"The most fundamental and lasting objective of synthesis is not production of new compounds, but production of properties."

George S. Hammond,
*Norris Award Lecture, **1968***

Hybrid nanostructures with tailored dimensions of pores exhibiting intensive absorption of light in the red-region - based on porphyrins

Eugenia Fagadar-Cosma

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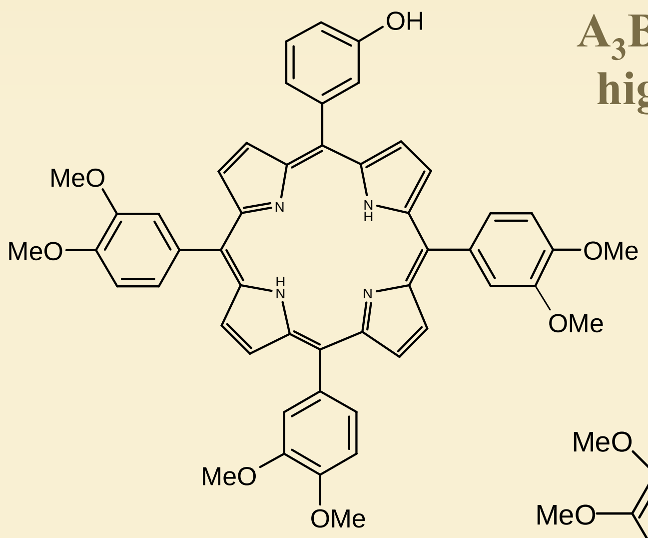
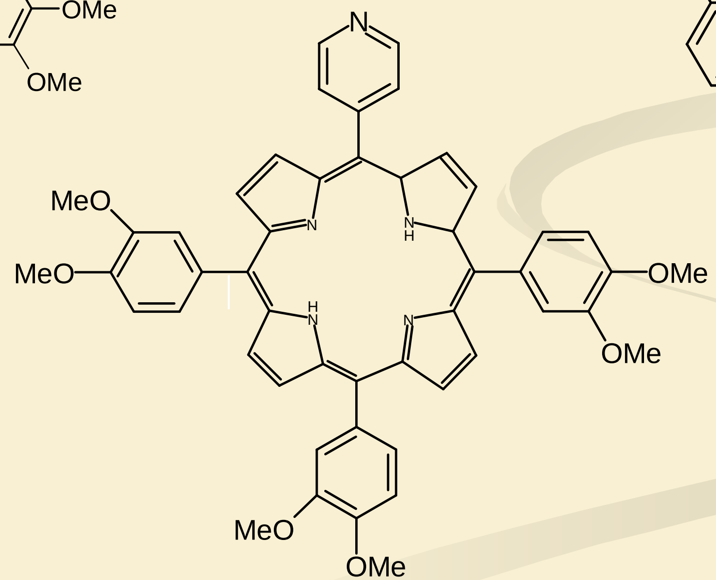
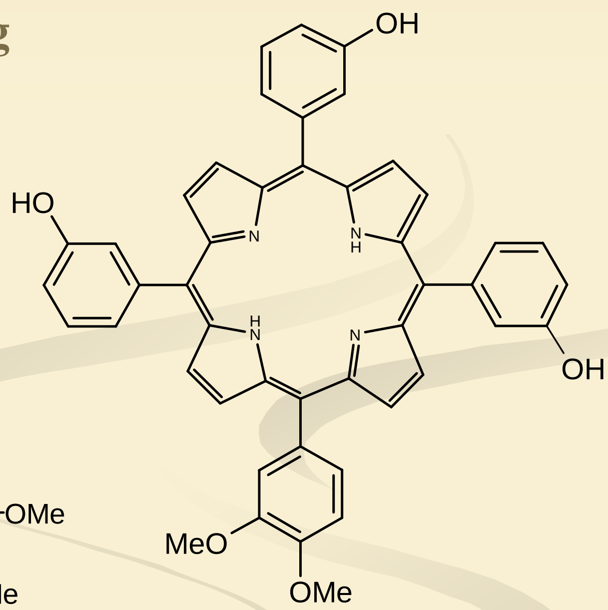
❖Due to their structure and versatile properties porphyrin derivatives are able **to develop supramolecular structures** performing functions like: **catalysis**, **light harvesting**, **dioxygen transport**, **electron transfer.**

❖ First aim: synthesis of asymmetric A_3B porphyrins peripherally diverse substituted **as new sources of ionophores, photosensitizers and dyes**



A_3B porphyrins - performing high values of fluorescence quantum yields (Φf)





E. Fagadar-Cosma, L. Cseh, V. Badea, G. Fagadar-Cosma and D. Vlascici, *Combinatorial Chemistry & High Throughput Screening*, **2007**, vol. 10 (6), 466-472

Our concerns in using porphyrins were related to accomplishments for:

❖ development of fundamental sciences **(and increasing international visibility: our small group of Romanian researchers published over 30 ISI original scientific papers in the field of porphyrins in the last 3 years)**

❖ approach to nanotechnologies, highly strategically technology domains **(**sensibility enhancers for **photovoltaic cells)**

❖ safety and durability for building engineering **(corrosion inhibition)**

❖ monitoring the quality of the environment **(sensors)**

❖ competitive non-invasive health treatments **(PDT therapy of cancer)**

The porphyrin molecules can be assembled in supramolecular architectures by different means:

- **functionalization**
- **immobilization in polymeric membranes or inorganic matrices**
- **electrode-deposition**

•*E. Fagadar-Cosma, O. Costisor, D. Vlascici, G. Fagadar-Cosma,, J. BIOL. INORG. CHEM., 2007,12 (Suppl. 1), 136*

