INTERNATIONAL WORKSHOP

ADVANCED MATERIALS

Duni, Bulgaria

11TH-14TH September 2018

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

“Materials Networking” project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 692146.
Horizon 2020 Project “Materials Networking”
“Advanced Materials” Workshop
11 – 14 Sept 2018, Duni, Bulgaria

ORGANIZERS

Faculty of Chemistry and Pharmacy, University of Sofia

Georgi Vayssilov
Rositca Nikolova
Anela Ivanova
Tony Spassov
Roumen Tsekov
Elena Vassileva

“Materials Networking” project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 692146.
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”.

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PROGRAM

**Tuesday, 11th September**

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<td>17:00</td>
<td>Opening</td>
<td>Georgi Vayssilov – project coordinator</td>
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<tr>
<td>17:10</td>
<td>OP1</td>
<td>Krassimir Danov</td>
<td>“Growth of wormlike micelles in nonionic surfactant solutions: Quantitative theory vs. experiment”</td>
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<tr>
<td>17:30</td>
<td>OP2</td>
<td>Slavka Tcholakova</td>
<td>“Rheology of foams formed from polymer-surfactant mixtures”</td>
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<tr>
<td>17:50</td>
<td>OP3</td>
<td>Lachezar Christov</td>
<td>“Numerical calculation of molecular weight characteristics of polymers produced by atom transfer radical polymerization”</td>
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<tr>
<td>18:10</td>
<td>OP4</td>
<td>Zhulieta Valkova</td>
<td>“Self-shaping’ of multicomponent drops”</td>
</tr>
<tr>
<td>18:30</td>
<td>OP5</td>
<td>Nadya Politova-Brinkova</td>
<td>“Self-regulation of foam volume and bubble size during foaming via shear mixing”</td>
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<tr>
<td>18:50</td>
<td>SO1</td>
<td>Fatmegyu Mustan</td>
<td>“Role of surface rheological properties for the kinetics of bubble Ostwald ripening in saponin-stabilized foams”</td>
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<tr>
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<td>Assya Bojinova</td>
<td>“Pharmaceutical drugs photodegradation by mechano activated ZnO catalysts”</td>
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<td>Valentina Lyubomirova</td>
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<td>10:00</td>
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<td>Júlia Garcia</td>
<td>“Synthesis and characterization of carbon supported Pt(Cu) core-shell nanoparticles for hydrogen oxidation in low temperature fuel cells”</td>
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<tr>
<td>10:10</td>
<td>SO3</td>
<td>Katarina Josifovska</td>
<td>“Endocrine Disruptors in water samples: A conjoined experimental and theoretical study under GC–MS conditions”</td>
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<tr>
<td>10:20</td>
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<tr>
<td>10:50</td>
<td>OP9</td>
<td>Todor Dudev</td>
<td>“Competition between abiogenic Al^{3+} and native Mg^{2+}, Fe^{2+} and Zn^{2+} ions in protein binding sites: Implications for aluminum toxicity”</td>
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<tr>
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<td>11:30</td>
<td>OP11</td>
<td>Kai S. Exner</td>
<td>“Recent model development in theoretical electrochemistry in order to close the apparent community gap between electrocatalysis and battery research”</td>
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<td>Iskra Koleva</td>
<td>“Stable subsurface carbon – a general feature of noble metal nanoparticles and surfaces”</td>
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<td>12:00</td>
<td>Lorena Vega</td>
<td>“Atomic arrangement of PtCu bimetallic nanoparticles determined using topological energy expressions”</td>
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<tr>
<td>12:10</td>
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<tr>
<td>16:00</td>
<td>Ana Koleva</td>
<td>“Coumarins and their behavior in ultrasound promoted metal-mediated reactions”</td>
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<td>16:20</td>
<td>Vladimir Gelev</td>
<td>“New stable isotope probes for NMR of proteins”</td>
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<td>16:40</td>
<td>Rumen Lyapchev</td>
<td>“Influence of the NHC-system on the auxiliary ligand behavior in palladium allyl complexes in solution”</td>
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<td>16:50</td>
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<td>“Designing conjugated polymers for visible light photocatalysis”</td>
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<td>18:00</td>
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<td>19:00</td>
<td>Tahmida Huq</td>
<td>Improving charge extraction from bismuth oxyiodide photovoltaics with 2-d metal dichalcogenide transport layers”</td>
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<tr>
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<td>Kai Philipps</td>
<td>“Next generation organic light-emitting diodes (OLED) based on thermally activated delayed fluorescence (TADF) polymers”</td>
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<tr>
<td>09:00</td>
<td>Petar Petrov</td>
<td>&quot;Exploiting polymer chemistry towards advanced functional nanocarriers development&quot;</td>
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<td>09:20</td>
<td>Aneli Nedelcheva</td>
<td>“The importance of integrated approach in pharmacognosy: Study based on Bulgarian medicinal plants listed in the European pharmacopoeia”</td>
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<tr>
<td>09:40</td>
<td>David Ng</td>
<td>“Polymer conjugates for therapeutic applications”</td>
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<tr>
<td>10:00</td>
<td>Elisaveta Mladenova</td>
<td>“Analytical approach for botanical origin determination of Bulgarian honeydew honeys and monofloral honeys”</td>
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<tr>
<td>10:20</td>
<td>Stiliyana Pereva</td>
<td>“On the efficiency of cyclodextrin-based inclusion complexes with ibuprofen”</td>
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<td>11:00</td>
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<td>Yuri Kalvachev</td>
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<td>“An environmentally benign antimicrobial nanoparticle based on a silver-infused lignin cores”</td>
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<td>Peter Georgiev</td>
<td>“Size-dependent dielectric function of single gold nanoparticle, s surface plasmon resonance”</td>
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<td>“The synthesis, stacking and charge transport of N-doped nanoribbons”</td>
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<td>Anielen Halda Ribeiro</td>
<td>“Using light-emitting nanoparticles to control defects in organic diodes”</td>
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<td>Elham Khodabakhshi</td>
<td>“Controlling charge transport and recombination in polymer/quantum dot-based OLEDs”</td>
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<td>Rumen Tomov</td>
<td>“Inkjet printing infiltration of Gd:CeO2 interlayer in commercial anode-supported SOFC”</td>
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<td>Jingwei Hou</td>
<td>“Linking defects, hierarchical porosity generation and desalination performance in metal-organic frameworks”</td>
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<td>Joan Coines</td>
<td>“Oxazoline or oxazolinium ion? The protonation state and conformation of the reaction intermediate of chitinase enzymes revisited”</td>
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<td>Martí López</td>
<td>“Tuning activity of transition metal carbides by surface metal alloying: Case of study of CO2 capture”</td>
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<tr>
<td>18:40</td>
<td>Martin Amoza Dávila</td>
<td>“Understanding the origin of magnetic anisotropy in S=1/2 mononuclear transition metal complexes”</td>
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<tr>
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<td>Agnieszka Mierczynska-Vasilev</td>
<td>“Magnetic removal of haze-forming proteins from white wines”</td>
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<td>19:10</td>
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<tr>
<td>09:00</td>
<td>Konstantin Neyman</td>
<td>“Density-functional modelling of nanocomposite materials for catalysis and new energy technologies”</td>
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<tr>
<td>09:30</td>
<td>Spas Kolev</td>
<td>“Approaches for improving the permeability and stability of polymer inclusion membranes for the clean-up of thiocyanate from gold mine tailings water”</td>
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SHORT ORAL PRESENTATIONS

SO 1  F. Mustan, S. Tcholakova, N.Pagureva, K. Golemanov, N. D. Denkov, E. G. Pelan, S. D. Stoyanov
Role of surface rheological properties for the kinetics of bubble Ostwald ripening in saponin-stabilized foams

SO 2  J. Garcia, I. Sirés, F. Centellas, E. Brillas i Pere Lluís Cabot
Synthesis and characterization of carbon supported Pt(Cu) core-shell nanoparticles for hydrogen oxidation in low temperature fuel cells

SO 3  K. Josifovska, Z. Zdravkovski, L. Pejov
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SO 4  I. Z. Koleva, O. Piqué, H. A. Aleksandrov, F. Viñes, G. N. Vayssilov, F. Illas
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SO 5  L. Vega, K. Neyman, F. Viñes
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SO 8  K. Philipps, Y. Ie, E. del Pino, C. Ramanan, P. W. M. B., J. J. Michels
Next generation organic light-emitting diodes (OLED) based on thermally activated delayed fluorescence (TADF) polymers

Low voltage current-driven organic electrochemical transistor for biomedical applications

SO 10  P. Georgiev
Size-dependent dielectric function of single gold nanoparticle surface plasmon resonance

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A. H. Ribeiro, X. Zhao, M. Bannwarth, K. Landfester, P. W. M. Blom, J. J. Michels
Using light-emitting nanoparticles to control defects in organic diodes

