EUPOC 2018

Biomimetic Polymers by Rational Design, Imprinting and Conjugation

20-24 May 2018, Como, Social Como Theatre

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Abstract Booklet & List of Partecipants

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EUPOC 2018 aims to provide an ideal forum for researchers to exchange and share innovative ideas on biomimetic polymers with rationally designed molecular recognition and response properties. The conference will cover fundamental aspects of molecular recognition, high efficiency bioconjugation, molecular imprinting, and novel strategies in synthetic design and nano-fabrication of multifunctional materials. Invited presentations will be given by leading experts from both academic and industrial settings.

Functional materials with biomimetic properties, e.g. selective molecular binding, response to stimuli and capability of specific signal transduction, are appealing for a large number of applications. Biomimetic polymers can be prepared through different approaches: those based on conjugation of well-defined molecular building blocks with synthetic polymers, and the use of template-guided synthesis to prepare molecularly imprinted polymers (MIPs). In the first approach, the molecular building blocks can be selected from nucleic acids, proteins or small organic molecules (synthetic receptors), which are linked to novel synthetic polymers via high efficiency conjugation chemistry. In the second approach, the active sites in MIPs are created by molecular templates (including metal-ligand complexes) during a crosslinking polymerization.

The functional performance of biomimetic polymers can be enhanced through nanofabrication and combination with many types of nanomaterials, e.g. quantum dots, upconvertion nanoparticles and photocatalysts. Biomimetic materials with multiple functions are also gaining importance in bioseparation, drug delivery, theranostics, forensic science, food analysis/traceability and environmental applications. Last but not the least, computational design using molecular dynamics, semi-empirical quantum mechanics and DFT methods are receiving much attention in developing high performance materials.

EUPOC 2018 will cover the following topics:

- Molecular recognition polymers by rational/computational design
- Biomimetic polymers through (bio)chemical conjugation
- Traditional and modern methods of molecular imprinting
- Biomimetic polymers for sensing, affinity separation and catalysis
- Biomimetic polymers for drug delivery, imaging, detection of biomacromolecules and cells
- Imprinted polyelectrolyte film, nanostructures and nanomaterials
- Switchable and multifunctional biomimetic polymers

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INVITED LECTURES

IL 1

POLYMER BIOMIMICS IN DIAGNOSTICS AND THERAPEUTICS)

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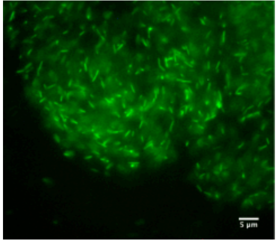
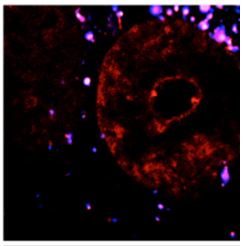
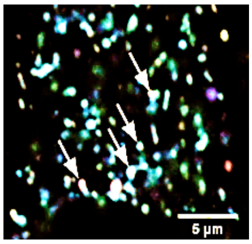
Biomimetic polymers have many applications ranging from anti-infectives, drug delivery and tissue engineering. However, the processes and mechanisms by which synthetic biomimetic polymers and particles bind to bacterial and mammalian cells, and how they transport within, are not always analogous to theor natural analogues . We have been working on materials which can probe cell surface binding and intracellular transport phenomena through a range of (bio)responsive functionality. These include polymers which can reversibly change from a chain-extended to a chain-collapsed state in response to temperature, pH, ionic strength or redox potential. The responses of these polymers can lead to a hydrophilic/hydrophobic switch at a surface, the unveiling of a ligand to bind to a receptor, or a release of a therapeutic payload at a target site. Recent studies have shown that even relatively simple 'model' polymer systems can behave in unexpected ways in varying cell types and populations. The talk will accordingly focus on polymers that can (a) bind to cell surfaces and interfere with bacterial Quorum Sensing (QS)[1] and redox systems[2] (b) selectively enter cancer cells by a polymer-mediated ligand switch,[3] and (c) change pathways inside a range of cells.[4]



Polymer-bacteria interactions



Selective cell entry



Pathway switching

We will show that new synthetic polymers can exhibit a variety of intriguing properties in the presence of a range of cell types, and that the knowledge gained from these studies can give useful insights into disease processes and new therapies.

Acknowledgments: The UK Engineering and Physical Sciences Research Council (EPSRC) for grants EP/G042462/1, EP/H005625/1, EP/I01375X/1, EP/N03371X/1, EP/N006615/1 and the Royal Society (Wolfson Research Merit Award WM150086) for funding.

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IL 2

TOWARDS THE RATIONAL DESIGN OF MOLECULARLY IMPRINTED POLYMERS

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Abstract

The recognition capabilities of molecularly imprinted materials are being successfully exploited in a growing number of application areas.[1] These developments have in turn driven attempts to establish strategies for the rational design of imprinted materials.[2] In this regard, the use of molecular dynamics simulations of pre-polymerization mixtures has proven to be a particularly useful for gaining molecular-level insights into events in these mixtures, prior to the onset of polymerization, that can be correlated to polymer performance, and even provide insights concerning polymer morphology. In this lecture, a background to these developments[3] shall be presented, along with examples of their use and current challenges.

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IL 3

MOLECULARLY IMPRINTED POLYMERS IN BIOMEDICAL APPLICATIONS

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Abstract

Molecular imprinting has attracted a great attention as a technology to produce synthetic polymer capable of antibody-like molecular recognition. Molecularly imprinted polymer (MIP) can be synthesized by forming a complex(es) with a template molecule and functional monomers, and then polymerization is carried out with a crosslinking reagent. The following removal of the template molecule leave binding cavities complementary in size and shape of the template molecules.[1].

Recently, we have developed post-imprinting modification (PIM),[2-7] which was inspired from biosynthesis of proteins, involving two steps such as peptide synthesis and the following chemical modification (post-translational modification). We have introduced this strategy to MIPs; an innovative strategy to achieve site-directed introduction of additional functionalities into MIPs after the imprinted cavity formation. I will present recent examples of PIM-based MIPs to show how PIM works in sensor applications.

Another recent advances in MIPs is biomedical applications. We have developed MIP-based nanocarriers for drug delivery systems.[8] Unexpectedly long circulation of albumin-imprinted MIP nanogels in blood streams was observed due to their stealth property acquired by post-cloaking serum albumin after administration. Detailed discussion will be made for demonstrating the effectiveness of MIP nanogels as nanocarriers in rug delivery systems.

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IL 4

IMPRINTED PHOTONIC HYDROGELS FOR THE SIZE AND SHELL-SELECTIVE RECOGNITION OF NANOPARTICLES

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Abstract

Sensors based on responsive photonic hydrogels[1] have stimulated a wide interest for visual medical diagnostics, pharmaceutical bioassays, and environmental monitoring. However, the use of these promising materials for the detection of nanoparticles (NPs) has thus far received little attention, although the sensing of nanoobjects is a rapidly evolving area of research[2,3]. To address this issue, we have combined the concepts of inverse-opal hydrogels and nanoparticle-imprinted polymers. In this talk, I will describe the elaboration of the resulting NP-imprinted photonic hydrogels consisting of a three-dimensional, highly ordered poly(methacrylic acid) macroporous array[4,5], in which nanocavities complementary to the target NPs, in this case colloidal quantum dots, are distributed (see Fig. 1). This novel type of NP-imprinted photonic hydrogel sensor displays high sensitivity and selectivity for the recognition of nanoparticles, thus opening new prospects for the development of equipment-free and cost-efficient sensing devices for NPs.

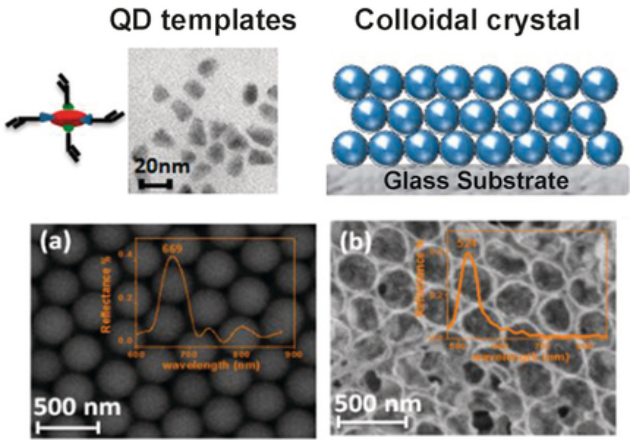

Figure 1: SEM images of a) the colloidal-crystal template of silica particles and b) the resulting inverse-opal structure of the NP-imprinted hydrogel. Inserts show the specular reflection spectra of the samples illuminated by a white-light source. A typical TEM image of the QD templates is shown at the top.

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IL 5

MOLECULARLY IMPRINTED POLYMERS FOR VIRUSES: A GRAND CHALLENGE

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Abstract

Biomimetic recognition utilizing molecularly imprinted polymers (MIPs) has proven its potential by providing synthetic receptors for numerous analytical applications including liquid chromatography, solid phase extraction, biomimetic assays, and sensor systems. The inherent advantages of synthetic receptors and functionalized membranes in contrast to biochemical/biological recognition and immobilization schemes include their robustness, synthetic versatility, and potentially lower costs. In principle, molecularly imprinted/templated materials are an ideal molecular capturing matrix tailorable for selective recognition or immobilization of a wide range of molecules. However, tailoring synthetic recognition elements to a target analyte requires thorough analysis and fundamental understanding of the governing molecular processes during the imprinting procedure, with the ultimate goal of rationally designing and predicting optimized synthesis pathways leading to molecular capture, recognition, and immobilization matrices with superior control on their physical geometry and molecular selectivity.

Of particular interest is the development of biomimetic recognition schemes for selectively binding proteins and large biomolecules, e.g., at the surface of biomedical devices for promoting or preventing adhesion of selected biomolecules, as well as for controlled molecular release. While materials with recognition capabilities even for larger biomolecules have achieved substantial advancements, the synthesis of molecularly imprinted materials with virus recognition properties remain challenging to date.

Here, an innovative synthetic strategy for biomimetic virus capture material is presented. An optimized sol-gel imprinting method finally yielded excellent binding selectivity, which could be achieved by a novel and generic strategy for suppressing non-specific binding via coating with deliberately selected blocking agents – a strategy termed 'enhanced selectivity by passivation'. Next to competitive studies with non-template viruses, applications in real-world biotechnological scenarios corroborate the practical potential of this approach.

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IL 6

OCHRATOXIN A AS WINE CONTAMINANT: IMPRINTED POLYMERS FOR CLEAN UP AND DETECTION

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Abstract

Food contamination from mycotoxins poses severe risks to human health, including cancer and serious hormonal disorders. Current analytical methods for determination of mycotoxin contamination in food at ppt- and sub-ppt-levels are negatively affected by the complexity of the matrix, which leads to the widespread use of immunoaffinity solid phase extraction cartridges as sample pre-treatment devices before of any HPLC quantification. As immunoaffinity cartridges have short half-life and high production costs, the use of alternative extraction methods based on target-selective materials is particularly attractive. Thus, recent years have seen a significant increase of “molecularly imprinted solid phase extraction” (MISPE) technique in food contaminant analysis.

Ochratoxin A (OTA, figure 1) is a well-known mycotoxin frequently detected in wine produced by mouldy grapefruits. It is a carcinogen for liver and kidney tissues, and it is considered to be the primary cause of the so-called “Balkan endemic nephropathy”, a degenerative affection of kidney widely diffused in several east-european countries. For these reasons, wine contamination by OTA is a relevant public health concern.

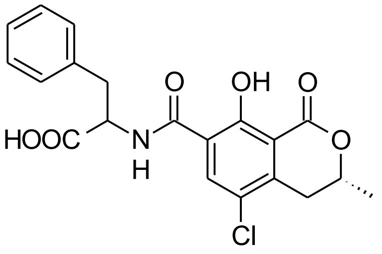

Figure 1: ochratoxin A

In this talk, the use of OTA-binding imprinted polymers will be discussed, with a focus on their design and development, the use of template mimics to avoid analytical interferences, the advantages/drawbacks of their use in the set-up of robust extraction protocols in wine, and the possible future trends in this field.

IL 7

SURFACE MOLECULAR IMPRINTING – FROM DETECTING NANOSIZED SPECIES TO TAILORING MATERIAL PROPERTIES

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Abstract

Nanosized analytes pose special challenges for sensing/rapid detection, because they are usually not accessible via light scattering in the visible range. On the other side, this size range is of special interest for such methods: it covers artificial, engineered nanoparticles as well as natural "particles", such as viruses. Molecularly imprinted polymers (MIP) represent a possibility to tackle those two issues: during synthesis, the prospective analyte acts template for self-assembly of the growing polymer leading to cavities that can selectively re-bind that analyte.

Molecularly imprinted nanoparticles have attracted comparably broad interest as receptors in sensing[1]. In contrast to that only few examples exist demonstrating engineered nanoparticles as templates. One notable exception is based in electropolymerized matrices for binding citrate-stabilized gold nanoparticles[2]. Herein we report successful surface imprinting of two different metal nanoparticles, Ag and Au, respectively, into polyurethane-based matrices. The resulting layers allow for detecting such particles in liquid phase in the ppm range by selective binding. Selectivity is governed by three factors: firstly, and most obviously, by nanoparticle size. Secondly, the nature of stabilizer shell plays a role. Again, this is understandable given that MIP and NP surfaces bind to each other. Thirdly, it is also possible to distinguish the different cores. The reason in the concrete case is mass-sensitive sensing: MIP layers bind particle numbers according to the respective binding equilibrium, but the device senses mass. The latter of course depends on density.

MIP sensor layers also offer the opportunity to tailor sensitivity. One example for this is Dengue virus sensing. Polyacrylate-based MIPs against inactivated virions lead to LoD below 100 pfu/ml (plaque forming units) in buffer solutions. Despite being an appreciable result from the sensing point of view, real-life sensing would require sensitivities that are at least 3-4 orders of magnitude lower. In a first step to bridge that gap zeta potential studies revealed that the virus exhibits positive surface charge. Hence, surfaces with negative zeta potential should lead to increased binding. The approach is indeed feasible: adding graphene oxide (GO) with a strong negative potential to the MIP and this forming a composite increases sensitivity by two orders of magnitude. This opens up a way for tuning MIP functionalities further through forming suitable composites.