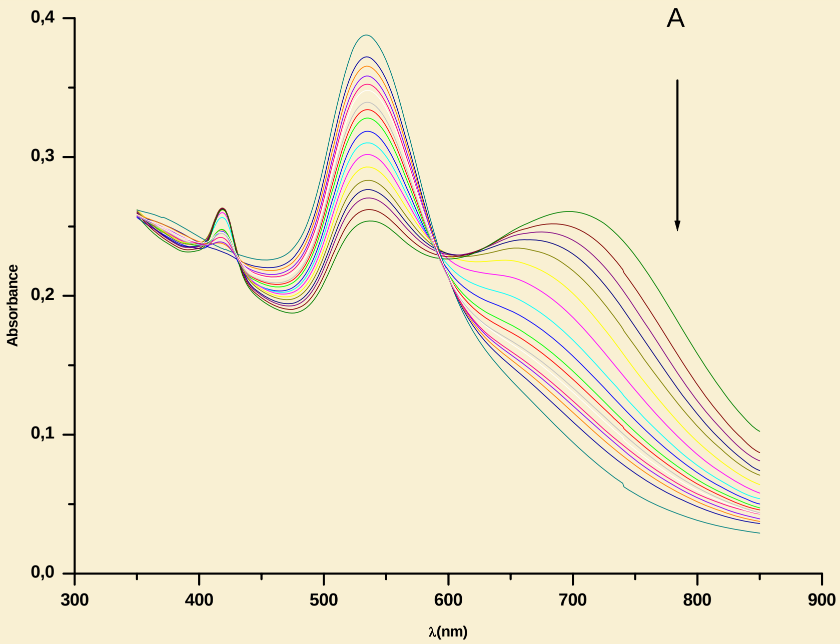
•*E. Fagadar-Cosma, B. Maranescu, C. Enache, C. Savii, G. Fagadar-Cosma, Revista de Chimie, 2006, 57(11), pp.1144-1147.*

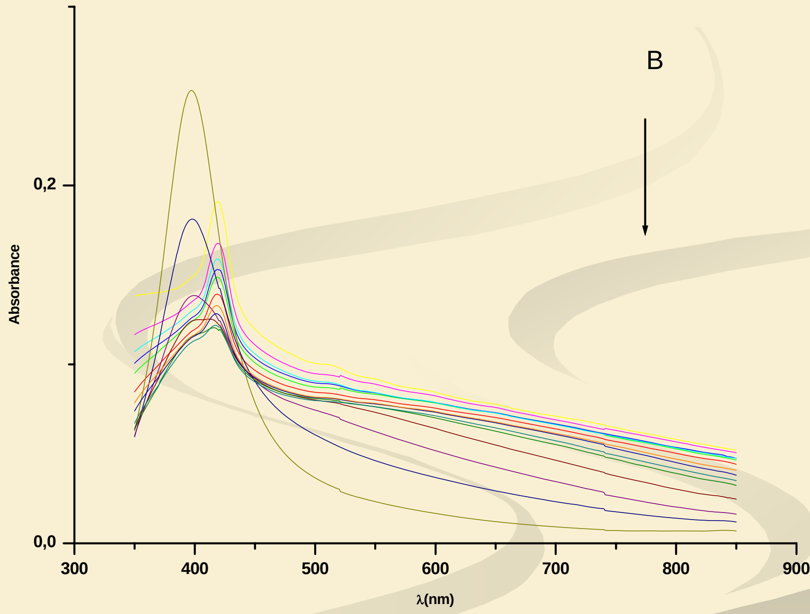
•*D. Vlascici, E. Fagadar Cosma, E. M. Pica, V. Cosma,O.Bizerea, G. Mihailescu, L. Olenic, Sensors, 2008, 8, 4995-5004*

An approach for obtaining wide-band absorption: gold and silver nanoparticles functionalized by 5,10,15,20-tetrakis-(4-carboxyphenyl)-21,23H-porphyrin new materials for photovoltaic cells with dyes

Water-soluble GNP (30nm) and AgNP (20 nm) are characterized by strong surface plasmon bands at 530 and 393 nm for gold and silver nanoparticles, respectively.

After addition of porphyrin, plasmon surface peaks of GNP and of AgNP are attenuated and a signal for newly formed complexes is appearing between 700-750 nm (isosbestic point and red shift of the new complex signal).

