



INTERNATIONAL WORKSHOP

ADVANCED MATERIALS

POMORIE, BULGARIA

10TH-13TH SEPTEMBER 2017

BOOK OF ABSTRACTS

PROGRAM

LIST OF PARTICIPANTS



SCOPE AND OBJECTIVES

The Workshop “Advanced Materials” is organized by the Faculty of Chemistry and Pharmacy, University of Sofia within the H2020-TWINN-2015 Project “**Materials Networking**”. The workshop aims at gathering together scientists from the partner organizations working in the area of advanced materials and related topics and thus identifying mutual areas of interests, exchange of knowledge and finding fields for following collaboration with the partner organizations.

Partner Organizations:

Department of Materials Science & Metallurgy, University of Cambridge, UK

Max-Planck Institute of Polymer Research, Mainz, DE

Faculty of Chemistry, University of Barcelona, ES

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PREFACE

The main objective of the TWINNING project is enhancement the scientific and technological capacity of the Faculty of Chemistry and Pharmacy at Sofia University (FCP-SU) and raising the research profile of the Faculty and its staff in the field of advanced functional materials via networking with three World-wide leading institutions – Department of Materials Science & Metallurgy, University of Cambridge, Max-Plank Institute of Polymer Research and Faculty of Chemistry, University of Barcelona. Faculty of Chemistry and Pharmacy at SU is a leading research centre in functional materials in Bulgaria and its networking and collaboration with global leaders in this research field will help in developing its potential to become European-wide known centre with increasing research and innovation contributions and achievements. Such achievements will increase the participation of the teams from FCP-SU in European and international projects and will promote higher performance of other research institutions in Bulgaria. Based on the expertise and achievements of the research groups in FCP-SU, the present project will contribute to two of the priority areas of the Bulgaria’s Smart Specialization Strategy with relevant thematic priorities “Materials for clean energy and environment protection” and “Materials with pharmaceutical and medical applications”.

PROGRAM

Sunday, 10th September

17:00	Opening – Georgi Vayssilov
17:10	Francesc Viñes
PL1	“Catalysts and catalysis through methods on models”
17:50	Hristiyan Aleksandrov
OP1	“Modeling of zeolite and metal systems relevant for catalytic applications: a theoretical study”
18:10	Lorena Vega
SO1	“On the accuracy of density functionals in describing transition metal surface properties”
18:20	Oriol Piqué
SO2	“C poisoning on noble and Pt-group metals”
18:30	Nadezhda Angelova
SO3	“Iron and aluminium based mixed nanostructured hydroxyphosphates as potential vaccine adjuvants: preparation and physicochemical characterization”
18:40	Antoan Rangelov
SO4	“Formation and characterization of inclusion complexes based on Starches”
19:00	Dinner

Monday, 11th September

09:00	Kai Zhang
PL2	“Nanostructured organic semiconductors for visible light photocatalysis”
09:40	Anela Ivanova
OP2	“Directed molecular design of organic light emitters”
10:00	Kai S. Exner
OP3	“Free energy diagrams from theory and experiment in electrocatalysis ”
10:20	Petko Petkov
OP4	“Breathing control by conformational isomerism in DUT-8(Ni): competition of strain against London dispersion ”
10:40	Coffee Break
11:10	Tony Spassov
OP5	“Nanoporous metals by selective dissolution of amorphous alloys ”
11:30	Petar Georgiev
OP6	“Acceleration effect of metal ions with smaller reduction potentials on the rate of citrate synthesis of noble gold and silver nanoparticles growth”
11:50	Martin Tsvetkov
OP7	“Some results on ¹⁷² Lu and ¹⁷² Hf doped MFe ₂ O ₄ (M= Zn, Ni, Co) obtained by time differential perturbed angular correlations, TDPAC, measurements”

12:10 OP8	Georgi Yordanov "Surface plasmon resonance studies of interactions between blood plasma proteins and nanoparticle drug carriers "
12:30 SO5	Ana Koleva "A new method for the synthesis of bis-2-oxo-chromans"
12:45	Lunch
15:20 OP9	Todor Dudev "α-Cyclodextrin: How effectively can its hydrophobic cavity be hydrated?"
15:40 OP10	Stefan Tsakovski "Impact of pH and inorganic ions on pharmaceuticals toxicity: environmental relevant case study"
16:00 OP11	Stoyan Gutsov "Aerogels - new materials with promising applications"
16:20 SO6	Gergana Gocheva "Structural characterization of folic acid and antifolates in aqueous solution"
16:30	Coffee Break
17:00 PL3	Markus Bannwarth "Monitoring crack appearance and healing in transparent coatings with damage self-reporting nanocapsules"
17:40 OP12	Elena Vasileva "Polyzwitterionic hydrogels for wound healing applications"
18:00 OP13	Aleksey Vasilev "Novel fluorogenic dsDNA binders. Synthesis by environmentally benign procedures"
18:20 OP14	Marta Reig "Molecular design of carbazole-based blue emitters for OLEDs"
18:40 SO7	Nikola Burdzhiev "Synthesis of substituted pyridines with application in metal-coordinated supramolecular assemblies"
19:00	Dinner

Tuesday, 12th September

09:00 OP15	Nikolay Denkov "Efficient self-emulsification via cooling-heating cycles"
09:20 OP16	Slavka Tcholakova "Preparation of porous materials by using direct foaming method"
09:40 OP17	Zahari Vinarov "Drug-loaded surfactant micelles in bio-relevant dissolution media: Impact of surfactant-bile interactions on drug solubility "
10:00 OP18	Svetoslav Anachkov "Rough raspberry particles: Wetting & universal emulsion stabilization"
10:20 SO8	Mihail Georgiev "Hardening of particle/water/oil three-phase dispersions due to capillary bridges with applications for new products and materials"
10:30	Coffee Break
11:00 OP19	Krasimir Vasilev "Nanoengineered plasma polymer films for biomedical applications "
11:20 OP20	Gergana Radulova "Surface shear rheology of adsorption layers from the protein hydrophobin and its mixtures with other proteins: experiment and theoretical model"

11:40 OP21	Anife Ahmedova "Coordination nano-capsules with improved therapeutic potential for cancer treatment"
12:00 OP22	Stanislava Yordanova "Naphthalimide derivatives - optical sensors and microbiological activities"
12:20- OP23	Mihail Avramov Development of underwater camera for precise ship inspection
12:45	Lunch
15:00 OP24	Rumen Tomov "Nano engineering of SOFC electrodes by inkjet printing infiltration"
15:20 OP25	Elisaveta Mladenova "Geographical origin of wine as defined by trace elements content"
15:40 OP26	Petar Petrov "Photoactive imidazolidene NHC complexes"
16:00 SO 9	Rumen Lyapchev "On the way to better catalysts: increasing catalytic performance of palladium imidazo[1,5-a]quinolin-1(2H)-ylidene complexes by tuning properties of the carbene ligand"
16:10 OP27	Tsvetomil Voyslavov "Assessment the level of self-cleaning of the soils around the former metallurgical plant – Kremikovtsi"
16:30 OP28	Stoyan Smoukov "Approaching the theoretical limit in polymer supercapacitors and multidimensional performance optimization"
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PLENARY LECTURES

Catalysts and catalysis through methods on models

F. Viñes, S.T. Bromley, K.M. Neyman, F. Illas

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Catalysis surrounds us in almost every aspect, from life related processes to automotives and manufactured chemicals. Focusing the attention on heterogeneously catalysed processes, two main branches of research and applicability are the synthesis/conversion of chemicals of industrial interest, and/or the usage of sunlight power as the energy source used in such processes. Heterogeneous (photo)catalysis highly depends on the reaction conditions, but also on the used catalyst, where factors such as chemical nature and composition, the exposure of active sites, the system particular size and shape, and its electronic structure are pivotal in tuning the catalytic performance. At the Computational Materials Science Laboratory (CMSL) of the University of Barcelona (UB) we conduct highly accurate *ab initio* simulations of such catalysts and the catalytic processes that occur at their surfaces on realistic models, in order to *i*) understand the catalysed reaction mechanism at the atomic level and *ii*) explain the experimental observations, both necessary steps to *iii*) rationally improve existent catalysts and/or reaction conditions, or even *iv*) propose new materials for these purposes. Here we present exemplary recent work on the catalytic greenhouse CH₄ gas decomposition,¹ and the direct and reverse water gas shift reactions on transition metal carbide systems,^{2,3} and the bandgap control on photoactive oxide materials by tuning size, shape, and polymorphism.⁴⁻⁵

