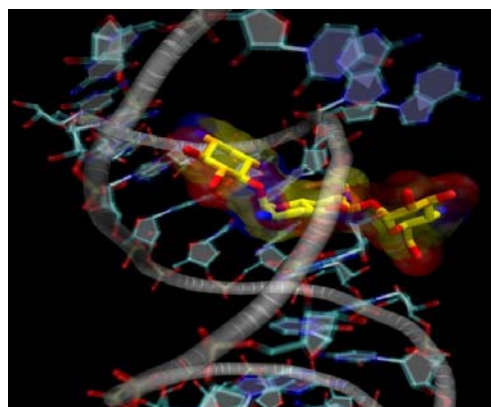
Our laboratory represents a new function within the Institute of Physical Chemistry, namely the "Chemical Biology of Natural Products and Designed Molecules", which was initiated in July 2005. Our studies incorporate molecular design and analysis, total synthesis, structure/activity relationship observations, combinatorial synthesis and biological investigations. Our research focuses on the study of biological systems, DNA, RNA and proteins, through their interaction with small molecules of natural or synthetic origin, targeting the development of new and improved pharmaceutical entities. Our goal is the total synthesis of natural products and designed analogues with improved potencies and pharmacological profiles, the development of new synthetic methodologies in solution and solid phase and the development of new *in vitro* biological assays for the evaluation of the new synthetic entities. Our design will be based on crystallographic information and molecular modelling studies. Currently, we are involved in the areas of Cancer (topoisomerase II inhibitors, apoptosis), bacterial infections (aminoglycosides and A-site ribosomal-RNA) and anti-virals (Hepatitis C virus, HIV). Some of our ongoing projects are described below in more detail.

### 1. Study of RNA components by the synthesis of small molecules

The research is intended to exploit RNA as a pharmaceutical target by the synthesis of rationally designed small molecules as lead structures and could potentially result in the development of novel antibiotics. The work initially focuses on substrates that bind specifically to the ribonucleic acid (RNA) components of the bacterial ribosome, which is a validated target for many known antibiotics.

Additionally, technologies currently used for the global analysis of protein function, exemplified by the biotin-small molecule conjugates, will be explored for the identification of novel RNA components as potential targets for small molecule interactions with therapeutic significance. Finally, exploration of RNA tertiary structure will be performed by the synthesis of "dynamic libraries", where the individual final products will be generated in the

presence of the biological target, resembling the outcome of a natural selection. Our approach will be expandable to other RNA-domains, like the GTPase associated domain in 23S rRNA, target of the antibiotic thiostrepton, or the internal ribosome entry sites (IRES), which are important targets for the treatment of viral pathogens such as polio and hepatitis C.



antibiotic thiostrepton, or the internal ribosome entry sites (IRES), which are important targets for the treatment of viral pathogens such as polio and hepatitis C.

This project represents an interdisciplinary approach, comprising of synthetic, spectroscopic, biological, and computational studies and is expected to elucidate the pharmacological profile of various RNA components and increase our understanding for their individual function. In addition to the obvious training opportunities for young researchers in the different scientific fields involved, its successful completion will place EU in the lead of the world stage in the field of RNA, will create new opportunities for the development of biotechnology and pharmaceuticals and will improve overall our quality of life.

### 2. Nanoscale functionalities for targeted delivery of biopharmaceutics

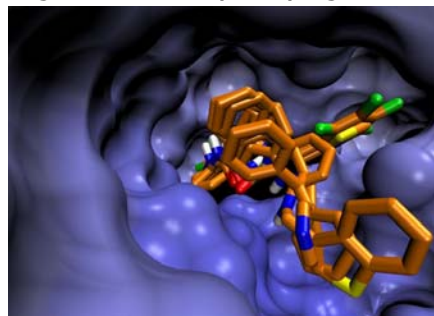
The present research aims at the development of innovative multidisciplinary approaches for the design, synthesis and evaluation of molecular, nano- and micro-scale functionalities for targeted delivery of therapeutic peptides and proteins (biopharmaceutics). New protein- and peptide-based drugs are being discovered every day and their increased availability offers new ways to treat diseases. However, the structure, physicochemical properties, stability, pharmacodynamics, and pharmacokinetics of these new biopharmaceutics place stringent demands on the way they are