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IL 8

IMPRINTED POLYMERS / SAW SENSORS: A SYNERGIC ROUTE FOR ACCURATE AND SELECTIVE CHEMOSENSING TECHNIQUE

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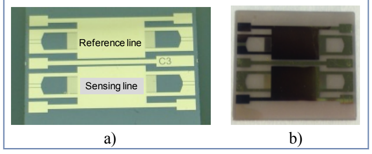
Abstract

Chemosensors have great potential applications in everyday life, ranging from food quality assessment and environment control to harmful substances detection and even illness diagnosis. The primary challenge is the choice and design of a of recognition layer that possess one or several binding affinities for the analyte(s) of interest. The imprinting technique, which consists in introducing selective molecular or ionic recognition sites in a polymeric matrix, conferring it bio-mimetic properties, is probably one of the most viable and promising approach. The rationale for using imprinted polymers is that they are easy to prepare, stable, cheap, versatile and can be used even in extreme environments, such as highly charged media. Several types of transduction techniques have been used in synergy with molecular or ionic imprinted polymers (MIP or III): electrochemistry, optical (mainly Surface Plasmon Resonance based technology) and gravimetry, via quartz crystal microbalance and surface acoustic wave (SAW) sensors.

Figure. 1 : SAW sensors before (a) and after (b) the deposition of an imprinted polymer



SAW sensors consist in a piezoelectric crystal or polymeric substrate on which are deposited Interdigital Transducers (Figure. 1a). Depending on the design of these latter, a SAW device may be a resonator or a delay line Among the variety of available non-labelled sensors, SAW devices are undoubtedly the most promising ones as they are able to independently extract the pure mass (and thus the binding of a considered analyte to a recognition layer) from the other parameters of influence such as viscosity and mainly ionic strength, which disturbs considerably electrochemical measurements. Functionalizing a SAW device with a MIP or an IIP is probably one of the most appropriate route for the design of highly sensitive, selective, reliable and accurate chemosensors (Figure. 1b).

Several MIP and IIP based SAW sensors will be presented. Besides demonstrating the potential of such sensors, in terms of sensitivity, selectivity, low limits of detection and versatility, the main goal of this talk is also to highlight their complementarity with other experimental or theoretical approaches (Figure. 2).

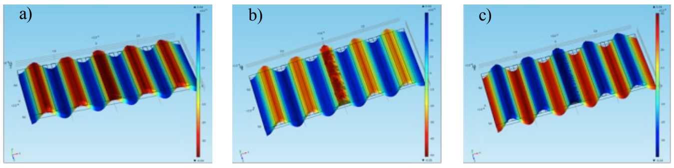


Figure. 2: Snapshots of the transvers displacement (at 14.6 ps) from COMSOL Multiphysics Simulation of a) a non-imprinted polymer, b) an IIP before and c) after extraction.

IL 9

TARGETING MYCOBACTERIA WITH TREHALOSE GLYCOPOLYMERS

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Abstract

Trehalose is a key component of the mycobacterial cell wall as well as the cytosol. The mycobacterium uses trehalose as an osmoprotectant and produces various trehalose-containing glycolipids in its cell wall, which are essential for its growth and proliferation. Additionally, trehalose dimycolate is proposed to be possibly involved in cell infection by specifically interacting with macrophage inducible C-type lectin (Mincle).

We found that trehalose-functionalized nanoparticles interacted strongly with *M. smegmatis*.[1] Furthermore, the trehalose nanoparticles selectively targeted *M. smegmatis* in the presence of mammalian cells, and showed promises as the drug delivery system for antibiotics against mycobacteria.[2] This opens up opportunities to develop trehalose-functionalized nanomaterials for diagnosis and therapeutics.

In this talk, the synthesis of trehalose-grafted multivalent glycopolymers will be presented. Examples of using trehalose glycopolymers as the scaffold for the detection of and antibiotic delivery to mycobacteria will be discussed.[3]

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IL 10

NIPAM-BASED NANOGELS AS DRUG DELIVERY VEHICLES

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Abstract

'Smart' polymers are part of a growing area of research, due to their great potential as delivery systems. Conventional approaches have shown the limitations of untriggered release, where Fickian diffusion drives non-specific cargo delivery. A variety of intelligent materials have been engineered to respond to stimuli such as pH, temperature, light and magnetic field, with temperature being the most studied. N-isopropylacrylamide (NIPAM)-based hydrogels have been extensively studied, since they show a volume phase transition temperature (VPTT) close to body temperature. In addition, in recent years, a number of different monomers showing thermoresponsive properties have been explored, with the aim of increasing the range of temperatures in which these materials can operate and thus, the number of different applications. Despite significant advances, the relationship between chemical composition of the polymerisation mixtures and the properties of the materials has yet to be fully understood. This significantly limits the development of further applications.

We have prepared a small library of nanogels using three thermoresponsive monomers in combination with varying percentages of methylene-*bis*-acrylamide (MBA) as crosslinker, to study the impact of chemical composition on morphology and thermoresponsive properties. We then introduced a pH-switch in the matrix by using a novel polymerisable proline-derivative, to develop dual temperature/pH responsive materials. We selected one of the formulations to demonstrate the potential application of the new nanogels as drug-delivery vehicles. The results of this study will be presented together with some additional data resulting from interesting studies that include both *in vitro* and *in vivo* experiments.

IL 11

DYNAMIC CHEMISTRY OF GLYCOSYLATED NANOSTRUCTURES

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Abstract

Carbohydrates play important roles in many biological processes due to their interactions with a wide variety of receptors. Although individual carbohydrate structures generally show weak affinity to their binding partners, the interactions can be enhanced by multivalent presentations at a variety of scaffolds. The resulting glyconanostructures and materials exhibit remarkable chemical and physical properties with high potential for modern biomedical applications.

In this presentation, different dynamic chemistry approaches for synthesizing and applying glycosylated nanostructures will be described. Carbohydrate entities can thus be conjugated onto different carrier structures of molecular and supramolecular nature, leading to well-defined, multivalent entities. The reversible, error-correcting feature of dynamic chemistry results in efficient access to new families of glyconanostructures of different geometry and size, and the modular approach enables the construction of a variety of structures for facilitated investigation of the binding effects.

The results demonstrate that this approach to carbohydrate presentation at nanoscaffold and nanomaterial surfaces leads to efficient and selective binding to cognate proteins, enabling new applications in carbohydrate-lectin recognition, profiling, biosensing, screening, cell imaging, and bacteria detection.

IL 12

BIOMIMICKING STRATEGIES TO ATTAIN ANTIFOULING SURFACES IN MARINE APPLICATIONS

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Abstract

Biofilm forming, bacterial adhesion, and settlement of fouling species e.g. in marine environments depend on several physic-chemical parameters related to the surface of the substrates and the foulants.

The first steps of fouling is often related to protein adsorption. Thus knowledge of the Coulombic charge and protein isoelectric point values are of pivotal importance to understand and control fouling. However, often only trace amount of unknown (adhesion) proteins are available for characterization, which poses a challenge to conventional analytical techniques. Here we introduce a new method that requires the use of only minute quantities (on the order of hundreds to a few thousands) of macromolecules covalently immobilized to the surface of Atomic Force Microscopy (AFM) colloidal probes to determine isoelectric points of proteins. We first validate our approach using well-known structures, and then study the surface charge of "footprint" adhesion proteins secreted by barnacle cyprid larvae of *Amphibalanus Amphitrite* during their search of settlement spots in sea water.

We measure adhesion forces of the tip- immobilized proteins against positively and negatively charged robust and smooth surfaces, made by sequential deposition of polyelectrolytes, as a function of pH [1]. The use of such reference substrates allowed us to study the influence of only one parameter (surface charge) while keeping the others (roughness, chemical composition) essentially unchanged [2]. Examples for combating marine and bacterial fouling will be shown to illustrate possible applications. These include the use of multilayer films obtained by (cross-linked) Layer-by-Layer electrostatic assemblies, as well as macromolecular brushes made by surface initiated polymerizations.

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ORAL CONTRIBUTIONS

OC1

DESIGN PRINCIPLES FOR FUNCTIONAL NANOSTRUCTURES OF HYBRID BLOCK COPOLYMERS

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Abstract

Conjugation of dendritically- or hyperbranched hydrophilic macromolecular blocks to hydrophobic segment(s) gives rise to hybrid block copolymers capable of self-assembly into nano-aggregates of diverse morphologies possessing multiple functionalities, e.g., targetable ligands available to specific interactions with biological environment. Such macromolecules mimic natural lipopolysaccharides that constitute one of the major components of the bacteria membranes and are responsible for molecular recognition and cell adhesion.

We propose a general theoretical framework that enables us to predict self-assembling behaviour of such macromolecules and structural/interactive properties of resulting nano-assemblies as a function of intramolecular hydrophilic/hydrophobic balance and molecular architecture of hydrophobic and hydrophilic domains. Different types of branching (topology) and functionalities of the branching points can be accounted for. In particular, we demonstrate that macromolecules with highly branched hydrophilic blocks exhibit a stronger trend to assemble into spherical micellar-like aggregates as compared to their linear chain homologs. The diagram of morphological states of the solution nanostructures comprising ranges of thermodynamic stability of spherical and cylindrical micelle-like aggregates and polymersomes is constructed and its systematic evolution as a function of degree of branching of soluble bock is analysed. We demonstrate that increasing degree of branching of hydrophilic block leads to stabilization of spherical aggregates as compared to cylindrical or lamellar-like ones. At the same time, the number of functionalizable terminal groups exposed to the surrounding media increases only weakly upon increasing branching degree of the soluble block due to simultaneous decrease in the aggregation number. This theoretical predictions provides important guide lines for design of vector systems for targeted delivery of biologicaly active molecules (e.g. anticancer drugs).

OC2

IBODIES: SYNTHETIC ANTIBODY MIMETICS AS TOOLS FOR MOLECULAR RECOGNITION AND IMAGING

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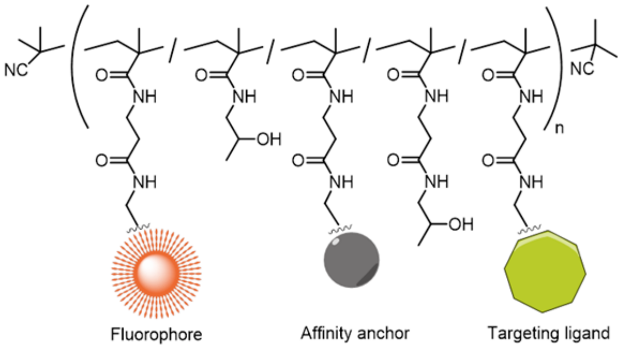
Abstract

Widely used tools for research, diagnostics and anticancer therapy are monoclonal antibodies. However, their use is compromised by high production cost, limited stability, and complicated chemical modification. Recently, we reported the design and development of synthetic polymer conjugates capable of replacing antibodies in number of *in vitro* applications used in biochemistry such as ELISA, flow cytometry, immunocytochemistry, and immunoprecipitation, and also useful for specific imaging of tumors. The conjugates, named "iBodies", consist of a hydrophilic copolymer decorated with low-molecular-weight compounds that function as targeting ligands, affinity anchors (typically biotin), and imaging probes (fluorophores or radiolabels).[1,2]



We chose and synthesized water-soluble and biocompatible *N*-(2-hydroxypropyl)methacrylamide (HPMA) copolymers since they have been used for the development of drug delivery carriers, imaging agents and polymer drugs[3]. Chosen carrier, the HPMA based copolymer, is a multivalent synthetic macromolecule with a number of reactive groups which enable covalent attachment of various ligands. These polymers were synthesized by controlled polymerization technique RAFT in the presence of trithiocarbonate chain transfer agent in organic solvents. Molecular weights of prepared copolymers were in range of 35 000 to 70 000 g/mol with polydispersities bellow 1,2. Content of co-monomers units with reactive thiazolidine-2-thione groups were between 8 - 20 mol%. These reactive groups allow covalent attachment of different ligands bearing primary amino group at common conditions and at room temperature.
We prepared specific conjugates targeting several important proteins, such as prostate specific membrane antigen, fibroblast activating protein and number of other medicinally relevant enzymes. We used these iBodies for enzyme inhibition, protein isolation, immobilization, quantification, and live cell imaging. Our data indicate this highly modular and versatile polymer system can be used to produce inexpensive and stable antibody substitutes.

This work was financially supported by grant of Czech Science Foundation (grant No.16-02938S) and by the Ministry of Education, Youth and Sports of the Czech Republic within the National Sustainability Program II (Project BIOCEVFAR LQ1604).

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OC3

MOLECULARLY IMPRINTED MATERIALS FOR A SUSTAINABLE FUTURE

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Abstract

Over the past decade we have focused our efforts on the development of novel polymerisable receptors for use in molecular imprinting, ranging from simple acrylamido pyridines[1] to ureas[2]. These architectures have proven the benefits of custom functional monomer design, as they result in materials that exhibit exceptional selectivity and affinity for the target of interest in highly competitive media. Building on this expertise, we wish to report on a series of recently developed receptors that further extend the tools available for the imprinting and sensing of compounds of environmental and biological importance, while addressing pressing issues of nutrient sustainability and circular economy. These include the first polymerisable squaramide receptors,[3] as well as a series of polymerisable ionic liquids, used in the recognition of anionic species and neutral (sulfonyl)ureas, respectively.

Polymerisable squaramides offer flexibility in terms of co-monomer choice and composition of polymerisation feed, while they are compatible with the use of cross-linking monomers. The latter, enables their incorporation as anion or cation recognition elements or polymer supported organo-catalysts in e.g. gel-type resins and molecularly imprinted polymers. We will demonstrate the use of such receptors in the capture, recycling and detection of phosphate – a non-renewable nutrient, essential for plant and animal growth, whose overuse is associated with eutrophication and pollution of fresh water bodies – and highlight the potential role of imprinted polymers in nutrient management and circular economy.

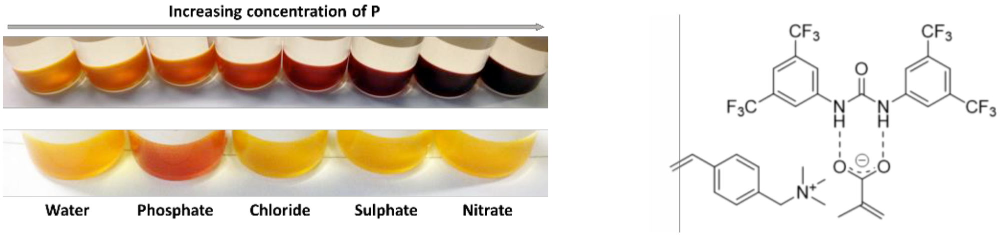

Fig. 1 Changes in polymer colour upon exposure to increasing concentrations of phosphate or competing anions (left), and IL monomer complexation of a urea organocatalyst (right).

Furthermore, inspired by our previous work on the use of the urea motif for anion recognition, we will report on a "reverse" approach and the first use of polymerisable ionic liquids for stoichiometric imprinting of (thio)urea organocatalysts and sulphonylurea drugs.[4] The resulting polymers were applied in the selective extraction of these compounds from complex matrices with near quantitative recoveries, while due to the use of an ion-pair monomer, they also exhibit exceptional long-term stability and minimal need for regeneration post-application. We will demonstrate how with a simple catalyst recovery protocol we were able to perform over 10 consecutive reactions without loss in performance, paving the way for greener catalytic processes.

