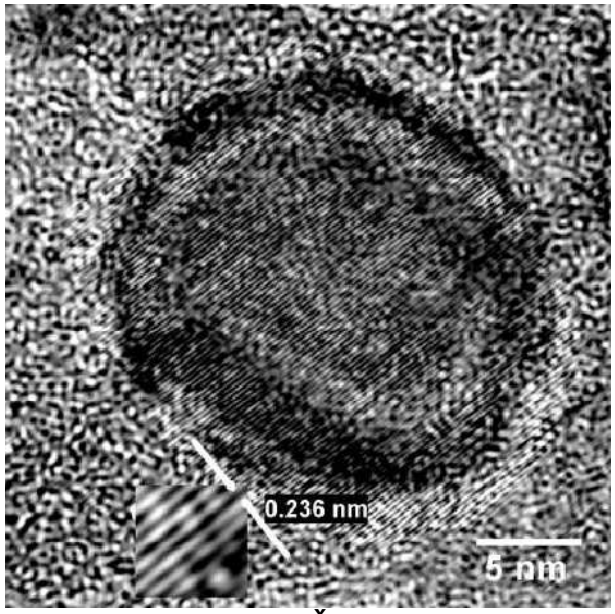
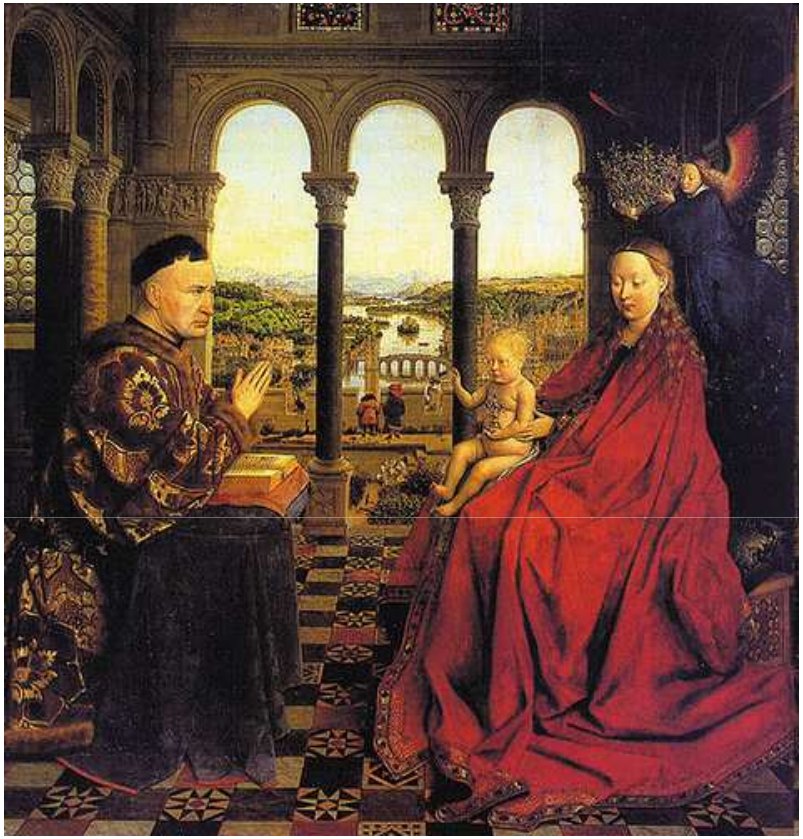
Advanced polymeric silver nanocomposites

Dr Panagiotis Dallas



Tato prezentace je spolufinancována Evropským sociálním fondem a státním rozpočtem České republiky.

Organic and supramolecular chemistry are forms of fine art



Nanoscience and polymer chemistry are direct analogues to civil engineering and architecture

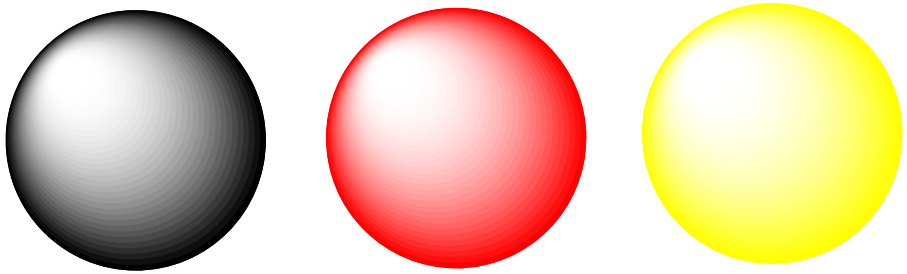
Tato prezentace je spolufinancována Evropským sociálním fondem a státním rozpočtem České republiky.

INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

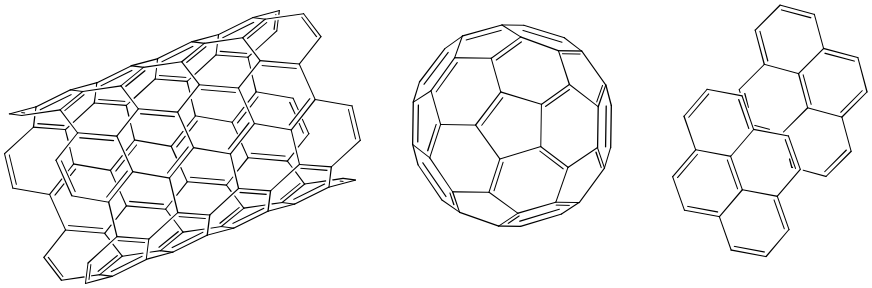
Nanomaterials (dimensions <50 nm) can possess significantly important MAGNETIC, OPTICAL, CATALYTIC AND BIOLOMEDICAL properties and by incorporating them in polymers these properties are inherited in the resulting nanocomposite.

The magnetic and optical properties of materials in the nanoscale are <u>size and shape dependent.</u>

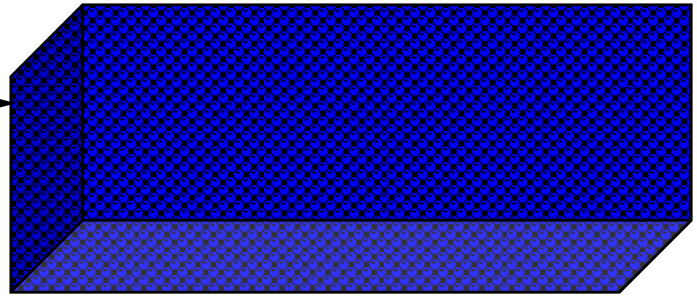
Nanoparticles can be surface functionalized with different organic molecules, e.g. iron oxides with carboxylate anions, noble metals with amines or thiols and even self assemble in perfectly arranged structures which is crucial in the manipulation of the nanoparticles' properties and in various applications, e.g. development of high density recording media.