delivered into the body. Carrier-based drug delivery systems can improve the bioavailability and diminish the toxicity of Peptidic/Proteinic (P/P) drugs. Furthermore, the carrier specificity can be enhanced, through proper functionalization, and the release of the therapeutic peptide/protein can be controlled on demand. Artificial nanostructures being of the same size as biological entities can readily interact with biomolecules both on the cell's surface and within the cell. Thus, the development of functionalized nanocarriers and nanoparticle-based microcarriers for P/P delivery is both an important scientific challenge and potentially a business breakthrough for the biopharmaceutical industry.

### 3. Design and synthesis of selective VEGF-R2 inhibitors

Angiogenesis is the process by which new blood capillaries sprout from pre-existing blood vessels, and it is well recognized that angiogenesis is an important mechanism governing tumor growth and metastasis. The recent clinical success of Avastatin<sup>®</sup> has provided a proof of principle for the potential of anti-angiogenic cancer therapy with anti-vascular endothelial growth factor (VEGF) agents. This dimeric glycoprotein interacts with two high-affinity transmembrane tyrosine kinase receptors, VEGF-R1 (originally Flt-1) and VEGF-R2 (or human KDR), and results in the proliferation of the endothelial cells and their development into new blood vessels.

One of the potential therapeutic approaches utilizes VEGF-R tyrosine kinase inhibitors that target the intracellular signal transduction. Within the last 5 years there has been considerable effort to produce selective VEGF-R inhibitors, therefore structures of several nanomolar binders of VEGF-R2 have been obtained. Computational chemistry analysis of these results will lead to the design, synthesis and biological evaluation of novel VEGF-R2 inhibitors.



## Publications 2008

1. Katsarou M.E., Efthimiadou E.K., Psomas G., Karaliota A., Vourloumis D., "Novel Copper(II) Complex of *N*-Propyl-norfloxacin and 1,10-Phenanthroline with Enhanced Antileukemic and DNA Nuclease Activities", *J. Med. Chem.* 2008, *51*, 470-478.
2. Psomas G, Alketa Tarushi, Efthimiadou E.K., Synthesis, characterization and DNA-binding of the mononuclear dioxouranium(VI) complex with ciprofloxacin. *Polyhedron* 2008, *27*, 133-138.
3. Efthimiadou E.K., Karaliota A., Psomas G., Mononuclear dioxomolybdenum(VI) complexes with the quinolones enrofloxacin and sparfloxacin: Synthesis, structure, antibacterial activity and interaction with DNA. *Polyhedron* 2008, *27*, 349-356.
4. Evnouchidou I., Momburg F., Papakyriakou A., Chroni A., Leondiadis L., Chang S-C., Goldberg A. L., Stratikos E. "The Internal Sequence of the Peptide Determines N-Terminus Cleavage by ERAP1" *PLoS ONE*, 2008, *3*, e3658.
5. Efthimiadou E.K., Katsarou M.E., Karaliota A., Psomas G., Copper(II) complexes with sparfloxacin and nitrogen-donor heterocyclic ligands: Structure-activity relationships *J. Inorg. Biochem.* 2008, *102*, 910-920.
6. Theodossiou T. A., Papakyriakou A., Hothersall J. S. "Molecular modeling and experimental evidence for hypericin as a substrate for mitochondrial complex III; mitochondrial photodamage as demonstrated using specific inhibitors" *Free Radic. Biol. Med.* 2008, *45*, 1581-1590.
7. Efthimiadou E.K., Karaliota A., Psomas G., Mononuclear metal complexes of the second-generation quinolone antibacterial agent enrofloxacin: Synthesis, structure, antibacterial activity and interaction with DNA. *Polyhedron* 2008, *27*, 1729-1738.
8. Efthimiadou E.K., Karaliota A., Psomas G., Structure, antimicrobial activity and DNA-binding properties of the cobalt(II)-sparfloxacin complex. *Bioorg. Med. Chem. Lett.* 2008, *18*, 4033-4037.
9. E.K. Efthimiadou, M.E. Katsarou, M. Fardis, C. Zikos, E.N. Pitsinos, A. Kazantzis, L. Leondiadis, M. Sagnou, D. Vourloumis, "Synthesis and characterization of novel natural product-Gd(III) MRI contrast agent conjugates." *Bioorg. Med. Chem. Lett.* 2008, *18*, 6058-6061.
10. A. Papakyriakou, D. Vourloumis, F. Tzortzatou-Stathopoulou, M. Karpusas, "Conformational dynamics of the EGFR kinase domain reveals structural features involved in activation." *Proteins* 2009, in press. (published on the web in 2008)
11. Evnouchidou I., Papakyriakou A., Stratikos E. "A new role for Zn(II) aminopeptidases: Antigenic peptide generation and destruction" *Curr. Pharm. Design* 2009, in press. (published on the web in 2008)