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OC 4

TEMPERATURE AND pH CONTROLLED SELF-ASSEMBLY OF A PROTEIN-POLYMER BIOHYBRID

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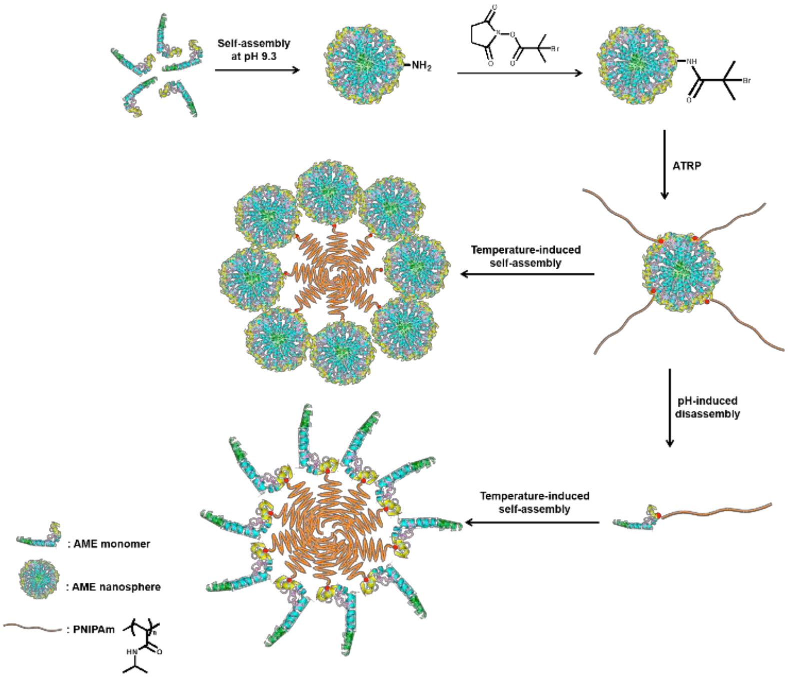
Abstract

A novel pH and temperature dual-responsive bioconjugate was prepared by grafting thermo-responsive polymer chains from a pH-responsive protein amelogenin nanospheres via atom transfer radical polymerization. The site-selective introduction of initiator molecules into the protein nanospheres allowed the preparation of well-defined protein-polymer biohybrid. In both basic and acidic solutions, this biohybrid could self-assemble into uniform and stable nanoparticles with a very narrow size distribution when heated above the lower critical solution temperature of the polymer. More interestingly, the nanoassembly process could be regulated by simply varying the pH and temperature.

As the protein and the polymer components can be further modified through protein engineering and controlled radical polymerization techniques, the amelogenin-based bioconjugate may serve as a promising platform material to be exploited for advanced drug delivery and for improved bioseparation purposes.



OC5

STAR CO-POLYMERS ARE AN EFFECTIVE DELIVERY SYSTEMS FOR HIV IMMUNOGENS ELICITING POTENT IMMUNE RESPONSES IN VIVO

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Abstract

Subunit vaccines based on minimal peptide immunogens are considered safe and customized alternative to traditional microbial vaccines, however their small size gives them poor pharmacokinetic and immunological properties. Conjugation of peptide immunogens to a nanoparticle delivery platform might solve these problems as it increases immunogen solubility, improves its interaction with immune cell surface receptors and significantly prolongs its persistence in the body.

In this study, star co-polymers were used as delivery platforms for HIV-1 peptide immunogen and the vaccines were tested *in vivo* in mice and nonhuman primates. In particular, we have designed and synthesized star co-polymers, consisting of bio-compatible poly[*N*-(2-hydroxypropyl)methacrylamide] (PHPMA) arms extending from a polya(midoamine) (PAMAM) dendrimer core. HIV-1 peptide minimal immunogens, derived from V3 loop of the surface envelope of HIV-1 protein, and synthetic adjuvant based on Toll-like receptor 7/8 agonist were conjugated to the PHPMA arms and PAMAM dendrimer core, respectively. The tunable architecture of the star co-polymers allowed covalent binding of a different number of antigens and various epitopes. The vaccine potency was further improved by binding of T-helper peptides together with HIV antigens to the star co-polymer. Due to the favorable hydrodynamic size (~20 nm), the star co-polymer conjugates trafficked preferentially to draining lymph nodes in mice where they were taken up by and activated various antigen presenting cell subsets to initiate strong germinal center reactions. Moreover, the vaccine elicited high antibody binding titers to the V3 sites of the HIV-1 envelope proteins in nonhuman primates.

We hope that our study opens the door for the development of safe and potent anti-HIV-1 prophylactic vaccines able to generate massive and durable production of broadly neutralizing antibodies.

This work was financially supported by the Czech Science Foundation (project 16-14957Y) and by the Ministry of Education, Youth and Sports of the Czech Republic within the National Sustainability Program II (project BIOCEV-FAR LQ1604).

OC6

A RATIONAL APPROACH TO MOLECULARLY IMPRINTED POLYMERS DESIGN: EXPERIMENT AND COMPUTATION

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Abstract

Molecular imprinting is a method that allows to generate biomimetic synthetic materials with molecular recognition properties similar to natural receptors in terms of affinity and selectivity[1]. For the design of molecularly imprinted polymers (MIPs) there is a wide variety of functional monomers, which allows to adapt these materials to any type of target molecule and to various applications such as separations materials; binding assays, biosensors, bioimaging, etc. Nevertheless, the vast majority of polymer synthesis protocols found in the literature are based on an empirical approach, using trial-and-error, and/or chemical intuition to find the recipe optimising the affinity between monomer and template in the pre-polymerization mixture and hence the recognition properties of the final polymer. Alternatives, such as combinatorial chemistry[2] and molecular modelling[3] have been proposed to rationalise MIP formulations. However, combinatorial screening is not a predictive tool, and it involves in addition laborious experimental verification. Therefore, when dealing with expensive templates and/or screening a large set of monomers, computational approaches appear the most appropriate.

In this work, a rational design study has been carried out to get a better understanding of monomer-template interactions, of the MIP formation and of the recognition mechanisms in MIP-ligand complexes by comparing experimental data with theoretical calculations. Three MIPs will be presented to illustrate our ration design: they are selective to precursors of malodorous compounds[4], to cancer biomarkers[5] and to dipicolinic acid[6]. Since monomer-template interactions are considered the driving forces for the selectivity of the final MIP, we have characterised these interactions in silico and experimentally. Spartan DFT calculations were performed on interactions in vacuum and in polar solvent. These in-silico binding energies were confronted to experimental data obtained by isothermal titration calorimetry (ITC) and nuclear magnetic resonance (NMR) spectroscopy methods. This approach combining experimental spectroscopic and calorimetric studies with computational chemistry is a powerful tool for better understanding the interaction mecanisms responsible of the monomer-template complex formation and its relation to the selectivity of the final MIP.

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OC7

SUPRAMOLECULAR ASSEMBLY OF LOW-MOLECULAR-WEIGHT WEDGE-SHAPED AMPHIPHILES FOR HIGH PERFORMANCE PROTON-CONDUCTIVE MEMBRANES

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Abstract

Self-assembled liquid-crystalline molecules attract interest due to their ability to form various well-defined nanostructures resembling the structure of tobacco mosaic virus (Fig. 1a) [1]. In particularly, ionic liquid-crystalline (LC) materials form well-organized 2D and 3D water channels for fabrication of efficient ion conducting materials for nano-reactors, filters and fuel cells. In the approach pursued by our group, fabrication of ion-selective membranes has been performed via supramolecular assembly of low-molecular-weight wedge-shaped amphiphiles that form well-ordered columnar hexagonal and cubic gyroid structures (Fig. 1b)[2]. This bottom-up synthetic route results in nanostructured membranes with a long-range order. Such approach can be advantageous as compared to conventional fabrication method employing amphiphilic copolymer-based systems as it can allow for a much better control over the ion channel size and topology.

In this work, the details of the structure formation processes occurring upon swelling in organic solvents vapour are explored[3,4]. Particularly, we report on the phase behaviour of a mesogen, which can exist in two different states at room temperature, a stable columnar and a metastable cubic gyroid phase. The latter reveals an exceptional stability and remarkable water sorption capacity accounted for by locally-ordered peripheral alkyl chains (Fig. 1c,d).The molecular modelling shows that the ion channel size correlates not only with water uptake but also with the molecular architecture such as the structure of the rigid molecular fragment bearing a polar group. These findings can help optimizing the ion transport for development of proton-conductive membranes.

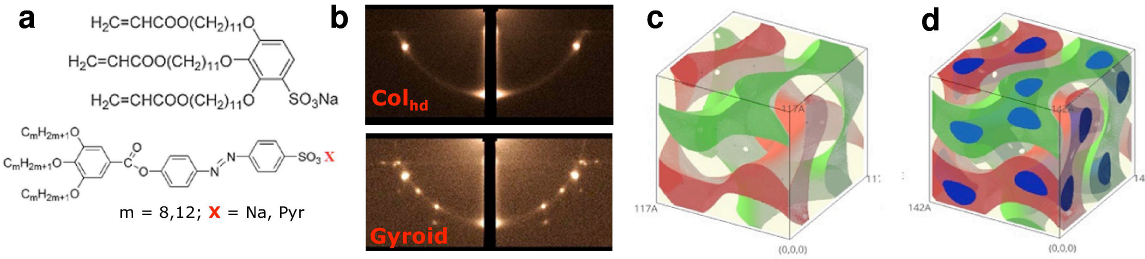

Fig. 1: chemical structure of studied mesogens (a); GIXD patterns of thin films in columnar and gyroid phase (b); and molecular model of gyroid phase in dry (c) and swollen (d) state.

The authors are grateful to the Ministry of Education and Science of the Russian Federation for financial support (contract No. 14.587.21.0052 (RFMEFI58718X0052)).

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OC8

A MONTE CARLO SIMULATION OF ETHYLENE AND A-OLEFINS POLYMERIZATION RATE AND POLYMER YIELD WITH ZIEGLER-NATTA CATALYSTS USING APPARENT KINETIC CONSTANTS OF INDIVIDUAL SITE TYPES

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Abstract

In this study, the Monte Carlo simulation method was applied to ethylene co(polymerization) over Ziegler-Natta catalyst reported by Chen et al. The Monte Carlo simulation was similar to sum square error (SSE) model to prediction of stage II and III of polymerization. Both model had slightly deviation from experimental results for activation stage (stage I). The modeling results demonstrated that in homopolymerization, SSE was superior to predict polymerization rate in current stage while for copolymerization, Monte Carlo had preferable prediction. The Monte Carlo simulation approved the SSE results to determine role of each site in total polymerization rate and revealed that homopolymerization rate changed from site to site and order of center was different compared to copolymerization. The polymer yield was reduced by addition of hydrogen amount however there was no specific effect on uptake curve which was predicted by Monte Carlo simulation with good accuracy. In the case of copolymerization it was evolved that monomer chain length and monomer concentration influenced the rate of polymerization as rate of polymerization reduced from 1-hexene to 1-octene and increased when monomer concentration proliferate.[1]

OC9

ION EXCHANGE BEHAVIOR OF MOLECULARLY IMPRINTED POLYMERS IN APROTIC SOLVENTS

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Abstract

Adsorption of neutral compounds onto molecularly imprinted polymers (MIPs) from aprotic solvents has been generally attributed to hydrogen bonding and van der Waals interactions. Ionic interactions have been also mentioned, but experimental proofs of the presence of ions in the prepolymerization mixture or after adsorption to the MIP are not easy to find. This presentation will show, that at least within an important subclass of MIPs, ion exchange behavior is an important contribution to binding and selectivity.

Conductivity experiments on prepolymerization mixtures in acetonitrile (a typical porogen) show significant ionic dissociation of the template – functional monomer complex. This indicates the likeliness of ion exchange by the MIP. Competitive adsorption experiments, where a quaternary ammonium ion can replace an adsorbed, originally neutral amine from the MIP, do also support the presence of ion exchange. Since this last observation has been made even in the nonpolar solvent toluene, one may reasonably conclude that binding in such solvents has a substantial ionic character.

Adsorption isotherms of MIPs have been generally attributed to Langmuir type binding sites. It will be shown that due to ion exchange processes, the Freundlich isotherm equation may be more appropriate for some MIPs than the Langmuir adsorption isotherm, even if there is no binding site heterogeneity present.

The selectivity pattern of MIPs for amine templates, like beta blockers, is shown to have peculiar properties due to the acid-base interaction with the acidic functional monomer, methacrylic acid. This pattern differs only slightly from the selectivity features of the nonimprinted control polymer. Thus, imprinting seems to have only a secondary role in creating the selectivity pattern of these MIPs. Despite of this, chiral selectivity can be well imprinted.

Acknowledgement:
Support by NKFIH 120075 project is acknowledged.

OC10

CONDUCTIVE IMPRINTED POLYMERS FOR THE DIRECT ELECTROCHEMICAL DETECTION OF β-LACTAM ANTIBIOTICS: THE CASE OF CEFQUINOME

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Biomimetic materials, such as molecularly imprinted polymers (MIPs), answer perfectly the demand of tunable electrode modifiers, required for the design of electrochemical biosensors for the selective detection of emerging contaminants, such as β-lactam antibiotics. MIPs can be directly integrated with the electrode surface by electropolymerization. Moreover, if the electropolymerization gives rise to electronically conductive polymers[1] (ECPs) a direct electrochemical detection of an electroactive analyte should be possible. The selectivity provided by the key-lock mechanism of MIPs cavities will add up to the specific electrochemical signal of the target leading to highly selective biomimetic sensors.

As a proof-of-concept for the creation of a complete biomimetic sensor array for β-lactam detection in milk[2], a MIP-sensor for cefquinome (CFQ) detection was designed. CFQ is a fourth generation cephalosporin applied only in veterinary treatments. It has a peculiar electrochemical behaviour, related to its 2-amino-5-thyazolyl acetamido substituent. The selection of the monomer for CFQ-MIPs, namely 4-aminobenzoic acid (4-ABA), was based on a rational design screening of electropolymerizable monomers performed with Sybyl 7.3 software package. Even though 4-ABA was known to give conductive polymers, its polymerization mechanisms has not been clarified yet[3]. A broad electropolymerization study was carried out to map the pH-dependence in relation to the electrochemical properties: conductive Poly(4-ABA) can be obtained at pH 1 and 7 while for intermediate pHs the polymers result to be isolating. Aiming to exploit a direct electrochemical detection, CFQ MIPs were synthetized by electropolymerization at pH 1 (0.1 M sulphuric acid) performing 7 consecutive cycles of cyclic voltammetry (CV, scan rate 50 mV/s), with a monomer:target ratio of 5:1 on multi-walled carbon nanotubes graphite screen printed electrodes (MWCNT-G-SPEs). The extraction of the analyte entrapped in the formed polymeric network was performed by letting in contact the modified electrode with phosphate buffer (PB) at pH 12 for 5 min. The modified electrodes were fully characterized by Electrochemical Impedance Spectroscopy, Scanning Electron Microscopy and CV proving the MIPs to be conductive and reproducible. Under optimum conditions, the lower cefquinome concentration detectable on the modified sensor was 50 nM in PB pH 2; not far away from the CFQ maximum residue limits in milk of 38 nM, established by the EU.