E. Khodabakhshi, B. Klöckner, J. J. Michels, R. Zentel, P. W.M. Blom
Controlling charge transport and recombination in polymer/quantum dot-based OLEDs

M. López, L. Broderick, J. Carey, F. Viñes, M. Nolan, F. Illas
Tuning activity of transition metal carbides by surface metal alloying: Case of study of CO2 capture

M. Amoza Dávila
Understanding the origin of magnetic anisotropy in S=1/2 mononuclear transition metal complexes
PLENARY LECTURES

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Density-functional modelling of nanocomposite materials

for catalysis and new energy technologies

Konstantin M. Neyman

ICREA (Institució Catalana de Recerca i Estudis Avançats), 08010 Barcelona, Spain

Departament de Ciència dels Materials i Química Física, Universitat de Barcelona, c/ Martí i Franquès, 1, 08028 Barcelona, Spain

e-mail: konstantin.neyman@icrea.cat

Active metal components are present in heterogeneous catalysts as nano-aggregates of thousands of atoms. Due to their sizes these nano-aggregates remain inaccessible for first-principles computations based on the density-functional theory. However, such species could be rather realistically represented by computationally tractable smaller metal nanoparticles (NPs), whose surface sites marginally change the reactivity with increasing particle size.¹ We illustrate this for Pd catalysts²–⁴ as well as for building of active sites on Pt/ceria catalysts.⁵–⁸ We show that employment of common slab models and thus neglecting the nanoscopic effects in these and similar systems can lead to severe misrepresentation of the surface reactivity. Proposed by us dedicated NP models expose a variety of active sites, whose structure and geometric flexibility notably better match those of the sites present in model and technical catalysts under experimental conditions. Thus, we advocate much broader usage of NP models in first-principles studies of nanomaterials for catalysis and energy technologies.

References:


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ORAL PRESENTATIONS
Growth of wormlike micelles in nonionic surfactant solutions: Quantitative theory vs. experiment

Krassimir D. Danov\(^1\), Peter A. Kralchevsky\(^1\), Simeon D. Stoyanov\(^2\), Eddie G. Pelan\(^2\)

\(^1\) Department of Chemical & Pharmaceutical Engineering, Sofia University "St. Kliment Ohridski", Sofia, Bulgaria

\(^2\) Unilever Research & Development Vlaardingen, 3133AT Vlaardingen, The Netherlands

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Despite the considerable advances of molecular-thermodynamic theory of micelle growth, agreement between theory and experiment has been achieved only in isolated cases. A general theory that can provide self-consistent quantitative description of the growth of wormlike micelles in mixed surfactant solutions, including the experimentally observed peaks in viscosity and aggregation number [1], is still missing. We consider the simplest system – nonionic wormlike surfactant micelles from polyoxyethylene alkyl ethers, \(C_mE_n\) [2] and construct a molecular-thermodynamic model that is in agreement with the available experimental data. We systematized data for the mean micelle aggregation number, from which the micelle growth parameter was determined at various temperatures, \(T\). None of the available models can give a quantitative description of these data. We constructed a new model, which is based on theoretical expressions for the interfacial-tension, headgroup-steric and chain-conformation components of micelle free energy. The wormlike micelles from \(C_mE_n\) surfactants grow with the rise of \(T\) because of shrinkage of their ethoxy headgroups due to enhanced segment-segment attraction. From data for single-component micelles we determined the headgroup cross-sectional area vs. \(T\). The aggregation numbers of the wormlike micelles in mixed solutions were predicted. Excellent agreement between the predicted and experimental values was obtained without using any adjustable parameters. The radii of the cylindrical parts and the spherical endcaps of micelles were determined. The constructed model can be further upgraded to obtain quantitative description of micelle growth in complicated systems, including binary and ternary mixtures of nonionic, ionic and zwitterionic micelles.

References:

Acknowledgments: The authors gratefully acknowledge the support from Unilever R&D and from the Horizon 2020 project ID: 692146-H2020-eu.4.b “Materials Networking”.

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Rheology of foams formed from polymer-surfactant mixtures

S. Tcholakova 1 and N. Denkov 1
1 Department of Chemical and Pharmaceutical Engineering, Faculty of Chemistry and Pharmacy, Sofia University, Sofia, Bulgaria
e-mail: sc@lepe.uni-sofia.bg

Solutions of surfactant-polymer mixtures often exhibit different foaming properties, compared to the solutions of the individual components, due to the strong tendency for formation of polymer-surfactant complexes in the bulk and on the surface of the mixed solutions. We study the effect of three classes of cationic polymers, Lupasols (based on polyethylenimine, PEI), Merquats (based on diallyldimethyl ammonium chloride, DADMAC) and Jaguars (Guar Hydroxypropyltrimonium Chloride), on the surface and rheological properties of foams, stabilized with the mixture of anionic (SLES) and zwitterionic (CAPB) surfactants, with and without myristic acid (MAc) present as a cosurfactant. The addition of Jaguar to the foaming solutions leads to [1]: (1) Significant increase of the foam yield stress for all systems studied; (2) Presence of consecutive maximum and minimum in the rheological curve stress vs. shear rate, for foams stabilized by cosurfactants with high surface modulus. These systems cannot be described by Herschel-Bulkley model anymore; (3) Presence of significant foam-wall yield stress for all foaming solutions. These effects are explained with the formation of polymer bridges between the neighboring bubbles in slowly sheared foams (for inside foam friction), and between the bubbles and the confining solid wall (for foam-wall friction). Polymers from Lupasol series [2] were found to suppress the cosurfactant effect of MAc on all surface and foam properties studied, which is related to the fact that Lupasol polymers bind strongly the MAc molecules in the bulk solution, thus reducing MAc surface activity and adsorption. The effect of Merquat polymers depend on their charge density, Merquat 740 with low charge density, affects strongly the dimensionless foam yield stress, foam-wall friction, and thinning behavior of BS+MAc films, whereas Merquat 100 with very high charge density has week effect on foam properties, due to the formation of relatively thin adsorption layers.

Numerical calculation of molecular weight characteristics of polymers produced by atom transfer radical polymerization

G. S. Georgiev, L. K. Christov

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Numerical realization of the original algorithm allows to calculate the molecular weight characteristics of the polymers, produced by atom transfer radical polymerization (ATRP). To this aim recurrent conversion relationships for monomer, initiator, active (A) as well as dormant (D) propagating, and dead (T) polymer chains are derived. The probability for transformation of A and D to T is also defined. By this probability the number parts of propagating (A and D) and dead (T) chains for each conversion step are determined. They are used for deduction of usable relations for calculating the number and weight degree of polymerization, and from here, the polydispersity index of the polymers produced after each conversion step. The relations for A and the mentioned above probability allow to outline the ruling parameters (such as the equilibrium constant for the A-D transition, monomer and Cu(II) concentrations) for effective control of polymerization rate and molecular weight characteristics of polymers obtained. However, they also show that the currently considered general ATRP mechanism does not allow effective control in wider boundaries of the polymerization rate and polymer molecular weight characteristics. A modified mechanism that overcomes these limitations and allows quantitative description of new control possibilities is proposed.
Recently it was shown that micrometer single-component emulsion drops, can break symmetry upon cooling and “self-shape” into fluid polyhedra, platelet-shaped hexagons, triangles, rhomboids, squares, toroids, O-shapes, and sub-micron in diameter fibers.[1,2] This process involves the formation of a plastic rotator phase of self-assembled oil molecules beneath the drop surface. However, most of the common substances used in industry appear as mixtures of molecules rather than pure substances. In this study,[3] we demonstrate the ability of multicomponent emulsion drops to deform upon cooling. The observed trends can be summarized as follows: (1) The general drop-shape evolution for multicomponent drops during cooling is the same as with single-component drops; (2) If a compound, which cannot induce self-shaping when pure, is mixed with a certain amount of a compound which induces self-shaping, then drops prepared from this mixture can also self-shape upon cooling. (3) The self-emulsification phenomena, which is observed with single-component, emulsion drops upon cooling and heating is also observed for multicomponent drops, reducing their volume more than 500 times only after one heating and cooling cycle.[4,5]

References:


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Self-regulation of foam volume and bubble size during foaming via shear mixing

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Liquid foams find a variety of applications in everyday life and industry as home and personal care products, in cosmetics, pharmaceuticals, etc. Here we study the factors affecting the foam generation in a planetary mixer with a series of surfactant solutions, having different dynamic surface tensions, surface dilatational moduli and bulk viscosities. The foam generation in this device consists of three well defined periods: (1) Induction period during which very slow increase of the foam volume is observed. The duration of this period depends significantly on the shear rate during foaming and on the volume of the surfactant solution; (2) Fast increase of foam volume; the rate of this process depends primarily on the shear rate and dynamic surface tension of the solutions; (3) Plateau region in which the foam volume remains constant. The experimental results show that the processes of air entrapment ends when a certain critical (dimensionless) shear stress of the foam is reached. Depending on the bulk and surface properties of the surfactant solutions, this critical stress is achieved for foams with different air volume fractions and mean bubble sizes. Thus, when solutions with higher bulk viscosity and/or higher surface modulus are used, the critical stress is reached at lower air volume fraction and with smaller bubbles. Power-law equations are shown to describe very well the effects of the foaming shear rate and solution viscosity on the final foam volume and mean bubble size.