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Nanostructured organic semiconductors for visible light photocatalysis

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Sunlight is a clean and inexhaustible source of renewable energy. Especially, the visible range of the solar spectrum accounts for 44% of the total energy as opposed to only 3% from the ultraviolet (UV) light. Inspired by nature’s ability to convert solar energy in photocatalytic processes, organic chemists have developed a vast number of photocatalysts in order to mimic the nature process. As a result, many molecular inorganic, transition metal-based complexes or organic dye compounds that absorb significantly in the visible spectrum were intensely studied to harvest solar energy and catalyze organic photochemical reactions. Nevertheless, there are still some intrinsic drawbacks associated with these homogeneous systems, for instance, high cost, toxicity of these rare metals, as well as limited availability in nature, and their additionally required post-reaction purification step for catalyst removal. It is therefore of great desire to develop stable, reusable and transition metal-free photocatalysts for organic synthesis. Compared to homogeneous catalysts, heterogeneous catalysts enjoy the advantage that they can be easily recycled by simple filtration due to their insoluble nature.

In this talk, a new class of non-metallic, organic semiconductor-based materials, in particular, conjugated nanoporous polymers, combining photoactive π -electron backbone and highly porous properties, will be presented as an efficient and stable platform for heterogeneous visible light-promoted chemical transformations. A structural design principle and important properties of the novel materials such as porosity, morphology or energetic band positions and their influence on the catalytic efficiency will be discussed. Examples of photoredox reactions such as molecular oxygen activation reaction,[1] C-C or C-N bond formations,[2] reductive dehalogenation reaction and C-H activation reaction [3] and direct bromination reaction on aromatic compounds will be shown. [4]

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Monitoring crack appearance and healing in transparent coatings with damage self-reporting nanocapsules

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The exposure of artificial materials to environmental stress causes their damaging and can eventually lead to catastrophic failure. Monitoring the intactness of materials, such as polymeric coatings, can alert from impending failure and significantly prolong their lifetime. Here, we introduce the novel concept of a health-state monitoring system for coatings that can display when a damage occurs and when it has been healed again. To achieve such a monitoring system, we integrated nanocapsules that can self-indicate their damaging *via* a color development into coatings. Hence, whenever the coating is damaged, the capsules break and highlight the damaged spot. As a second feature, the color development is reversed in the presence of (self-)healing compounds to allow tracking of the healing process. Thus, in a first step damages are being highlighted *via* color “turn-on” and, in a subsequent second step, a propagating healing reaction “turns-off” the damage indication system to trace the healing reaction and allow full control over the healing process. This reversible self-reporting system can pave the way towards a new generation of materials with multiple autonomous reporting functions to display the current health state of materials – from occurring damages to successful healing.

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2. Z. J. Wang, S. Ghasimi, K. Landfester, K. A. I. Zhang, *Adv. Mater.* 2015, 27, 6265–6270.
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ORAL PRESENTATIONS

**Modeling of zeolite and metal systems relevant for catalytic applications:
a theoretical study**

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Nanosized zeolites are materials with applications as catalysts and adsorbents. Silanol-free nanosized MFI-type zeolite was synthesized by introducing tungsten moieties within the crystal framework of the material and was characterized by various experimental and theoretical techniques [1]. Our quantum-chemical calculations showed that W heals defect sites in the framework - silanol nests, by forming flexible W–O–Si bridges. These W–O–Si fragments were found to be more stable than Si–O–Si in the all-silica MFI zeolite. It was found that tungsten incorporation in nanosized MFI crystals also modifies other properties such as hydrophobicity and Lewis acidity, as well as increases their stability. Thus, the new material opens new perspectives for catalytic and separation applications.

Nickel nanorticles are active and inexpensive catalysts for various industrially important reactions such as dry reforming of methane (DRM) ($\text{CO}_2 + \text{CH}_4 \leftrightarrow 2\text{CO} + 2\text{H}_2$), but they deactivate rapidly mainly due to the coke deposition on the catalyst. Two elementary reaction steps are crucial for the processes of DRM and coke formation on Ni particles: interaction of monoatomic C species with O or another C species to form either CO or C₂ species. In order to understand deeper these reaction steps we clarified various important aspects such as: stability of various sorption positions of monoatomic C and O, as well as of CO and C₂ species on/in surface/subsurface regions of periodic Ni(111) slab and Ni₇₉ nanoparticle models [2]. These models represent large nickel particles and nickel nanoparticles of ~1 nm size, respectively.

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Directed molecular design of organic light emitters

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The quest for more powerful blue emitters to be applied in organic light-emitting diodes is one of the demanding tasks of contemporary nanotechnologies. An approach to enhance substantially the intrinsic efficiency of luminescent organic molecules is the so-called thermally activated delayed fluorescence (TADF).¹ A prerequisite for its occurrence is a negligible energy separation between the lowest singlet and triplet excited states, which is challenging to achieve. The talk summarizes the results from systematic molecular design aimed at suggesting a molecular framework with high potential for TADF-based light emission. A set of donor-spacer-acceptor molecules are modelled with (TD)DFT to reveal the relative importance of several molecular factors for accomplishing the desired luminescence characteristics. The size of spacer, the position of binding to it, the torsion angle between the donor and the acceptor, and variation of the D-A conjugation length turn out to be the crucial determinants.² Following the derived molecular guidelines, several compounds are put forward as promising emitters. The best among them is 6-(5-tert-butyl-1,3,4-oxadiazol-2-yl)-N,N-diphenyl-9H-fluoren-1-amine with predicted fluorescent transition at 432 nm and probable TADF with $\Delta(S_1-T_1) = 0.84$ eV.

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Free energy diagrams from theory and experiment in electrocatalysis

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Electrocatalytic reactions are of ubiquitous importance, since those can be found in a large array of applications such as in fuel cells or in large-scale industrial processes. The chlorine evolution reaction (CER) constitutes the anodic reaction of the chlor-alkali process, in which dimensionally stable anodes (DSA) consisting of a mixture of TiO₂ and RuO₂ are employed as electrocatalyst. Hence, a single-crystalline RuO₂(110) model electrode may be envisioned as an appropriate model system in order to gain molecular insights into the CER.

Previous *ab initio* studies of CER over RuO₂(110) identified the active site of the electrode surface, namely the terminally bonded oxygen atoms O_{ot} (1,2), as well as the reaction mechanism (3). The corresponding Volmer-Heyrovsky mechanism consists of the adsorption and discharge of a chloride anion on the active O_{ot} site (Volmer step) that is followed by the direct recombination of the adsorbed chlorine species (OCl_{ot}) with another chloride anion from the electrolyte solution (Heyrovsky step). Experimental measurements of the CER over RuO₂(110) reveal two Tafel regions with different Tafel slopes (4). While the Tafel slope for small overpotentials is reconciled with the Heyrovsky step as rate determining reaction step (rds), the Tafel slope in the second Tafel region is ascribed to the Volmer step being the rds (5). This fact enables to convert the experimental Tafel plot into a free energy landscape, which allows for a direct comparison with the corresponding theoretical free energy diagram based on first-principles kinetics (6). Therefore, the free energy surface is the proper vehicle to transport kinetic information between *ab initio* theory and experiment back and forth.

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Breathing control by conformational isomerism in DUT-8(Ni): competition of strain against London dispersionPetko Petkov¹ and Thomas Heine²¹*University of Sofia, Faculty of Chemistry and Pharmacy, J. Bourchier blvd. 1, 1164, Sofia, Bulgaria*²*Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstr. 2, 04103 Leipzig, Germany*
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The analogy between metal–organic frameworks (MOF) and porous network compounds based on purely inorganic building units, such as aluminosilicates (zeolites) or aluminophosphates, is much related to reticular synthesis aiming at the control of the pore structure and coordination space in such kind of materials [1]. Chemical and thermal robustness of MOFs, including structural rigidity during reversible adsorption/desorption, have been key features in terms of possible industrial applications in catalysis and gas storage/separation [2-4] and herein MOFs are challenging established porous materials.