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OC11

NOVEL MOLECULARLY IMPRINTED POLYMERS (MIPS) FOR THE RECOVERY AND RECYCLING OF (THIO)UREA ORGANOCATALYSTS

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Abstract

Organocatalysts have been applied as a "greener" alternative to metal-ion catalysis, and diaryl(thio)ureas have been developed to activate substrates via explicit double hydrogen bonding.[1] In these organocatalytic processes high catalyst loadings are typically employed, however, the catalysts are often discarded during the reaction workup process, due to a lack of viable recovery processes, resulting in excess waste and added costs.

Here, we wish to report on the development of novel "molecular sponges" for the recovery and recycling of valuable organocatalysts from a range of chemical reactions. Hence, we prepared stoichiometrically imprinted polymers against Schreiner's urea catalyst, a widely used organocatalyst, using 4-vinylbenzyltrimethylammonium methacrylate (VBTMA) as the functional monomer and utilising the urea affinity for carboxylate anions (Fig. 1).[2] This monomer has already successfully been applied by our group for the extraction of the sulfonylurea moiety of glibenclamide (an antidiabetic drug) from serum samples.[3] Solution association between the catalyst and the novel functional monomer was studied by ^{1}H-NMR titrations and an association constant $K_a > 10^5$ M^{-1} was measured in DMSO-d_6. Detailed analysis of the binding on the subsequently prepared imprinted and non-imprinted polymers showed the capability of the polymer to recognise the template, the analogue Schreiner's thiourea catalyst and a cinchona based thiourea catalyst. The present design yields robust imprinted polymers that can be repeatedly used without loss in performance. Furthermore, these novel materials exhibit exceptionally high binding affinity, as well as enhanced capacity and selectivity for the model template. The polymers were applied as Solid Phase Extraction materials and extraction protocols were developed for the recovery of (thio)ureas from reaction mixtures. The results show an exceptional recovery up to 100% over 5 cycles for a Baylis-Hillman reaction and up to 90% over 5 cycles for a Diels-Alder reaction, without loss of catalytic activity.

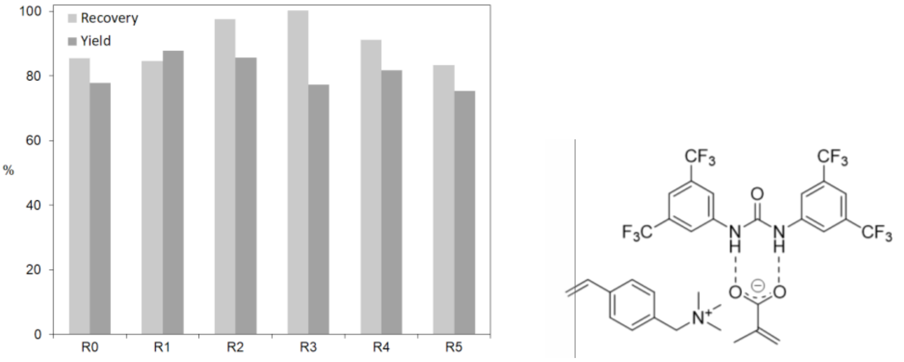

Fig. 1 Schreiner's urea catalyst *recovery and reaction yield over 5 cycles for a Baylis-Hillman reaction (left) and c*hemical structure of VBTMA ion pair monomer, showing proposed primary interaction with Schreiner's *urea (right).*

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OC12

MOLECULAR IMPRINTING WITH POLYDOPAMINE FOR RECOGNITION OF BIOTOXIN MOLECULES

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Abstract

Dopamine (DA), a mussel-inspired molecule, can be coated on various substrates through self-polymerization under alkaline solution. The formed polydopamine (PDA) film has a highly cross linked structure which is highly desired for the molecular imprinting techniques. In addition, surface imprinting by self-assembly monolayer systems also show great potential advantages due to simple construction, fast template removal and rapid sensor response time. Since PDA is hydrophilic and biocompatible, containing plenty of noncovalent functionalities, such as amino and hydroxyl groups as well as π-π bonds, it may establish multiple interaction with the amino acids on the proteins. In our work, we developed a simple, cost-efficient method for the generation of molecular imprinted film on quartz crystal microbalance (QCM) sensors. Peanut agglutinin (PNA), which is a simulant to ricin, was used as the target. This method is based on self-polymerization of dopamine in the presence of template PNA at room temperature. A solution of dopamine hydrochloride (2mg/ml), PNA (1mg/ml), ammonium persulfate (0.12mg/ml) was mixed in Tris-buffer. After stirring for 30 minutes at room temperature, 100 µL of the solution was deposited on the gold crystal and dried in the air overnight. The template extraction is done by soaking in 2% SDS-HAc solution for 4 hours. During the preparation of the protein imprinted coating layer, the pH conditions and the ratio between PDA and PNA were investigated. When the pH value is 7.5 and the ratio between PDA and PNA is 2:1, the frequency change is about 17 Hz during the injection of 10 ppm PNA solution. BSA was employed to test the selectivity of the MIP layer. After the injection of 10 ppm BSA solution, the frequency change is about 8 Hz. The ratio between PDA and PNA was then changed to 1:1 in order to create more imprinted cavities during the MIP process. Subsequently, the frequency response was increased by more than five times.

OC13

MOLECULARLY-IMPRINTED SILICA AEROGELS FOR A SELECTIVE ADSORTION OF METHYLXANTHINES AND PAHs

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Abstract

Molecularly-Imprinted Silica Aerogels (MISA) were successfully designed and investigated in the selective adsorption of methylxanthines and polycyclic aromatic hydrocarbons (PAHs). The characterization of these materials and their comparison to their non-imprinted peers reveals the successful removal of the template molecules. The adsorption of theophylline onto various surface-functionalized caffeine-imprinted silica aerogels revealed the superiority of phenyl-functionalized ones. The template to silicon precursor and water to silicon precursor molar ratios were also found to have a pronounced effect on the adsorptive capacity and selectivity of the molecularly-imprinted aerogels where optimal results were used in the competition experiments. The competitive adsorption experiments performed with caffeine-imprinted silica aerogels between caffeine and theophylline revealed a higher affinity towards caffeine. The adsorptive competition between several PAHs onto 2-naphthol-imprinted silica aerogels showed also the same behavior towards the template molecule. The comparison of the adsorptive capacities of molecularly-imprinted silica aerogels with their non-imprinted peers reveals the undoubtful pronounced effect of imprinting on increasing the adsorption capacity of the materials and expressing their selectivity towards target molecules.

OC14

RATIONAL DESIGN OF POLYMER BRUSH: HIGHLY VERSATILE AND EFFICIENT ADSORBENTS FOR SELECTIVE REMOVAL OF EMERGING CONTAMINANT NEONICOTINOIDS FROM THE AQUATIC ECOSYSTEM

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Abstract

The pervasive usage of neonicotinoid insecticides has flickered concern over their effects on non-target systems. Neonicotinoids pose a high risk to aquatic ecosystems due to their low soil binding, high soil persistence, and high water solubility. The aim of this work is to sense and selectively remove neonicotinoids from the aquatic ecosystem using polymer-brush functionalized molecularly imprinted polymers (MIPs). In order to obtain highly selective recognition polymer brush, the molecularly imprinted polymers (MIP) have been designed using quantum chemical methods to screen the optimal monomer and its ratio to neonicotinoids from virtual library of functional monomers. We have evaluated the performance of five DFT methods (PW6B95, PBE0-D3, B3LYP-D3, M06, and M062X) to describe the binding energies between pre-polymerization complexes. The DFT methods were evaluated against the CCSD(T) reference data by considering the pre-polymerization complexes and their binding energies. The best method relative to the CCSD(T) was found to be PW6B95-D3. The M06 method has also showed good performance, particularly when combined with Grimme's D3-dispersion scheme. The PW6B95-D3/PCM method is used not only for studying the structure of the template and the monomer-monomer interactions, but also to assess the stoichiometry, noncovalent binding energies, solvation effects and thermodynamics properties such as binding energy. Among the virtual library of 15 functional monomers, methacrylamide gives the most stable interaction energy with the template followed by acrylamide and n-isopropylacrylamid according to the thermodynamic values. On the basis of the computational interpretations, the best three MIPs were synthesized experimentally. The topological properties of MIPs were characterized by FTIR, TEM and TGA. When compared with the non-imprinted polymer (NIP), the MIP brush showed an excellent affinity and selectivity towards neonicotinoids in seawater samples with binding capacity (B_{max}) with 99.35 mg/g, imprinting effect of 3.63, and a dissociation constant of 31 mM. The theoretical results are in good agreement with the experimental binding studies. A molecularly imprinted solid phase extraction paired with HPLC method (MISPE-HPLC) has been castoff for the analysis of neonicotinoids in seawater samples. The method was validated for its linearity (R_2=0.9942) and accuracy (88.22%–99.98%). This study reveals that computational methods are convenient and powerful tool to provide an innovative polymeric material for neonicotinoids detection and its removal from seawater.

OC15

MAGNETIC IMPRINTED POLYMERS FOR PROTEIN RECOGNITION

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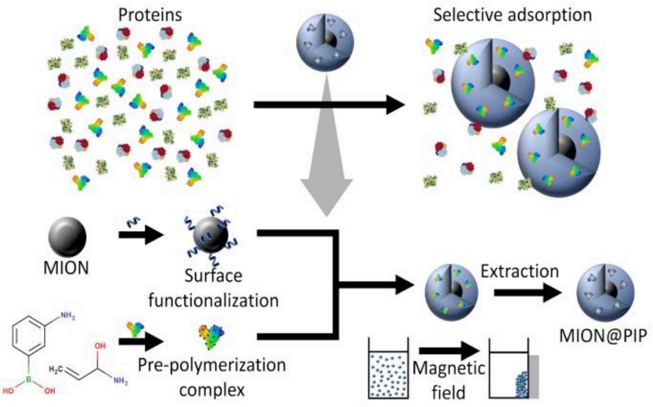
Abstract

Molecularly imprinted polymers (MIP) are cross-linked polymer networks presenting very specific recognition sites for a template molecule[1]. Due to specific interactions between functional monomers and template, one can create a synthetic antibody, which are of great interest for biotechnologies. Synthetic pathways were developed to obtain protein imprinted polymers (PIP), used for analytical or diagnosis purposes[2], but also to enhance nanoparticles stealth[3]. A great interest is nowadays focused on their use in nanomedicine, e.g. for in vivo protein targeting[4].

Coupling PIP to magnetic iron oxide nanoparticles[5] (MION) offer the possibility to detect and manipulate proteins in vitro or in vivo. In this field, we recently developed a novel synthetic pathway combining bulk and grafting approaches of polymerization to obtain magnetic imprinted polymer nanoparticles[6]. The adsorption property of the resultant PIP was demonstrated by rebinding experiments. The as prepared bovine serum albumin imprinted hybrid nanoparticles present a very high adsorption capacity of 300 mg/g, 3.75 times higher than the one of non-imprinted polymer, and selectivity toward the template protein compared to other albumins. Green-fluorescent protein imprinted magnetic polymer also show such great properties and preliminary tests concerning the targeting of cells using these materials showed very promising results.



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OC16

CAPTURE AND SENSING OF GLYPHOSATE IN AQUEOUS SAMPLES: ARE MOLECULAR IMPRINTED POLYMERS THE ANSWER?

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Abstract

Glyphosate (N-phosphonomethyl glycine) is a non-selective, broad spectrum herbicide, sold under the tradename of "Roundup". Both glyphosate and its main metabolite, aminomethyl phosphonic acid (AMPA), are easily absorbed into soil, leading to concern over soil saturation and subsequent leaching into nearby bodies of water due to the broad distribution over large areas.[1] EU regulations limit the levels of glyphosate, and all pesticides, in drinking water to 0.1 $\mu g\ L^{-1}$.[2]

The aim of this project is to develop materials that can capture and signal the presence of glyphosate, alongside AMPA, using stoichiometric molecularly imprinted polymers (MIPs). Molecular imprinting is based on the creation of solution state complexes between the template and a functional monomer, containing complementary functional groups, that can create weak non-covalent interactions, such as hydrogen bonds. These complexes can then be "frozen" by co-polymerisation with an excess of co-monomer, thus creating a polymer that contains a cavity that is complementary to the template molecule in size, shape and functional groups, allowing the polymer to selective capture and release the template. The polymers explored in this work utilise polymerisable squaramide-based receptors, which have previously been shown to have a high affinity towards anionic species.[3]

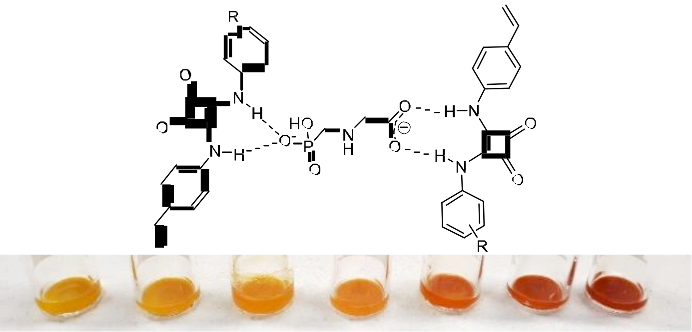

Figure 1 Template-monomer complex between a squaramide receptor and glyphosate (top) and polymer colour change upon exposure to increasing concentrations of glyphosate in water (bottom)

The affinity of these monomers towards the tetrabutylammonium salts of both glyphosate and AMPA, was assessed using titration experiments. The best performing monomer demonstrated an association constant of $>10^4\ M^{-1}$ for both targets and were then incorporated into polymers. To evaluate the binding strength and polymer capacity, rebinding experiments were performed, with the highest capacity observed of TBA glyphosate in water was 107.2 $\mu mol\ g^{-1}$. Within the rebinding experiments the polymers demonstrated a colour change from yellow to red on increasing concentrations of template. Following on from this, solid phase extraction will be used to selectively capture the target molecules from environmental water samples.