References:

Acknowledgments:
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MANOVA studies on toxicity and endocrine disrupting potential of packaging materials exposed to different extraction schemes

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In the scientific literature related to the widely understood issue of packaging materials designed to have contact with food (so called food contact materials), there is much information on raw materials used for their production, as well as their physiochemical properties, types and treatment parameters. However, not much attention is given to the issues concerning migration of toxic substances from packaging and its actual influence on the health of the consumer.

The goal of this study was to estimate the impact of particular foodstuff packaging type, food production and storage conditions on the degree of leaching of potentially toxic compounds (including endocrine disruptors) to foodstuffs using the acute toxicity test Microtox and XenoScreen YES/YAS assay. The selected foodstuff packaging materials were metal cans used for fish storage and composite one for liquids storage (Tetrapak) and cups.

Multi-factor analysis of variation (MANOVA) was used to evaluate the effects of the three main factors solvent, temperature (temperature regime for cup), contact time and their interactions on the respected dependent variable (acute toxicity or estrogen disruption potential).

From all stimulants studied the most toxic were can and Tetrapak lining acetic acid extracts that is an indication for significant migration of toxic compounds. This migration increased with increase of contact time and temperature and justified the hypothesis that food products with low pH values cause significant damage internal resin filling.

Can lining extracts of all simulation media (excluding distilled water and artificial saliva) proved to contain androgen agonists even at 25°C and extraction time of 12h. For Tetrapak extracts significant endocrine potentials for acetic acid, DMSO and saliva were detected.

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Pharmaceutical drugs photodegradation by mechano activated ZnO catalysts
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The pharmaceutical drugs have been considered as emerging pollutants due to their continuous input and persistence in the aquatic ecosystem even at low concentrations. They have been detected worldwide in environmental matrices, indicating their ineffective removal from water and wastewaters using conventional methods. In this study we present photocatalytic purification of water from Paracetamol and Chloramphenicol by ZnO powders under UV-light illumination. Commercial ZnO is mechano activated (treated for 5, 15, 20, 30, 40 and 60 min). The mechanoactivation is performed varying the atmosphere in air, or in suspension of ethanol and methanol. The changes in the studied material (phase composition, structure and particle size of the samples) and morphology have been investigated by means of X-ray diffraction and Scanning electron microscopy. The degradation rate of Paracetamol and Chloramphenicol increases with time of mechanical activation up to 30 min and then decreases. The optimal time of mechanoactivation are experimentally established.

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Analytical problems in the mass spectrometric analysis of environmental samples

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Environmental analytical chemistry measurements are essential in the assessment of the quality of environment and public health. Besides the typical pollutants, unsuspected environmental problem might be the emission of a large number of concomitant elements. Therefore environmental assessment demands the determination of as many elements as possible at broad concentration intervals. In recent decades, inductively coupled plasma mass spectrometry (ICP-MS) has emerged as the most promising multielement technique for trace analysis of environmental samples.

Complex environmental matrices however might give rise to spectral and matrix interferences leading to reduction of sensitivity. With the appropriate method development – choice of isotopes, calibration strategy, plasma conditions, optimization and use of dynamic reaction cell with two gases and introduction of rejection parameters (RPα) for reduction of the signal of matrix elements these limitations can be circumvented.

Besides the sensitive determination of numerous elements by Q-ICP-MS a serious advantage for element determination in solid samples is provided by LA-ICP-MS. One of the most serious drawbacks of LA-ICP-MS application is the lack of solid Certified Reference Materials in an appropriate form for many sample matrices. In this case matrix-matched laboratory standards should be prepared.

The optimization of the analytical procedures enables the reliable determination of very large number of elements in environmental samples by ICP-MS/LA-ICP-MS.

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“Materials Networking” project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 692146.
Competition between abiogenic Al$^{3+}$ and native Mg$^{2+}$, Fe$^{2+}$ and Zn$^{2+}$ ions in protein binding sites: Implications for aluminium toxicity

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The abiogenic aluminium has been implicated in some health disorders in humans. Protein binding sites containing essential metals (mostly magnesium) have been detected as targets for the “alien” Al$^{3+}$. However, the acute toxicity of aluminium is very low. Although substantial body of information has been accumulated on the biochemistry of aluminium, still the underlying mechanisms of its toxicity are not fully understood. Several outstanding questions remain unanswered: (1) Why is the aluminium toxicity, unlike that of other “alien” metal cations, relatively low? (2) Apart from Mg$^{2+}$ active centers in proteins, how vulnerable are other essential metal binding sites to Al$^{3+}$ attack? (3) Generally, what factors do govern the competition between ‘alien’ Al$^{3+}$ and cognate divalent metal cations in metalloproteins at physiologically relevant conditions? Here, we endeavor to answer these questions by studying the thermodynamic outcome of the competition between Al$^{3+}$ and a series of biogenic metal cations, such as Mg$^{2+}$, Fe$^{2+}$ and Zn$^{2+}$, in model protein binding sites of various structures, compositions, solvent exposure and charge states. Density functional theory (DFT) calculations in combination with polarizable continuum model (PCM) computations are employed. For the first time the presence of different Al$^{3+}$ soluble species at physiological pH is properly modeled in accordance with the experimental observations. The results imply that the combination between concentration and physicochemical factors renders the Al$^{3+}$ → M$^{2+}$ (M = Mg, Fe, Zn) substitution and subsequent metalloenzyme inhibition a low-occurring event at ambient pH: the more active aluminium species, [Al(H$_2$O)$_6$]$^{3+}$, presents in very minute quantities at physiological conditions, while the more abundant soluble aluminium hydrate, {[Al(OH$_2$)$_4$](H$_2$O)$_2$}$^{-}$, appears to be thermodynamically incapable of substituting for the native cation.

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DFT-based molecular design of alkaline-ion batteries

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The quest for new types of batteries has been unceasing ever since the batteries were invented. This is even more topical nowadays when the amount of devices powered by batteries we use grows constantly and the environmentally friendly clean energy obtained by renewable sources has to be stored, redistributed, and used on demand.

The molecular design related to batteries addresses modelling of electrodes, electrolytes and non-aqueous solvents. The first objective of our study is the description of the behaviour of the charge carriers with the non-aqueous environment. The interaction of lithium and sodium ions – separately or mixed – with ethylene carbonate (EC) was studied by means of stepwise expansion/contraction of the ions’ solvation shell of explicit EC molecules in implicit solvent medium in order to quantify: i) the coordination number of the metal ions and of the counterions; ii) the free energy of solvation/desolvation of the ions; iii) the competition between the ions in batteries based on a dual-metal-ion electrolyte.

The second target of our research are the electrode materials. Typically, the cathodes used currently are layered structures of mixed transition metals oxides. The anodes are either graphite or again transition metals oxides. The design of organic structures capable to replace the traditional inorganic formulations has been our lasting goal, mostly focused on novel anodes. Here is reported the first attempt to model cathodes by means of functionalizing graphene with conjugated organic dyes, thus providing porous conducting materials for metal ions intercalation. The possible modes of functionalization with anthraquinone were considered and the most favourable energetically structure was chosen for determination of the theoretical capacity of the material and the electrode potential as a function of the amount of intercalated metal ions.

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Recent model development in theoretical electrochemistry in order to close the apparent community gap between electrocatalysis and battery research

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Atomic scale-insights into the performance of electrode materials or solid-state catalysts require thermodynamic considerations as first step in order to determine potential surface structures that are relevant for subsequent kinetic studies.\textsuperscript{1} In heterogeneous catalysis as well as electrocatalysis, the \textit{ab initio} atomistic thermodynamics approach\textsuperscript{2,3} has been recognized as powerful tool by compiling thermodynamically stable surface phases as function of the corresponding environmental parameters in the form of stability diagrams or by a priori computational screening in order to propose promising (electro-)catalysts by the construction of Volcano plots.\textsuperscript{4}

Quite in contrast, the \textit{ab initio} thermodynamics approach has been introduced in battery research only recently by transferring the concept of surface Pourbaix diagrams from electrocatalysis to lithium-ion batteries.\textsuperscript{5} In this talk, recent investigations that aim at applying well-established concepts such as stability diagrams or Volcano plots from the field of (electro-)catalysis for the investigation of electrode materials in lithium-ion batteries are presented and critically discussed.\textsuperscript{6,7}

\textit{References:}

**Coumarins and their behavior in ultrasound**

**promoted metal-mediated reactions**

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Sonication provides an unusual mechanism to generate high-energy chemistry due to the extraordinary temperatures and pressure generated by the cavitation bubble collapse. (1–3) It is known that this kind of energy can be used to generate radicals and to initiate electron-transfer processes during reactions.