Magnetic (Fe_2O_3, FePt, EuS) Fluorescent (CdSe, CdS) Metallic (Ag, Au, Pt, Pd)

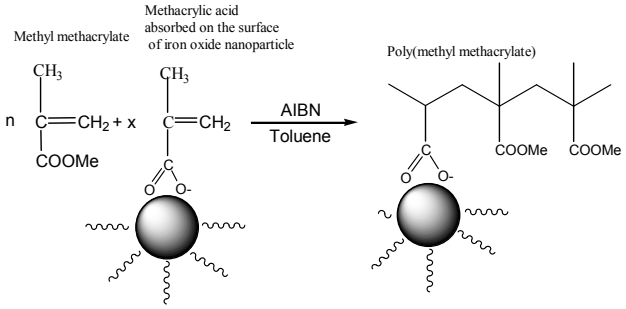


Carbon nanotubes (1-D) and fullerenes (0-D)-graphene (2-D) now joins the family (network of carbon double bonds)

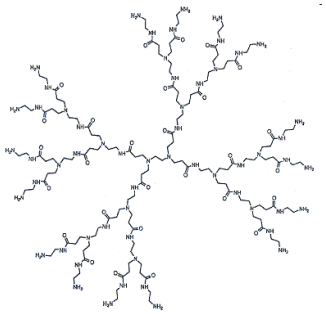


Tato prezentace je spolufinancována Evropským sociálním fondem a státním rozpočtem České republiky.

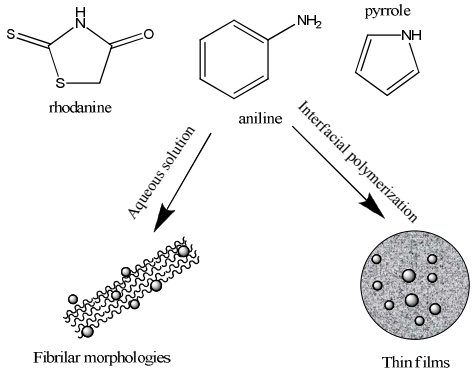
- **Common plastics (**nylon, pmma, polystyrene)



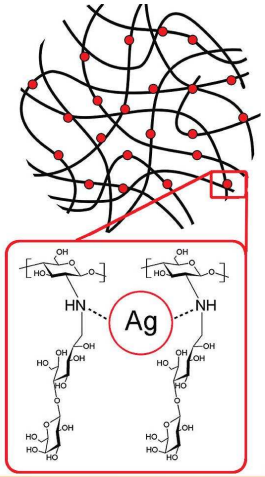
- **Dendrimers**



- **Conductive polymers**
- **Conjugated polymers**



- **Biopolymers:** Carboxymethylcellulose, polysaccharides.[5]



Principle requirements:

- Homogenous dispersion of nanoparticles inside the matrix
- Fine size distribution
- Controlled morphology- going beyond polymer filled nanocomposites

Advantages:

✓ **Plastics** are transparent (>90% for pmma) and have high tensile strength.

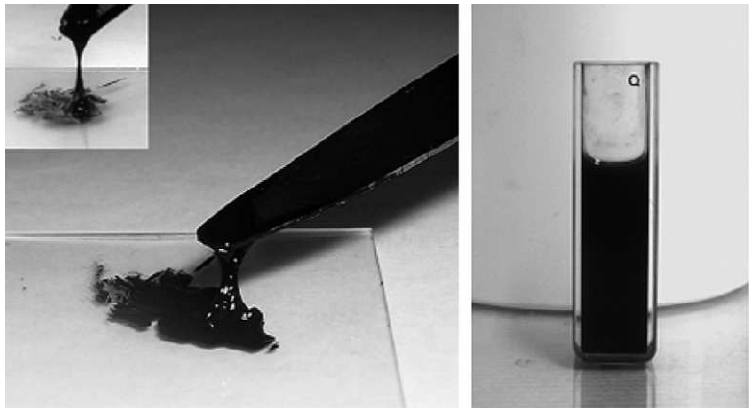
✓ **Dendrimers** are completely symmetrical and functional macromolecules.

✓ **Biopolymers** are biocompatible and low cost materials.

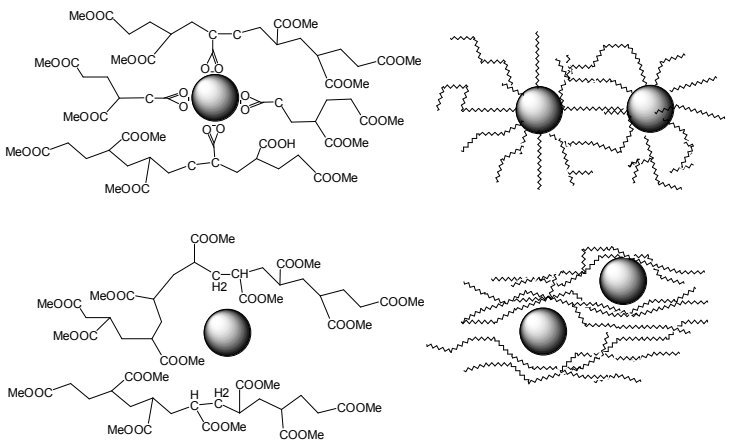
✓ **Block copolymers** tend to self assemble to perfectly organized nanostructures

[1] © Travan A. et al. ***Biomacromolecules 2009,*** *10,* 1429

- A prescribed morphology is required for the optimum accomplishment of the properties of both components.
- **Liquid like behavior:** Functionalization of the surface with silanes or organic molecules that exhibit a low temperature melting point can lead to meltable or liquid nanoparticles (Nanoscale Ionic Materials-NIMS). [2]
- **Solubility in various solvents:** Nanoparticles lack solubility so appropriate coating makes them either organophilic or hydrophilic.
- Polymers, ligands and surfactants control the size and shape growth of the nanoparticles and the surface functionalization of the nanoparticles and polymer chains can **manipulate the interparticle distance and interactions**. [2]
- **Utilization of the polymer's functionality:** The polymers functional groups makes them versatile tools for building networks or attaching them on surfaces following a layer by layer approach.
- **Self assembly of nanoparticles:** According to the polymers tendency to form ordered and symmetric patterns. [3]



*Meltable carbon nanotubes can be also soluble in toluene. [4] © **Carbon 2007**, 45, 1583-1585, Bourlinos, A.B. et.al*



*Chemical bonding of iron oxide nanoparticles with pmma after surface functionalization with methacrylic acid. [5] © **Nanotechnology 2006**, 17, 2046-2053, Dallas, P. et.al*

Tato prezentace je spolufinancována Evropským sociálním fondem a státním rozpočtem České republiky.

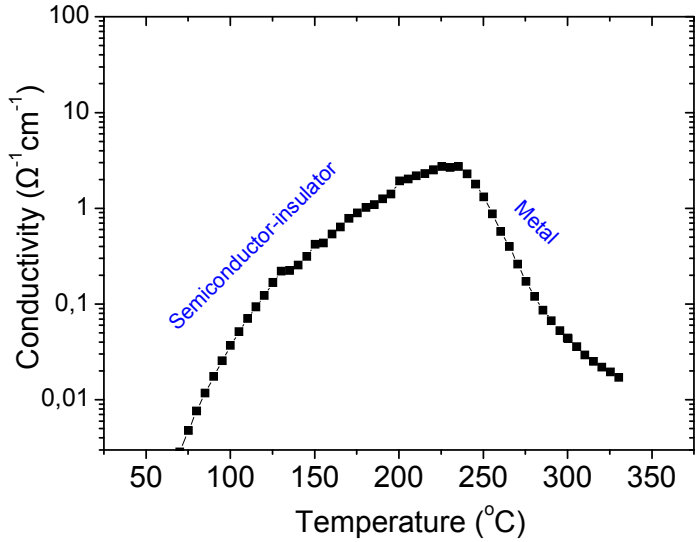
INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

[2] a) A.B.Bourlinos. ***Adv.Mater. 2005, 17(2),*** 234-237 b) R.Rodriguez. ***Adv.Mater. 2008***, 20(22), 4353-4358