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OC17

MOLECULARLY IMPRINTED POLYMERS CONTAINING REDOX OR FLUORESCENT PROBES FOR SENSING APPLICATIONS

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Molecularly Imprinted Polymers (MIPs) are synthetic polymers designed to mimic natural biological receptors like antibodies. In the classical non-covalent approach, a template molecule interacts with a functional monomer and a cross-linker in a porogen solvent. After polymerization, the removal of the template generates the recognition cavities inside the three-dimensional copolymer network. Ion Imprinted Polymers (IIPs) are prepared in a similar manner by choosing functional monomers having chelating properties with respect to a target ion. Combined with various transduction mechanisms, MIPs and IIPs are the key stones of a large panel of chemical sensors thanks to their high recognition properties, easy synthesis and high stability[1]. A significant improvement of the sensors performances can be reached when the functional monomer also acts as a sensing element[2]. This is what we intend to do by (1) incorporating a redox probe as the functional co-monomer during MIP synthesis[3] and (2) including a fluorescent monomer inside an IIP.

In the first strategy, the electrochemical answer of the redox probe is impacted by the template presence when this one is recognized by the MIP, thus leading to its easy detection (Fig.1). This concept of electrochemical MIPs was first validated for benzo(a)pyrene[4] quantification and has been extended to that of Bisphenol A (BPA). Combining the ferrocenylmethyl methacrylate redox probe with 4-vinylpyridine functional co-monomer led to MIP microbeads particles which were then shaped into easy-to-handle screen-printed electrodes. A limit of detection for BPA of 13 ng/L was reached in that case, thanks to MIP microbeads as sensitive and active part of these advanced electrodes[5].

In parallel, we designed an innovative fluorescent monomer sensitive to lead(II) ions, which was further incorporated inside IIPs. The detection of this toxic metal is based on the generation of a fluorescent signal via a photoinduced electron transfer OFF-ON mechanism upon lead binding by the IIP (Fig. 2).

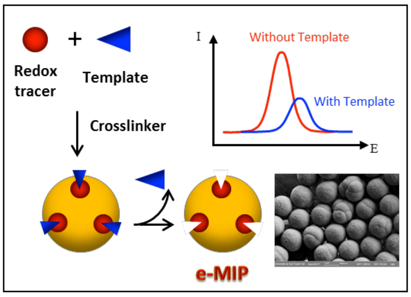

Fig. 1. Concept of electrochemical MIPs

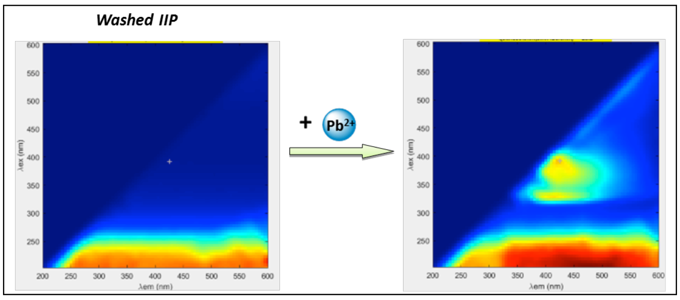

Fig. 2. Impact of lead(II) addition on the IIP fluorescence signal

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OC18

MAGNETIC NANOPARTICLES AS HOT SPOTS IN MOLECULARLY IMPRINTED POLYMER MATRIX FOR CONTROLLED DRUG RELEASE.

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Abstract

Molecularly imprinted polymers (MIPs), which possess selective affinity and sustained release behavior toward specific biomolecules have found applications in biosensing, drug delivery, bioseparation as well as diagnostics and therapeutics. The advantage in drug delivery of such a system is the possibility of regulating drug release by increasing the residence time of the therapeutic agent within the polymeric matrix, by means of either covalent or non-covalent interactions in specific binding sites.

Magnetic nanoparticles (MNPs) have attracted considerable attention for magnetic targeting and hyperthermia applications owing to their ability to generate heat when exposed to an alternative magnetic field (AMF) without penetration depth limit. Magnetic materials for therapeutic agents release based on thermosensitive polymers or vesicles have been developed. In this case, the approach was to induce an increase of permeability of the vector by heat dissipation under AMF excitation. Another way to release drug is to use hyperthermia to break bond between superparamagnetic iron oxide nanoparticles and the target in presence of oscillating magnetic fields. Recently, multifunctional ligands linked to iron oxide nanoparticles took benefits from local heating of nanoparticle's surface to release a fluorophore on demand.[1] Our approach is motivated by these last developments, i.e. to use local heating as the key parameter to trigger drug release.

We synthesised an innovative magnetic delivery nanodevice for targeted cancer therapy showing active control over drug release by using hyperthermia effects.[2] Our material, wich combines the drug controlled release ability of MIP with magnetic properties of iron oxide nanoparticles, allows the control release of doxorubicine (DOX) in athermal conditions. *In vitro* and *In cellulo* release of DOX were investigated and showed a massive DOX release under AMF without temperature elevation of the medium.

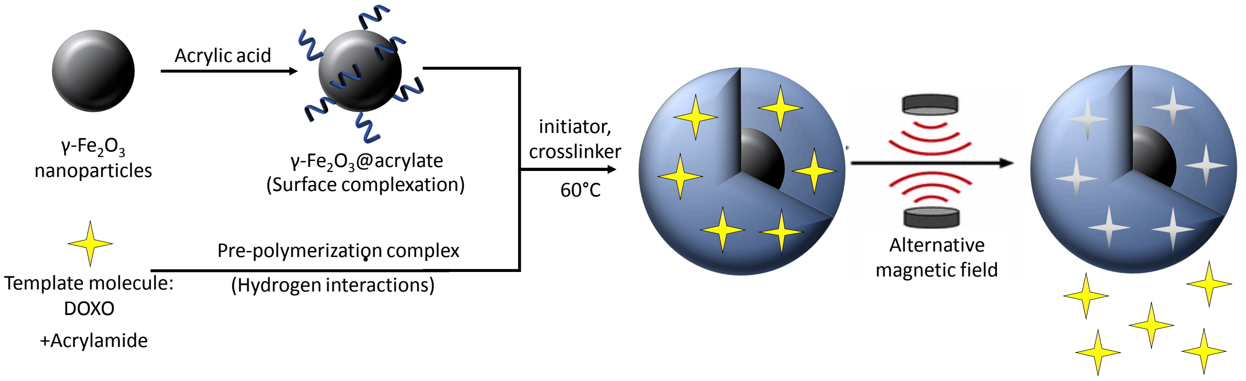

Figure 1. Two-step synthesis of Fe_2O_3@DOX-MIP via a subsequent grafting of an acrylic acid compound and the growth of the polymer at 60 °C. AMF induces DOX release.

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(a) (b)

OC19

HAEMOGLOBIN DETECTION USING NANOCOMPOSITE OF MOLECULARLY IMPRINTED POLYMERS AND CARBON QUANTUM DOTS

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Abstract

Fluorescent molecularly imprinted polymers (MIPs) as label free nanosensor has drawn much attention due to high selectivity and sensitivity. Fluorescent carbon dots (CDs) is a class quantum dots with properties such as water solubility, biocompatibility, high quantum yield, and excellent optical and chemical stability. Nanosensors based on MIPs and CDs have been reported to achieve recognition and detection for many chemical compounds[1].

In this work, a new type of nanosensor incorporating CDs and MIPs was formed by protein-stabilized emulsion for sensitive determination of haemoglobin (Hb), as shown in Figure 1a. With the probe sonication, the size of MIPs decreased to 1 µm. Compared with previous work[2], no silica was used here, so that corrosive hydrofluoric acid was not necessary. Moreover, the imprinting was carried out at room temperature, so the structure of Hb was more stable during the process. When Hb bound to the MIP, the interactions between Hb and the CDs resulted in fluorescence quenching. At Hb concentration of 0.1 mg/ml, 5 mg/ml of the MIPs could bind more than 85.7% of Hb, in contrast, the same amount of non-imprinted polymers (NIPs) only bound 19.5% of Hb. As shown in Figure 1b, various concentrations of Hb ranging from 0.01 mg/ml to 0.5 mg/ml was mixed with the MIPs, and the limit of detection was found to be 0.01 mg/ml. With the high sensitivity, the nanosensor could potentially be used to detect trace amount of Hb.

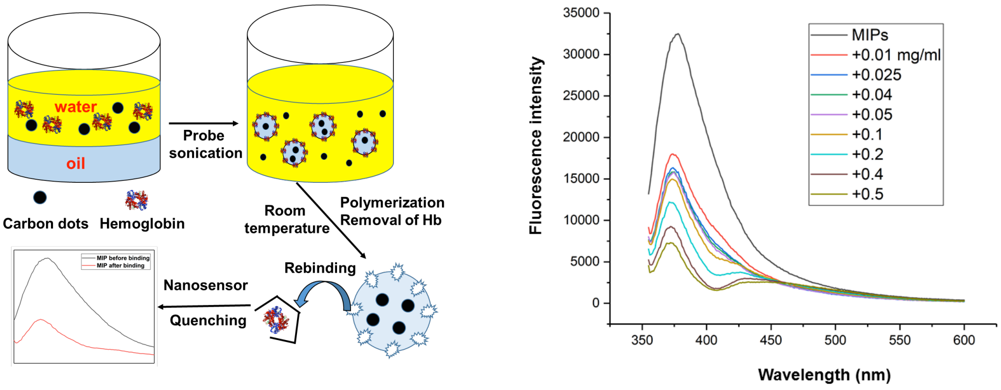

Figure 1. (a) Schematic illustration of the preparation of nanosensors. (b) Fluorescence quenching of MIPs (1 mg/ml) with Hb at different concentrations, ranging from 0.01 mg/ml to 0.5 mg/ml.

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OC20

MOLECULARLY IMPRINTED POLYMERS AS SORBENTS FOR THE REMOVAL OF MCPA FROM WATER

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Abstract

2-methyl-4-chlorophenoxyacetic acid (MCPA) is a commonly used phenoxy herbicide for selective control of weeds. Since its development in the 1940s, MCPA has been widely overused leading to a number of problems due to its high solubility in water and lack of binding with soil. MCPA can cause huge damage to aquatic environments and may pose a threat to human health through the contamination of potential sources of drinking water.[1] Due to these concerns, WHO set a maximum value for MCPA in human drinking water at 2 µg L^{-1}.[2] Current methods for MCPA removal from water are either not removing MCPA at a suitable level or are too expensive to implement on a wide scale. MIPs could provide an efficient and cost-effective method for the removal of MCPA from water.

The aim of this project is to develop a molecularly imprinted polymer (MIP) capable of removing MCPA from water. Three MIPs have been developed to address this problem, using commercial monomers 2-(diethylamino)ethyl methacrylate (DEAEMA) and 4-vinylpyridine (4-VP), and a tailor made urea-based monomer.[3] It has been shown through equilibrium rebinding and solid phase extraction experiments that the urea-based vinyl monomer-containing polymers were far superior to the commercial monomer-containing polymers, both in terms of their ability to bind MCPA in aqueous environments and their selectivity for MCPA. The ability of the urea-based vinyl monomer-containing polymers to act as efficient and cost-effective alternatives to current methods of MCPA removal from water through the production scale-up and testing of these polymers with environmental water samples will also be discussed.

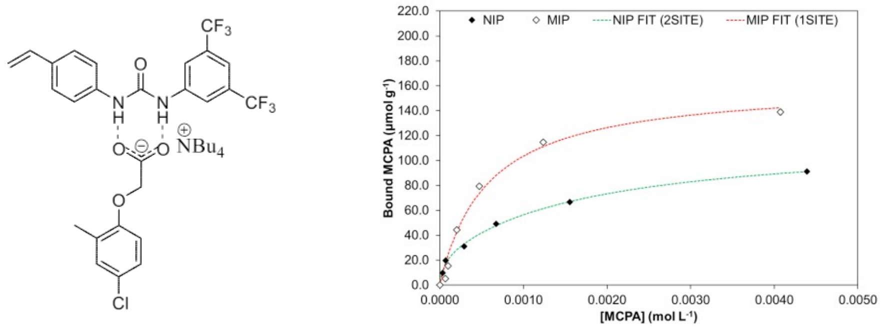

Fig 1: Proposed complex formation between urea-based vinyl monomer and MCPA (left); equilibrium rebinding of urea-based vinyl monomer-containing polymers and MCPA in water (right).

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OC21

UREA- AND SQUARAMIDE- BASED MONOMERS FOR MOLECULAR IMPRINTING OF BILE ACIDS

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Abstract

Liver cancer is the second most common cause of cancer death worldwide, with a reported mortality-to-incidence ratio of 0.95 in 2012.[1] Hepatocellular carcinoma (HCC) is estimated to account for 70% to 90% of liver cancer cases worldwide, largely due to risk factors such as hepatitis C and hepatitis B viruses, cirrhosis and fatty liver disease.[2] In recent metabolomic studies, several bile acids have been identified as potential biomarkers of HCC, such as glycocholic acid (Fig 1.).[3]

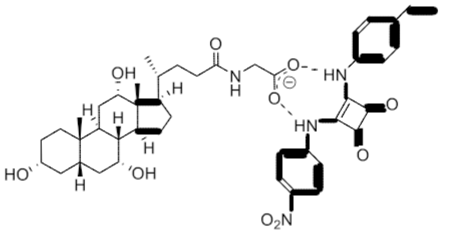

Fig 1. Proposed mode of interaction between glycocholic acid anions and novel squaramide receptor.

Molecularly imprinted polymers (MIPs) are polymeric materials imprinted with a template molecule to yield cavities of a specific size and shape for the molecule of interest. The field has observed a shift from the use of commercially available monomers for imprinting towards the employment of tailor-made functional monomers for recognition of specific motifs. Here, we will discuss the use of polymerisable urea and squaramide functional monomers in the molecular imprinting of bile acids.[4,5] The strength of the non-covalent interaction associated with these functional monomers may be tuned via control over the acidity of the protons involved in hydrogen bonding. Furthermore, we will demonstrate the colorimetric anion sensing capability of the *p*-nitroaniline-substituted squaramide monomer with bile acids (Fig 2).

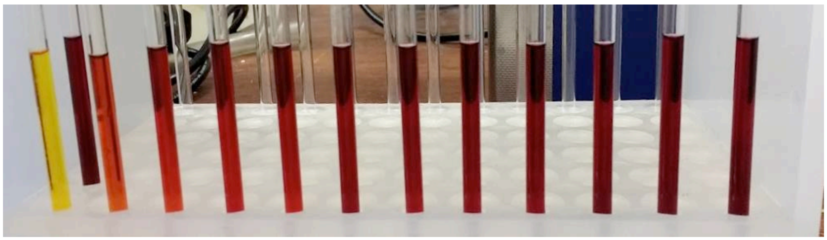

Fig 2. Colour changes observed during ^1H NMR titration of squaramide vs. tetrabutylammonium glycocholate in DMSO.