Ultrasound techniques are also used as an environmentally friendly technology in green chemistry and provide another option for improving common reactions that require high temperatures, long reaction times and give unsatisfactory yields. Another aspect is the acceleration of metal-mediated organic reactions under ultrasound due to activation of the metal surface, which is an efficient method for removing impurities and oxidized metal layers. Meanwhile, it can reduce the particle size, bring about modified surfaces of the metal and at the same time speed up the formation of organometallic reagents. (4)

Here we would like to compare the reaction pathways of two reactions promoted by ultrasound irradiation having organometallics as main reagent. Moreover, the chemical behavior of 3-substituted coumarins was examined accounting the specific Michael-type reactions or radical dimerizations. On the other hand, organomagnesium and organozinc reagents were investigated for their role in the studied reaction conditions as hard nucleophiles and radical initiators.

**References:**


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New Stable Isotope Probes for NMR of Proteins

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NMR spectroscopy offers a unique glimpse of the conformation, dynamics, and interactions of biomolecules. The two broad challenges in observing large proteins by NMR, low signal-to-noise ratio and signal overcrowding, represent the flip-side of the extremely high information content of NMR spectra. Selective labeling at specific sites with the stable isotopes 13C, 1H, 2D, 15N, 19F is an increasingly popular method to simplify and improve the NMR spectra of macromolecular systems. Here we describe the development of several new probes for labeling and observation of membrane proteins.
E-Z photoisomerization in photoswitchable molecular machines for triplet-triplet annihilation upconversion accelerated molecular organic solar thermal systems

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The isomerization between two different states of molecular switches, when are exposed to light, attracts considerable attention during the last few decades. The vast applications are spread in molecular logics [1, 2], electronics, organic semiconductors in organic field effect transistors, to enable on/off switching of the electric current by light [3–5]. If the isomers are not isoenergetic, the capture and store of solar energy is quite possible [6]. Such materials in principle are called molecular organic solar thermal systems (MOST) [7] and the stored energy equals the energy difference between the two isomers. An energy barrier prevents relaxation from the high to the low energy isomer. Theoretical upper limit to the solar energy conversion efficiency possible for a pure MOST system is 10.6% [8], but recently it has been demonstrated that by coupling the MOST system to a photon up-conversion one [9], sub-bandgap absorption is enabled, and a substantial increase in the theoretical maximum efficiency is possible. This break-through actually arouses the interest to the development of new more effective and low cost MOST materials.

In the present work we describe an improved synthetic method for the synthesis of four (two novel) styryl cyanine betaines with sulfoalkyl-benzothiazolium and phenyl-15-aza-crown-5 end groups. Their E-Z photoisomerization properties were studied in details (experimentally and computationally) and their potential to be used as MOST materials were demonstrated. This type of dye-barium complexes are the first organic systems photoisomerized only by TTA-UC illumination.

References:

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Designing conjugated polymers for visible light photocatalysis

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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.

Conjugated polymers (CPs) have recently emerged as a new class of visible light-active, organic and heterogeneous photocatalysts for photoredox reactions. The CPs have been established as a potential alternative to resolve critical drawbacks of traditional molecular and homogeneous photocatalysts due to their structural durability, non-toxicity, low cost by the absence of noble metals, and high designability. Tremendous attempts have been made for the design and synthesis of CPs for a variety of visible light-promoted photocatalytic chemical transformations. In this talk, the recent developments in controlling structural, photophysical and electronic properties of CPs, and to extract the underlying design principles with respect to the molecular structure, macroscopic feature, i.e. morphology, porosity and chemical functionality, and processibility of CPs for the enhancement of their photocatalytic activity. [1-3]

Synergistic micellar growth in mixed surfactant solutions: 
Rheology and cryo-TEM imaging

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We studied the synergistic growth of giant wormlike micelles in ternary solutions, which contain a zwitterionic surfactant (CAPB, cocamidopropyl betaine), an anionic surfactant (SLES, sodium lauryl-ethersulfate) and a fatty acid. For a given fatty acid concentration, the viscosity $\eta_0$ exhibits a sharp and high peak (Fig. 1), which in the case of octanoic acid (HC8) reaches 41 000 times the viscosity of water [1]. The peak height decreases as a function of the fatty acid chainlength until it completely disappears for hexadecanoic acid. The cryo-TEM imaging revealed complex phase behaviour: (i) growing rod-like micelles to the left of the peak; (ii) entangled wormlike micelles at the peak (Fig. 1); and (iii) multi-connected structures for octanoic acid versus shape transition into disc-like micelles for dodecanoic acid after the peak [1,2]. The two scenarios in (iii) explain the viscosity reduction by making a direct correlation between rheology and microstructure.

References:

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Visible light-driven photocatalytic activity of magnetic recoverable ternary g-C₃N₄/rGO/ZnFe₂O₄ nanocomposites

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The g-C₃N₄/rGO/ZnFe₂O₄ ternary nanocomposite photocatalysts with different ferrite/g-C₃N₄ ratio (1:4, 1:2, 3:4, 1:1) were successfully fabricated by a stepwise solvothermal method in ethylene glycol as a solvent. The samples were characterized by a number of physicochemical methods: X-ray diffraction, FTIR, UV-VIS diffuse reflectance, photoluminescence spectroscopy and N₂ adsorption/desorption in order to evaluate the successful synthesis and their properties. All of the samples, including the stand-alone g-C₃N₄ and ZnFe₂O₄, were tested for adsorption and photocatalytic degradation of aqueous malachite green model solution (10⁻⁵ M) under visible light irradiation (λ>400 nm). The results show that the prepared nanocomposites have higher sorption and photocatalytic activity than the pristine g-C₃N₄ and ZnFe₂O₄ and can be successfully used for water purification from organic azo-dyes. Due to their magnetic properties the photocatalysts can be easily recovered and re-used.

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On the Multistate of 2’-hydroxyflavylium-Flavanone System. Illustrating the Concept of a Timer with Reset at the Molecular Level

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Abstract: The multistate of species regarding 2’-hydroxyflavylium derivatives have a peculiar behavior due to the formation in moderately basic solutions of a flavanone from the mono-ionized trans-chalcone. The firmly established theory to account for the thermodynamics and kinetics of the flavylium based multistate of species in acidic medium was extended to the basic medium. The key experimental procedure to carry out this study is a sequence of reverse pH jumps from all pH range to a final pH sufficiently acid to have flavylium cation as the sole species. The reverse pH jumps can be performed from the equilibrium and pseudo-equilibrium. Acidification of the flavanone to pH=1 does not give back flavylium cation. In contrast, the di-ionized species trans-chalcone is obtained in a very fast process from the flavanone at pH>12. A cycle constituted by a sequence of pH jumps illustrates the concept of a timer at the molecular level with reset capacity.

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Exploiting polymer chemistry towards advanced functional nanocarriers development

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The synthesis and self-assembly of amphiphilic block copolymers in aqueous media is a valuable strategy for developing advanced functional nanocarriers of various biologically active substances. The versatility of synthetic methods in polymer chemistry allows preparation of polymeric nanocarriers having beneficial set of properties like biocompatibility, longevity, high stability in vitro and in vivo, high loading capacity, controlled drug release profile, and ability to accumulate in the target zone of the body.

Here, we report results from our current study aiming at developing novel block copolymer carriers of biologically active substances such as curcumin, caffeic acid phenethyl ester (CAPE) and insulin. Well-defined biocompatible and biodegradable amphiphilic block copolymers possessing precisely set molecular parameters, properties and functionality were synthesized via ring-opening polymerization, atom transfer radical polymerization and/or click reactions. Next, block copolymer micelles of tailored structure and composition were obtained by (cooperative) self-assembly of copolymers in water. The micelles were then loaded with biologically active substance via hydrophobic or electrostatic interaction, achieving a high loading efficiency. In vitro experiments revealed a sustained release profile and an enhanced antitumor or antioxidant activity of the micellar formulation as compared to the free drug. Some of the newly developed functional system exhibited great potential for targeted delivery of anti-cancer drugs in mitochondria, thus causing programmed tumor cell death.

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“Materials Networking” project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 692146.
The importance of integrated approach in pharmacognosy: Study based on Bulgarian medicinal plants listed in the European pharmacopoeia

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The ninth edition of European Pharmacopoeia (Ph. Eur. 9, Supplement 9.5) includes a total of 302 individual monographs of herbal substances and herbal preparations. Over 38% are based on 84 species of the Bulgarian flora: 86 monographs of herbal substances and 29 of herbal preparations. Biosystematic studies on them have been conducted with varying intensity over the last decades. Presented here is developed and applied model of integrated approach through the methods of pharmacognosy, ethnobotany and phytochemistry in outlined three groups of species:

(i) Biosystematically (including phytochemical) well studied species, representatives of the Bulgarian flora, with scientifically reconstructed ethnobotanical data, with a potential for geographical identity (limited area of distribution/ Balkan endemic plants): Achillea clypeolata Sm (Compositae) pharmacognostic profile.