## Conferences 2008

1. Dionisios Vourloumis, "Chemical Biology of Small Molecules Interfering with Protein-Synthesis" 13<sup>th</sup> National Conference in Medicinal Chemistry, Athens, Greece, March 14–15, 2008.
2. Dionisios Vourloumis et al. "Chemical Biology of Small Molecules Interfering with Protein-Synthesis" 9<sup>th</sup> International Conference in Medicinal Chemistry: Drug discovery and design, University of Patra, Greece, March 26–28, 2008.
3. Dionisios Vourloumis et al. "New Contrast Agents for Magnetic Resonance Imaging targeting Cancer Cells", 2<sup>nd</sup> *price Award*, 9<sup>th</sup> International Conference in Medicinal Chemistry: Drug discovery and design, University of Patra, Greece, March 26–28, 2008.
4. Dionisios Vourloumis et al. "Rational Design of Vascular Endothelial Growth Factor Receptor-2 (VEGFR-2) Inhibitors based on Molecular Dynamics Simulations" 9<sup>th</sup> International Conference in Medicinal Chemistry: Drug discovery and design, University of Patra, Greece, March 26–28, 2008.
5. Dionisios Vourloumis et al. "Chemical Biology of Small Molecules Interfering with Protein-Synthesis" ESF-COST High-Level Research Conference: Natural Products Chemistry, speaker and session chair, Biology and Medicine, Acquafredda di Maratea, Italy, May 18–23, 2008. Book of Abstracts 2008, pages 60 – 61.
6. Anastasopoulou Panoula, Zografos Alexandros L., Katsoulis Ioannis, Athanasios Papakyriakou, Kythreoti Georgia, Mavridis Ioannis, Vourloumis Dionisios "Chemical Biology of Small Molecules Interfering with Protein-Synthesis", BOSS XI, 11<sup>th</sup> Belgian Organic Synthesis Symposium, Ghent, Belgium, July 13 - 18, 2008. Book of Abstracts 2008, P26.
7. E. Efthimiadou, M. Katsarou, M. Fardis, C. Zikos, E.N. Pitsinos, A. Kazantzis, L. Leondiadis, D. Vourloumis "New contrast agents exploiting natural products for targeted magnetic resonance imaging", 7<sup>th</sup> Joint Meeting of AFERP, ASP, GA, PSE & SIF: Natural Products with Pharmaceutical, Nutraceutical, Cosmetic and Agrochemical interest, Athens, Greece, August 3 – 8, 2008. Book of Abstracts 2008, PG103.
8. E. Efthimiadou, M. Katsarou, M. Fardis, C. Zikos, E.N. Pitsinos, A. Kazantzis, L. Leondiadis, D. Vourloumis "New contrast agents exploiting natural products for targeted magnetic resonance imaging", XX<sup>th</sup> International Symposium on Medicinal Chemistry, Vienna, Austria, August 31 - September 4, 2008. Abstract published in *Drugs of the Future* 2008, 33, Suppl. A, P226.
9. Kythreoti Georgia, Zografos Alexandros L., Katsoulis Ioannis, Athanasios Papakyriakou, Anastasopoulou Panoula, Mavridis Ioannis, Vourloumis Dionisios "Chemical Biology of Small Molecules Interfering with Protein-Synthesis", XX<sup>th</sup> International Symposium on Medicinal Chemistry, Vienna, Austria, August 31 - September 4, 2008. Abstract published in *Drugs of the Future* 2008, 33, Suppl. A, P249.
10. E. Efthimiadou, M. Katsarou, M. Fardis, C. Zikos, E.N. Pitsinos, A. Kazantzis, A. Karaliota, L. Leondiadis, D. Vourloumis "New contrast agents for magnetic resonance imaging targeting cancer cells", 8<sup>th</sup> International Conference of Anticancer Research, Kos, Greece, October 17-22, 2008. Abstract published in *Anticancer Research* 2008, 28, 3272-3273, P183.