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OC22

MOLECULAR IMPRINTING FOR THE GLUTEN EPITOPE DETERMINATION

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Abstract

Molecularly imprinted polymers (MIPs) are nature-inspired artificial receptors[1] with the ability to bind reversibly and, therefore, are suitable to recognize the target analytes. The fabrication of MIPs against small molecules or peptides is now straightforward whereas imprinting of large molecular structures, such as proteins, is still challenging.[2,3] A possible solution is to imprint just defined epitopes instead of a whole protein.[4]

Gluten, that chemically corresponds to storage proteins deposited in the starchy endosperm cells of the developing grain, is the allergen that triggers autoimmuno reactions in people suffering from celiac sprue (CS). It is estimated that CS affects the 1-2% of the European population with direct healthcare costs estimated at about 3 bn EUR/year.[5] The only effective therapy is strict dietary abstinence from gluten. In fact, even a small contamination of food with gluten can cause serious adverse reactions from digestive system. Food considered as "gluten-free", thus safe for CS suffering people, should contain less than 20 mg/kg of gluten.

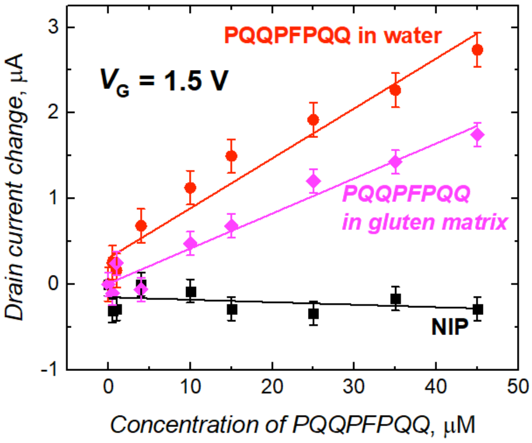

Figure 1. Calibration curves constructed for gluten epitope analyte, PQQPFPQQ, using molecularly imprinted polymers (MIPs, **red** and **magenta** curves) and a non-imprinted polymer (NIP, **black** curve) as recognition units as well as extended-gate field-effect transistors (EG-FETs) as transducers. All of the measurements were performed for the gate voltage, V_G = 1.5 V

In the present study, a toxic gluten epitope, PQQPFPQQ, was chosen as a template for imprinting. The MIP film was prepared by electrochemical polymerization of bis(bithiophene) derivatives, bearing either cytosine or carboxylic acid substituent, in the presence of the template and a cross-linking monomer. After the MIP deposition, the template was washed from the polymer film. Subsequently, the film composition was characterized by X-ray photoelectron spectroscopy (XPS) as well as its morphology and thickness were examined by atomic force microscopy (AFM).

Performance of this chemosensor was tested under laboratory conditions. Extended-gate field-effect transistor (EG-FET) chemosensor signals were measured for an aqueous solution of the PQQPFPQQ analyte as well as its interferences with 1 or 2 mismatched amino acids. Moreover, the chemosensor responses were measured toward the PQQPFPQQ analyte in gluten samples digested with pepsin at pH ≈ 2.0 (Figure 1). Finally, analytical parameters of the devised chemosensor were evaluated.

The present research was supported by European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No. 752438 (GEMS).

OC23

P_SENSE - A NOVEL, USER-FRIENDLY OPTICAL SENSOR FOR PHOSPHATE

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Abstract

Phosphate is one of the essential nutrients required for plant growth, development and quality and it is used globally as a major ingredient of fertilisers. However, its overuse has deemed it the main cause of water quality failure, as it can lead to eutrophication of fresh water bodies. As a limited resource, the use of phosphate should be optimised and managed efficiently.[1]

For these reasons, *P_Sense*[2] is developing a sensitive, portable, real-time phosphate sensor that is easy to use by non-expert personnel and does not require any additional reagents or external instrumentation for the analysis of soil and water for phosphate. This tool can help farmers and environmental agencies alike to manage, control and optimise the levels of phosphate in real-time, avoiding environmental damage and the enormous financial burden on the management of pollution by public agencies and the private sector.

At the heart of *P_Sense* is an imprinted polymer based on a new family of polymerisable squaramide receptors, which exhibit high affinity for anionic compounds and signal the binding event by a dramatic colour change.[3] By incorporating these novel building blocks into imprinted polymers, we demonstrate, *for the first time*, that not only is the presence of phosphate observable by naked eye *in water*, but due to the shape and size selectivity imparted to the polymers during the templating process, these colour changes are *only observed in the presence of P* and not when other competing anions, e.g. chloride, nitrate or sulphate, are present (Fig. 1).

Here, we will discuss our progress towards the development an advanced prototype sensor, from monomer and polymer development, to colour calibration and the incorporation of the sensor in a portable phosphate analysis device.

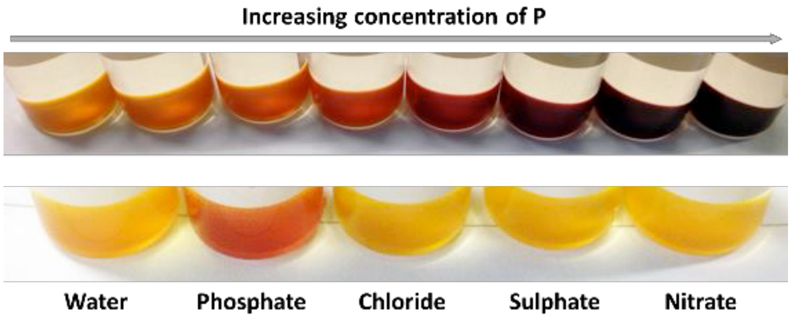

Figure 1: Colour change in the MIPs with increasing concentration of P (top) and polymer response to the presence of water, phosphate, chloride, sulphate, and nitrate (bottom).

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[3] P. Manesiotis, A. Riley and B. Bollen, J. Mater. Chem. C 2014, 2, 42, 8990-8995

OC24

Thermal biomimetic sensor for point-of-care bacteria detection

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Introduction

Over the past decade, various biomimetic sensor platforms based on synthetic, bio-inspired receptors have been developed. In terms of macromolecular targets, surface-imprinted polymers (SIPs) have emerged as interesting candidates for incorporation into point-of-care detection systems. In 2012, the authors of this work introduced a surprisingly versatile tool for label-free sensing; the so-called heat-transfer method (HTM) that could be combined with SIPs for the detection of *e.g.* bacteria.[1,2] Although the results from these experiments were promising, the relatively narrow dynamic range of the sensor limited its application for e.g. on-site bacteria detection. Therefore, the sensitivity of the thermal sensing principle has been improved in this study by analysing the propagation of a thermal wave through the receptor layer rather than a constant current (thermal wave transport analysis or TWTA). Using this improved read-out strategy makes it possible to detect bacteria in urine in concentrations relevant for the diagnosis of urinary tract infection (UTI).[3]

Experimental

Aluminium chips were coated with polyurethane and imprinted with *E. coli* to create synthetic receptor layers. A thermal current with an average temperature of 37°C, an amplitude of 0.1°C and a frequency of 0.03 Hz was send through the SIP-coated chip and the phase shift of the transmitted wave was analysed in response to the concentration of bacteria in spiked urine samples.

Results & Discussion

The sensor is able to discriminate between eight selected bacterial species that are relevant in terms of infectious diseases (data not shown).[3] Additionally, the sensor is able to detect bacteria in urine in concentrations between 10^4-10^5 CFU mL^{-1}, the relevant regime for UTI (Figure 1).

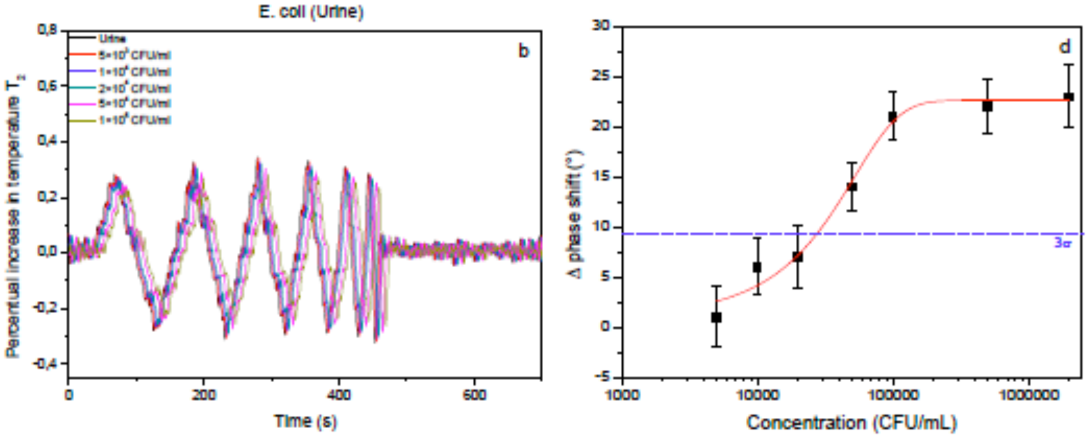

Figure 1: Detection experiment in spiked urine samples. The presence of bacteria in spiked urine samples leads to a concentration-dependent increase in the observed phase shift on the transmitted wave (left panel). These data were used to construct a dose-response curve (right panel) illustrating the limit-of-detection and dynamic range of the sensor.

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[2] van Grinsven B., Eersels, K.; et al. Physica Status Solidii 2018, DOI: 10.1002/pssa.201700777
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OC25

IMMOBILIZATION OF SUB-MICROMETER MOLECULARLY IMPRINTED PARTICLES ON CRYOGEL FOR HEMOGLOBIN PURIFICATION

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Cryogels, supermacroporous hydrogels, as a class of monolithic stationary phase are a product of cryogelation technology[1]. Cryogels have interconnected channels in the micrometre range, and can be used as a robust matrix for embedding different types of particles and adsorbents. Combination of the porous structure of cryogels with the selectivity of affinity adsorbents form a unique composite material that is suitable for separating a wide range of molecules[2]. In this project, we studied composite cryogels bearing MIP particles for purification of hemoglobine (Hb). The MIP particles were synthesized by Pickering emulsion polymerization using Hb as template[3]. In order to form composite cryogel, additional reactive groups (amino and epoxy groups) were introduced to the surface of the particles during the polymerization. A suspension of the MIP particles was pumped through an epoxy- or amino-modified cryogel column to allow the particles to be immobilized on the cryogel (**Fig. 1**).

In a second approach, Hb-imprinted cryogel was prepared by radical polymerization of hydrophilic monomers in water under cryo-condition. The direct Hb imprinting in cryogel resulted in a soft hydrogel material containing large flow through pores. Both the composite cryogels and the Hb-imprinted cryogels displayed specific binding to Hb when evaluated in batch mode binding experiments. To evaluate Hb-separation under flow condition, a mixture of BSA and Hb was passed through the different gels, and the proteins collected in the different fractions were analysed by SDS-PAGE. As shown in **Fig. 2**, the composite MIP cryogel displayed the best effect of Hb purification.

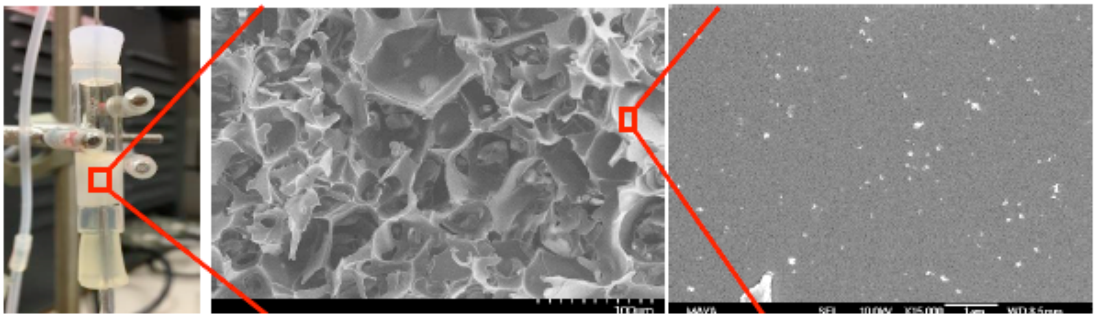

Fig. 1. *Left to right: Image of a composite cryogel hosted in a glass column. The SEM images show the porous structure of the cryogel and the immobilized MIP particles.*

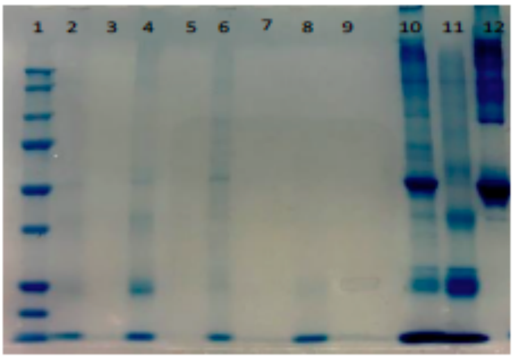

Fig. 2. *SDS-PAGE analysis of protein mixture (BSA 1 mg/mL and Hb 0.3 mg/mL) before and after treatment with different cryogels.*
Lane 1: Molecular weight marker; Lane 2: mixture of BSA and Hb, eluted from NIP-cryogel; Lane 4: mixture of BSA and Hb, eluted from MIP-cryogel; Lane 6: mixture of BSA and Hb, eluted from composite NIP-cryogel; Lane 8: mixture of BSA and Hb, eluted from composite MIP-cryogel; Lane 10: mixture of BSA (1 mg/mL) and Hb (0.3 mg/mL); Lane 11: Hb (0.3 mg/mL); Lane 12: BSA (1 mg/mL).
Lanes 3, 5, 7 and 9: fractions collected at the regeneration steps.

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OC26

TOWARDS BIOLOGICAL APPLICATIONS OF HYDROGEL-BASED MOLECULARLY IMPRINTED POLYMERS

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Abstract

Molecular imprinting of large biomolecules such as proteins has risen in popularity over the past 10-15 years, but it has not been without challenges. Given the metastable nature of biological molecules, one needs to take into account how the template biomolecule will respond to its environment during MIP polymerisation and subsequent washing and rebinding stages. The format of the MIP (bulk, thin film or nanoparticle) is also crucial in determining binding affinity.

Our Group has investigated a range of biomolecules including proteins, viruses and ribosomes for imprinting within hydrogels. We demonstrate that the imprinting factor (relative binding of protein to MIP vs NIP) can be radically improved post imprinting under optimised pH and buffer conditions, suggesting that the buffer components act as an essential mobile phase to chaperone the protein into protein selective cavities within the MIP (but not NIP). We have also shown that MIP cavities can be used as novel nucleants for the protein crystallization[1,2], by allowing the agglomeration of a sufficient number of protein molecules and thus overcoming the energy barrier for crystal formation. The latter phenomenon in conjunction with atomic force spectroscopic studies suggest that imprinted cavities accommodate a cluster of protein molecules rather than individual proteins.

We prepared bulk acrylamide and functionalised acrylamide based MIPs imprinted with purified porcine reproductive and respiratory syndrome virus-1 (PRRSV-1). Our preliminary results demonstrate the proof-of-concept for a highly effective and specific neutralisation of PRRSV-1 infectivity with polyacrylamide and poly N-hydroxymethacrylamide MIPs. Crucially PRRSV-1 was not neutralised with non-imprinted control polymers and the PRRSV-1 imprinted MIPs did not neutralise the unrelated bovine viral diarrhoea virus (BVDV).