(ii) Representatives of the Bulgarian flora, ±biosystematically studied, well-known ethnobotanical data and use in ethnomedicine, widespread and with modern categorization as a potential source of substances with possible human health risks (presence of pyrrolizidine alkaloids, PAs), implementation of measures for limited use and control: Tussilago farfara L. (Compositae) pharmacognostic profile.

(iii) Geographically determined group, non-European species, with scientifically reconstructed ethnobotanical data, intensive current use (monographs, Ph. Eur.), increasingly important species. Case study for plant species with a distribution area covering the Asian continent or parts thereof (including Asian endemic species).

Studies over the last decade have demonstrated how the implementation of an integrated approach to plant research provides objective and reliable characterization of species (taxa) as medicinal plants and a realistic assessment of their prospects as a resource and source of natural compounds with biological activity.
Polymer Conjugates for Therapeutic Applications

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Nanomedicine, designed for cancers and other elusive diseases, have been investigated in many platforms and systems. Most commonly, strategies typically involve the formation of a designated nanoparticle system through synthetic polymer or inorganic chemistry. The pharmacophore is subsequently encapsulated within the construct through stimulus responsive or supramolecular interactions. Once administered in vivo, active and passive targeting (i.e. enhanced retention and permeation effect) directs the nanomedicine to the diseased locations.

Beyond using synthetic materials as carriers, natural macromolecules such as proteins can also be excellent candidates. Proteins carry out many functions in Nature including transport, catalysis and cellular signalling. It is thus intuitive that proteins naturally fit in these multiple roles clearly demonstrating their phenomenal potential towards both material and therapeutic applications. However, as protein functions are highly specific, it is frequently necessary to chemically engineer these macromolecules in a way to modify their physical and chemical profile such as stability, reactivities and function.

In this talk, we will demonstrate the synthetic concepts towards designing polymer bioconjugates and transform them into broad application areas in smart materials (i.e. stimulus responsive hydrogels) and therapeutics (i.e. cancer and HIV).

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Analytical approach for botanical origin determination of Bulgarian honeydew honeys and monofloral honeys

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Honey is defined as a naturally sweet mixture produced by bees (Apis mellifera) from the nectar of blossoming flowers (monofloral or polyfloral honey), from secretions of parts of the living plants or excretions of plant-sucking insects on the living part of plants (honeydew honey), that the honey bees collect, transform and combine with specific substances of their own (such as enzymes), deposit, dehydrate, store and leave in the beeswax honeycombs to ripen and mature. All components (carbohydrates, minerals, enzymes, amino acids, pigments, variable amounts of sugar-tolerant yeasts, pollen, traces of vitamins, organic acids and wax) are due to maturation of the honey; some are added by the bees, and some are derived from the plants. However, it is assumed that honey from the same floral source can also vary due to seasonal climatic variations or to a different geographic origin. The existing European Commission honey directive describes requirements related to the concentrations of acidity, apparent reducing sugar (calculated as invert sugar) and apparent sucrose, 5-hydroxymethylfurfural (HMF) content, mineral content (ash), moisture and water-insoluble solids. In case of doubt or fraud, there is no standardized analysis available that can discriminate or determine the botanical (floral or vegetable) and geographical (regional or territorial) origin of the honey. The aim of the study presented is to define descriptors that can classify and differentiate monofloral honeys (black locust, lime, sunflower, thistle, rape) and honeydew honeys (coniferous and oak) produced in Bulgaria according to the main plant species and production territory. The investigation combines sample collection of monofloral honeys or honeydew honeys with guaranteed botanical and geographical origin, reliable analysis of physicochemical parameters (color, water content, specific rotation, electrical conductivity, pH, total acidity, hydroxymethylfurfural, diastase activity, proline content) and chemical elements content (Al, Ca, Cd, Fe, K, Mg, Mn, Na, Pb, Sr) with suitable statistical treatment of results obtained. Final conclusions will show the possibilities of conventional analytical methods to evaluate the quality of monofloral honey and honeydew honey produced in Bulgaria and necessity of more sophisticated methods like isotope ratio measurements or NMR analysis for more reliable identification and classification.

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“Materials Networking” project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 692146.
On the efficiency of cyclodextrin-based inclusion complexes with ibuprofen


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Cyclodextrin (CDs) have important applications in many fields of natural sciences – chemistry, pharmacy, gas storage, catalysis, foods, cosmetics. This interest and already 40 years of research on CDs is due to their structure – they have a hydrophobic cavity and a hydrophilic exterior, thus they can be used as hosts of molecules with proper size, which can be entrapped into their cavity. Ibuprofen and naproxen are non-steroidal anti-inflammatory drugs with high bioavailability and permeability, but low water solubility. Very few researches investigate the complex efficiency and how this can improve the solubility of the drugs in water, their properties and also shed a light to the mechanism of complex formation. We propose a modified ball milling method (with the use of a solvent), which is very effective, compared to the classical pharmaceutical methods – it is cheap, environmentally friendly and can be applied in an industrial scale. With the help of thermal analysis (Differential Scanning Calorimetry and Thermal Gravimetry), we were able for the first time to quantitatively determine how efficient is this modified synthetic method. We proved that for CD/ibuprofen complexes 1 molecule ibuprofen, replaces 7 molecules water from the cavity of the cyclodextrin.

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Growing Polymeric Micro- and Nanoparticles with Regular Anisotropic Shapes – Towards a Scalable Bottom-Up Synthesis

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Shape-anisotropic polymeric micro- and nano-particles are of significant interest for the development of novel composite materials, lock-and-key assemblies, and drug carriers. Currently, syntheses require external confinement in micro-fluidic devices or lithographic techniques associated with significant infrastructure and low productivity, so new methods are necessary to scale-up such production efficiently. Our recent discovery of artificial morphogenesis,1 where rotator phase transitions internal to emulsion droplets shape them into a multitude of prescribed shapes, promises to revolutionize the generation of novel shaped microparticles. We have demonstrated it for dozens of oil/surfactant systems,2 as well as mixtures of oils,3 but the shapes were only stable upon freezing. A method is urgently needed to turn these shapes into permanently stable particles.

Here we report bottom-up polymerization of regular shape-anisotropic particles (polygonal platelets with different numbers of edges, with and without protruding asperities, and fibrilar particles with controllable aspect ratios), with size control over 4 orders of magnitude (~50 nm–1 mm). Polymerization also enables the study of much smaller shapes than could previously be studied in water suspensions, and we study the fundamental limits of the self-shaping transition process driving these transformations for monomer oil droplets of stearyl methacrylate (SMA) monomer oil. We show the method is compatible with a variety of polymerizing monomers and functional modifications of the particles (e.g., composites with magnetic nanoparticles, oil-soluble additives, etc.). We also describe postsynthetic surface modifications that lead to hierarchical superstructures. The synthesis procedure retains the great potential of artificial morphogenesis in scalability and material-efficient nanomanufacturing, with minimum infrastructure and process requirements and little maintenance of the equipment. 4

References:

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Hierarchical mordenite as a heterogeneous catalyst

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Due to its structure and high Si/Al ratio zeolite mordenite has high thermal and acidic stability. Mordenite-type of zeolites have been used as catalysts in many industrially important reactions such as hydrocracking, hydroisomerization, alkylation, acid-catalyzed isomerization of alkanes and aromatics, reforming. In order to increase the specific surface area and to overcome the problem of the limited access to the active sites, OSDA-free synthesized mordenite undergoes fluoride etching as a post-synthetic treatment. The post-synthetic treatment is performed with hydrofluoric acid in combination with ammonium fluoride. Thus the porosity is enhanced additionally without changing considerably the Si/Al ratio of the zeolite framework. All samples have been characterized by X-ray diffraction analysis, nitrogen adsorption, scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) and solid-state nuclear magnetic resonance (NMR) spectroscopy. The catalytic activity of the samples obtained has been investigated in the reaction of m-xylene transformation. All mordenite samples having undergone post-synthetic treatment exhibit catalytic activity higher than that of the parent sample.