## International Patents

1. D. Vourloumis, D.E. Murphy, T.J. Prins, F. Ruebsam, C.V. Tran, S.J. Berthel, R.F. Kester, R. "Oxime Glucokinase Activators." U.S. Provisional Patent Application No. **23198 US** (pending).

## Funded Projects

1. Marie Curie Excellence Grants, "Study of RNA components by the Synthesis of Small Molecules", Contract No. MEXT-CT-2006-039149, Dr. Dionisios Vourloumis, € 1.620 k€, 2/2007–1/2011).
2. 'NMP' INTEGRATED PROJECT, "Nanoscale Functionalities for Targeted Delivery of Biopharmaceutics", Contract No. NMP4-CT-2006-026723, € 537 k€, 10/2006-9/2010).
3. ENTER2004, GSRT, "Design of Selective Inhibitors of Vascular Endothelial Growth Factor Receptor-2 (VEGF-R2) Using Structural Methods for the Treatment of Cancer." Contract No. 04EP63, Dr. Dionisios Vourloumis, € 58.5 k€, 2/07-10/08)
4. "Development of innovative bio-active magnetic nanomaterials for diagnosis and monitoring of pathogenic conditions by magnetic tomography", PEP Attikis, 10 k€, 2006-2008.

## Personnel

D. Vourloumis: research director (permanent researcher); A. Zografos, I. Katsoulis, G. Kythreoti, A. Papakyriakou, M. Katsarou, Victoria Nahmias, Constantina Pyrkotis: (7 post doctoral associates,

external funding); E. Efthimiadou, G. Mavridis: (2 PhD students, NCSR "D" fellows); P. Anastasopoulou, A. Papadopoulou: (2 PhD students, external funding); N. Lymperea, K. Xanthopoulos (2 undergraduate students); C. Georgaki: (administrative assistant, external funding).

### **Collaborations**

T. Hermann (UCSD, San Diego USA, RNA biochemistry), E. Theodorakis (UCSD, San Diego USA, Organic Synthesis), D. Georgiadis (UOA, Athens Greece, Organic Synthesis/Spectroscopy), A. Karaliota (UOA, Athens Greece, Inorganic Chemistry), S. Stratikos (NCSR "Demokritos", IRRP).