Research group of prof. Kaskel studied in details the “gate opening” mechanism in the highly flexible DUT-8(Ni) MOF with unprecedented unit cell volume change, up to 254%, caused by adsorption of gases, using combined single crystal X-ray diffraction, in situ XRD and EXAFS techniques.[5] The dependence of flexibility in this family of MOFs is still not clear, and the control on the gate opening is not well understood yet. By this reason we performed computational modeling of different conformational isomers of DUT-8(Ni). Our simulations show that gate opening depends on the conformation of the non-linear NDC linkers and also on the type of the metal center.

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Nanoporous metals by selective dissolution of amorphous alloys

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Rapidly quenched multicomponent metallic glasses are exposed to chemical and electrochemical selective dissolution. Amorphous alloys of precious metals as well as of transition metals are investigated. To achieve desired micro- and nanoporous structures the dealloying conditions (types and concentrations of the electrolyte, temperature) were optimized. The effect of the electrode potential on the dissolution process is also found to be crucial. For some of the amorphous ribbons (e.g. Zr-based) the etching takes place with constant rate in three dimensions, indicating a surface controlled dissolution process. The etching velocity is found to be very high, as the whole dealloying process proceeds in several minutes. As a result three-dimensional homogeneous microporous structures are obtained. Besides, the evolution of the morphology and microstructure of the nanoporous materials at different stages of dealloying is investigated by SEM and High Resolution Transmission Electron Microscopy (HRTEM) equipped with EDAX microanalysis. The resulting ligaments size ranges from tens to hundred nanometers. The changes in the ligament composition and microstructure at different dealloying times are correlated to the alloy composition and mechanism of dealloying. Additionally, the microstructure evolution is related to the electrocatalytic activity of porous alloys. The electrocatalytic activity for Hydrogen evolution of the dealloyed ribbons is compared to the as-cast alloys and other known electrocatalytic materials.

Acceleration effect of metal ions with smaller reduction potentials on the rate of citrate synthesis of noble gold and silver nanoparticles growth

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Hypothesis: Citrate synthesis of gold nanoparticles (GNPs) and silver nanoparticles (SNPs) can be accelerated by addition of europium(III), iron(III), copper(II) and silver(I) ions in initial reaction mixture [1].

Experimental: The kinetics of GNPs and SNPs growth was followed by means of UV-Vis absorption spectroscopy and Atomic force microscopy (AFM) imaging [2].

Findings: All used metal ions with smaller reduction potentials can accelerate gold and silver nanoparticle growth in comparison to classical citrate synthesis. The mechanism of nanoparticle formation follows two step Finke – Watzky (F–W) kinetic model. The values of nucleation and growth rate constants are obtained and compared with that for citrate synthesis. The temperature effect on the rate of formation was observed.

Keywords: Gold and silver nanoparticle synthesis, Finke – Watzky kinetic model, Growth acceleration

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Some results on ^{172}Lu and ^{172}Hf doped MFe_2O_4 (M= Zn, Ni, Co) obtained by time differential perturbed angular correlations, TDPAC, measurements

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It is now more than 70 years since ferrites debuted as an important new category of magnetic materials and were prized for a range of properties that had no equivalents in existing metal magnetic materials. Today ferrites are employed in a truly wide range of applications and new high- performing ferrite- based materials are appearing one after another.

There are numerous ways to modify and alter the properties of spinel ferrites such as controlling their morphology and changing their chemical composition. One of the most popular ways to control the properties of semiconductor materials is by doping them with different ions in small concentrations and ferrites are no exception. Recently rare earths, RE, doped ferrites rised attention due to the intrinsic properties of these elements. To understand however how the doping ions affect the properties of the ferrites we first need to understand how they affect the crystal structure (are they substituting any of the metal cations, are they forming a different phase or are they incorporated into the internodal space of the crystal). Due to the low concentrations of the RE and the nanodimensional state of the ferrites the conventional powder XRD and Mössbauer spectroscopy are not enough to answer this question. One of the most powerful techniques that can answer this question is the $\gamma\gamma$ -TDPAC method due to it`s detectability of low concentrations. We`ll introduce the $\gamma\gamma$ -TDPAC method and present some results obtained by measurments on Lu and Hf modified Zn-,Ni-, Co- ferrites synthesized by coprecipitation method.

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Surface plasmon resonance studies of interactions between blood plasma proteins and nanoparticle drug carriers

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Nanoparticles for parenteral delivery of bioactive substances are expected to interact with blood plasma proteins immediately after their administration forming a dynamic adsorption layer on the particle surface known as protein corona [1]. The kinetics of formation and the composition of the protein corona are important factors largely affecting the nanoparticle biodistribution, lifetime in blood circulation and in vivo fate [1].

In this presentation we describe the use of surface plasmon resonance (SPR) technique for studies of nanoparticle-protein interactions [2,3]. The SPR technique has been proven to be one of the most powerful technologies to determine specificity, affinity and kinetic parameters during the binding between various macromolecular substances. We report on the utilization of SPR to measure the interactions between blood plasma proteins and polymer drug nanocarriers [3]. The proposed methodology was found suitable for measurement of interactions of both drug-free and drug-loaded nanocarriers with blood plasma proteins and allowed quantitative evaluation of both rate and equilibrium constants of interactions. Presented results demonstrated that SPR can be considered as a promising technique for real time investigation of both kinetic and equilibrium parameters of the nanoparticle-protein interactions, which could be of importance for the development of drug nanocarrier systems and their biomedical evaluation and application.

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α -Cyclodextrin: How effectively can its hydrophobic cavity be hydrated?Silvia Angelova[†], Valia Nikolova[‡], Stiliyana Pereva[‡], Tony Spassov[‡], Todor Dudev[‡][†] *Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*[‡] *Faculty of Chemistry and Pharmacy, Sofia University “St. Kl. Ohridski”, 1164 Sofia, Bulgaria**t.dudev@chem.uni-sofia.bg*

Cyclodextrins (CDs) are among the most widely used native host systems with ability to form inclusion complexes with various molecular objects. This ability is so strong that the “hydrophobic” CD cavity never remains empty – even in the guest-free state it is filled with water molecules. However, no consensus has been reached concerning both the total number of hydrating water molecules and their preferred binding location in the CDs. Several outstanding questions regarding the CD hydration still wait to be answered: (1) Which spots of the CD cavity (“hot spots”) have the highest affinity for the guest water molecules? (2) How stable are water clusters inside the cavity? (3) Which mode of water binding - sequential or bulk - is thermodynamically more favored? (4) What is the upper limit of the number of water molecules bound inside the host cavity? (5) What factors do control the CD hydration process? Here, using α CD as a typical representative of the cyclodextrin family, we endeavor to answer these questions by combining experimental measurements (differential scanning calorimetry and thermogravimetry) with theoretical (DFT) calculations. Energies of the α CD hydrate formation are evaluated and the role of different factors, such as the number and mode of binding (sequential vs. bulk) of water molecules, type of hydrogen bonds established (water-water vs. water- α CD), and the dielectric properties of the medium, on the complexation process is assessed. The results obtained shed light on the intimate mechanism of water binding to α CD and disclose the key factors governing the process.

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Impact of pH and inorganic ions on pharmaceuticals toxicity: environmental relevant case study

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Assessment of the impact of pharmaceuticals residues on living organisms is a very complex subject. Apart from taking into account the toxicity of individual compounds also environmental factors should be taken into account (e.g. irradiation, pH, coexistence of other substances). In this paper attempts were made to assess the impact of coexisting ions and changes in pH on the toxicity of selected ten pharmaceuticals against two bioassays. Bioassays selected for study are used to measure the endocrine potential (XenoScreen YES/YAS®) and to measure acute toxicity (Microtox®).

As can be noticed Microtox® test gives the most definitive outputs concerning the determination of interaction type between drugs and chemical species. Synergism is proven for almost all drugs and chemical species and only two separate cases of antagonism are found. The significant interactions drug/pH are rare and for the great majority of experiments uncertainty is shown.