Parent and hierarchal mordenite were modified with zirconia by incipient wetness impregnation in order to vary surface acidity type and strength. Acidic properties of the obtained materials were investigated by TPD of adsorbed ammonia and FT-IR spectra of adsorbed pyridine. Catalytic performance was studied for the glycerol esterification with acetic acid. Zr increased reaction turnover activity compared to raw zeolite substrate due to abundant Brønsted and Lewis moiety presence. The demonstrated biomass valorization processes to bio-based platform chemicals are of interest, as they employ biodiesel production waste. Zr-modified hierarchical mordenite shows the best catalytic performance in the studied reaction, most probably due to the optimal Brønsted/Lewis acid sites ratio and better access to them. The Zr-modified hierarchical mordenite is a highly active, cost effective, stable and reusable catalyst.
An environmentally benign antimicrobial nanoparticle based on a silver-infused lignin cores

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Silver nanoparticles have antibacterial properties, but their use has been a cause for concern because they persist in the environment. Here, we show that lignin nanoparticles infused with silver ions and coated with a cationic polyelectrolyte layer form a biodegradable and green alternative to silver nanoparticles. The polyelectrolyte layer promotes the adhesion of the particles to bacterial cell membranes and, together with silver ions, can kill a broad spectrum of bacteria, including Escherichia coli, Pseudomonas aeruginosa and quaternary-amine-resistant Ralstonia sp. Ion depletion studies have shown that the bioactivity of these nanoparticles is time-limited because of the desorption of silver ions. High-throughput bioactivity screening did not reveal increased toxicity of the particles when compared to an equivalent mass of metallic silver nanoparticles or silver nitrate solution. Our results demonstrate that the application of green chemistry principles may allow the synthesis of nanoparticles with biodegradable cores that have higher antimicrobial activity and smaller environmental impact than metallic silver nanoparticles.

References:

“Materials Networking” project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 692146.
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. Important for applications, we not only extensively test our coating for their antibacterial efficacy against medically relevant pathogens in isolates but also assess their potential cytotoxicity to mammalian cell and inflammatory consequences. I will also outline our work on developing advanced nanoengineered plasma polymer coatings capable of directing cellular behaviour including adhesion, proliferation, differentiation and migration. We have developed unique capabilities to control and tailor entire spectrum of surface properties such as chemistry, wettability, ligand densities, nanomechanics and nanotopography in a substrate independent fashion. 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 and I will outline how we guide the differentiation of stem cells by tailoring surface chemistry, nanotopography or density of signalling molecules. A recently developed device for selective cancer cell capture for complex liquids will also be presented.

**Selected References:**


The synthesis, stacking and charge transport of N-doped nanoribbons

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We designed and synthesized three novel thia-diazoloquinoxaline containing long N-Nanoribbons with 8, 13 and 18 rings, which show high electron affinities (EAs) of ~4.1 eV derived from the onset of reductive peaks in cyclic voltammetry. Crystal structure analysis demonstrated in-plane extension through close contacts of thiadiazoles and layered packing enabling in-plane and interlayer electron transport. Organic field-effect transistor devices provided electron mobilities, which supplies a potential way to enhance the charge transport in long N-heteroacenes.
Inkjet printing infiltration of Gd:CeO$_2$ interlayer in commercial anode-supported SOFC

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Abstract: The key technical challenges in Solid Oxide Fuel Cells (SOFC) development today are performance, durability and cost. The use of solution techniques to impregnate an already optimized electrode scaffold provides a fast and efficient way to evaluate new electrode materials. It can also offer low cost routes to manufacture desired electrode structures and to fine tune its key properties. Single step inkjet printing infiltration with doped ceria (Sm and Y) and cobalt oxide inks was performed in order to modify the properties of the doped ceria interlayer in commercial (50x50x1 mm size) anode supported SOFCs. Deep penetration of the inks through the La$_{0.8}$Sr$_{0.2}$Co$_{0.5}$Fe$_{0.5}$O$_{3-\delta}$ porous cathode to the Gd$_{0.1}$Ce$_{0.9}$O$_2$ interlayer was achieved by optimization of the jetting parameters. The low temperature calcination (750°C) resulted in densification of the porous interlayer and decoration of the cathode scaffold with nano-particles (~ 20-50 nm in size). The I-V testing showed maximum power density gain between 82–97% for the infiltrated cells at 800°C. The polarization resistances of the reference and the infiltrated cells revealed only small changes in the activation and concentration polarizations losses due to the low density of the nano-decoration on the surface of the La$_{0.8}$Sr$_{0.2}$Co$_{0.5}$Fe$_{0.5}$O$_{3-\delta}$ scaffold. This work demonstrated that single-step inkjet printing infiltration, a non-disruptive low-cost technique, could produce significant and reproducible performance enhancements in commercial SOFCs.

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Linking defects, hierarchical porosity generation and desalination performance in metal-organic frameworks

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Composite membranes with defective metal-organic frameworks (MOFs) connect the emerging fields of MOF topological modification, MOF-polymer interfacial engineering and composite material functionalization. Although defective MOFs can be fabricated via thermal or chemical treatment, the relationship between hierarchical MOF structure and their performance in a polymeric matrix has so far not been investigated.\textsuperscript{1} Here we show how a modulator fumarate-based MIL-53(Al) microwave synthesis process results in defective MOFs. This ligand replacement process leads to materials with hierarchical porosity, which creates a higher mesopore volume and Brønsted acidity without compromising the crystalline structure and pH stability (Figure 1). Compared with stoichiometric ratios, increasing the reaction time leads to more effective defect generation. The subsequent incorporation of defective MOFs into polyvinyl alcohol pervaporation membranes can effectively promote the fresh water productivity in concentrated brine treatment, with salt rejection of >99.999% (Figure 2).\textsuperscript{2} The membranes also have good long-term operational stability with effective antifouling behavior. We provide evidence that topological engineering of the MOF surface is related to their physical and chemical behaviors in a polymeric matrix, opening up the possibility of MOF defect engineering to realize selective separations, catalysis and sensing within a polymeric matrix.

Figure 1 Schematic diagram of the defective MOF fabrication process

Figure 2 Membrane pervaporation performance with different MOF materials.

References:
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Oxazoline or oxazolinium ion? The protonation state and conformation of the reaction intermediate of chitinase enzymes revisited

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Chitin, one of the most abundant carbohydrates in nature, is hydrolyzed by chitinases, enzymes that has gained interest because of their medical and industrial applications.1 Family GH18 chitinases, unlike most retaining glycosidases,2 follow a substrate-assisted mechanism in which the 2-acetamido group of one N-acetylglucosamine unit reacts with the sugar anomic carbon, forming an intermediate which is commonly described as an oxazolinium ion.3,4 By means of QM/MM metadynamics simulations on chitinase B from Serratia marcescens, we show that the reaction intermediate features instead a neutral oxazoline, with an oxazolinium ion being formed only on the pathway towards the reaction products. The role of a well-defined hydrogen bond network that orchestrates catalysis by protonation events, is discussed.

References:


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Magnetic removal of haze-forming proteins from white wines

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Bentonite fining to remove haze-forming proteins is a key step in the production of white and rosé wines, but has some drawbacks including wine losses and waste disposal issues¹. A novel technology for the rapid, selective, magnetic removal of pathogenesis-related proteins from wine shows potential as a bentonite alternative².

A careful tuning of the surface chemical functionality of magnetic nanoparticles was used to more successfully and selectively capture pathogenesis-related proteins from wines which can then be separated from the system by applying an external magnetic force and therefore allow for the rapid and selective removal of protein haze.

The analysis showed that the acrylic acid coated magnetic nanoparticles effectively removed proteins and did not significantly change the phenolic composition of the wines. This new technology may become an alternative to conventional bentonite treatment. Furthermore, such rapid separation technology for the binding and removal of proteins could benefit other areas such as diagnostics, water treatment, biotechnology and therapeutics.

References:

Acknowledgments:

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Polymer inclusion membranes (PIMs) are a relatively recently developed type of liquid membranes which offer significant advantages compared to the other types of liquid membranes (e.g., bulk, emulsion and supported liquid membranes) [1-3]. PIMs are usually composed of a base polymer and an extractant, trapped between the entangled polymer chains. In some cases they may also incorporate a plasticiser or modifier. In most of the PIMs reported in the literature the base polymer is either poly(vinyl chloride) (PVC) or cellulose triacetate (CTA). A PVC-based PIM incorporating the commercial anion-exchanger Aliquat 336 has been applied successfully to the clean-up of thiocyanate from gold mine tailings water [4, 5]. Thiocyanate prevents reuse of gold mine tailings water in the flotation of gold ore. In a subsequent study we have demonstrated that poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), used as a base polymer instead of PVC, improves significantly the performance of the corresponding PIM in the separation of thiocyanate [6]. The efficiency of this separation process has been further improved by utilising semi-interpenetrating polymer networks of PVDF-HFP and poly(ethylene glycol dimethacrylate) (PEG-DMA) instead of just PVDF-HFP [7].