### **Contact**

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# **Service Laboratories**

## ENVIRONMENTAL ANALYSIS

### Objectives/Activities

Contamination of water supplies with organic pollutants such as PAHs, PCBs and cyanotoxins is one of the most important global problems. Recent EU Directives propose the determination of these target pollutants in drinking and surface water and set their maximum concentration. Resulting from the above, it is mandatory to monitor these analytes using appropriate methods. The availability of rapid, reliable screening method is prerequisite when a large number of samples must be analyzed, but on the other hand there is an urgent need of a confirmatory method for the analysis of these contaminants which belong to the priority pollutants list. Disadvantages of conventional methods of analysis can be overcome by using liquid chromatography-mass spectrometry (LC/MS/MS). In the frame of the accreditation of our laboratory in PAHs determination in potable and surface water by using LC/MS/MS it has been funded (2005-2009) by Antagonistikotita (Ministry of Development) with 311.3 KEuro. This has upgraded the instrumentation of our laboratory (HPLC/UV-Vis or FL or CD, IC, GC/ECD or FID and GC/MS), mainly by the purchase of the LC/MS/MS analytical device and gave new opportunities to our research and service activities.



Current interests of our Laboratory are focused into the following:

- Method Development for the determination of toxic pollutants in trace level in water, foodstuff and environmental samples (pesticides, PCBs, PBRBs, chlorophenols, PAHs, BTX, VOCs, drug residues, cyanotoxins, organic halides)
- Method Development for the determination of Polychlorinated Biphenyls (PCBs) in water and Organic Halides in foodstuff (honey) by Solid Phase Microextraction (SPME) in combination with GC/ECD and GC/MS.
- Method Development for the determination of Polycyclic Aromatic Hydrocarbons (PAHs) in potable and surface water by using LC/MS/MS.
- Method Development for the determination and identification of cyanotoxins in surface and drinking water by using SPE and LC/MS-MS.
- Elaboration of MSc and PhD Thesis.
- Accreditation of the laboratory in PAHs determination in potable and surface water by using LC/MS/MS (being the only Laboratory in Greece for that purpose).
- Services for the determination of toxic organic residues in trace level.

### Personnel

A. Hiskia: director (permanent researcher); T. Triantis: (quality manager); A. Tsimeli (analyst), S. Zervou, I. Dimitrakopoulos, T. Caloudis: (adjunct scientist).

### Funded Projects

1. "Development of analytical infrastructure of the Environmental Analysis Laboratory, EKEFE Demokritos", Antagonistikotita (Ministry of Development), Coordinator Dr. A. Hiskia, 311,3 K€, 2006-2008.
2. "Chemical Analysis of sediments for the determination of heavy metals and chlorinated organic compounds", in the frame of services to EDRASOMICHANIKI SA, 3,6 K€.
3. «Chemical analysis of soil samples for the determination of Polychlorinated Biphenyls (PCBs)», in the frame of services to HELLENIC PETROLEUM S.A., 4,0 K€.
4. «Chemical analysis of air filters for the determination of Benzo(a)pyrene», in the frame of services to PLINIOS SA, 7,31 K€.

5. «Chemical analysis of soil and water samples for the determination of Polycyclic Aromatic Hydrocarbons (PAHs)”, in the frame of services to PREFECTURE of DRAMA, 3,0 K€.

### **Infrastructure**

Spectrophotometers UV-VIS-near IR, GC equipped with FID, ECD and TCD, HPLC equipped with UV-VIS and FLD, GC/MS, HPLC/MS/MS triple tetrapole, IC, Polarographic unit, TOC, SPE and SPME apparatus, oven, ultrasound bath, analytical balances, pHmeter, Rotary evaporator, ultrapure water apparatus.

### **Collaborations**

Dr. Jussi Meriluoto (Abo Akademi University, Finland, Method development for the determination and identification of cyanotoxins in surface and drinking water by using SPE and LC/MS-MS), Prof. D. Dionysiou (University of Cincinnati, USA, AOP for cyanobacteria toxins destruction), Dr. S. Lacorte (Dep. of Environ. Chem., CID-CSIC, Barcelona, Analytical method development), Dr. T. Caloudis, (EYDAP, trace organic analysis in water)

# ISOTOPIC ANALYSIS, RADIOCARBON DATING, AND RADON MEASUREMENTS

## Objectives/Activities

The laboratory of Isotope Hydrology is offering services principally to Public Organizations, Universities, Technical Universities, Communities, Agencies and private individuals.