For YES+ and YAS+ (both agonistic effects) many cases of well-expressed synergism for all chemicals with a limited number of drugs (diazepam, fluoxetine hydrochloride, estrone, chloramphenicol for YES+ test) and (diazepam, progesterone, androstenedione, estrone for YAS+ test) are found. The tests YES- and YAS- do not indicate cases of synergetic interaction except for the couples Br⁻/diazepam and NH₄⁺/ketoprofen. On the other hand, the last two tests (YES- and YAS-) reveal some specific cases of antagonistic interaction with the participation of only two drugs (diclofenac (sodium salt) and fluoxetine hydrochloride) with several chemical species. Antagonism is also proven for YES+ test but mainly for diclofenac (sodium salt) and androstenedione in mixtures mainly with cations.

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Aerogels - new materials with promising applications

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This work focuses on the dependence preparation conditions—structure—physical properties of hydrophobic silica aerogels, all of them prepared under subcritical drying, thus aiming at potential application as case insulation filling in heat pumps. The so prepared, millimeter scaled nanoporous hydrophobic silica aerogel granules were analyzed with standard electron microscope and atomic force microscopy, IR spectroscopy, UV/Vis spectroscopy, differential scanning calorimetry and thermal conductivity measurements [1]. The physical properties of the aerogels were compared with commercial aerogel granules. Moreover, a new physicochemical method for incorporation of red emitting $\text{Eu}(\text{phen})_2(\text{NO}_3)_3$ complex into hydrophobic aerogels is demonstrated for the first time [2].

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Polyzwitterionic hydrogels for wound healing applications

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Skin, which is the largest organ in the human body, could be easily injured by burning, traumas, etc. Skin regeneration is a result of complex interactions between cells, extracellular matrix and soluble mediators. Wound healing could be easily hampered if any of the components of the healing process is compromised. Wound dressings are designed to ensure an appropriate environment for skin regeneration and to protect the wound from bacteria, negative mechanical forces, etc. Hydrogels, which are networks, produced by chemical or physical crosslinking of hydrophilic polymers, are soft tissue-like, flexible and transparent - properties which make them excellent candidates for wound healing management.

Polyzwitterons (PZI) have recently emerged as biomaterials with the lowest non-specific protein adsorption, even compared to the golden standard - poly(ethylene glycols). Besides, PZI swell more in salt solutions than in pure water. Thus, PZI hydrogels could provide at the same time antifouling properties and high ability to absorb wound exudate. That makes them able to: preserve moisture wound environment; painless dressing replacement and easy wound monitoring.

In this work, two types of PZI networks - polysulfobetaine (PSB) and polycarboxybetaine (PCB) were synthesized by using poly(ethylene glycol) diacrylate as crosslinking agent. They were characterized in terms of their swelling ability and intelligent responses towards temperature, salt concentration and pH changes of the media. Moreover, they were tested for cytotoxicity and inhibitory activities towards bacterial biofilms as well as to myeloperoxidase and collagenase - two of the enzymes causing wounds chronicity. The potential of the hydrogels for wound healing was confirmed by *ex vivo* experiments with clinical wound exudates.

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Novel fluorogenic dsDNA binders. Synthesis by environmentally benign procedures

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Continuing our previous studies [1, 2] novel asymmetric monomeric monomethine cyanine dyes TO-7Cl and 5a–5d, which are analogs of the commercial dsDNA fluorescence binder Thiazole Orange (TO), have been synthesized. The synthesis was achieved by using a simple, efficient and environmentally benign synthetic procedure to obtain these cationic dyes in good to excellent yields. Interactions of the new derivatives of TO with dsDNA have been investigated by absorption and fluorescence spectroscopy. The longest wavelength absorption bands in the UV-VIS spectra of the target compounds are in the range 509–519 nm and these are characterized by high molar absorptivities (63000–91480 l mol⁻¹cm⁻¹). All investigated dyes from the series are either not fluorescent or their fluorescence is quite low, but they become strongly fluorescent after binding to dsDNA. The influence of the substituents attached to the chromophores was investigated by combination of spectroscopic (UV-VIS and fluorescence spectroscopy) and theoretical (DFT and TDDFT calculations) methods.

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Molecular design of carbazole-based blue emitters for OLEDs

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The development of Organic Light-Emitting Diodes (OLEDs) that emit in the blue region has attracted intensive research, since these materials can be applied in combination to green and red colour emitters in full-colour displays and white OLEDs (WOLEDs). Taking into account the inferior performance of blue OLEDs in front of the red and green ones, many research efforts are still currently put forward to the development of new luminescent dyes with blue emission [1]. Indeed, proper operation of OLED devices with blue-emitting materials is subjected to its intrinsic large band gaps that difficult the injection of charges into the emitting layer, and the lower sensitivity of the human eye in this part of the electromagnetic spectrum, which decreases the efficacy [2]. In addition, blue OLEDs are more prone to degradation showing poor long-term stability and shorter lifetimes [3].

Among the many known luminescent materials with blue emission, carbazole derivatives are found to be promising as emitting layers in non-doped blue OLED devices [4]. Carbazole-based materials are well-known for its luminescent and hole-transporting properties [5]. This heterocycle shows an emission band in the UV zone of the spectrum that can be shifted to lower energies by extending its π -conjugated system. Thus, the design of new carbazole-based dyes that could present both blue fluorescent properties and charge transport characteristics is an attractive challenge.

Here we show an effective strategy to obtain blue-emitting materials based on the carbazole heterocycle by extending its π -conjugated system and by tuning the photophysical properties through the introduction of a triple bond as a π -conjugated linker [6,7].

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Efficient self-emulsification via cooling-heating cycles

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Emulsification requires drop breakage and creation of large interfacial area between immiscible liquid phases. Usually, high shear or high pressure emulsification devices which generate heat and increase emulsion temperature are used to obtain emulsions with micrometer and sub-micrometer droplets. Recently we reported a new efficient procedure of self-emulsification [1] which is based on spontaneous bursting of the dispersed drops into hundreds and thousands of smaller droplets, during freezing and melting, without any mechanical energy applied to the emulsion. In all three mechanisms discovered, the energy of phase transition to the rotator phase and to the solid alkane, accumulated during drop cooling and freezing, is transformed into interfacial energy of the smaller drops in the final emulsion. Using appropriate cooling rates and surfactant-alkane combinations, we observed this phenomenon with all types of surfactants (nonionic, cationic and anionic) and with all alkanes (chain-length varied between C₁₄ and C₂₀) we have tested. Thus we have confirmed that the studied phenomenon is rather general, as it is not limited to a narrow range of surfactant-alkane pairs. This method is of high potential interest for producing pharmaceutical emulsions and dispersions of temperature-sensitive drugs. Not only the drop size could be reduced at minimal heat and mechanical stresses, but also the lipid drug carriers could be frozen in a desired shape, and surface-modified to achieve selective particle uptake in specific organs and/or controlled release from slow dissolution or from slow enzyme lipolysis in the intestinal fluids and blood plasma.

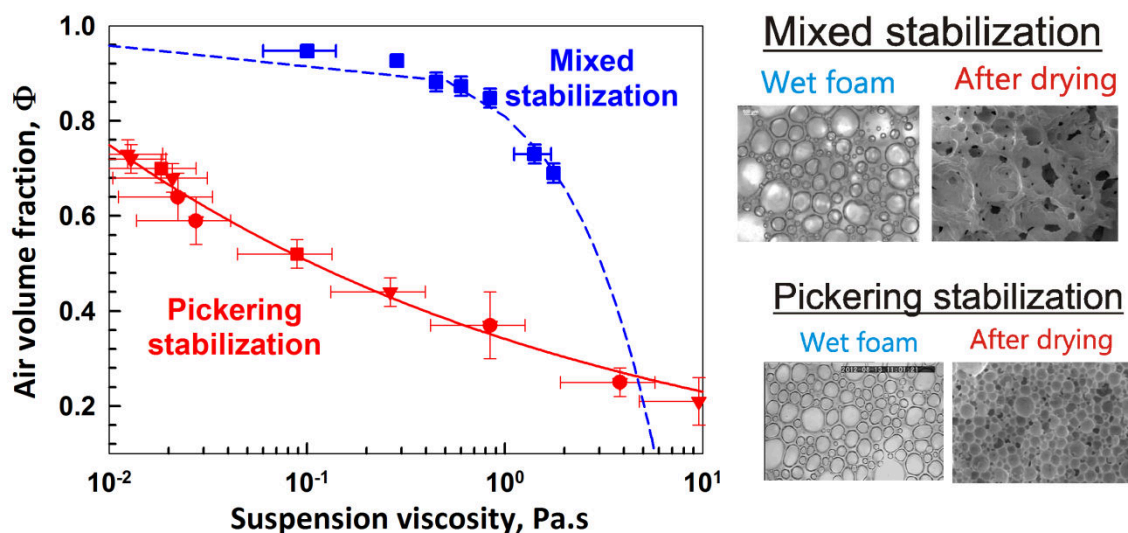
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Preparation of porous materials by using direct foaming method