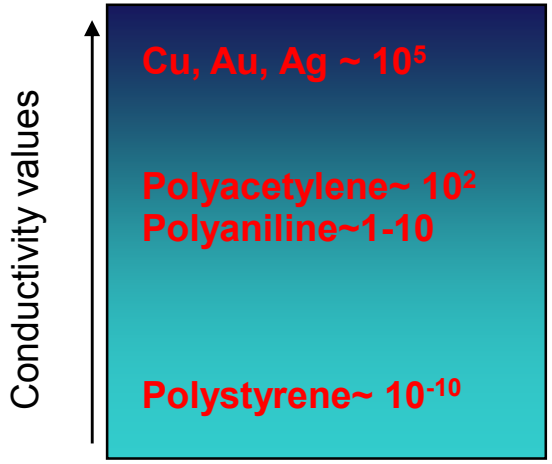
[3] S.I.Lim, C.J.Zhong. ***Acc.Chem.Res. 2009,*** 42(6), 798

Properties of conjugated and conductive polymers

- Even if the electrochemical polymerization of **pyrrole and aniline** was firstly performed in 1915, the interest expanded after the discovery of conductivity in **polyacetylene by Prof.H.Shirakawa (1977)**
- **2000: Nobel prize in *Chemistry* awarded to Prof.H.Shirakawa, Prof.A.MacDiarmid and Prof.A.Heeger for their discovery and development of conductive polymers.**
- **Electronic conductivity.** Usually it follows a semiconducting behavior, however there are many reports demonstrating a metallic conductivity.
- **Low band gap absorptions**



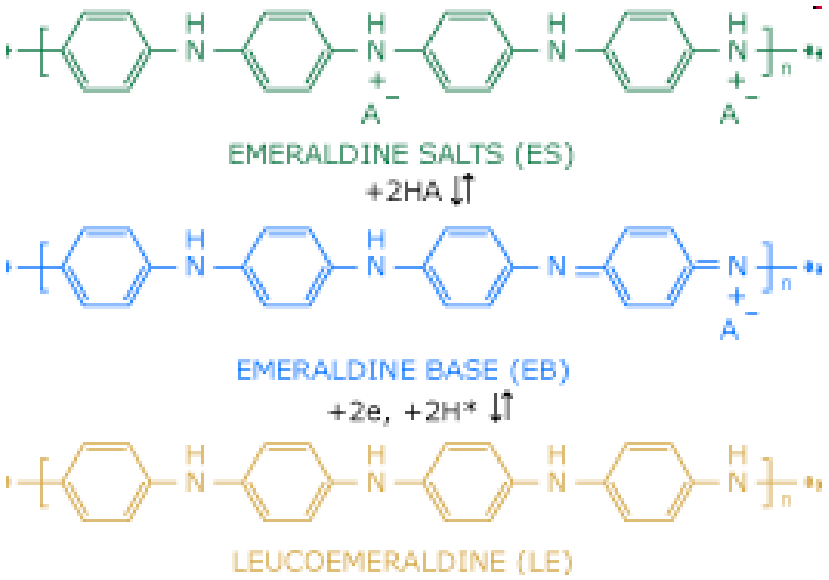
Metal-insulator transiotion in polyaniline nanoneedles due to Peierls instability (1-D conductors are intrinsically unstable) [7]



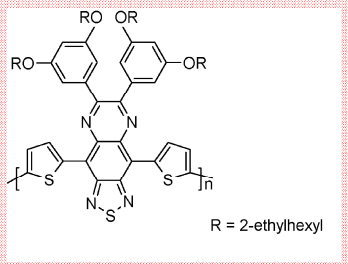
[6] K. Lee., et al ***Nature 2006, 41***, 65.
[7] © P. Dallas.,et al. ***Polymer 2007***, 48, 3162

Applications of conjugated and conductive polymers

- **Sensor applications:** The bridging amine units enable them to serve as excellent redox sensors for various organic and inorganic molecules (e.g. NH_3, N_2O_4, glycose) [8]
- Specifically: polyaniline exhibits different oxidation states, each one with different colour and accordingly UV-Visible absorptions. Only the emeraldine salt form is conductive and the presence of the above mentioned species induced immediate changes in the conductivity of the polymer thus serving as excellent sensor.
- Even if they have lower conductivity than conventional metals they have major advantages like low weight, easy preparation and processability, dispersion in various solvents and low cost.



Photovoltaics and solar cells due to low band gap and strong absorptions in the visible light region. [9]

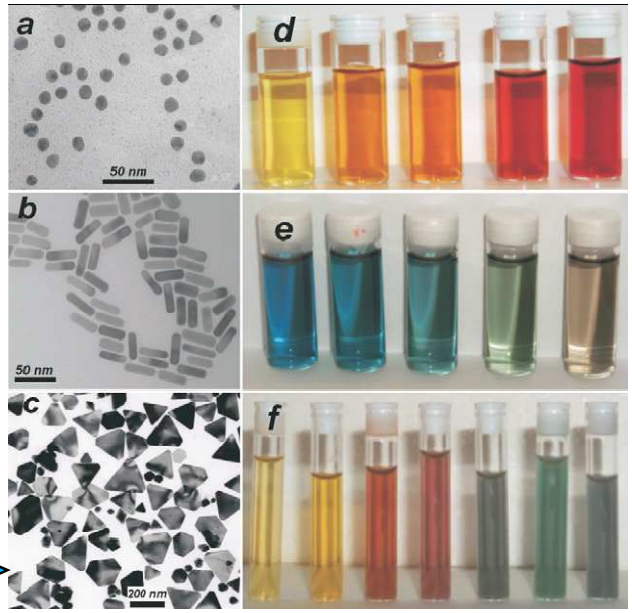


The pioneering work of Prof.Sir Richard Friend (Cavedish Laboratory, University of Cambridge, England) paved the way for Light Emitting Diodes and flat panel screens based on polymers.

[8] (a) X. Li., et al ***J.Phys.Chem.C. 2009, 113***, 69-73.
(b) M. Zhao.,et al. ***J.Phys.Chem.C 2009***, 113, 4987-4996.
[9] A.P.Zoombelt. ***Org.Lett. 2009,*** 11(4), 903-906

Interesting aspects of silver nanoparticles

- Catalytic activity: Reduced size increases the fraction of surface atoms which are crucial in catalysis. Ligand- or polymer stabilized colloidal noble metals have been used for many years as catalysts for the hydrogenation of unsaturated organic molecules. Additionally, there is a special interest in developing “green” methodologies for catalyzing organic reactions in aqueous solutions.
- Antibacterial activity
- Surface plasmon resonance



Left: Au nanospheres and nanorods (a,b) and Ag nanoprisms (c)

Right: AuAg alloy nanoparticles with increasing Au concentration (d), Au nanorods of increasing aspect ratio (e), and Ag nanoprisms with increasing lateral size (f). [10]

4th Century AD: Lycurgus cup
1857: Michael Faraday reported the color of colloidal gold

The free electron of the noble metal nanoparticles surface interact with UV and Visible light and the excitations result in different absorptions easily observed in the corresponding spectrum.
All these absorptions are size and shape dependent.