The services referring to isotopic analysis are:

- Concentration of  $^{18}\text{O}$ , D in solid and water samples
- Concentration of  $^{13}\text{C}$  in solid and water samples
- Radon in water samples and indoors (indoor pollution)
- Concentration of Tritium in water samples
- Radiocarbon dating and concentration of  $^{14}\text{C}$  in solids, liquids and atmospheric samples

## Personnel

N. Zouridakis: research director/group leader (permanent researcher)

E. Arnidi: (technical staff, under contract).

## Services

In 2008 for scientific collaborations and the several services (University of Athens, HCMR, Polytechnic School of Xanthi, NPUA) were made isotopic analysis of  $^{18}\text{O}$  in 880 water and 260 determinations of Tritium concentration.

## Incomes-Outcomes in 2008

Annual incomes	57.251,4 €
Annual outcomes	34.556,38 €

The Laboratory of Isotope Hydrology has signed contracts for Laboratory Services with IGME of 110.000 € during the years 2006, 2007, 2008.

## Estimate Costs of Isotopic Analysis

The costs for Laboratory Service without taxes are:

Radiocarbon dating of charcoal, wood	250 €
Radiocarbon dating of cells, herbs, $\text{CaCO}_3$	280 €
Radiocarbon dating of mortars	350 €
Radiocarbon dating of bones	500 €
Radiocarbon dating of water	600 €
Isotopic analysis of $^{18}\text{O}$ in water samples	80 €
Isotopic analysis of D in water samples	100 €
Determination of Radon's concentration in water samples	60 €
Determination of Radon's concentration indoors	80 €
Determination of Tritium concentration in water	150 €
Isotopic analysis of $^{18}\text{O}$ in solid samples	100 €

## INTITUTE INSTRUMENTATION AND SERVICES

The following Research facilities provide support for the research projects in IPC and also offer services to other research Laboratories or industry.

- **NMR** ([nmrlab@chem.demokritos.gr](mailto:nmrlab@chem.demokritos.gr)), Scientists in charge: Dr. K. Yannakopoulou, Dr. M. Pelecanou, Dr. L. Leontiadis,

The laboratory, established in 1990, is equipped with a Bruker **AVANCE 500** MHz spectrometer with an indirect broadband and a direct broadband probe and a Bruker **AVANCE III 250** MHz spectrometer with a dual probe. The mission of the lab is to support high quality research carried out by the groups of the participating institutes (Physical Chemistry, Biology, Radioisotopes and Radiodiagnostic Products) and the NCSR "Demokritos" in general, thus actively participating in the research and development activities of the center.

A portion of spectrometer time is devoted to providing service requested mainly from other academic institutions and occasionally from the industry.

- **Macromolecular Crystallography Lab (X-RAY)**

(<http://ipc.chem.demokritos.gr/raxis/index.html>)

Scientists in charge: Drs. Irene M. Mavridis, Metaxia Vlassi, George Nounesis

The laboratory was established in 1998, after the creation of the "Network of Macromolecular Crystallography" by 10 academic laboratories in the Athens area. It is equipped with a Rotating anode (Rigaku) generator, Image Plate Raxis IV (Molecular Structure corporation), Low Temperature apparatus (Oxford Cryosystems) an offer by the Hellenic Pasteur Institute, computing and molecular graphics facilities, Circular Dichroism spectrometer (Jasco J-715). The mission of the lab is to support research carried out by the participating laboratories of the network (three of which are institutes in NCSR Demokritos: Physical Chemistry, Biology, Radioisotopes and Radiodiagnostic Products), thus actively help structural biology research in Greece. The laboratory is also equipped with a 4-circle diffractometer, mainly for use of the Institute of Physical Chemistry.