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Foaming of particulate suspensions, followed by foam drying, is developed as an efficient method for production of highly porous materials with various applications. A key factor for success is the appropriate choice of surfactants which both modify the particle surface and stabilize the foam. In this presentation we will compare the efficiency of this method for silica suspensions containing two surfactants which lead to very different types of foam stabilization. Cationic TTAB leads to particle-stabilized foams (Pickering stabilization) whereas zwitterionic CAPB – to surfactant-stabilized foams [1]. Thus we determined the general (common) features shared between the various surfactant systems: (1) The foaminess is controlled exclusively by the suspension viscosity under shearing conditions which mimic precisely the foaming process; (2) The foam stability to drainage and coarsening is controlled exclusively by the suspension yield stress; (3) The surfactant adsorption on the particle surface should occur in the time scale of seconds to minutes, thus ensuring appropriate rheological properties of the foaming suspension.



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Drug-loaded surfactant micelles in bio-relevant dissolution media:**Impact of surfactant-bile interactions on drug solubility**

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More than 50 % of new drug molecules have poor water solubility, limiting clinical application. One approach to increase drug solubility is solubilization in surfactant micelles. However, the oral delivery of solubilized formulations presents an additional challenge, due to the endogenous surface-active substances in the gut (bile salts, phospholipids). These bio-surfactants interact strongly with classical surfactants thus altering drug solubility, which results in variable and difficult to predict oral bioavailability. Therefore, we aim to reveal the impact of bile-surfactant interactions on drug solubility, by studying the influence of surfactant molecular structure on drug solubilization in bio-relevant media.

We studied the solubilization of Fenofibrate (Log P = 5.3) by 13 surfactants with different chain length (C12-C18) and head group (cationic, anionic, nonionic and zwitterionic). Porcine bile extract containing bile salts and phospholipids was used for bio-relevant media preparation. Sodium taurodeoxycholate (97 %) was used as a pure bile acid for model experiments. Drug solubility was determined by HPLC and micelle size was measured by light scattering.

Drastic decrease of Fenofibrate solubility in presence of bile was observed for anionic and cationic surfactants at surfactant concentration of 0.5 wt %. In contrast, drug solubilization in nonionic surfactants was not significantly affected. Experiments at different surfactant-to-bile extract ratios showed near-ideal behaviour for Tween 20:bile mixtures – Fenofibrate solubility decreased linearly with the increase of bile extract fraction. However, increasing bile extract fraction from 0 to 20 mol. % resulted in a pronounced drop in Fenofibrate solubility for both sodium dodecyl sulfate and tetradecyl trimethylammonium bromide, see Figure 1. Identical results were obtained when bile extract was replaced with a pure bile salt (sodium taurodeoxycholate), thus confirming that surfactant-bile interactions are key. Dedicated experiments aimed to reveal the mechanism showed that nonionic surfactants do not form mixed micelles with the bile salts, thus retaining their solubilization capacity, whereas charged surfactants form mixed micelles with bile, which have low drug solubilization capacity. These findings advance the understanding of drug solubility in complex, bio-relevant media and could be used to improve the in-silico models for prediction of oral bioavailability that currently neglect such type of bile-surfactant interactions.

Rough raspberry particles: Wetting & universal emulsion stabilization

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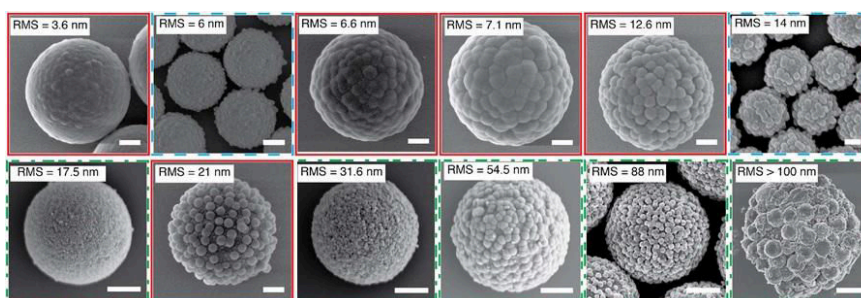
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Surface heterogeneities, including roughness, significantly affect the adsorption, motion and interactions of particles at fluid interfaces. However, a systematic experimental study, linking surface roughness to particle wettability at a microscopic level, is currently missing. Here¹ we synthesize a library of all-silica microparticles with uniform surface chemistry, but tunable surface roughness and study their spontaneous adsorption at oil–water interfaces. We demonstrate that surface roughness strongly pins the particles’ contact lines and arrests their adsorption in long-lived metastable positions, and we directly measure the roughness-induced interface deformations around isolated particles. Pinning imparts tremendous contact angle hysteresis, which can practically invert the particle wettability for sufficient roughness, irrespective of their chemical nature. As a unique consequence, the same rough particles stabilize both water-in-oil and oil-in-water emulsions depending on the phase they are initially dispersed in. These results both shed light on fundamental phenomena concerning particle adsorption at fluid interfaces and indicate future design rules for particle-based emulsifiers.



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Nanoengineered plasma polymer films for biomedical applications

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In my talk, I will present recent developments from my lab on various biomaterial coatings that are facilitated by plasma deposition. These include antibacterial coatings, drug release platforms and cell guidance/capture surfaces.

Undesired bacterial adhesion and subsequent colonisation of medical devices is a substantial medical problem causing complex and sometime fatal infections. We have developed various strategies for generation of antibacterial coatings that can be applied to medical device surfaces. These involve means such as silver nanoparticles, antibiotics, nitric oxide, quaternary ammonium compounds (QACs) or simply coatings that have intrinsic low fouling properties. All these coatings are facilitated by plasma deposition, a technique that provides functional films placed to the surface of any type of material. Important for applications, we not only extensively test our coating for their antibacterial efficacy against medically relevant pathogens but also assess their potential cytotoxicity to mammalian cell and inflammatory consequences. We have also developed methods for the synthesis and surface immobilisation of hybrid antibacterial nanocapsules and nanoparticles, including such capable of triggered release.

In a second part of my talk I outline our work on developing advanced nanoengineered plasma polymer coatings capable of directing cellular behavior. We have developed unique capabilities to control and tailor surface properties such as chemistry, wettability, ligand densities, nanomechanics and nanotopography in a substrate independent fashion. We can also tailor all these surface properties in a gradient manner. I will demonstrate how we use surface gradients of nanoparticles density to study the influence of surface nanotopography on the behavior of various cell types, including immune cells. I will present a strategy for developing gradients of surface elastic moduli and the cell response to these surfaces. I will also outline how we guide the differentiation of stem cells via surface chemistry, nanotopography or density of signalling molecules.

I will also briefly present drug delivery and release platforms that we have developed including a method for solvent free encapsulation of drug particles. A recently developed device for selective cancer cell capture for complex liquids will also be presented.

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Surface shear rheology of adsorption layers from the protein hydrophobin and its mixtures with other proteins: experiment and theoretical model

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The hydrophobins represent a class of amphiphilic proteins. At air/water and oil/water interfaces they form adsorption layers with the highest surface elasticity and viscosity among all investigated proteins. Moreover, the hydrophobins are rather “sticky” molecules, which are used for surface coatings and to fix functional molecules at interfaces. We investigated the surface shear rheology of class II hydrophobin HFBII layers at liquid interface in two different dynamic regimes – fixed rate of strain and oscillations [1–3]. The rheological data obtained in both regimes comply with the same viscoelastic thixotropic model, which is used to determine the surface shear elasticity and viscosity, E_{sh} and η_{sh} . The resulting values for the E_{sh} show that the elasticity is insensitive to the rate of strain in a wide range of the investigated shear rates. The mixing of hydrophobin HFBII with other conventional proteins could reduce E_{sh} and η_{sh} proportional to the fraction of the conventional protein. However, our experiments show that the effect of mixing can be rather different depending on the nature of the additive. If the additive is a globular protein, like β -lactoglobulin and ovalbumin, the surface rigidity is preserved, and even enhanced. In contrast, the addition of the disordered protein β -casein leads to softening of the HFBII adsorption layer. Similar (an even stronger) effect is produced by the nonionic surfactant Tween 20 [4]. These results could contribute for quantitative characterization and deeper understanding of the factors that control the surface rigidity of protein adsorption layers with potential application for the creation of stable foams and emulsions with fine bubbles or droplets.