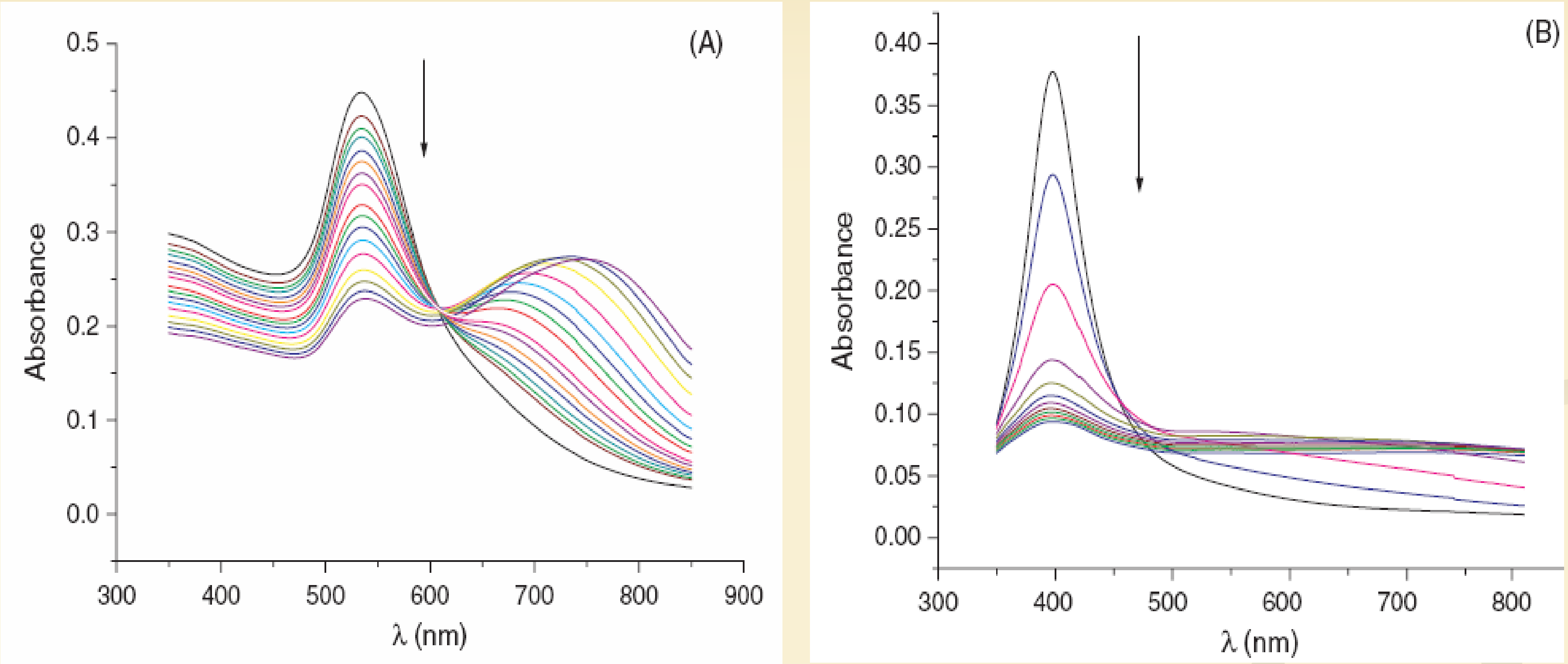




UV-Vis spectra for porphyrin functionalized with GNP (A), AgNP (B) with pH modified

Gh. Mihailescu, L.Olenic, S. Pruneanu, E-Fagadar-Cosma, P.Ardelean, E. Indrea, S. Dreve, TD. Silipas, Journal of Optoelectronics and Advanced Materials 2008, 10(9), 2252-2255

- Gold and silver colloids are bearing surface negative charge. This charge must be compensated by adding acid in order to favor functionalization, by protonating internal nitrogen atoms of the porphyrinic ring.

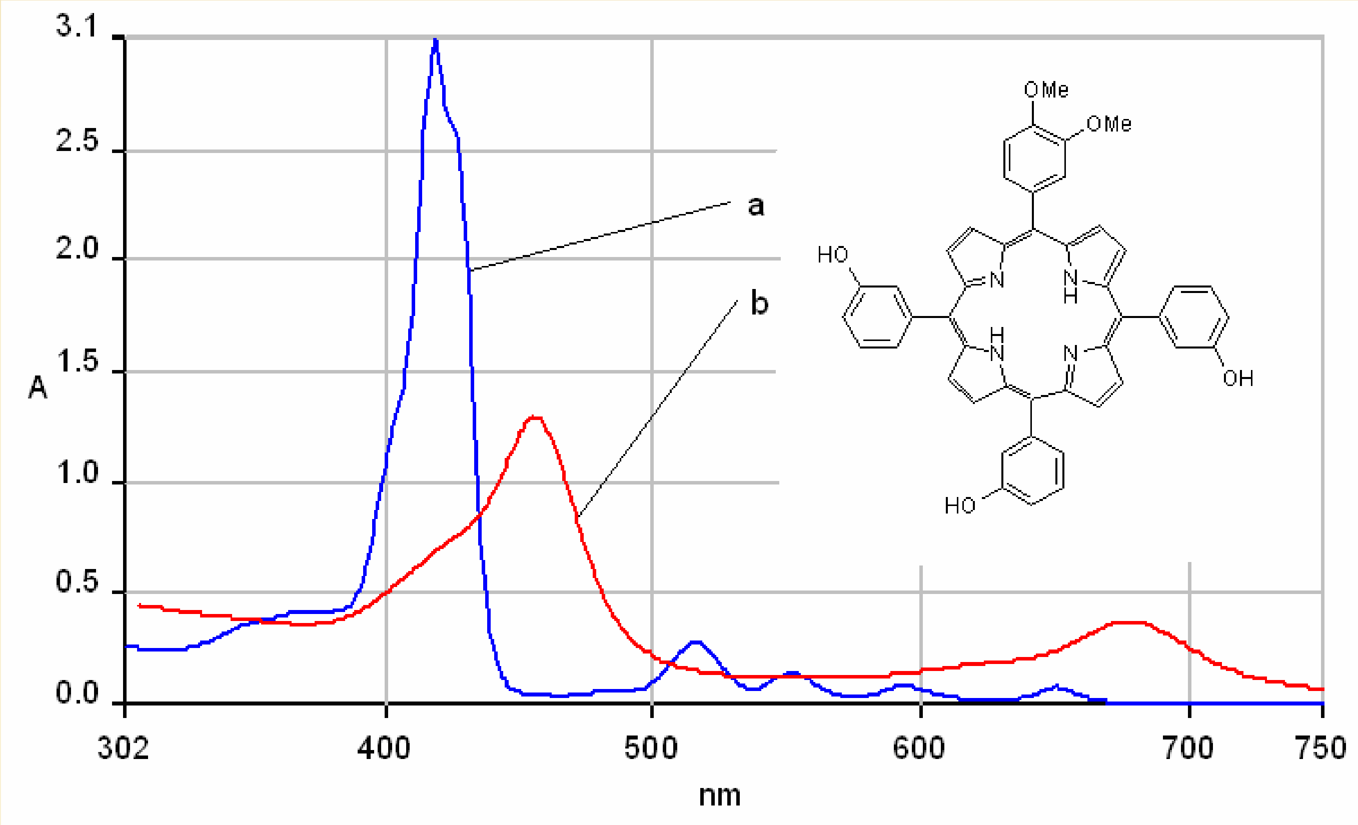


UV-Vis spectra for porphyrin with GNP (A) and AgNP (B) with modified pH-detail.

G. Mihailescu, L. Olenic, S. Garabagiu, G. Blanita, E. Fagadar Cosma, and A. S.Biris, Coupling Between Plasmonic Resonances in Nanoparticles and Porphyrins Molecules, Journal of Nanoscience and Nanotechnology, Vol. 10, 4, 2010, doi:10.1166/jnn.2009.1388