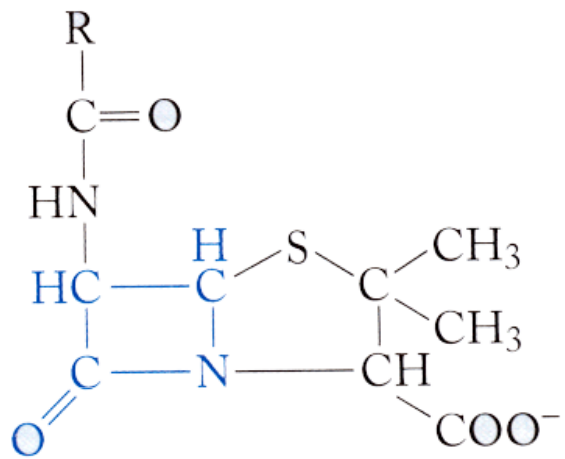
Tato prezentace je spolufinancována Evropským sociálním fondem a státním rozpočtem České republiky.

INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

[10] © Luis M.Liz-Marzan. ***Mater.Today. 2004**, 26.*

Organic molecules and natural products as antibacterial agents

- *Silver has been known for centuries as an effective antibacterial agent.*
- **1930: Sir Alexander Fleming** refines penicillin extracts
- Bacteria have evolved mechanisms against these **β-lactam antibiotics by hydrolyzing the lactamic ring**. On the other hand they have not yet evolved mechanisms of action against silver.



Penicillin

Tato prezentace je spolufinancována Evropským sociálním fondem a státním rozpočtem České republiky.

Antibacterial activity of silver

Even if the exact mechanism is not clearly resolved numerous studies indicate the following interactions between silver and bacteria [11]:

- Silver cations bind to negatively charged components of proteins and nucleic acids, thereby causing structural changes and deformations. In general, they are well known to interact with electron donor functional groups like thiols, phosphates, hydroxyls, imidazoles, amines.
- It is considered that silver cations inhibit ATP synthesis via binding to the ATP synthesis enzyme molecules in the cell wall and are even entering the cell and binding with DNA.
- It has been confirmed the incorporation of silver into the cell membrane structure
- The outer membrane of e-*coli* cells: it is predominantly constructed from tightly packed lipopolysaccharide (LPS) molecules, which provide an effective permeability barrier. Metal depletion may cause the formation of irregular-shaped pits in the outer membrane.

- *Already has been reported the interaction of silver with viruses like HIV-1.* [12]

WARNING!

Dangers from *over-use* of antibacterial agents:

- **Allergies**
- **Asthma**
- **Weak immune system especially for kids**

[13] a) P.Gibson et al. Pediatric Pulmonology 2003, 36, 209–215 b) F.Marra. et al. Chest 2009 (in press) c) J.P.Zock. et al. *American Journal of Respiratory and Critical Care Medicine* 2007, 176. 735-741

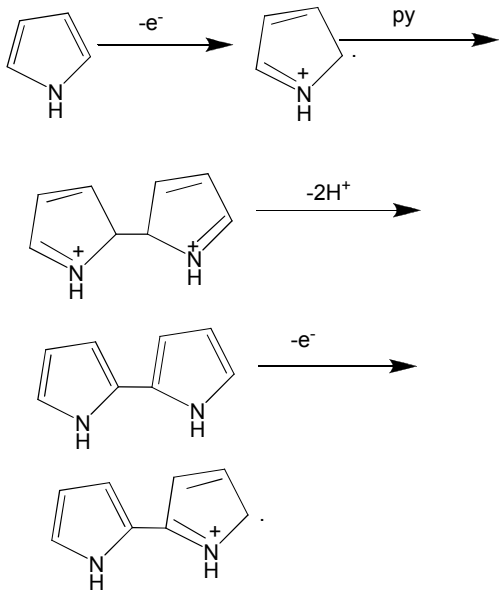
Tato prezentace je spolufinancována Evropským sociálním fondem a státním rozpočtem České republiky.

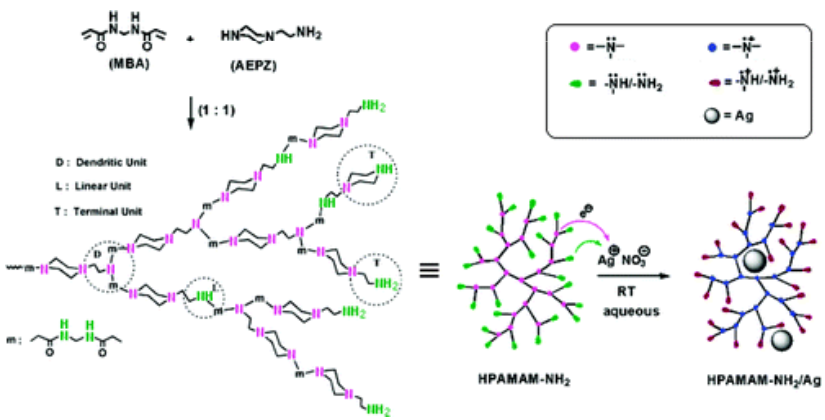
INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

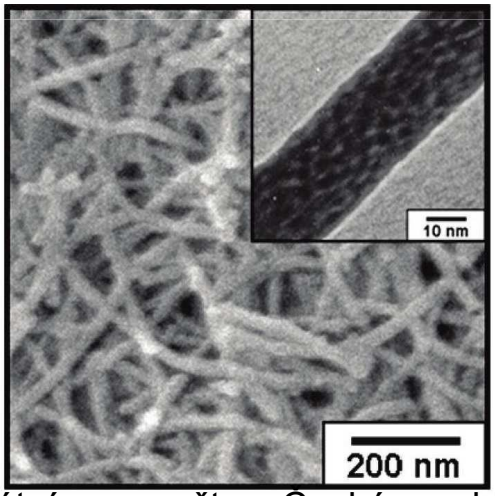
[11] a) I.Sondi et al.J.Colloid Interf.Sci. 2004, 275, 177-182 b) J.Jain et al. Mol.Pharmaceutics. 2009 (in press) **10.1021/mp900056g**
[12] J.L.Elechiguerra. et al. Journal of Nanobiotechnology 2005, 3, 6

One-step reduction of silver cations

- The oxidation potential of silver makes it ideal candidate for the initiation of oxidation polymerization of various monomers, for example **pyrrole or rhodanine.**
- **Dendrimers** can also immediately reduce silver cations towards metal nanocomposites. [14]©