References:

Acknowledgments: This research has been conducted in close collaboration with Prof. RW Cattrall, Dr C Xu, Dr Y O'Bryan, Dr YB Truong, and Dr IL Kyratzis and has been partially funded by the Australian Research Council and Stawell Gold Mines (Linkage grant LP0989449).
SHORT ORAL PRESENTATIONS
Role of surface rheological properties for the kinetics of bubble Ostwald ripening in saponin-stabilized foams

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Bubble Ostwald ripening (OR) leads to a gradual increase of the mean bubble size in foams with time. The rate of OR can be reduced significantly or even arrested completely, using appropriate solid particles and/or surfactants as foam stabilizers. To reveal the reasons for the reduced rate of OR in saponin-stabilized foams, we performed measurements of the rate of bubble diminishing, for single air bubbles placed below a solution surface, with a large series of saponin bio-surfactants¹. These saponin surfactants form adsorption layers with surface elasticity, spanning a very wide range – from almost zero up to several thousand mN/m. The measured rate of bubble OR showed no correlation with the surface elastic modulus (dilatational or shear), as measured at 0.1 Hz frequency of surface oscillations. A reasonable correlation was observed only with the surface stress (deviation from the equilibrium surface tension), measured at very slow rate of surface deformation, which mimics much better the actual processes of bubble OR in foams – higher surface stress corresponds to lower OR rate. New theoretical expression, accounting for the out-of-equilibrium surface tension during bubble shrinkage and for the gas flux across the meniscus regions surrounding the foam films, was derived and used to calculate theoretically the rate of bubble diminishing. The comparison of the theoretical predictions with the experimental data shows clearly that the main reason for the reduced rate of OR in the studied systems is the high resistance to gas transfer of the saponin adsorption layers. The deviations from the equilibrium surface tension, although noticeable, have smaller effect. The complementary experiments with actual foams showed that the rate of OR is even lower (compared to the rate measured with single bubbles) which is explained with the thicker non-equilibrium foam films, formed between the neighbouring bubbles in ripening foams.

References:

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Synthesis and characterization of carbon supported Pt(Cu) core-shell nanoparticles for hydrogen oxidation in low temperature fuel cells

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Fuel cells can contribute to the solution for the current energy crisis, since the electrochemical process from which energy is obtained has high efficiency and a low environmental impact. However, the main problem of fuel cells is that electrodes contain 20% of Pt, which is an expensive and not abundant metal, yet at low temperatures Pt is easily poisoned with CO, which is present in hydrogen obtained by reforming.¹ A strategy for the reduction of the Pt content in the fuel cell catalyst is to synthesize nanoparticles with a core-shell structure, where cores are from a sacrificial metal and they are recovered by a Pt shell. It has been proved that nanoparticles with a core of Cu produce an electronic effect on the shell of Pt improving its CO tolerance. Carbon supported Pt(Cu) nanoparticles have been synthesized by an electrochemical procedure, but it is hard to produce large amounts of catalysts.² In this work, Pt(Cu) core-shell nanoparticles supported on a high surface area carbon powder have been produced by electroless deposition of Cu using formaldehyde as a reducing agent, followed by a partial galvanic replacement with Pt. The TEM and XRD characterization of the catalyst show Pt(Cu) nanoparticles of around 1.5 nm with 10 wt.% Pt, which is lower than that in the commercial catalyst.

References:

Acknowledgments:

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Endocrine disruptors in water samples: A conjoined experimental and theoretical study under GC–MS conditions
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In the past years there has been growing concern of possible harmful consequences of exposure to xenobiotic compounds that are capable of modulating or disrupting the endocrine system of both wildlife and humans.

A sample preparation method based on single-drop microextraction followed by a combined gas chromatography – mass spectrometry (GC–MS) analysis is proposed for the determination of two well-known endocrine disruptors, namely Bisphenol A and Triclosan in water. 3 mL water samples spiked with various concentrations of Bisphenol A and Triclosan were extracted by a single 3 μL drop of organic solvent, where the conditions for the extraction temperature and time were optimized. Derivatization that is required for GC determination of these compounds was carried out using N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) inside the injection syringe barrel. The established method was applied to water samples from Vardar River, tap water from four different locations from Skopje as well as to samples from bottled water.

The developed chromatographic techniques in this work include the use of a mass spectrometer as a detector for determining the chemical entity of the molecular species. Considering the complexity of the studied molecules, the possibility of simultaneous existence of a large number of conformational isomers and potentially different pathways of their breakdown under conditions of mass spectrometric experiments, we have carried out a theoretical study of silylated derivatives of Bisphenol A and Triclosan by a conjoined static and dynamic approach, in which the density functional tight binding (DFTB) methodology is combined with molecular dynamics (MD) simulations.

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Within the static approach, the potential energy surfaces (PESs) of the silylated derivatives were explored in
details. To predict the finite-temperature behavior of the studied molecules, we performed MD simulations in the
microcanonical (NVE) ensemble with the atom-centered density matrix propagation scheme (ADMP).

Stable subsurface carbon – a general feature of noble metal nanoparticles and surfaces

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Late transition metals like Ni, Cu, Ag, Au are widely used as heterogeneous catalysts\textsuperscript{1} for many reactions of
industrial interest, e.g. ammonia synthesis, exhaust gases treatments, and Fischer-Tropsch reaction.\textsuperscript{2,3} During
the catalytic processes involving organic reagents, the carbon poisoning could involve formation of C\textsubscript{n}
moieties even at low coverages. Such species can adsorb strongly on the active, low-coordinated sites of the
catalyst and thus to hinder the reagent adsorption on the metal nanoparticles.

In order to estimate if the surface or subsurface positions are more stable for monoatomic C species, we
have modelled various structures with a carbon atom adsorbed/absorbed on/in Cu, Ag, and Au (111)
extended surfaces as well as M\textsubscript{79} (M = Cu, Ag, and Au) nanoparticle models. The activation energy barriers
for the surface→subsurface carbon diffusion were also calculated.

The periodic DFT calculations have been performed using the VASP code with the PBE exchange-
correlation functional and plane wave basis set with a 415 eV cutoff for the kinetic energy.

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Atomic arrangement of PtCu bimetallic nanoparticles determined using topological energy expressions

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Metal nanoparticles (NPs) are employed in many technological fields, including heterogeneous catalysis and energy technologies. Bimetallic NPs allow fine-tuning their chemical activity and reducing their cost. In particular, the interest in PtCu NPs is to reduce the Pt usage, by alloying it with a less expensive metal Cu. Chemical reactivity of bimetallic NPs depends on their composition, size, shape and preference of atoms to be located in interior versus surface facet, edge and corner positions. This very complex structure-stability dependence makes finding the most energetically preferred atomic arrangements of nanoalloys a challenge, which can be addressed using a recently developed in our group topological energy ($E_{\text{TOP}}$) approach [1]. Herewith we applied this approach, which relies on exploring topological Monte Carlo arrangements of PtCu nanoparticles using energetic descriptors obtained by Density Functional Theory (DFT) optimizations of realistic models. We studied a series of PtCu NPs containing 116, 140 and 201 atoms and featuring Pt:Cu atomic ratios 1:3, 1:1 and 3:1. In all these models Pt atoms show a clear preference for location in the outer surface shell, following the stability trend depending on their positions Terrace $>$ Edge $>$ Corner. Notably, for all studied NPs with 3:1 Pt:Cu ratios a Cu@Pt core-shell structure has been predicted to be the most energetically stable.

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Influence of the NHC-system on the auxiliary ligand behavior in palladium allyl complexes in solution

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Despite the wide variety of different types of NHC structures, complexes bearing imidazo[1,5-a]quinolin-1-ylidene NHC-ligand are not so well studied and the properties of their respective allyl complexes are unknown.

To investigate their properties we synthesized series of imidazoquinolininium salts (A1) bearing substitues with different volume (R). From those carbene precursors several allyl complexes were prepared which demonstrate fluxional behaviour in solution. Their behavior was observed with NMR-spectroscopy. The behaviour of the allyl ligand and the complexes in general is influenced by the volume of the substituent (R).

To compare the steric effects we also prepared series of less bulky imidazo[1,5-a]pyridinium salts (B1), bearing the same substituents (R), and their respective allyl complexes (B2).
Improving charge extraction from bismuth oxyiodide photovoltaics with 2-d metal dichalcogenide transport layers

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Bismuth oxyiodide (BiOI) has recently been shown to be a promising lead-free alternative to halide perovskites for photovoltaics. BiOI replicates the electronic structure of halide perovskites, and is tolerant to anti-site and vacancy defects. Notably, BiOI has been found to be at least two orders of magnitude more air-stable than methylammonium lead iodide.¹ Although record external quantum efficiencies of 80% have been achieved, the power conversion efficiency (1.8%) is limited by inefficient hole extraction in a ITO[NiOx]BiOI[ZnO]Au device stack, due to downwards band-bending of BiOI at the NiOx interface. In this work, 2-d molybdenum sulphide (MoS₂) is investigated as an alternative hole transport layer. Through plasma treatment, the work function is increased to >5.1 eV. A detailed photoemission spectroscopy investigation reveals that this results in upwards band-bending of BiOI next to the MoS₂ interface, which can enable improved charge extraction. We discuss control of the preferred orientation of BiOI on MoS₂ to achieve devices with improved efficiency.