New inorganic-organic hybrid silica-porphyrin nanomaterials

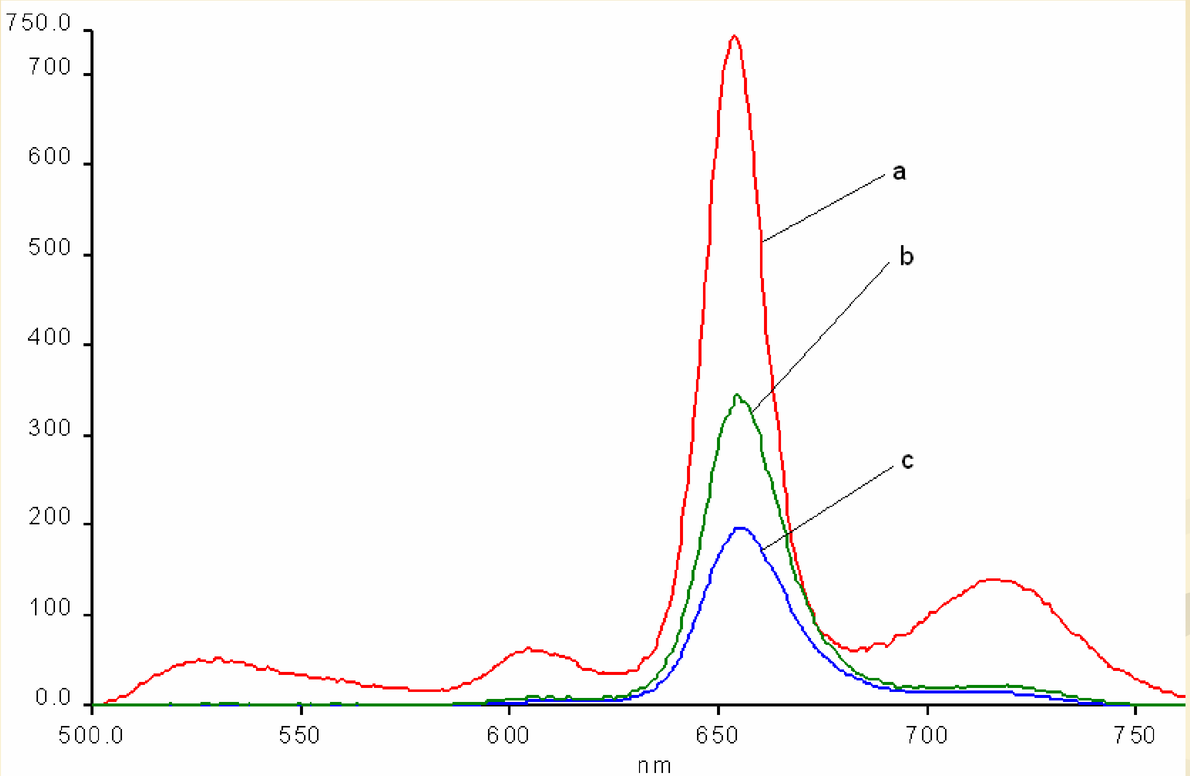
for development of applications in optics, electronics and catalysis.



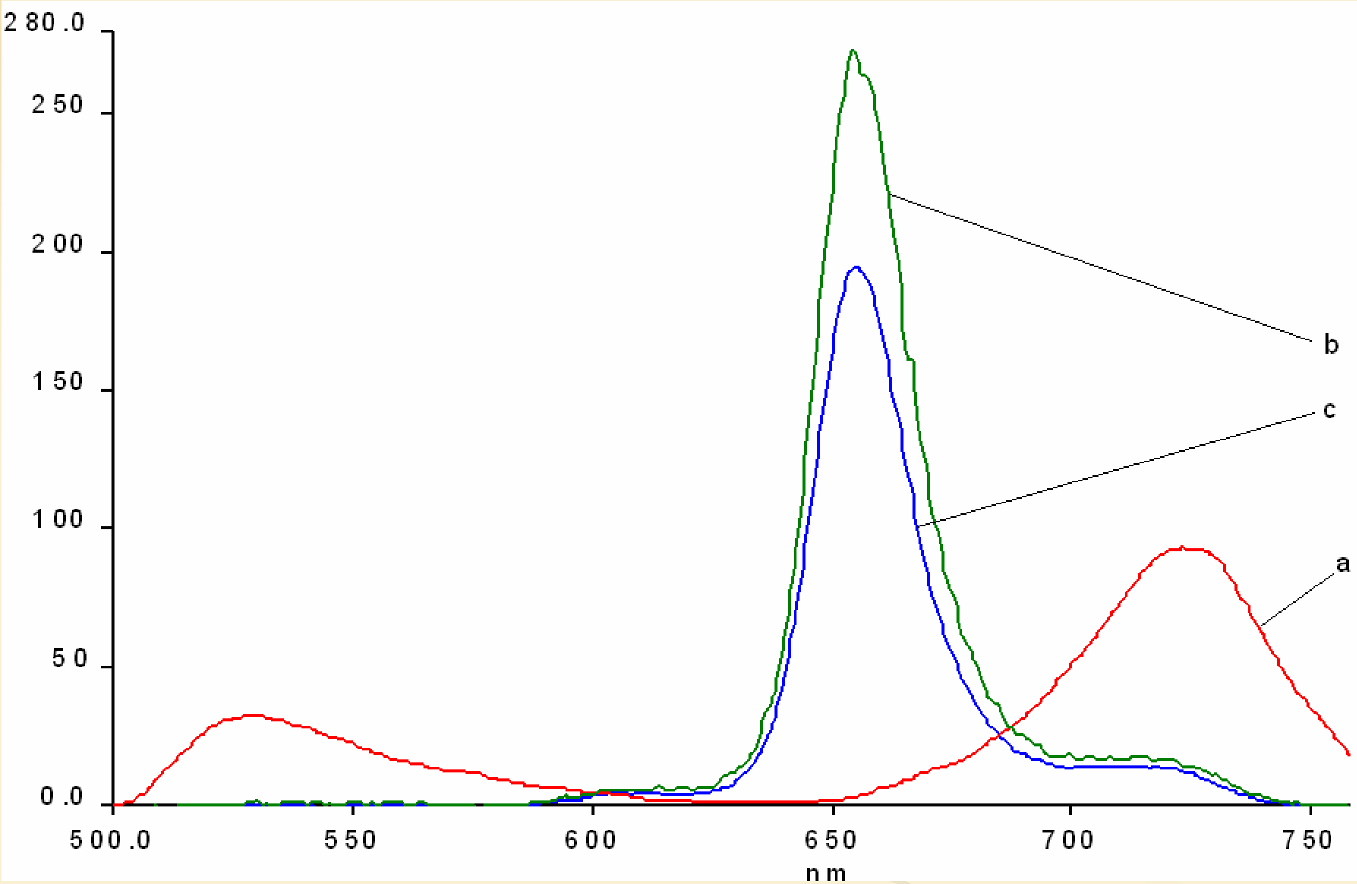
The broad Soret and Q I bands are both batochromic shifted, and supplementary, the QI band is manifesting an important hyperchromic effect.