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Coordination nano-capsules with improved therapeutic potential for cancer treatment

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Metallosupramolecular cages and capsules gain increasing popularity as both molecular containers [1] and anticancer agents [2]. For successful combination of these properties, however, thorough analysis of the effect of guest encapsulation on the host's cytotoxic properties is highly required. Here we report on the modulation of cytotoxicity of Pt(II) and Pd(II)-linked coordination capsules upon encapsulation of guest molecules such as pyrene and caffeine. The anticancer activity of the capsules against various human cancer cells (HT-29, T-24, HL-60 and its resistant counterparts HL-60/Dox and HL-60/CDDP) significantly altered upon the guest encapsulation. The encapsulation of guest molecules causes decrease in cytotoxicity of the capsules. The observed trends in the anticancer activity of the capsules and their host-guest complexes correlate with their different stabilities toward glutathione, as was estimated by NMR-based kinetic experiments. Mechanistic insights into the observed activity are obtained by fluorescence microscopic imaging of tumor cells treated with the capsules and their pyrene complexes. The data suggest the glutathione-triggered disassembly of the capsular structures as a potential activation pathway for their cytotoxicity [3].

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Naphthalimide derivatives - optical sensors and microbiological activities

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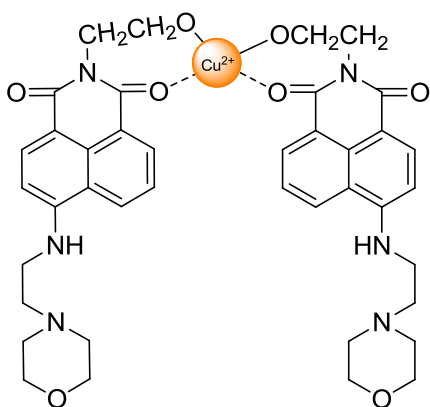
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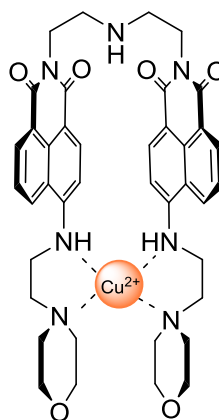
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Four 1,8-naphthalimide derivatives were obtained and their photophysical properties in different solvents were investigated. It has been shown that studied compounds have solvent dependent absorbance and emission. Cu(II) and Zn(II) complexes of the compounds were also obtained and characterized. Antimicrobial composite PLA-metal complexes materials have been prepared for the first time. The microbiological activity of composite materials PLA-metal complexes in thin polymeric film has also been investigated. The results suggest that the new metal complexes could find application in designing new antimicrobial preparations to control the spread of infections. [1] Microbiological activity of the metal complexes has been investigated in vitro against different Gram-positive and Gram-negative bacteria and two yeasts. The results indicate that they can be applied as antimicrobial agent to be used in biomedical and agrochemical applications. [2]



Proposed Cu (II) complex [1]



Proposed Cu (II) complex [2]

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Development of underwater camera for precise ship inspection

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Objectives of the Product

The camera is using innovative principle for scanning with a laser beam of underwater constructions - bottom of ships as it stays in water (no dry dock), port construction inspection, control of dams, ship propellers defects inspection, internal inspection of tanks of oil tanker, pontoon pier inspection.

Similar approach is known for extra-water welding robots for both quality scanning and seam tracking purposes. The proposed camera can be used for seam tracking during welding with underwater robots. (for underwater welding motion control of the robot).

The purpose of the product is to be used in conjunction of underwater robot for inspection of the microstate of ship bottoms. Quality of welds and junction in the underwater parts of the ship can be done. The inspection is done for welding problems e.g buzz, tack, or other welding imperfections. The decision about “weld OK” or “weld Not OK” is done by limits stored in the camera controller and possible to be adjusted by the operator console for the specific inspection case.

Structure of the system:

The system consists of a

- sensor part which is capable to deliver images of the scanned object at rate of up to 50 frames/s(fps) at full resolution or up to 1000 fps for a defined smaller sub-region of the video sensor.
- Controller part based on Intel NUC PC
- Operator console – consists of PoE+ injector or switch with 1G speed capable to work in aggressive extra-water maritime conditions
- Connections – The sensor part is connected to the controller with 2-10m cable. The controller is connected to the operator console with 100m.

Economic and commercial exploitation of results

Possibility to manufacture the ordered number of cameras for interested customers. The target customers are companies working in repair and quality control of ships.

- Examples of companies that can use this camera, type of activity
 - Ship repair companies, Ship manufacturers
 - Ship inspection authorities
 - Light water (up to 100m) inspection of pipelines and cables
 - Inspection of platforms for ground oil and gas (up to 100m)
 - Ports installation construction
 - Internal inspection of tanks of oil tanker when filled with water
 - Underwater Robot development companies for integration of the scanning camera as a tool
 - Pontoon Pier inspection
 - Control of dams – especially metal gateways
 - Military inspections - submarine parts - underwater
 - Ship propellers defects from cavitation inspection to decide if a propeller needs to be changed or repaired.

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Nano engineering of SOFC electrodes by inkjet printing infiltration

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Feasibility of inkjet printing for fabrication and modification of SOFCs functional coatings was studied. Inkjet printing is simple and cost-effective non-contact technique applicable to variety of surfaces which allows utilization of very thin fragile and/or non-even porous supports. The effect of nano-decoration of anode and cathode scaffolds by inkjet infiltration was assessed. Two - step fabrication of the electrodes was implemented. In the first step the porous electrode scaffold was created by printing suspension composite inks. During the second step inkjet printing infiltration was utilized for controllable loading of active elements and formation of nano-grid decorations thus radically reducing the activation polarization losses. Anode and cathode symmetrical cells were characterized by impedance spectroscopy in order to reveal the relation between the microstructure and their electrochemical performance. The traditional infiltration procedures are often based on manual use of micro-dispensers to suspend sessile drops onto the porous electrode surface followed by exposure to low-grade vacuum promoting ink permeation into the scaffold. Such treatment is non-scalable, time consuming and wasteful since a significant portion of the infiltrated precursor is lost in the process. In contrast, inkjet printing offered inherently much faster and cost efficient processing path by reproducibly dispensing droplets in the range of nL to pL volumes at high rates (kHz) and high velocity (1-20 m/s). Infiltrated microstructure was created by consistently printing droplets with micrometer spatial resolution ensuring reproducibility between the infiltration runs and zero ink waste effect. By regulating Reynolds (Re) and Weber (We) numbers of the jetted ink one can effectively control the spread of the drops on the surface as well as their permeation depth. Inkjet systems offers wide scale of application - from experimentation platforms working with customized inks, up to mass manufacturing systems that can print rapidly and competitively on industrial scale.

Geographical origin of wine as defined by trace elements content

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Wine is one of the most traditional and widely-consumed alcoholic beverages worldwide. The presence of metals in the wine is important from a toxicological and organoleptic point of view. It is proven that soil and climatic conditions are primary factors determining element composition of grapes and wines. The aim of the present study is to evaluate the chemical elements migration in the system soil-grape-wine for Bulgarian samples. According to results obtained for trace elements content it will be determined classification of Bulgarian wines by geographical origin. Thirty-two soil samples were analyzed using two single step extraction procedures with 0.05 mol/L EDTA and 0.43 mol/L CH₃COOH, respectively, in order to evaluate the extractable metal contents in the soils. Total element content in the grape vine, including elements, which are leached from the soil, and elements, which are result from an aerosol contamination, is determined in 33 vine leaves samples after acid mineralization. The content of same elements is quantified after acid digestion in 33 wine must samples (prior fermentation process). Selected chemical elements were quantified in each technological step through winemaking process including in the final product wines. After the statistical treatment of the results obtained specific relations between trace chemical elements were identified.