- **Elemental Analyzer** ([elyan@chem.demokritos.gr](mailto:elyan@chem.demokritos.gr)) Scientist in charge: E. Yannakopoulou

The laboratory was established in the 90s. It is equipped with a Perkin-Elmer 2400 (C,H,N) Elemental Analyzer, which performs a fast and accurate analysis of elements C,H,N. The method is based on the combustion of the sample in an oxygen atmosphere at 925°C. The Elemental Analyzer provides services to all institutes of NCSR "Demokritos", as well as to other research and academic institutions and private section.

- **AFM** ([asap@chem.demokritos.gr](mailto:asap@chem.demokritos.gr)) Scientist in charge: A. Sapalidis

The laboratory, established in the 90s, is equipped with the MultiMode scanning probe Nanoscope III microscope from Digital Instruments. NanoScope III controller is capable of scanning the maximum scan size (16x16  $\mu\text{m}$ ) as low as few nanometers with full 16-bit resolution on all scan waveforms and on each axis. This versatile, high-resolution metrology and imaging tool performs a complete range of AFM techniques for surface characterization of properties like topography, elasticity, friction, adhesion, and electrical/magnetic fields.

The mission of the lab is to support high quality research carried out by the groups of the Physical Chemistry Institute together as well as the other institutes in 'Demokritos'. A portion of microscope's

time is devoted to providing service requested mainly from other academic institutions and occasionally from the private sector.

- **FT-IR** ([fkats@chem.demokritos.gr](mailto:fkats@chem.demokritos.gr)) Scientist in charge: Dr. F. Katsaros

The laboratory is equipped with a Thermo Scientific Nicolet 6700 FTIR spectrometer with N<sub>2</sub> purging system. In addition a single reflection ATR (Attenuated Total Reflection) SmartOrbit accessory, equipped with a single-bounce diamond crystal can be used. This accessory offers many advantages, including the ability to analyze hard, abrasive, or caustic materials, without any sample preparation. The spectrometer supports the research activities carried out by many groups of NCSR Demokritos. It also provides services to academic and industrial users.

- **Thermal analysis lab** ([kpapadok@chem.demokritos.gr](mailto:kpapadok@chem.demokritos.gr))  
Scientist in charge: Dr. K. Papadokostaki

The laboratory, established in 2003, is equipped with a **TA Instruments** 2920 Temperature Modulated Differential Scanning Calorimeter (**MDSC**). MDSC offers all the benefits of standard DSC and provides further information for greater understanding of material properties, because it can separate overlapping events that are difficult or impossible to do by standard DSC. The lab supports research carried out by the Institute of Physical Chemistry and Demokritos Centre in general, related to thermal characterization of polymers and other materials used in various scientific and technological areas. It also provides service to industry.

- **Micro Raman** ([likodimo@chem.demokritos.gr](mailto:likodimo@chem.demokritos.gr)) Scientist in charge: Dr. P. Falaras, Dr. A. Kontos, Dr. V. Likodimos

The laboratory, established in 2007, is equipped with a Renishaw inVia Reflex micro-Raman microscope utilizing an Ar<sup>+</sup> ion laser ( $\lambda=514.5$  nm) and a high power near infrared (NIR) diode laser ( $\lambda=785$  nm) as excitation sources. The spectrometer is equipped with 1800 and 1200 lines/mm diffraction gratings together with holographic notch and dielectric edge Rayleigh rejection filters and a high sensitivity deep depletion CCD detector. Raman spectra can be continuously acquired over an extended spectral range of 100-3500 cm<sup>-1</sup> in a single scan (SynchroScan mode), while measurements down to 10 cm<sup>-1</sup> from the laser line, can be performed by the use of the near excitation tunable filter (NEXT). Confocal Raman measurements are implemented by varying the spectrograph entrance slit and CCD area, while the laser line can be focused on the sample surface using the  $\times 5$ ,  $\times 20$ ,  $\times 50$  and  $\times 100$  objectives on a Leica DMLM microscope at variable laser power. Polarization measurements can also be performed.