The overlapped UV-vis spectra of free-porphyrin (line a), and of the hybrid silica material obtained by impregnation of porphyrin THDMPP into the silica matrix synthesized via one step acid sol-gel procedure (line b), in THF

- **The intensity of the main peak and of the second peak are remarkable increased in the hybrid materials comparatively with that of the free porphyrin.**



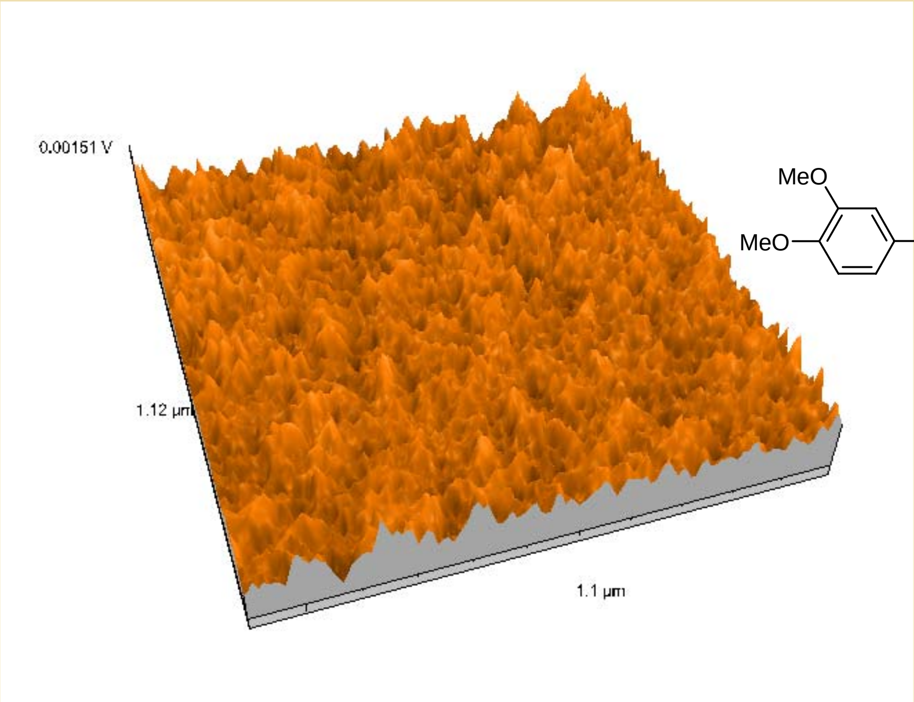
Superposed emission spectra of hybrid nanomaterials obtained by impregnation of porphyrin THDMPP into the silica matrix synthesized: *via one step acid sol-gel procedure (line a); via two steps acid-base sol-gel procedure (line b) and of free porphyrin (line c), in THF, at the same concentration c=4x10^{-5}M*

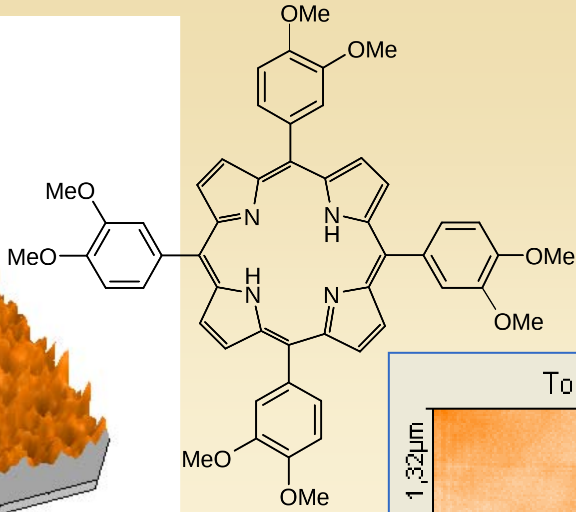


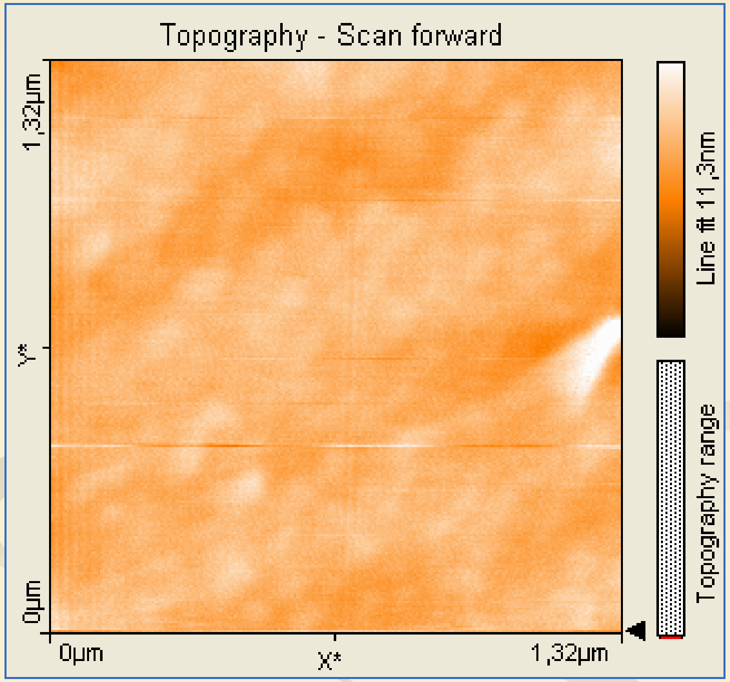
Superposed emission spectra of hybrid nanomaterials obtained by impregnation of porphyrin THDMPP into the silica matrix synthesized: via one step acid sol-gel procedure (line a); via two steps acid-base sol-gel procedure (line b) and of free porphyrin (line c), in THF, at the same concentration c=4x10^{-5}M, after the gels are aged