Finally, we have recently tested the use of our MIPs for translatome profiling. In particular, we reported the first molecular imprinting of ribosome template using a bulk polymer imprinting approach[3]. Although, we were able to recapitulate the specific translational response in human cells using MIPs from 1,000 cells, the method is currently still not very practical as it requires mechanical breaking to obtain 'bulk' MIP particles, which could affect the reproducibility and efficiency of ribosome binding. This will be discussed.

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OC27

MACROPOROUS MOLECULARLY IMPRINTED FILMS FOR CHEMOSENSING OF MACROMOLECULE

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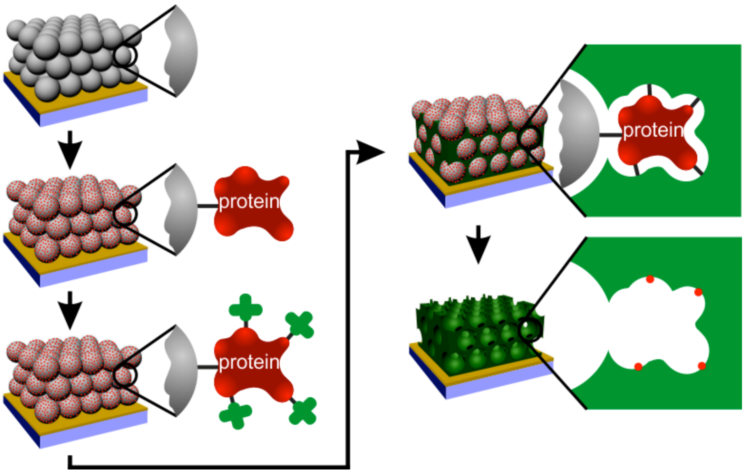
Abstract

Chemosensors selective with respect to human chorionic gonadotropin (hCG) protein hormone were devised. A macroporous film of molecularly imprinted polymer (MIP) was designed as recognition unit of the chemosensor to provide selectivity. Two alternative platforms of analytical signal transduction were explored, namely an electric platform using the extended-gate field-effect transistors (EG-FETs) and capacitive impedimetry (CI). A precise control over the structure of the material was successfully achieved by combining inverse opal structuring, surface imprinting, and semi-covalent imprinting of proteins (Scheme 1). A colloidal crystal templating with optimized potentiostatic polymerization of 2,3′-bithiophene enabled depositing an MIP film as an inverse opal. Prior immobilization of the hCG protein on the colloidal crystal allowed for formation of molecularly imprinted cavities exclusively on the internal surface of the pores. Furthermore, all binding sites were located on the surface of the imprinted cavities at locations corresponding to positions of functional groups on the surface of protein molecules. This precise controlling of the positions of recognition sites was possible due to initial derivatization of the surface immobilized protein molecules with suitable functional monomers (Scheme 1). This synergistic strategy resulted in a material with superior recognition performance. Selectivity of the chemosensor with respect to protein interferences was very high. Moreover, the limit of detection was in the femtomolar concentration range.



Scheme 1. Illustration of the procedure of poly(2,3′-bithiophene) inverse opal imprinting with protein hormones.

OC28

"POLYMULTIVALENT" POLYMER–PEPTIDE CLUSTER CONJUGATES FOR AN ENHANCED TARGETING OF CELLS EXPRESSING $\alpha_v\beta_3$ INTEGRINS

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Cancer tumor targeting is a central challenge in oncology both considering early diagnostics and therapy efficacy. It can be achieved by developing systems exhibiting a high affinity for receptors over-expressed by the tumors compared to healthy tissues.

In this context, we developed new "polymultivalent" conjugates combining both multifunctional polymer chains and multivalent ligand clusters that are able to target the αvβ3 integrins over- expressed at the level of tumor angiogenesis[1]. A library of polymer- peptide conjugates (Fig. 1) were prepared by efficient covalent coupling of a controlled number of tetrameric cRGD peptide clusters[2] onto well-defined and biocompatible RAFT polymers[3] (Figure 1).

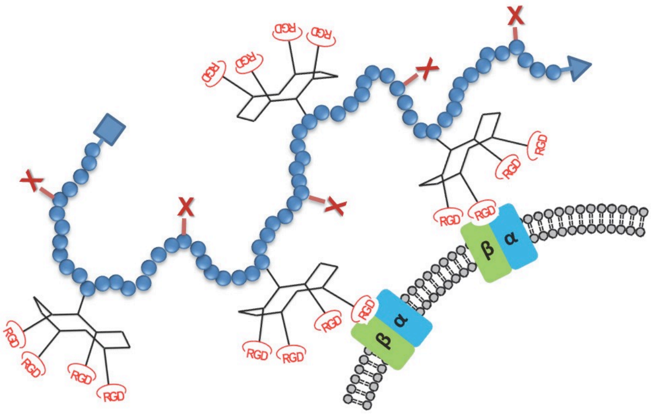

Figure 1: Schematic representation of the "polymultivalent" polymer-peptide conjugates

In vitro assessments evidenced a significantly improved affinity of these "polymultivalent" conjugates towards cells expressing αvβ3 integrins thanks to multivalency effects. Conjugates were then labelled with Cy5.5 dyes for further studies by confocal microscopy and flow cytometry. Internalization of the fluorescent conjugates (highly bright thanks to the multiple dyes bound to the polymer) in cells expressing αvβ3 integrins was shown to be both very efficient and specific.[4]

This new class of highly potent conjugates thus hold great promises for the vectorization of diagnostic and/or therapeutic entities toward αvβ3-integrin-rich environments. The conjugates can be applied as biospecific fluorescent probes to study various biological processes, both *in vitro* and *in vivo*. Furthermore, they may be used for the early diagnosis and the treatment of a large number of cancer tumors over-expressing αvβ3 integrins, especially because of their associated neo-angiogenesis.

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OC29

POLYURETHANE COLLOIDAL PARTICLES MIMICKING ANTIMICROBIAL PEPTIDES

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Antimicrobial peptides (AMPs) are essential components of the host innate immune response as a first line of defense to combat pathogenic microbes[1]. AMPs have a complex hierarchical structure formed by the self-assembly of simple building blocks like amino acids mediated by supramolecular interactions. The fundamental structural principle underlying all classes of AMPs is the ability of the molecule to adopt a shape in which clusters of hydrophobic and cationic amino acids are spatially organized in discrete sectors of the molecule, enabling them to induce a selective disruption of the bacterial cytoplasmic membrane[1]. In this context, we developed colloidal particles based on a novel polyurethane functionalised with a polyionic liquid. These particles mimic the patchy mesoscopic structural organization of AMPs.

A cationic hydrophobic liquid monomer (HDIL) was grafted from the amphiphilic polyurethane (NHP407) by a redox initiated aqueous heterophase polymerization. A cationic hydrophilic monomer (HIL) was sequentially added and polymerized (HPIL) to a hydrophobic polyionic liquid block (HDPIL). The chemical structure of the synthesized colloidal particles was elucidated from the recorded ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra and morphological characterization was analysed by cryo-TEM. It is clearly observed that the patchy colloidal particles of self-organized mesophases were formed by discrete nanodomains of charged ionic liquid moieties (Figure 1). The dark areas in the cryo-TEM image can be ascribeed to the ion pairs of cations and anions, resulting in a higher electron density compared to non-ionic polyurethane blocks. The aqueous dispersion of NHP407-g-(HDPIL-b-HPIL) has a *ζeta* potential of magnitude + 55 mV stemming from the quaternary ammonium moieties of the respective HDPIL and HPIL blocks. The minimum bactericidal concentration (MBC) determined by the broth microdilution method was as low as 3.9 µg/mL and 31.25 µg/mL *against S. epidermidis and S. aureus* respectively. The colloidal dispersion at ~15 µg/mL, reduced 99% of *S. aureus* viability within 30 minutes. The IC_{50} of the designed colloids on L929 fibroblasts was higher than the minimal inhibitory concentration determined on susceptible *S. aureus* and *S. epidermidis*, showing a selectivity index of 7.06 and 14.12 respectively. The focus of the future experiments is to have a precise control over the individual block length, which would pave a pathway for reaching a higher selectivity index.

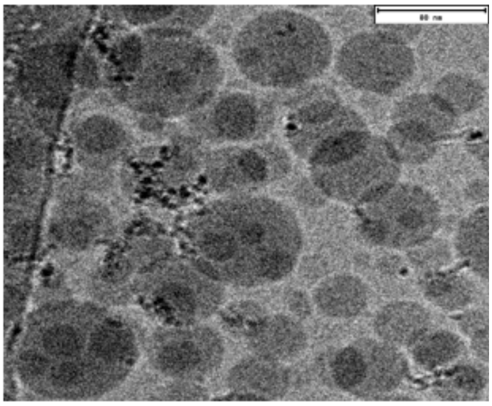

Figure 1. Cryo-TEM image of aqueous dispersion of NHP407-g-(HDPIL-b-HPIL).

Acknowledgment: The work was developed in the framework of the Hymedpoly project. HyMedPoly received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 643050

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OC30

THE FINAL FRONTIERS IN MODELING AND DESIGNING MOLECULARLY IMPRINTED POLYMERS

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Abstract

Despite ongoing experimental and theoretical progress, molecular imprinting remains a field of controversy in materials science in particular related to the question whether templating a polymer matrix is based on statistical effects, or whether this process may be considered the deliberately controlled entailment of specific binding sites for a particular template molecule. While a wealth of experimental papers since the seminal works of Wulff and Mosbach have been published indicating more - or sometimes less - selectivity, an absolute proof for this open question has not been shown to date.

In this presentation, a breakthrough approach will be shown to potentially answer this pertinent question once and forever. Teaming up with one of the leading groups on large-scale molecular dynamics (MD) simulations of complex systems, we have developed a simulation concept that for the first time provides an MD strategy for generating 'virtually imprinted polymers' (VIPs), testing such VIPs within a second set of MD simulations enabling 'virtual chromatography experiments', and – last but not least - applying local density of states (LDOS) calculations for the first time in classifying and selecting suitable functional monomers.

Within these truly fundamental studies, we introduce the first theoretical demonstration for molecular templating processes in atomistic detail for the example of virtually imprinted polymers for 17-β-estradiol, and demonstrate selective binding via virtual chromatography experiments even vs. its enantiomer, which is in accordance with previously obtained experimental results. The obtained simulation results unambiguously prove the existence of a distinct imprinting effect similar to the concepts commonly described in the MIP literature. Achieving selective retainment in a virtual imprinting/chromatography experiment and even generating virtual chromatograms clearly disproves the hypothesis that molecular imprinting is a statistical effect. Furthermore, we visualize for the first time that the presence of the target molecule during the imprinting procedure is mandatory, as the spatial structure of the selective binding sites determined by the arrangement of the functional monomers is crucial for entailing selective binding properties. In addition, a comprehensive strategy towards rationally screening and selecting suitable functional monomers from a library based on LDOS calculations complements this study.

In conclusion, the fundamental concepts discussed in this presentation provide a solid step towards truly predictive modeling of molecular imprinting strategies that could be expanded in future to almost any level of complexity.

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OC31

MICROFLUIDIC THERMAL SENSOR FOR DRUG DETECTION IN WHOLE BLOOD

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Introduction

Over the past few years, the combination of MIPs and the so-called heat-transfer method has led to the development of biomimetic sensor platforms for the detection of various compounds ranging from low-molecular weight targets such as neurotransmitters,[1,2] to bigger entities such as peptides and proteins.[3] Recently, the concept was extended from a laboratory device to a disposable, portable prototype that allows for point-of-care detection of neurotransmitters in whole blood samples.[4]

In this work, a disposable microfluidic flow cell was developed allowing the end-user to simultaneously detect five different drug molecules in whole blood samples. In addition, the methodology allows for differential measurements comparing the response of a sensitive MIP channel to that of a non-imprinted reference channel (NIP channel).

Methods

Microfluidic cells were made by casting hydrophilic poly-dimethyl siloxane (PDMS) onto 3D-printed polylactic acid (PLLA) molds. These flow cells were coupled to a single heater and a single fluid inlet, allowing blood samples to be administered passively through capillary force. Heat transfer measurements were performed in five active (coated with nano MIPs) and one reference channel (NIP) simultaneously.

Results & Discussion

A proof-of-principle experiment using the current microfluidic flow cell illustrates its potential for detecting small molecules (serotonin was used as a model target) in physiologically relevant concentrations in whole blood (Figure 1 left).[4] The concept can be readily extended towards the detection of so-called "designer drugs" in blood. As these compounds are continuously changed to avoid legal restrictions, little is known about the dangers associated with abusing these substances. A low-cost sensor that allows to detect multiple drug classes in blood in minutes, would allow first line healthcare workers to identify substance abuse and take appropriate measures to prevent overdose- related deaths. A microfluidic flow cell designed for this purpose that allows the end-user to measure up to five different drug-imprinted MIPs and a non-imprinted reference in real-time, is shown in the right panel of Figure 1.

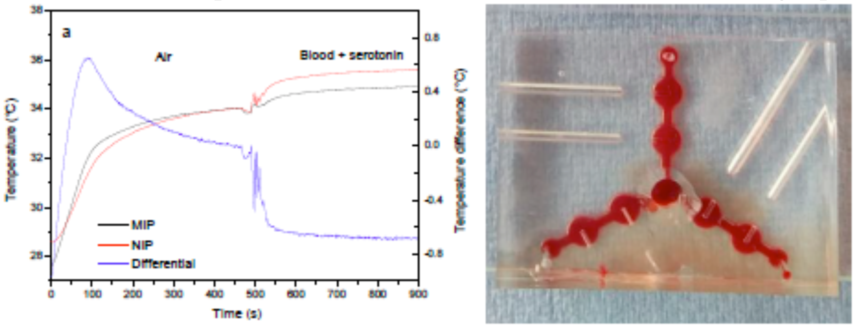

Figure 1: Proof-of-principle detection of neurotransmitters in whole blood (left panel) and the microfluidic flow cell for multi-drug testing (right panel)

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OC32

POLY(AMIDOAMINE)/PROTEIN CONJUGATES

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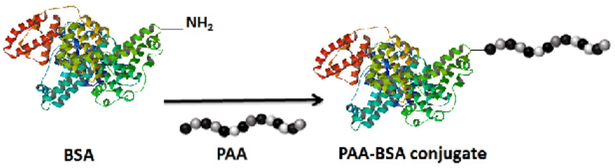
Abstract

In the past 20 years, bioconjugation between polymers and proteins has attracted significant attention to the pharmaceutical industry. Polymers have been used to improve the stability and lower the immunogenicity of proteins. However, efficient intracellular delivery remains a challenge and often restricts the use of proteins with an extracellular target. Poly(amidoamine)s [1] (PAAs) are pH responsive polymers and have been used to promote intracellular delivery of different biomacromolecules via interpolyelectrolyte complexes. We hypothesised that PAA/protein conjugates could potentially promote the cytosolic delivery of a therapeutic protein.