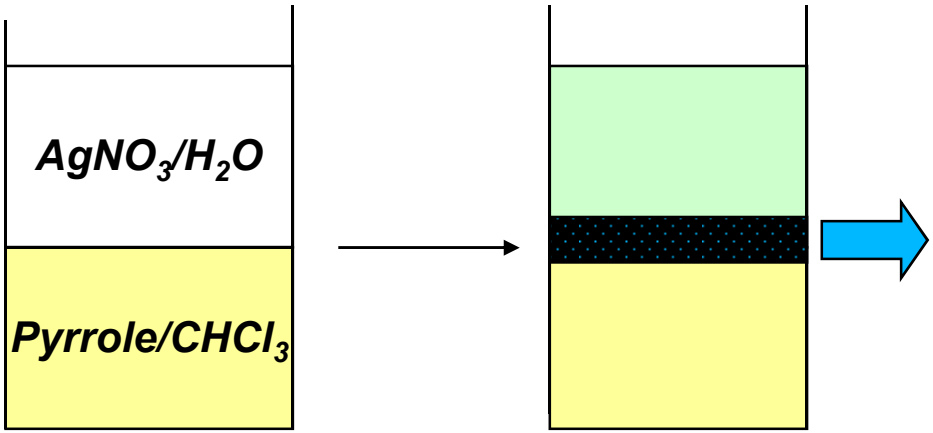


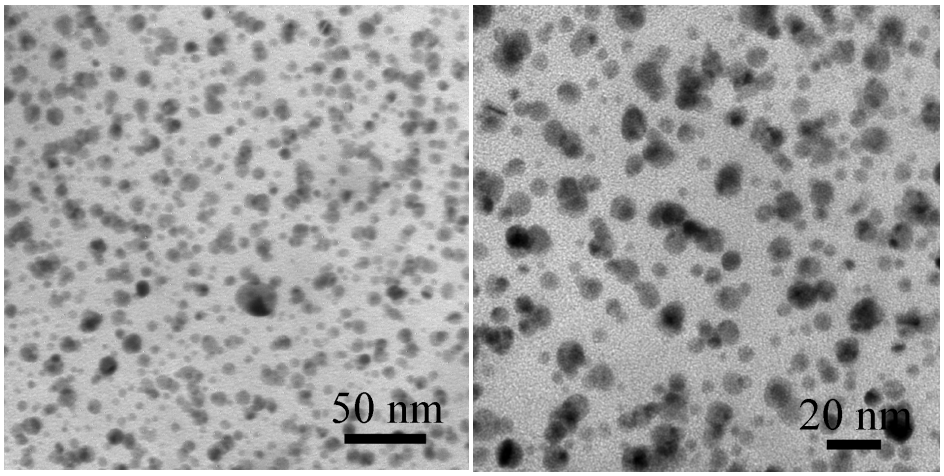


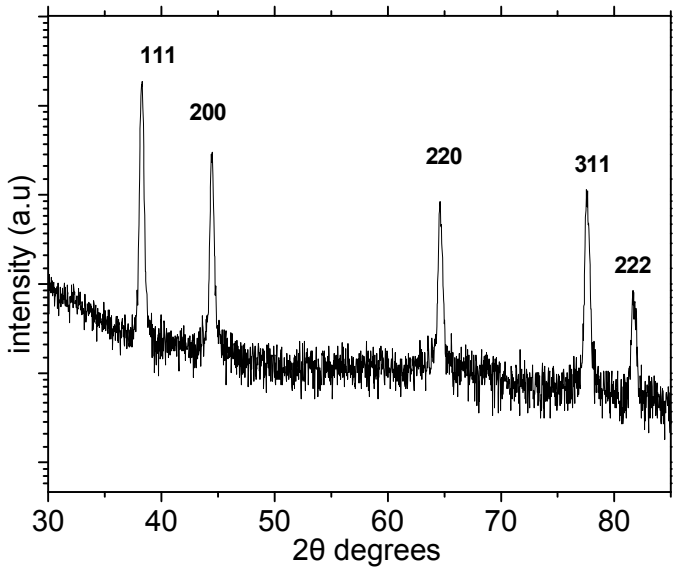
Tato prezentace je spolufinancována Evropským sociálním fondem a státním rozpočtem České republiky.

[14] © H.Kong., et al. ***Biomacromolecules 2008**, 9, 2766-2681.*

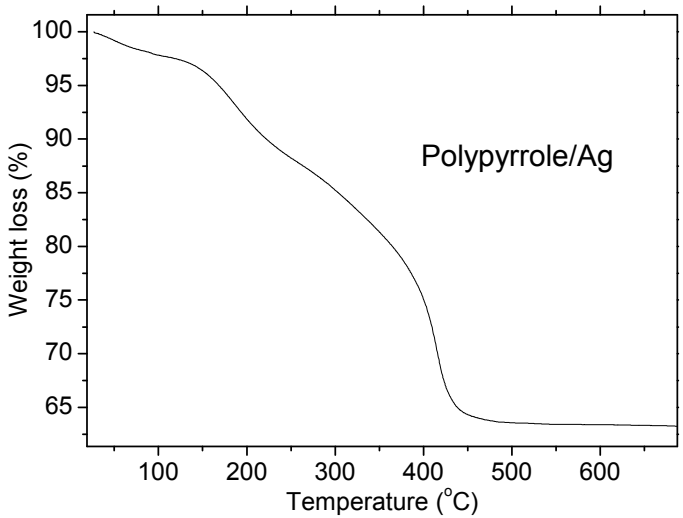
Silver polypyrrole composites: thin films through interfacial polymerization







Left: X-ray diffraction pattern indicating the crystal plains of metallic silver
Right: The % wt percentage of silver in the nanocomposite can be estimated through thermal analysis

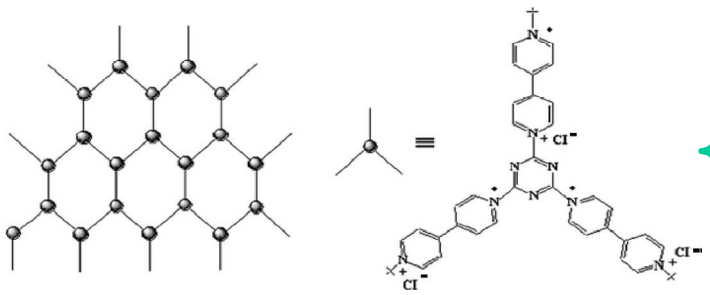


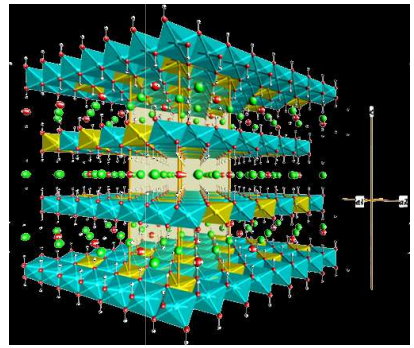
Tato prezentace je spolufinancována Evropským sociálním fondem a státním rozpočtem České republiky.

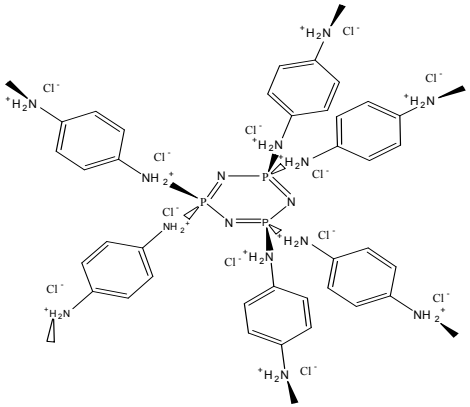
INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

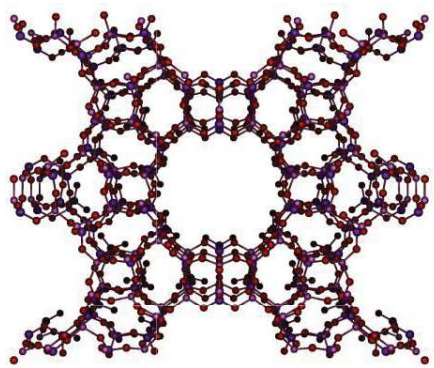
[15] © P.Dallas., et al. ***Polymer 2007**, 48, 2007-2013.*