BET analysis data of THDMPP-silica hybrid materials

Sample	Pore Size Diameter D_p [ads] (nm)	Pore Size Diameter D_p [des] (nm)	Surface Area S_{BET} (m^2/g)	Pore Volume V_p (cc/g)
Hybrid THDMPP-silica acid catalyzed	1.38	1.78	326.6	0.139
Control silica acid catalyzed	1.95	2.23	532.65	0.301
Hybrid THDMPP - silica acid-base catalyzed	1.82	2.60	465.05	0.162
Control-silica acid- base catalyzed	3.40	3.81	1074.54	0.792







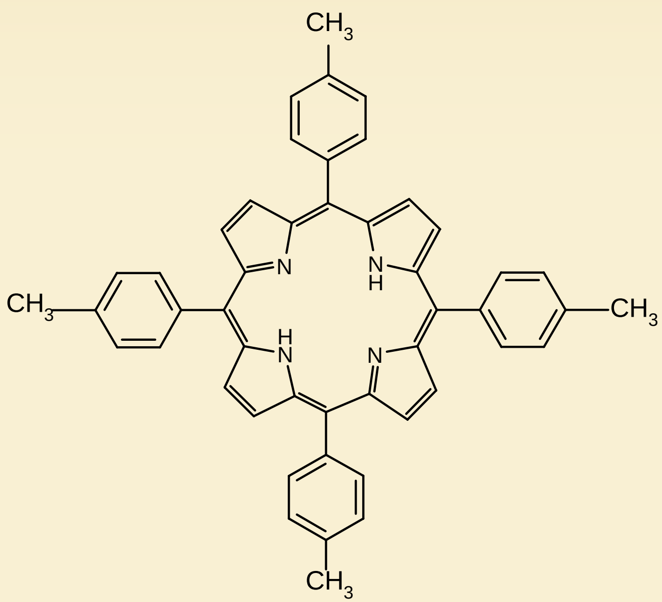
AFM images, 3D in contact mode, *of hybrid silica-porphyrin obtained by in situ acid/base catalyzed sol–gel method; and topography from a section of (1.32 µm 1.32 µm).*

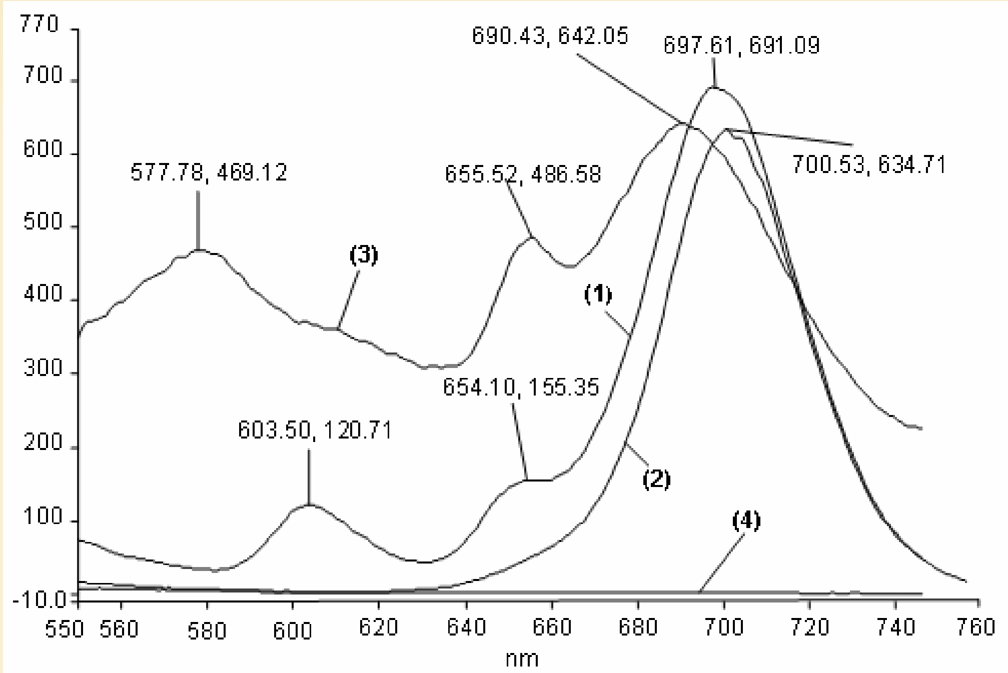
The dimensions of columnar microparticles are maximum 52.94 nm in length, 66.17 nm in width and 19.23 nm in height. From topography scanning, the material seems to be ordered in oriented rows of the islands and the depths.

E. Fagadar-Cosma, C. Enache, D. Vlascici, G. Fagadar-Cosma, M. Vasile and G. Bazylak, Materials Research Bulletin, in press, **doi:10.1016/j.materresbull.2009.08.010**

Silica hybrid materials embedding *meso*-tetratolylporphyrin

- **Acidic catalysts** provide transparent gels of **low porosity**, whereas with **basic catalysts** translucide gels of **high porosity** are made
- **Monocation is trapped in the gel together with the dication**





Emission spectra of porphyrin-silica hybrid: one step-acid catalysis, molar ratio HCl:TEOS = 0.01:1 (line 1- peaks at 603 and 654 nm belong to the monocation H_3TTP^+); acid catalysis, molar ratio HCl:TEOS = 0.03:1 (line 2-all the porphyrin is transformed in dicationic derivative H_4TTP^{2+}); two-step acid-base catalysis, molar ratio HCl:TEOS = 0.01:1, NH3:TEOS = 0.0102:1 (line 3); control silica matrix sample (line 4), λex= 420 nm

The silica nanomaterials immobilizing porphyrins have been prepared to act as:

- **photocatalysts in micro-channel** chips based on photocatalytic abilities in dechlorination, epoxidation, and sterilization under visible light irradiation
- **selective sensors for bio-molecules, NO_2 or NO, fluorescent chemosensors for metal ions, pH sensors**
- In photodynamic therapy (PDT), many fluorescent porphyrins are selectively absorbed and can later kill cancerous cells by means of the singlet oxygen generated when the tumor is irradiated with red laser light (k = 630–800 nm), in the presence of oxygen. It is well known that optimal tissue penetration occurs with light of wavelength between 610 and 800 nm, the same range in which many porphyrins show fluorescence

Potentiometric determination of ions offers advantages such as high selectivity, sensitivity, good precision, simplicity, portable, non-destructive analysis and low cost. Many porphyrins and metalloporphyrins were used in the last years as ionophores for developing new polymeric membrane ion-selective electrodes.