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Photoactive imidazolidene NHC complexesPetrov, P.Y.¹; Lyapchev, R.H.¹; Yordanova, S.B.¹; Stoyanov, S.S.¹; Dangalov, M.G.²; Vasilev, N.G.²¹ Sofia University “St. Kliment Ohridski”, Sofia, Bulgaria² Bulgarian Academy of Sciences, Sofia, Bulgaria

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With focus on the electronic interactions within a metal-carbene system we present the synthesis of two types of photoactive NHC precursors and of their Pd and Pt complexes [1,2]. Their NMR, absorption and emission spectra give insight on the electronic interactions within the metal-ligand systems.

The first, naphthalimide type NHC complexes prove to be thermally stable and provide excellent catalytic activity, while quinoline-based counterparts undergo thermal degradation in catalytic conditions. Both types of complexes photodissociate their NHC ligands upon irradiation, to produce the respective carbene dimers [3].

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Assessment the level of self-cleaning of the soils around the former metallurgical plant – Kremikovtsi

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The aim of our research is to study the natural self-cleaning ability of soils around the metallurgical plant – Kremikovtsi, closed since 2009. On the basis of results from previous survey, with soil samples collected nearby operating Kremikovtsi plant, we had prepared a new sampling plan including sample points of contaminated soils according to the current Bulgarian soil legislation [1]. The new set of samples was processed and analyzed in accordance with internationally accepted ISO standards for soils [2, 3, 4]. Appropriate analytical techniques (FAAS/ETAAS) were used for quantification of both pseudo-total concentrations and concentrations of selected toxic elements in soil extracts obtained according to the classical BCR extraction. The content of polycyclic aromatic hydrocarbons (PAHs) in soil samples was determined by gas chromatography after a Soxhlet extraction. Comparing the data from the previous studies and the newly obtained results, self-purification coefficients for the sampling points were calculated with respect to the different analytes (toxic chemical elements and PAHs).

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Approaching the theoretical limit in polymer supercapacitors and multidimensional performance optimization

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Supercapacitors promise recharging of phones and other devices in seconds and minutes as opposed to hours for batteries. But current technologies are not usually flexible, have insufficient capacities, and for many their performance quickly degrades with charging cycles. By using phase separation we have created polymer supercapacitors that solve all three problems at once. We show increased use of the active material and approach the theoretical storage capacity. We also demonstrate flexibility and resilience to charge/discharge cycling. We do extensive characterizations with a system of freestanding poly(3,4-ethylenedioxythiophene)/poly(ethylene oxide) (PEDOT/PEO) semi-interpenetrated network (sIPN) films. We simultaneously achieve improvements in three crucial elements of supercapacitor performance: specific capacitance (182 F/g, a 70% increase over neat PEDOT), cycling stability (97.5% capacitance retention after 3,000 cycles), and flexibility (the electrodes bend to < 200 μm radius of curvature without breaking). Our simple and controllable sIPN fabrication process presents a framework to develop a range of polymer-based interpenetrated materials for high-performance energy storage technologies.

SHORT ORAL PRESENTATIONS

On the accuracy of density functionals in describing transition metal surface properties

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Here we assess the performance of various density functional theory exchange-correlation functionals of extended use (Vosko-Wilk-Nussair – VWN, Perdew-Burke-Ernzerhof – PBE, PBE for solids – PBEsol, revised PBE – RPBE, and Tao-Perdew- Staroverov-Scuseria – TPSS) in describing surface properties of all transition metals with face-centred cubic (fcc), body-centred cubic (bcc), or hexagonal close-packed (hcp) crystallographic structure. Results on calculated surface energies, work functions, and interlayer distances are compared to available experimental data, including direct comparisons to surface-specific values, but also to surface average values, tackled by averaging values through Wulff constructed equilibrium nanoparticle shapes^[1,2]. Results highlight that surface properties are best simulated using the PBEsol functional, although PBE is advised when considering both bulk^[3] and surface properties.

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C poisoning on noble and Pt-group metals

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Coinage (Cu, Ni, Ag, Au) and Pt group (Pt, Pd, Ir, Rh) metals display a face-centred cubic (*fcc*) crystal structure, and are usually used in heterogeneous catalysis. It is well known that when using these metals as catalysts for reactions dealing with organic molecules, they present deactivation over time. Among many reasons, this deactivation can be due to carbon poisoning, a phenomenon caused by carbon atoms produced from secondary reactions taking place on the metal catalyst surface.¹⁻³

We show here a thorough study on the interaction of carbon atoms with most common (001), (011), and (111) surfaces of these *fcc* metals by first-principles methods. Specifically, optimization simulations carried out at density functional theory (DFT) level on proper surface slab models have been done placing a carbon atom in different positions of the surface, and also in the subsurface region, to investigate the possible formation of carbidic phases, which are known to affect the surface on-going reactions. Adsorption and absorption energies are obtained, along with mean C-Metal distances at the corresponding final geometries. The main results reveal that noble metals, as expected, interact less strongly with C atoms. On the other hand, there is a high interaction for the rest of late transition metals, highlighting the possible C poisoning. C atoms are found to have a tendency to penetrate on the late transition metals or to form carbidic layer on the surface, which could affect the surface activity. Surprisingly, aside from Ni, Pd, and Pt, results also suggest the formation of Ag and Cu carbidic phases.

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Iron and aluminium based mixed nanostructured hydroxyphosphates as potential vaccine adjuvants: preparation and physicochemical characterization

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Adjuvants are substances that, when combined with an antigen in a vaccine formulation, potentiate the immune response against that antigen [1]. Amorphous aluminum hydroxyphosphate is among the currently approved adjuvants for application in some vaccines for human use, while studies on its iron analogue, ferric hydroxyphosphate, are quite limited. In this article we report on the preparation and physicochemical characterization of nanostructured iron and aluminium based mixed hydroxyphosphates as potential vaccine adjuvants. The transmission electron microscopy analysis of the pure and the respective mixed hydroxyphosphates revealed a network of primary platy nanoparticles (20-50 nm in size), which aggregated in aqueous medium to form secondary micron-sized particles. The ultra-structural characteristics of the prepared hydroxyphosphates were similar to that of the aluminum hydroxyphosphate currently used in some human vaccines. The obtained nanostructured hydroxyphosphates were characterized by energy dispersive X-ray spectroscopy for elemental composition, zeta-potential measurements for determination of isoelectric point, X-ray powder diffraction, infrared spectroscopy, protein adsorption capacity, and dissolution rate.

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Formation and characterization of inclusion complexes based on starches

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Starch is a biopolymer mixture of predominantly linear amylose and branched amylopectin. It is well known that in the presence of suitable ligand amylose can form a helix with hydrophilic outer surface and hydrophobic inner channel, generally known as V-amylose. The ligand molecule or a part of it usually resides in the helix, but can also be trapped between helices, to form an inclusion complex with the amylose. We investigated the phenomenon of complex formation for a variety of starches, both modified and native. Some of the ligands used are well known in the literature for their complexing ability, while others have not been used for complex formation with starches before to the best of our knowledge. We used a hydrothermal and solid encapsulation methods to investigate the possibility of complex formation between starch molecules and gasses (mainly N₂O) for the purposes of food industry. The results indicate that the typical V-Amylose helix could not be formed with this ligand, however other types of complexes were formed and about 2% (w/w) of gas could be found in some of the samples.

Similar hydrothermal and novel mechanochemical approaches were used to obtain inclusion complexes of Wheat Starch (WS) with Lysophosphatidylcholine (LPC). Complexes were characterized via X-Ray Diffractometry (XRD), Differential Scanning Calorimetry (DSC), and Solid-state ¹³C NMR spectroscopy. LPC was chosen as a guest molecule because of the high complexing ability and the interesting properties of the amylose-LPC complexes. Increase in ball-milling time led to sharpening and increase in intensity of the complex peak at $2\theta=23^\circ$. LPC displayed protective properties in regards to starch granules: even after 10 hours of ball-milling some of the starch peaks could still be observed in the diffractogram, although significantly reduced. Both hydrothermal and mechanochemical methods allowed complexation of the entire amount of added LPC.

The possibility of complex formation between starches and the NSAID Ibuprofen is currently being investigated. Few methods for preparation of complexes are being used, including hydrothermal and mechanochemical, and the goal is to achieve complexes with controllable release rate. Some promising results and insights were obtained.