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Next generation organic light-emitting diodes (OLED) based on thermally activated delayed fluorescence (TADF) polymers

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In organic light-emitting diodes (OLEDs), due to spin statistics, singlet and triplet excitons are created in a 1:3 ratio. In conventional fluorescent emitters, only the singlet excitons are radiative, implying that 75% of the formed excitons decay non-radiatively, which is a major loss process. Because of the small energy difference \( \Delta E_{ST} \) between singlet (S\(_1\)) and triplet (T\(_1\)) excited states in thermally activated delayed fluorescence (TADF) emitters, triplet excited states can transfer to singlet states via reverse intersystem crossing, followed by radiative decay via “delayed fluorescence” which explains their excellent performance.[1] Solution processing allows low-cost and large-area OLED applications. However, the fabrication of small molecule–based TADF OLEDs requires vacuum processing due to poor film formation from solution processing. In recent years a variety of TADF polymers and dendrimers were developed with the aim of an easily solution-processable, highly efficient OLED.[1]

To investigate the influence of chemical structure on the TADF properties and the percolation threshold for charge transport we synthesized a variety of green-emitting TADF polymers. The fact that they share an identical TADF substructure, based on the previously published TADF emitter DMAC-BP[2] allows us to isolate the effect of chain connectivity. These materials also enable us to compare the properties of \( \pi \)-
conjugated versus non-conjugated linkages between the donor units in the TADF polymers. Furthermore, comparison is made with the small molecule counterpart. We varied the length of the non-conjugated linkers, as well as alkyl side chains, as well. Steady state optical spectroscopy revealed a pronounced solvatochromic behavior for all polymers. Additionally, time resolved photoluminescence spectroscopy demonstrated TADF. Spectroscopic differences between the various structures observed. The fabrication and characterization of OLED devices with active layers based on these new materials is currently in progress. 


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Low voltage current-driven organic electrochemical transistor for biomedical applications

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Detection of ion concentrations plays a fundamental role in biomedical diagnostics, health and environmental monitoring, water and food controlling, as well in the security and agriculture industry. 1 Here we show an organic electrochemical transistor (OECT) in a current-driven configuration providing highly sensitive ion detection at low voltages. 2 The ion sensitivity normalized to the supply voltage is larger than 1200 mV V -1 dec -1 , which is the highest value ever reported for ion-selective transistors. The bias current determines the range of ion concentration and the sensitivity is not limited by the supply voltage, thus overcoming the fundamental limit. A potential application is demonstrated by the integration of the current-driven OECT with an ion-selective membrane, exhibiting a sensitivity of 1035 mV V -1 dec -1 , normalized to the supply voltage. We were able to extend this concept by interfacing organic electronics with biological systems. The integration of OECTs with human cells, enables the assessment of barrier tissue layer properties in a non- “Materials Networking” project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 692146.
invasive and label-free method. Measuring the paracellular transport provides information about the
integrity and function of the barrier tissue as disruption or dysfunction can be an indicator for disease or
toxicity. The OECT, resembled in the inverter-like topology, is sensitive to cell coverage and shows minute-
respond to toxins due to barrier rupture. Pushing this technology to greater sensitivity, this proposed
approach may open opportunities in toxicology, drug delivery, disease diagnostics and fundamental research
in molecular biology.

References:

Size-dependent dielectric function of single gold nanoparticle surface plasmon resonance

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Simple theoretical model for finite size effects of single gold nanoparticle surface plasmon resonance
was proposed. The analytical model solution was verified to describe semi-empirical calculation data for
gold nanoparticles. Size dependence of the surface plasmon resonance frequency from UV-Vis absorbance
spectra was used, and compared to mean diameters of size distributions from Atomic Force Microscope,
Transmission Electron Microscope, and Dynamic Light Scattering. The simple model was based on Lorentz
oscillator and Drude model with analytical solution similar to semiempirical adapted Drude formula
presented by Kriebig. A good agreement between theory and experiments for small spherical gold
nanoparticles with diameters from 5 to 20 nm was observed.

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Using light-emitting nanoparticles to control defects in organic diodes

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Polymer light emitting diodes (PLEDs) have attracted enormous attention owing to their compatibility with scalable processing techniques and flexible electronics. The light emitting polymer (LEP) layer in such devices is typically processed from an apolar organic solvent, which in case of up-scaled device production will be placed under heavy scrutiny due to environmental constraints. It is therefore advantageous if this layer is processed as aqueous nanoparticle dispersion. An additional advantage is the fact that the confinement of a nanoparticle offers the possibility to prevent large-scale phase separation in case the active layer contains an additional component, such as a dopant molecule or an electrically insulating diluent. The latter is of particular interest, since we have recently shown that diluting a semiconducting polymer with an insulating host eliminates electron trapping in the former. This results in a balanced charge carrier transport and increased device efficiency.[1] In this contribution we present the preparation of PLED devices from stable aqueous mini-emulsions[2] of the well-known poly(p-phenylene vinylene)-derivative Super Yellow. The particles and resulting spin-coated films have been thoroughly characterized by dynamic light-scattering and scanning electron microscopy. We demonstrate how smooth films can be prepared despite the particulate nature of the emulsion. Our continuous effort in preparing high quality thin films of these light emitting polymer nanoparticles has now led to acceptably low leakage currents, as well as full-area light emission.

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Quantum dot (QD) based light-emitting diodes (QLEDs) are competitive alternatives to purely organic light-emitting diodes (OLEDs) in terms of color purity, luminescence intensities, and external quantum efficiencies (EQEs). Hybrid QD/organic polymer light-emitting diodes combine the advantageous emitting properties of the QDs with the flexibility in device construction of polymeric materials. In QD/polymer hybrid LEDs, adding QD emitters in the polymer host usually leads to strong charge trapping or charge transfer, which can adversely affect device performance. In a desired host-guest system with a blue-emitting donor polymer and a red-emitting QD acceptor, the emission process should preferably occur via long-range Förster energy transfer (FRET), without charge trapping or charge transfer. Therefore, the design challenge for such a system would be optimizing energy transfer, while at the same time spacing host and guest sufficiently far apart to avoid charge transfer.\textsuperscript{1,2}

Herein, to address this challenge, we designed a novel QD/polymer hybrid material in which the surface of QDs is covered with an electrically insulating shell of optimal thickness. This way, we manage to separate donor and acceptor far enough to prevent short-range processes such as charge trapping and charge transfer, though allowing FRET. This is achieved in two steps: i) shielding the emitting CdSe core of the QD with a ZnS shell having a wider bandgap and ii) grafting insulating polymer chains, i.e. polystyrene, onto the ZnS surface. The PS layer furthermore enhances miscibility with the host. We blended the red-emitting CdSe/ZnS/PS core shell QDs (acceptor) with poly(di-n-octylfluorene) (PFO) as the host (donor). In order to reach to optimum conditions, different series of QD/PS-hybrids have been synthesized and applied in single carrier and dual charge carrier devices and the morphology of the emitting layer was also investigated. In the optimal system, FRET from PFO to QDs indeed governed the electroluminescence of the PFO+QD/PS-hybrid films, with near complete elimination of charge trapping.
Tuning activity of transition metal carbides by surface metal alloying: Case of study of CO$_2$ capture

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CO$_2$ is one of the main actors of the greenhouse effect and its removal from the atmosphere is becoming an urgent need. CO$_2$ capture and storage (CCS) and usage (CCU) technologies are intensively investigated to decrease CO$_2$ concentration. Both CCS and CCU require appropriate materials to adsorb and activate CO$_2$. Recently, it has been theoretically and experimentally shown that transition metal carbides (TMC) are able to capture, store, and activate CO$_2$. [Energy Environ. Sci. 2016, 9, 141] To further improve the adsorption capacity of these materials, a deep understanding of the atomic level processes involved is essential. In the present work, we theoretically investigate the effects of surface metal doping on TMCs by taking TiC as a textbook case while using Cr, Hf, Mo, Nb, Ta, V, W, and Zr as dopants. By using periodic slab models with large supercells and state-of-the-art density functional theory based calculations we show that CO$_2$ adsorption is enhanced by doping with metals down a group but worsened along the $d$ series. Adsorption sites, dispersive forces, and coverage appear to play a minor, secondary constant effect. The dopant-induced adsorption enhancement is however highly biased by the charge rearrangement at the surface. In all cases, CO$_2$ activation is kept but doping can shift the desorption temperature by up to 135 K.

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Understanding the origin of magnetic anisotropy in $S=1/2$ mononuclear transition metal complexes

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Magnetic anisotropy is a key property which, along with the molecular spin, generates molecules that exhibit single molecule magnet behavior. For systems with total spin $S=1/2$, the presence or absence of magnetic anisotropy can be explained by means of the molecule's $g$-tensor. Using ideal models to screen the most common geometries for coordination numbers 2 to 8 in mononuclear transition metal complexes, we employed the Ab initio Ligand field Theory (AILFT)\(^1\) formalism as implemented in the electronic structure package ORCA\(^2\) to build a qualitative model which predicts the behavior of the magnetic anisotropy in molecular systems with $S = 1/2$. We have subsequently validated this qualitative model and corroborated our predictions by means of available experimental information\(^3\). We will also show the potential use of this model to design new molecules exhibiting large magnetic anisotropy.

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