Ionophore	Type of ion selective sensor	Composition of PVC membranes (%)	Liniar domain of potentiometric response(M)	Detection limit (M)	Slope (mV/ pIon)	Application
Rh Tetraphenyl porphyrin chloride (RhTPPCl)	Thiocyanate-selective	1% ClRhTPP, 33% PVC, 66% DOP şi 20% mol. TOMACl	$1 \cdot 10^{-1} – 1 \cdot 10^{-5}$	$7 \cdot 10^{-6}$	59.8	Thiocyanate from biological samples
Zr(IV)-tetraphenyl porphyrin dichloride ($ZrTPPCl_2$)	Fluoride-selective	1% Cl_2ZrTPP, 33% PVC, 66% *o*-NPOE şi 20% mol. NaTPB	$1 \cdot 10^{-1}-5 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	90.2	Fluoride from urina, waters, tooth paste, dental materials
5,10,15,20-tetrakis (4-methoxy phenyl)-21H,23H-porphine Cu (II), (CuTMP)	Iodide-selective	1% CuTMP, 33% PVC, 66% o-NPOE şi 10% mol TDMACl	$1 \cdot 10^{-1} – 1 \cdot 10^{-5}$	$8,5 \cdot 10^{-6}$	51.7	Iodide from drugs
5,10,15,20-tetrakis-(4-methoxyphenyl)-porphyrin-Co(II) (CoTMeOPP)	Thiocyanate-selective	1% CoTMeOPP, 33% PVC, 66% NPOE şi 35% mol. TOMACl	$1 \cdot 10^{-1} – 1 \cdot 10^{-5}$	$6 \cdot 10^{-6}$	65.8	Thiocyanate from biological samples

- *D. Vlascici, E. Fagadar Cosma, E. M. Pica, V. Cosma,O. Bizerea, G. Mihailescu, L. Olenic,, Sensors 2008, 8, 4995-5004*
- *G. Fagadar-Cosma, D. Vlascici, E. Fagadar-Cosma, J. BIOL. INORG. CHEM., 2007,12 (Suppl. 1), 218;*
- *Vlascici, D.; Fagadar-Cosma, E.; Spiridon Bizerea, O., Sensors, 2006, 6, 892-897.*

Zn(II) Tetrapyridylporphyrin (ZnTPyP)	Iodide-selective	1% ZnTPyP, 33% PVC, 66% o-NPOE 20%mol TDMACl	$1\cdot10^{-1} – 1\cdot10^{-5}$	$7,4\cdot10^{-6}$	52.4	Iodide from drugs
Co(II) *meso*-Tetra-*p*-tolyl porphyrin (CoTTP)	Salicylate-selective	1% CoTTP, 33% PVC, 66% *o*-NPOE şi 15%mol TDMACl	$1\cdot10^{-1} –1\cdot 10^{-5}$	$8\cdot10^{-6}$	65.5	Salicylate from pharmaceutical products
5,10,15,20-Tetraphenyl porphyrin (H_2TPP)	Nickel-selective	1%TPP, 33% PVC, 66% DOS, 20%mol. NaTPB	$1\cdot10^{-1} – 5\cdot10^{-6}$	$4\cdot10^{-6}$	29.7	Nickel in chocolate
meso-Tetra-*p*-tolyl porphyrin(H_2TTP)	Nickel-selective	1,4%TTP, 56%DOS, 42% PVC, 0,6%NaTPB	$1\cdot10^{-1} – 5\cdot10^{-6}$	$4.4\cdot10^{-6}$	29.2	Nickel in chocolate
Tetra-(3-hydroxyphenyl) porphyrin	Lead-selective	2%I, 32,3% PVC, 1% KTClPB, 64,7% NPOE	$1\cdot10^{-1} – 1\cdot10^{-5}$	$3\cdot10^{-6}$	25.8	Lead from water samples
Tetra-(3-hydroxyphenyl)porphyrin	Silver-selective	2%I, 32,3% PVC, 1% KTClPB, 64,7% DOS	$1\cdot10^{-1} – 8\cdot10^{-6}$	$8\cdot10^{-6}$	64.5	Chloride in different meat products
5, 10, 15, 20-tetrakis(3,4-dimethoxyphenyl) porphyrin	Copper-selective	2%I, 32,3% PVC, 1% KTClPB, 64,7% DOS	$1\cdot10^{-1} – 2.5\cdot10^{-6}$	$2\cdot10^{-6}$	27.8	Copper from synthetic samples

The membranes were prepared using three different plasticizers: (bis(2-ethylhexyl)sebacate (DOS), dioctylphtalate (DOP), *o*-nitrophenyl octyl ether (NPOE). Sodium tetraphenylborate (NaTPB) or potassium tetrakis(4-chlorophenyl)borate (KTClPB) were used as additives in the case of charged carrier ionophores and trioctylmethyl-ammonium chloride or tridodecylmethyl-ammonium chloride in the case of the neutral ones.

AWARDS for PATENTS and ISI Papers

2008: SECOND PRIZE OF ROMANIAN AUTHORITY FOR SCIENCE AND TECHNOLOGY for research and developments projects; Domain: Materials and inovative processes.
MATNANTECH, CEEX: 48/26.07.2006, *Multifunctional nanocomposites based on supramolecular architectures exhibiting optoelectronic, photochemical, electrochemical and biological properties precursors for advanced materials. "MAVOPTEL“*, Director: Otilia COSTISOR; Scientific Coordinator: Eugenia FAGADAR-COSMA

2008: G*old Medal to International* PRO INVENT, VIth eddition, 2008, Cluj-Napoca, for the invention, N*ITRITE–ION SELECTIV POTENTIOMETRIC ELECTRODE*, Brevet RO NR. 200600190 (22), (23.03.2006), Vlascici D., Pică E. M., Fagadar-Cosma E., Bizerea O., Costisor O., Cosma V.