Newly developed triazine based polymers

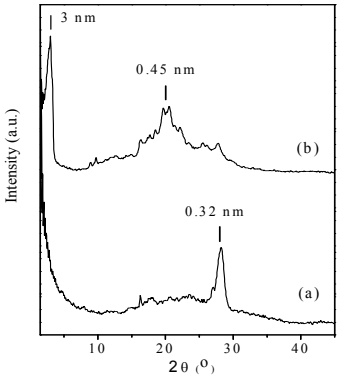


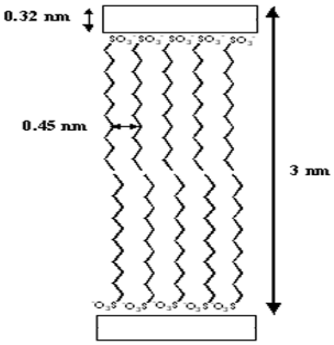




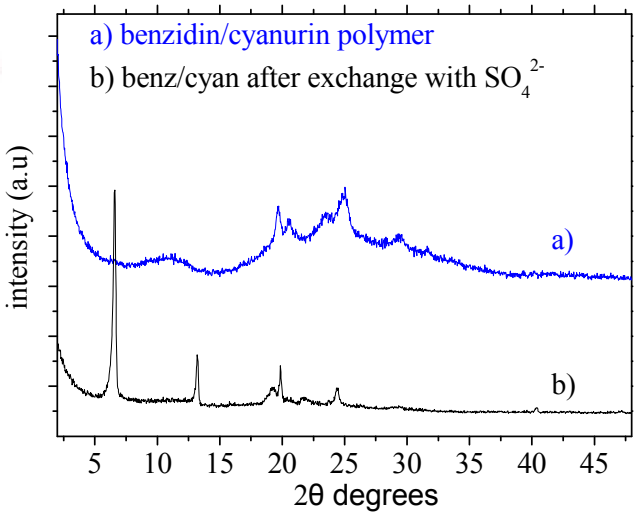


- These polymeric networks are synthesized through nucleophilic attach of aromatic diamines like 4,4' bipyridine, 1,4 phenylenediamine or benzidin in the reactive chlorine anions of either cyanuric or phosphonitrilic chloride.
- Chlorines are acting as counterbalancing anions and can be exchanged with other or inorganic anions thus expanding the d-spacing of the network (see XRD patterns below).
- They can be considered as organic-inorganic hybrid analoques of zeolites and layered double hydroxides.



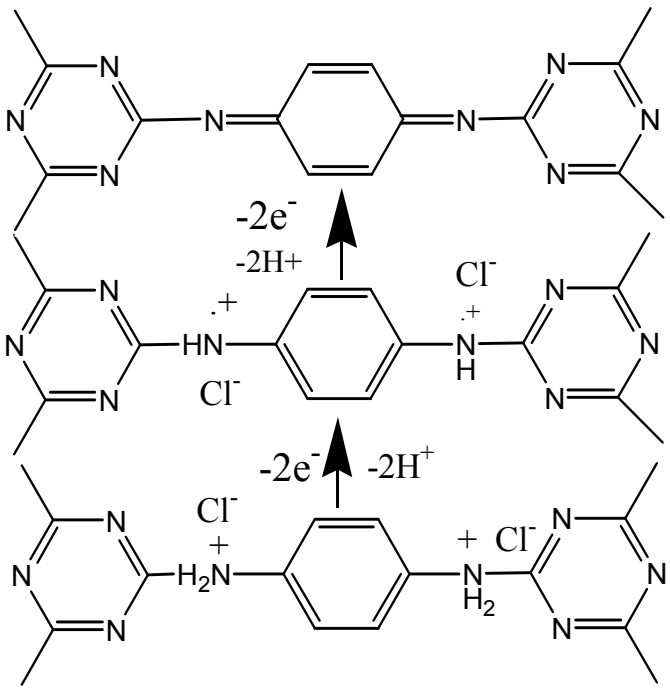


Cyanuric chloride:
Monosubstituted and planar
Phosphonitrilic chloride:
Disubstituted and the sites have
an in and out of plane orientation.



[16] © P.Dallas., et al. ***Polymer 2008***, 49, 1137-1144.
[17] © A.B.Bourlinos., et al. ***Eur.Pol.J. 2006,*** 42, 2940-2948