The mission of the lab is to support high quality research on the vibrational properties of materials and the characterization of devices carried out in the Institute of Physical Chemistry and NCSR, in general. A portion of spectrometer time is devoted to providing service requested from other academic institutions as well as the private sector.

# **Education Activities**

## Graduate Studies at the Institute of Physical Chemistry

**Responsible:** Dr K. L. Stefanopoulos

**Deputy:** Dr G. Romanos

The training of young scientists (PhD or Master's candidates, post-doctoral fellows) is one of the most important activities of the Institute of Physical Chemistry.

High quality research activities constitute the core of the graduate studies offered. It is supplemented by advanced courses, offered either by NCSR "Demokritos" or by collaborating Universities, as well as lectures by invited speakers from Greece and abroad.

Since the Institute is not entitled by law to operate an independent graduate school, all graduate students are enrolled in university graduate programmes. Indeed, the Institute is actively participating in several such programmes that are financially supported by the Greek Ministry of Education (EPEAEK).

The majority of the graduate students working at the Institute receive financial support either by NCSR "Demokritos" (scholarship) or through their participation in research programmes (national, European or international). Thus, out of about fifty (50) graduate students that perform research at the Institute, seventeen (17) are financially supported by NCSR "Demokritos".

Finally, during 2008, eight (8) PhD and five (5) Master's degrees were awarded to graduate students of the Institute.

In specific:

### Ph.D dissertations

1. S. Antonaraki, "*Study of Degradation Mechanisms of organochlorinated Pollutants: Photolytically with hydrogen peroxide and photocatalytically with 12-tungsto phosphate acid*", School of Chemical Engineering, National Technical University of Athens
2. S. Chatziefthimiou, "*A Crystallographic Study of the Structure of Biological Macromolecules. I. Immunoglobulin domains 9-11 of myomesin. II. Inclusion complexes of cyclodextrins*", Department of Chemistry, University of Athens
3. M. Dakanali, "*Synthesis of polycyclic systems, key structural features of bioactive natural products*", Department of Science, Agricultural University of Athens
4. X. Kontogianni, "*Synthesis of functional dendritic polymers. Study of drug encapsulation and controlled release*", Department of Chemistry, University of Athens
5. V. Nousiou, "*Computational study of spatiotemporal oscillations in heterogeneous catalytic reactions*", Department of Chemistry, University of Athens
6. Th. Oikonomou, "*Biofunctionality of DNA Sequences*", School of Medicine, University of Athens
7. S. Papageorgiou, "*Heavy metal adsorption from wastewater with metabolites extracted from marine biomass*", Department of Chemistry, University of Athens
8. I. Tsogas, "*Supramolecular Systems Derived from the Interaction of Liposomes with Dendritic Polymers*", Department of Chemistry, University of Athens

### Master's dissertations

1. M. Galanou, "*Functional liposomes as carriers of bioactive substances and their application to cancer cell destruction using Photodynamic Therapy*", Department of Chemistry, University of Athens
2. I. Mavridis, "*Chemical Biology of small molecules interfering with Protein-Synthesis*", Department of Chemistry, University of Athens
3. A. Scandali, "*Photocatalytic Degradation of Gas Pollutants using Nanostructured Titania*", Department of Materials Science & Engineering, University of Ioannina



4. N. Sterioti, "*Molecular recognition of PEG-stabilized liposomes*", Department of Chemistry, University of Athens
5. K. Tsimeli, "*Development of an integrated laboratory system for the monitoring of cyanotoxins in surface and drinking waters with LC-MS/MS method. A survey for the presence of cyanotoxins in surface and drinking waters of Athens*", Department of Chemistry, University of Athens