2008: G*old Medal to 2nd National* Conference of Researchers and Inventors from Romania, *CNCIR, Bucharest, 11-12 Dec. 2008 for the ISI paper: Combinatorial synthesis and characterization of new asymmetric porphyrins as potential photosensitizers in photodynamic therapy, Combinatorial Chemistry & High Throughput Screening, 2007, 10(6), 466-472, Fagadar-Cosma E., Cseh L., Badea V., Fagadar-Cosma G., Vlascici D.*

2008: G*old Medal to 2nd National* Conference of Researchers and Inventors from Romania *CNCIR, Bucharest, 11-12 Dec. 2008*

and

2009: G*old Medal* and PRIX SPECIAL ARCA DE L'UNION DES INVENTEURS DE CROATIE at *37th International Exhibition of Inventions, New Techniques and Products of Geneva*, 1-5 April 2009

and

2009: Gold Medal and Special Prize POLISH FEDERRATIOON OF ENGINEERING ASSOCIATIONS - *NOT®* at *3rd International Warsaw Invention & Innovation Show IWIS 2009*, Varsaw, Poland, 1-3 June 2009,

for the invention : *Procedure for construction of stochastic sensors based on porphyrins and diamond or graphite paste for the determination of ascorbic acid at molecular level,* OSIM, no. A/00898/17.11.2008 van Staden R. I., Fagadar-Cosma E. L.,

2009: G*old Medal to International* PRO INVENT, VIIth edition, 2009, Cluj-Napoca, for the invention: *Procedeu de realizare a unui senzor potentiometric pe baza de ionofor porfirinic cu selectivitate inalta pentru argint,* Request for patent O.S.I.M., Bucureşti, România, A/00634/18.08.2008, Fagadar-Cosma E., Vlascici D., Pica E. M., Costisor O., Cosma V., Olenic L., Bizerea O.

International and National Collaborations
with Universities and Research Institutes - for intersectorial applications

Electrochemical characterization of advanced nanomaterials based on metalloporphyrins and their applications as electrocatalytic active materials for oxygen reduction, ***Kiev National University of Technologies & Design***, *Group of Professor Viacheslav Barsukov (Department of Electrochemical Power Engineering & Chemistry)*

Investigation of new porphyrin derivatives and their self-assembling and self-organization in solutions using methods of molecular hydrodynamics and optics, ***Institute of Macromolecular Compounds Russian Academy of Sciences, G****roup of Elena Tarabukina, Coordinator , Laboratory of molecular physics of polymers*

Photochromic behavior of nano-structurable porphyrin-polysiloxanes systems, *Prof. Dr. Nicolae Hurduc,* ***Technical University «Gheorghe Asachi» Iasi***

Polyurethane Gels with Silver Nanoparticles and Porphyrins or Ag-Porphyrins for the Treatment of Skin Diseases, *Dr. Stefania Gavriliu,* ***National Institute for Research and Development in Electrical Engineering ICPE-CA, Bucharest,*** *Dr. Constantin Ciobanu,* ***"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania***

Magnetic-fluorescent nanocomposites for biomedical applications-based on porphyrin, *Dr. Luminita Patron*, ***Institute of Physical Chemistry "Ilie Murgulescu" of the Romanian Academy, Bucharest***

SENSORS for monitoring life, food quality and the degree of pollution in the environment, *Prof. Dr. Camelia Bala, Conf. Dr. Lucian Rotariu,* ***University of Bucharest****, Conf. Dr. Dana Vlascici,* ***West University of Timisoara****, Dr. Viorica Cosma, Prof. Maria Pica,* ***Technical University Cluj-Napoca***

Corrosion inhibition effect of porphyrinic aggregates onto the metallic structures, *Dr. Gheorghe Fagadar-Cosma,* ***"Politehnica" University Timisoara and*** *Dr. Ioan Taranu,* ***National Institute for Research and Development in Electrochemistry and Condensed Matter***

Testing of photochemically-active supramolecular devices by deposition of porphyrins on crystalline TiO2 support- for construction of photovoltaic cells, *Dr. Gheorghe Mihailescu,* ***INCDTIM Cluj-Napoca***

The Langmuir– Blodgett film properties of different free base porphyrins for sensing of chemical substances, *Prof. Dr. Mihai Popescu M., Dr. Adam Lorinczi, Dr. Rodica Cristescu R,* ***National Institute for Lasers, Plasma and Radiation Physics- Bucharest-Magurele***

Evaluation of the risks of the nanoparticles for the health and environment by flow cytometry and complementary techniques, *Dr. Daniela Bratosin,* ***National Institute for Biological Sciences Research & Development- Bucharest***

EC FP6 Research Infrastructure action –

Integrated Infrastructure Initiative - Contract # RII3-026145

EU-NMR

Dr Luc Nagels, **Department of Chemistry, University of Antwerpen, Antwerpen**

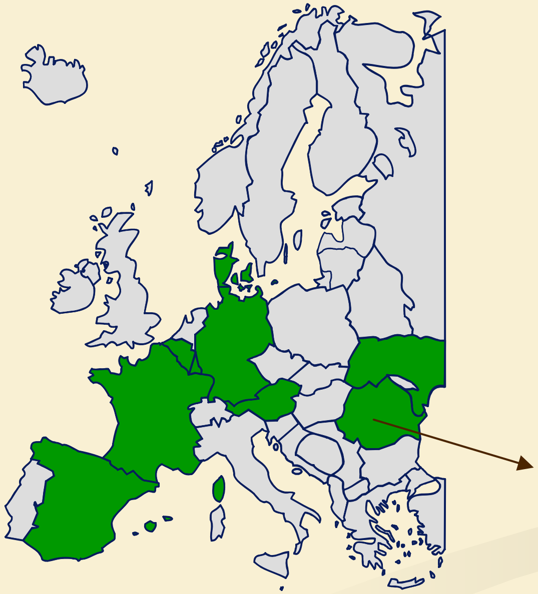
Prof. U. L. Gunther, Dr. Sue Rhodes, HWB-NMRCR-UK Institute for Cancer StudiesUniversity of Birmingham

Dr. Grzegorz Bazylak, Faculty of Pharmacy, Collegium Medicum, Nicolaus Copernicus University, Poland

Dr. Eugenia Fagadar-Cosma, Institute of Chemistry Timisoara of Romanian Academy

FP 7 –Proposal, COLLABORATIVE PROJECT, submitted 14 Jan 2010

Joint call with Energy, Environment and Transport



Institute of Chemistry Timisoara of Romanian Academy