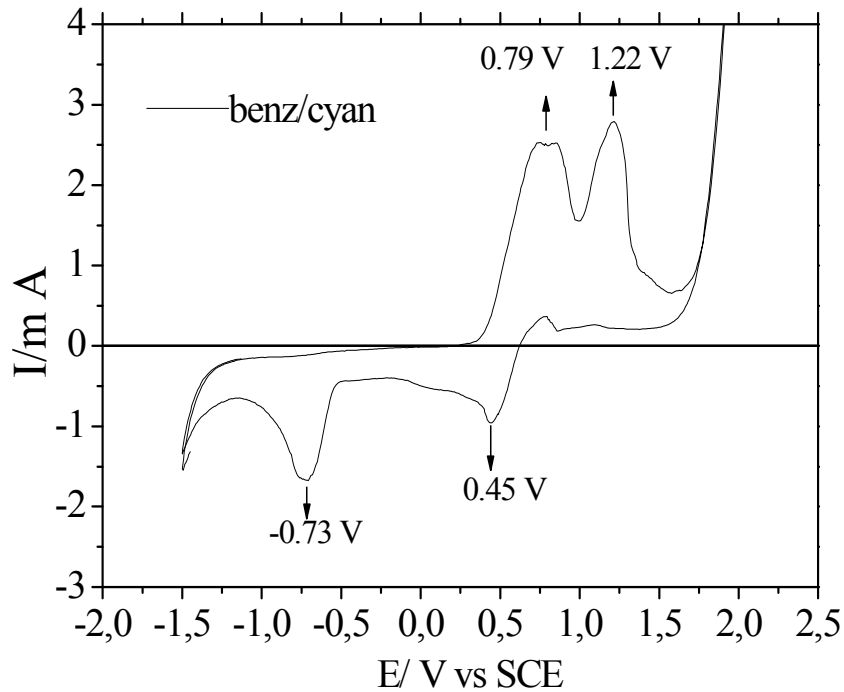
Electrochemical and redox activity



Dark green

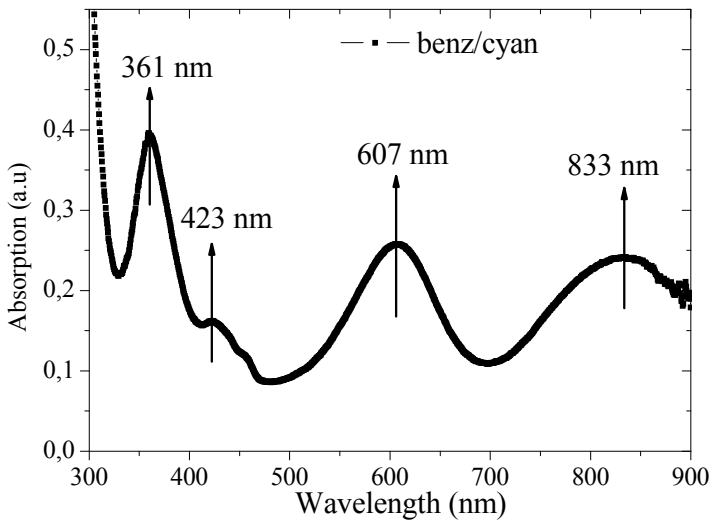
Blue

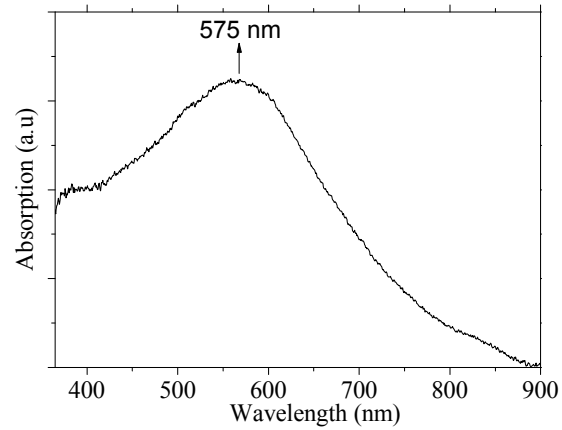
Light purple



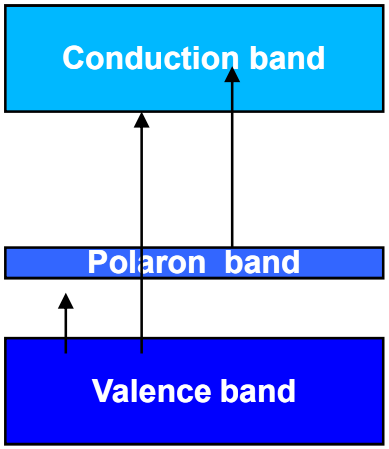
Due to the bridging protonated amine untits the polymer are chemically and electrochamicelly active. Cyclic voltammetry steps induce significant changes in the color and the oxidation state with an impact in the absorptions of the UV-Visible region

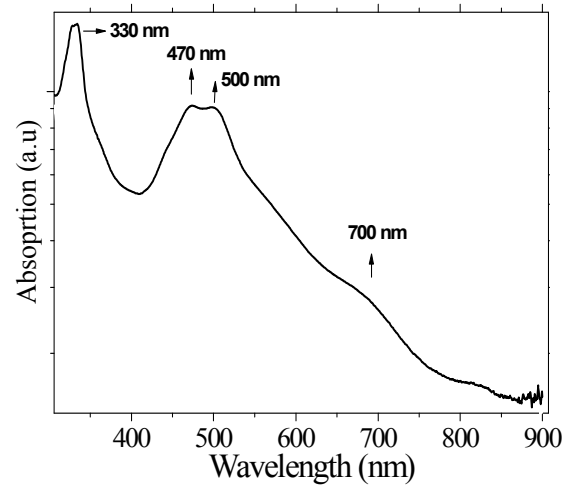
Optical properties





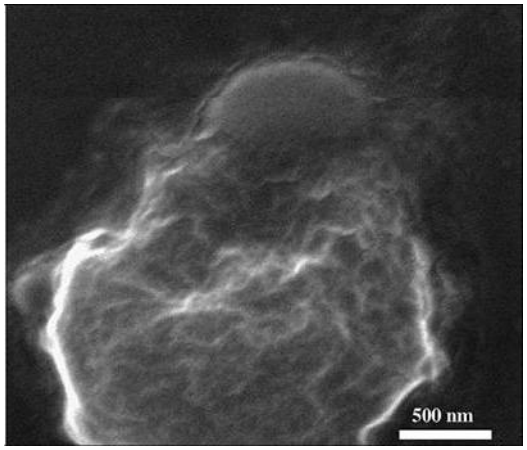
Polyaniline exhibits a well established formation of a polaron band which results in three distinct absorptions in the UV-Visible spectra. Similar was the spectrum of benzidin/cyanuric polymer (up).
It can be assigned to a partial formation of radical cations in the bridging amine units. EPR studies have been very powerful tools for the study of such materials.

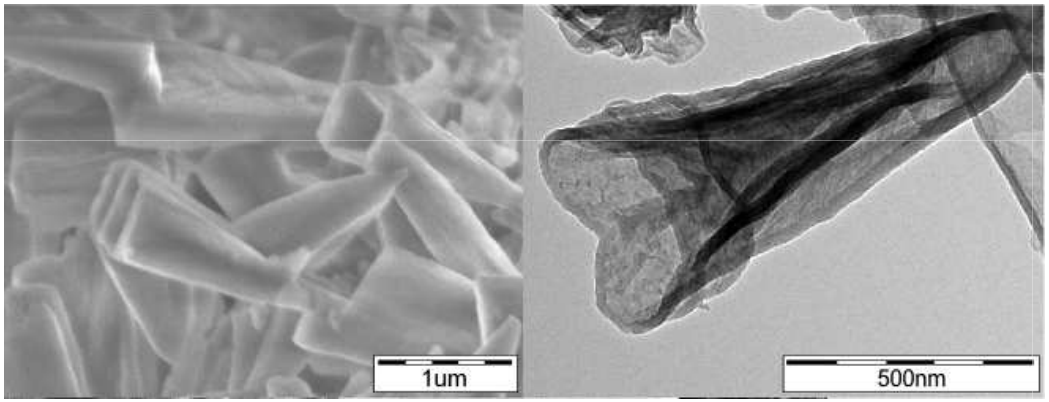




UV-Visible spectrum of 3-D phosphotriazine based polymers before and after oxidations with $S_2O_8^{2-}$.

Morphology of the polymers





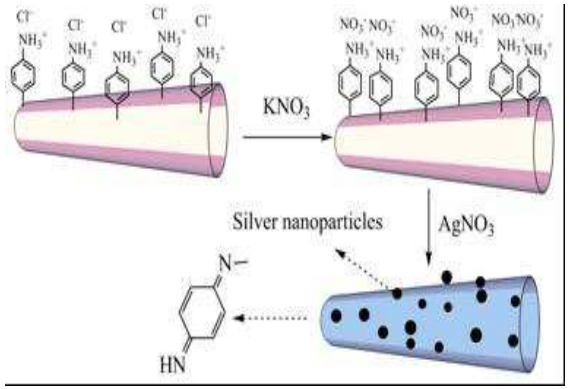
The macroscopic morphology of the polymers
is following the microstructure and the
macromolecular chains orientation.

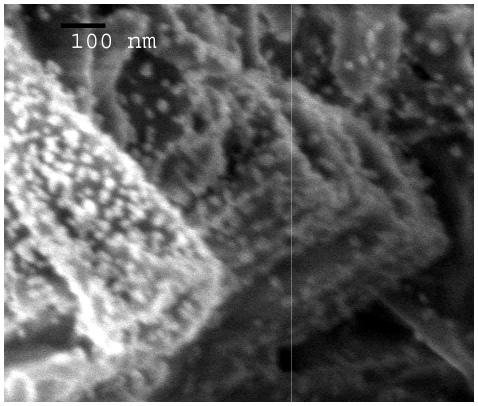
(I) An Electron Microscopy study of the 2-dimensional cyanuric derivative reveals the presence of individual or fused submicrometer grains with a striated surface texture, platy morphology and multi-layered structure at the edges. These features combined are suggestive of a lamella phase.
(II) The 3-dimensional growth of the phosphonitrilic derivatives results in elongated, hollow morphologies.