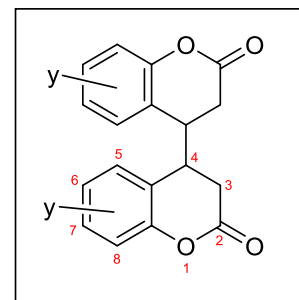
A new method for the synthesis of bis-2-oxo-chromans

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Coumarins and their oxo-chromane analogs are a large class of compounds that have attracted the group interest for a long time due to their biological activities. They have shown to be useful as antitumor, anti-HIV agents and as CNS-active compounds. Furthermore, they have been reported to have multiple biological activities – anti-coagulant, anti-inflammatory, anti-microbial, antioxidant as well as good enzyme inhibition properties.¹



During the research of the properties of coumarin compounds and their derivatives, several biscoumarins and their oxo-chromane analogs were isolated from plants and later been synthesized.² There are different types of dimerized coumarin systems from which 3,3'-, 4,4'-, 3,8'-, 3,6'-, 8,8'- and 8,6'-biscoumarins are known.

We are interested in finding simple procedure for the synthesis of 4,4'-bis-2-oxo-chromans. For this type of compounds few synthetic procedures were reported in the literature based on electroreductive hydrocoupling⁴, photoreactions⁵ or electrochemical reduction.⁶ All of these methods have some disadvantages – long reaction time, unsatisfactory yields or requirement of complex equipment. Therefore the present paper reports the application of ultrasound irradiation in the formation of bis-2-oxo-chromans and their derivatives.

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Structural characterization of folic acid and antifolates in aqueous solution

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The bioactivity of many pharmaceuticals (including chemotherapeutics) depends on the efficient delivery to the malignant target tissue. Their incorporation in drug delivery systems (DDS), guided to the neoplastic cells by targeting ligands, is more often used in clinical practice nowadays. This approach is the so-called active targeting and is based on the recognition of the ligand from a specific cell surface receptor. In this study, the α -folate receptor (α -FR) is chosen as the target of our model DDS. Folic acid (FA) is the natural ligand of α -FR and its analogues (antifolates) are also known to bind with it [1]. As a first step from the investigation of such complex multimolecular system, the structure of FA and of a small set of antifolates is characterized. Molecular dynamics is used to study their behavior. The atomistic simulations are performed in conditions that mimic the biological environment - aqueous solution, ionic strength, body temperature, and ambient pressure. The specificity of the interaction of each ligand with the receptor is driven by certain molecular characteristics, which are evaluated and critically compared.

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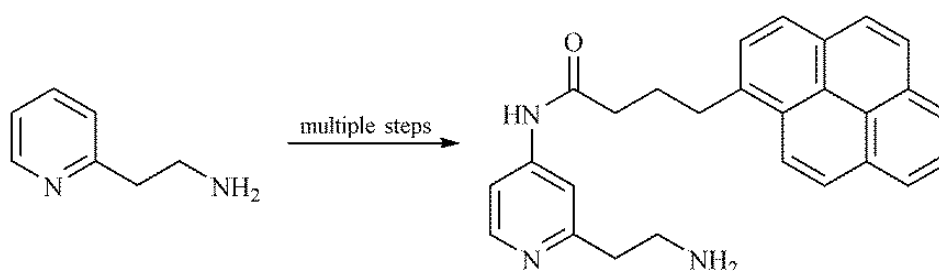
Synthesis of substituted pyridines with application in metal-coordinated supramolecular assemblies

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Self-assembly processes as a source of novel functional materials have attracted much attention in the field of supramolecular chemistry. Such materials have the potential to be used as suitable carriers of anticancer agents because they can increase the selectivity based on the enhanced permeability and retention effect. Recently Matsumoto *et al.* reported the formation of copper(II) complexes of *N*-(2-substituted imidazol-4-ylmethylidene)-2-aminoethylpyridines that form pH dependent self-assembled tetranuclear or hexanuclear structures capable of decomposing at right pH value.¹ This provoked our interest in the synthesis of modified 2-aminoethylpyridine possessing appropriate cytotoxic moiety. The pyrene fragment is expected to provide the desired antitumor activity. Pyrene is known for its strong interaction with the nucleic bases and ability to intercalate between them in the double strand structure of DNA, thus providing the desired cytotoxicity. Thereby, the suitably substituted pyridine that we have synthesized will be employed in the design of multidentate Schiff bases with the desired complexation ability and biological properties.



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Hardening of particle/water/oil three-phase dispersions due to capillary bridges with applications for new products and materials

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The subject of this study is the rheological behavior of three-phase dispersions particles/water/oil. In this area, there is a vast unexplored concentration gap between the phase domain of particle networks (particle volume fractions $\phi_p < 30\%$)¹ and the domain of wet granular materials ($\phi_p > 70\%$)². The objective of our studies is to experimentally investigate and theoretically interpret the rheological properties of dispersions in the intermediate region, $30\% < \phi_p < 70\%$. They possess the remarkable property that the addition of a minimal amount of the second (disperse) liquid phase leads to strong solidification of the dispersion owing to the interconnection of the particles by capillary bridges. The yield stress, Y , of the dispersions is investigated for various ϕ_p values. Quantitative theoretical model is developed, which relates Y with the maximum of the resultant of capillary bridge force as a function of shearing angle. The model agrees very well with the experimental data. For water-in-oil bridges, Y is systematically lower than for the respective oil-in-water bridges (Figure 1) because of electrostatic repulsion between the particles across the oil phase³, which opposes the capillary-bridge attraction.

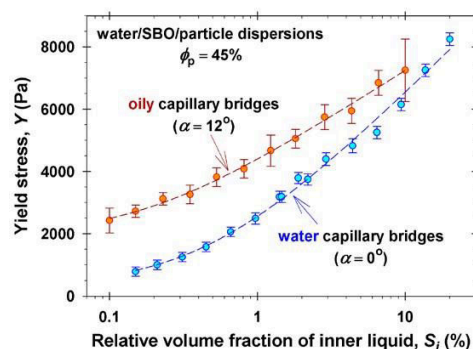
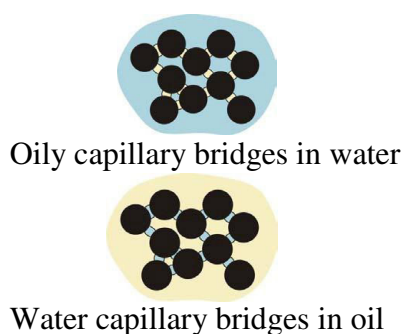


Figure 1. Oily vs. water capillary bridges: comparison of the measured yield stress; SBO

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On the way to better catalysts: increasing catalytic performance of palladium imidazo[1,5-a]quinolin-1(2H)-ylidene complexes by tuning properties of the carbene ligand

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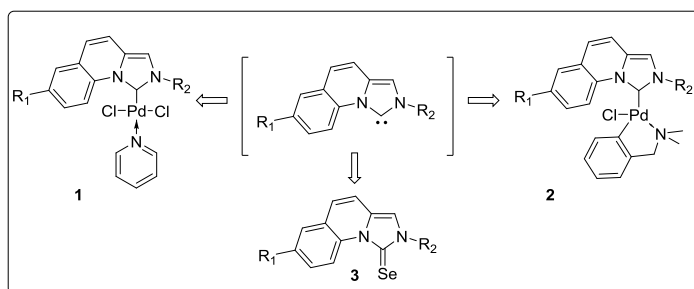
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Despite the wide variety of different types of NHC structures, there is almost no information for the synthesis and especially for the catalytic performance of palladium complexes, bearing imidazo[1,5-a]quinolin-1(2H)-ylidene NHC-ligand.

We present the synthesis of two types of palladium imidazo[1,5-a]quinolin-1(2H)ylidene complexes (**1** and **2**) having two different nitrogen additional ligands - pyridine¹ and DMBA². Their catalytic properties were tested in Suzuki reaction. In order to improve their activity, the substituents R₁ and R₂, which influence the electron and steric properties of the NHC ligand, were varied. Selenoureas (**3**) were synthesized and analyzed by ⁷⁷Se NMR spectroscopy to evaluate the π-acceptor ability of the new ligands.



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