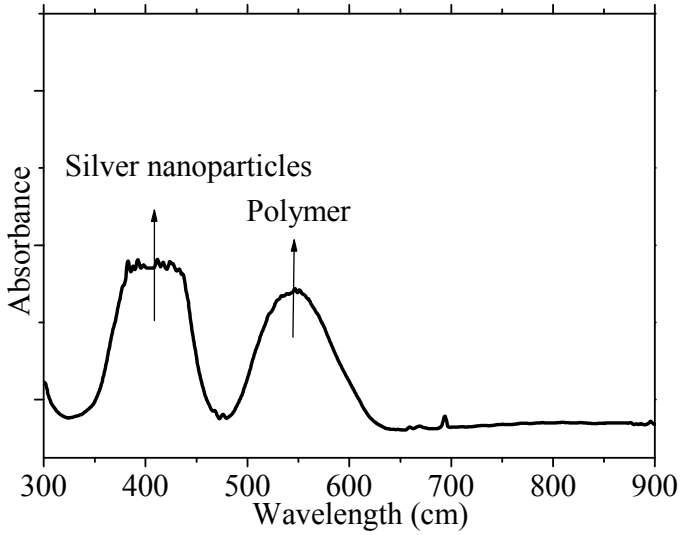
Tato prezentace je spolufinancována Evropským sociálním fondem a státním rozpočtem České republiky.

INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

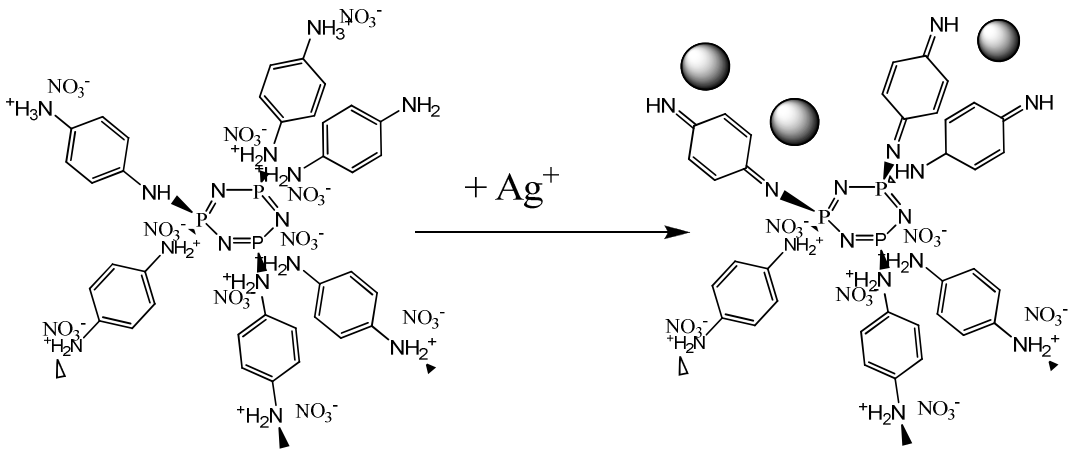
Synthesis of silver nanocomposites on the surface of triazine based polymers







- Redox reaction with silver cations results in silver nanoparticles that inherit the composites with high antimicrobial activity.
- Amines, amides, imines and thiols are excellent capping agents for noble metals as such the nanoparticles are well attached on the surface of the polymer



Tato prezentace je spolufinancována Evropským sociálním fondem a státním rozpočtem České republiky.

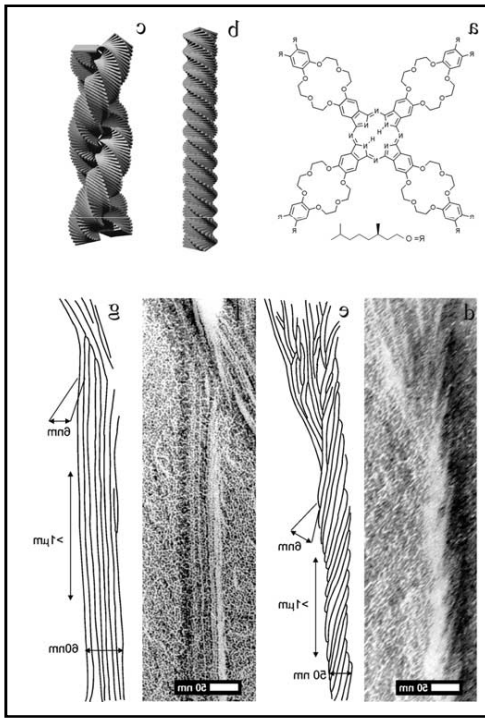
Future prospects for polymer chemistry

Porous polymeric networks with palladium nanoparticles are promising candidates for hydrogen storage materials and fuel cell technology. [19]

Palladium nanoparticles are excellent absorbents of hydrogen

The porous network of the support will enable the penetration and encapsulation of gas molecules, e.g. hydrogen. Its functional sites can selectively arrange the palladium nanoparticles.

Supramolecular chemistry (Nobel prize in 1987: J.M.Lehn, D.J.Cram, C.J.Pedersen) is a form of (chemical) art that enables the control of non-covalent interactions like hydrogen bonding for the construction of hyper-molecules with advanced functionalities and symmetry. This can light the way for new and advanced polymers that will enable the perfect formation and control of nanomaterials according to their structure.



Crown ether phthalocyanine self assemble to nematic Nano-structures: potential applications in non-linear optics, chemical sensors, nanodevices.

[18] a) A.Thomas et al. ***Macromol.Rapid. Commun. 2009,*** 30, 221
b) F.Cacialli ***Mater.Today 2004,*** 24
[19] Y.E.Cheon. et al. ***Angew.Chem.Int.Ed. 2009,*** 48, 2899-2903

- **The use of nanocomposites will reach 45 million kg by 2011. As such the challenges are in the hands of polymer chemists to optimize the performance and the synthesis of new composite materials.**
- **Further reading:**

Nanocomposites and interparticle distance control:

I. Vaia, R.A., Maguire, J.F**.** ***Chem. Mater.*** **2007,** ***19,*** 2736-2751.

II. Crooks, R.M., et al. ***Acc.Chem.Res. 2001, 24(3),*** 181.

III. Lim, S.I., Zhong, C.J. ***Acc.Chem.Res. 2009,*** 42(6), 798.

IV. M.Zorn., ***ACS Nano. 2009, 3(5),*** 1063-1068

Silver/polymer nanocomposites:

V. Gladitz, M., Reinemann, S., Radusch, H.J. ***Macromol. Mater. Eng. 2009, 294,*** 178–189.

VI. Rhim, J.W. et al. ***J. Agric. Food Chem***. ***2006***, 54, 5814-5822.

VII. C.N.Lok et al ***J.Proteome Res. 2006***, 5, 916-924.

Recent advances in polymer science:

VIII. A.Thomas et al. ***Macromol. Rapid Commun. 2009, 30,*** 221-236.

Tato prezentace je spolufinancována Evropským sociálním fondem a státním rozpočtem České republiky.

INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

Acknowledgements

- Dr.A.B.Bourlinos
- Prof.R.Zboril
- Dr.D.Jancik
- Dr.D.Niarchos
- Dr.D.Petridis
- Dr.V.Georgakilas

**The original research work presented here, was conducted in both the Centre of Nanomaterial Research of Palacky University and the Institute of Materials Science, NCSR "Demokritos", Athens, Greece.*

Contact information: Dr Panagiotis Dallas, Centre of Nanomaterial Research & Department of Physical Chemistry, Palacky University, Olomouc, Czech Republic. E-mail: panosdallas@gmail.com

Tato prezentace je spolufinancována Evropským sociálním fondem a státním rozpočtem České republiky.

INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