BSA and catalase were selected as model proteins. Poly(amidoamine)/protein conjugates [2] were synthesised using a "grafted to" approach, by hydrogen-transfer between the PAA's vinyl end groups and the NH_2 groups present on the surface of the protein. The conjugates were recovered by freeze-drying, purified by anionic exchange and size exclusion chromatography and were further characterised using different techniques (Table 1). Enzymatic assays indicated the conjugates displayed an esterase activity similar (C1) or reduced ~35% (C2) compare to BSA.

Table 1. Physicochemical characterization of the conjugates.

	M_n (Da)	M_w (Da)	Đ	D_h[a] (nm)	Đ[a]	ξ (mV)	BSA[b] (mg/mg)	NH_2[c] (%)
C1	140,700	208,900	1.5	$37.5_{\pm1.7}$	$0.47_{\pm0.02}$	$+15.4_{\pm0.4}$	$0.76_{\pm0.03}$	$15.9_{\pm0.8}$
C2	218,600	530,400	2.4	$75.1_{\pm1.8}$	$0.54_{\pm0.02}$	$+20.2_{\pm1.0}$	$0.43_{\pm0.09}$	$24.8_{\pm1.0}$
BSA	102,500	120,200	1.2	$5.9_{\pm0.3}$	$0.31_{\pm0.01}$	$-11.7_{\pm1.9}$	-	-
PAA	7,000	13,200	1.9	$73.5_{\pm10.7}$	$0.47_{\pm0.07}$	$+44.8_{\pm2.3}$	-	-

M_n: number average molecular weight. M_w: weight average molecular weight. Đ: polydispersity. M_n, M_w and Đ were determined by SEC relative to protein standards for the conjugates and BSA and relative to PEG standards for PAA. D_h: hydrodynamic diameter. ζ: zeta potential. [a] Determined by DLS. [b] mg of BSA per mg of conjugate. [c] % of primary amine modified following conjugation to PAA. Mean±SD, n=3.

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OC33

TRACEABLE THIOL-SENSITIVE NANOGELS FOR INTRACELLULAR CONTROLLED DRUG RELEASE

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Abstract

The design of selective drug delivery nanocarriers is a promising approach to release active agents in cellular districts, counteracting central nervous system disorders[1-2]. However, the hydrophilic drugs loading within nanocarriers presents the main drawback of the unwanted rapid diffusion, limiting the pharmacological activity in the target site. To overcome this aspect, we proposed the design of double conjugated nanogels where the drug was linked to the network through a thiol-sensitive bond. These nanodevices were composed by polyethylene glycol (PEG) and polyethyleneimine (PEI) both chemically functionalized: PEG was linked to rhodamine (RhB, used as drug mimetic) through a disulfide bond and PEI modified with Cy5 dye using click chemistry to ensure the nanogel traceability (Fig. 1A). The selectivity as drug delivers is related to the S-S bond that can be disrupted by glutathione or cysteine cell component, commonly present in cytosol, releasing rhodamine as loaded. We tested the rhodamine release in glutathione solution, representative of its human body concentration, obtaining a faster release than in PBS. Moreover, according to the importance of target drug carriers in the damaged central nervous system exploiting the phagocytic activity of microglia, we tested our nanogels in microglia culture. The colocalization of Cy5 and rhodamine signals showed that the mimetic drug was internalized by cells. After 4 days, the delocalization of rhodamine signal than Cy5 (Fig. 1B) confirmed its release from nanogel, within cytosol[3], suggesting that these nanogels were able to carry hydrophilic molecules towards specific target and release them selectively.

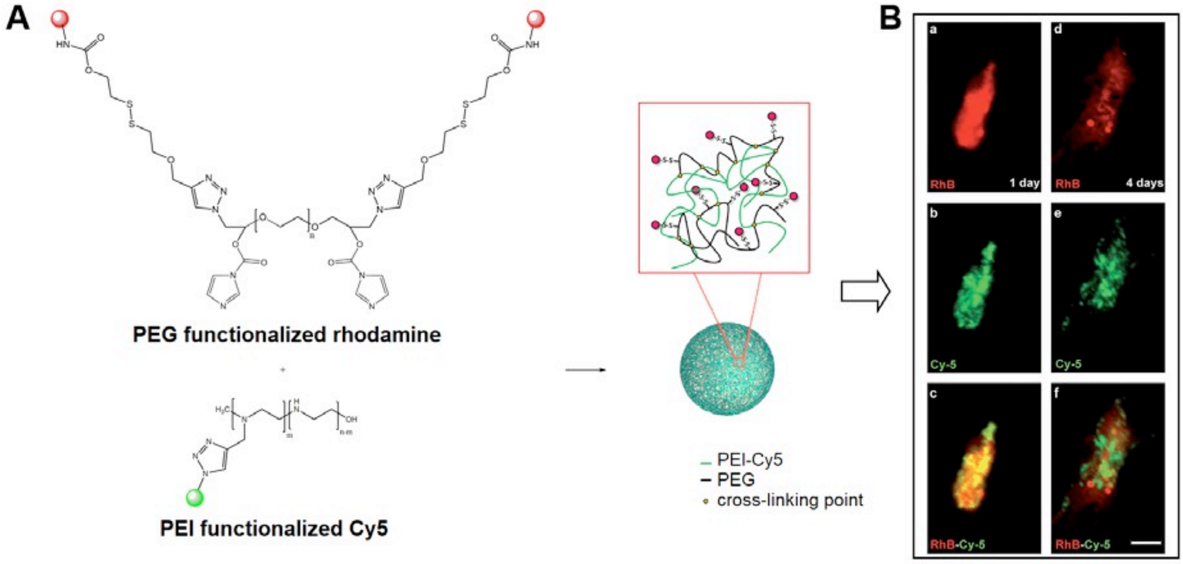

Fig. 1. A: Scheme of functionalized nanogels, with rhodamine (red dots) and Cy5 (green dot). B: Nanogel internalization in microglia and signal delocalization of rhodamine (red) and Cy5 (green) after 4 days.

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OC34

ISOMERISM-COMPETITIVE VECTORS TOWARD BIOMEDICALLY RELEVANT MIMICRY THROUGH RADICAL CYCLOCOPOLYMERIZATION

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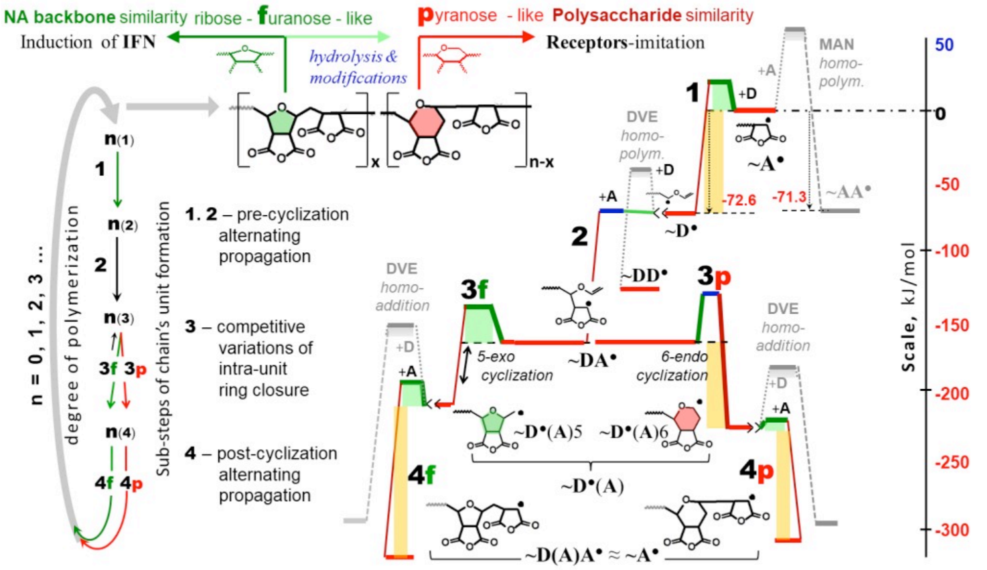
Abstract

Radical copolymerisation of maleic anhydride (**MA**) is prominent platform for diverse biomimetics development. Involvement of the graft-reactive anhydride centres into a polymeric backbone significantly facilitates mimetic-aimed diversiform side-chain modifications. However, key basis for permissible scopes of a desired macromolecular mimicry could be predetermined directly under copolymerisation process in relation with nature of main-chain-forming comonomers and the reactions controlling. In the current report we focus on the antiviral-relevant mimicry of polymeric backbone produced by MA cyclocopolymerization with divinyl ether (**DVE**). Although the resulted DVE-alt-MA (1:2) copolymers have been widely applied as precursors for outstanding family of interferon (**INF**) inductors, immune modulators, and multimodal antiviral protectors[1], the detailed mechanisms and factors for regulating the bio-relevant furane/pyran-like isomerism of intra-chain units were far from clear understanding. We investigated this aspect via quantum chemical modelling the competitive routes of chain propagation and ring closure sub-steps in view for careful precise estimation of kinetic (E_a) and thermodynamic (ΔH_r) factors – the crucial regulating drivers (in part, see the energetic map of general sub-step routes).



The obtained data allow quantitative analysis of relative probabilities for mainly possible and side-expected sub-reactions of chain units' formation with evident kinetic priority of "furane" (5-exo) ring closure, but reverse thermodynamic favour of "pyrane" (6-endo) alternative. The adequate modelling methodology selection and application; theory – experiment verification; practical recommendations for "f/p" isomerism regulation (with detailed stereo-selectivity) for antiviral mimicry are discussed.

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OC35

SELF-CLEANING POLYMER MEMBRANES BY CHEMICAL CONJUGATION OF DIGESTIVE ENZYMES

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Abstract

Membrane technology is a modern scientific field with a variety of current and future applications in water purification, wastewater treatment, medicine (*e.g.* hemodialysis), as well as in the food, biotechnological, and pharmaceutical industries. An enormous problem in all areas is called *membrane fouling*: the unwanted clogging of the pore structure with organic and inorganic substances, biomolecules, or even microorganisms.

The required cleaning of a fouled membrane is associated with the use of aggressive and environmentally harmful chemicals, as well as significant costs and efforts in terms of process control and occupational health. If applied over long time, oxidative agents also lead to an erosion of the material up to the point where membrane must be exchanged. Numerous approaches have been described in the literature to counter the fouling problem. By immobilizing enzymes on the membrane surface, a new system was created which is able to enzymatically degrade adsorbed substances, and thus to generate a **self-cleaning surface** (Fig. 1a). This approach combines a passive fouling reduction by modifying the membrane surface and an active degradation of fouled substances[1,2].

In this study, **covalent immobilization of digestive enzymes** consisting of proteases, amylases, and lipases on polyvinylidene fluoride (PVDF) resulted in **biocatalytic active polymer membranes** with self-cleaning capability. Activation of enzymes and therefore **"switching on"** the membrane system was achieved by adjusting pH and temperature leading to an active degradation of fouled substances on its surface (Fig. 1b). Fouling and self-cleaning experiments with solutions of protein, lipid, carbohydrate, and a mixture were performed and resulted in high regeneration of water permeation flux. Furthermore, long-time performance, stability, and filtration of real samples including river water, and household sewage were tested. Comprehensive membrane characterization was conducted by investigation of immobilized enzyme concentration, enzyme activity, mercury porosimetry, XPS, SEM, and finally, zeta potential, as well as water contact angle measurements.

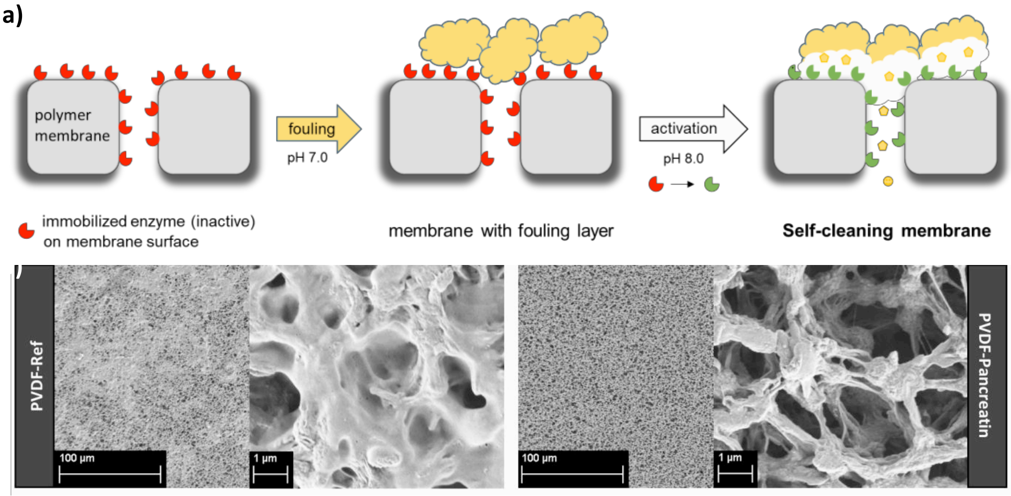

Fig. 1: *(**a**) Schematic principle of self-cleaning membranes. Digestive enzymes covalently immobilized on the mem- brane surface are activated by changing the buffer pH within a range of 7.5-8.5 and digest the fouling-causing substrates. (**b**) SEM images of PVDF reference membrane (left) and enzyme modified PVDF (right) after fouling and self-cleaning experiment using protein solution.*

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OC36

NANOPARTICLE-SUPPORTED POLYMER BRUSHES FOR TEMPERATURE-REGULATED GLYCOPROTEIN SEPARATION

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Abstract

Glycoproteins play an important role in many biological processes, and are frequently used as biomarkers for different diseases. Effective separation of glycoproteins is one important step in many research areas and diagnostics. In this work, we synthesized a series of nanoparticle-supported boronic acid polymer brushes for affinity separation of glycoproteins (Figure 1). The polymer brushes were prepared by surface-initiated atom transfer radical polymerization of glycidyl methacrylate and *N*-isopropylacrylamide, followed by stepwise modification of the pendant as well as the end functional groups to introduce the boronic acid moieties through Cu(I)-catalyzed alkyne-azide cycloaddition reaction. We investigated the impact of the polymer structure on glycoprotein binding under different pH and temperature conditions, and established new methods that allow glycoproteins to be more easily isolated and recovered with minimal alternation of solvent composition. Our experimental results suggest that for separation of glycoproteins, terminal boronic acids located at the end of polymer chains play the most important role. The thermo-responsibility of the new affinity adsorbents, in addition to the high capacity for glycoprotein binding (120 mg ovalbumin/g adsorbent), provides a convenient means to realizing simplified bioseparation not only for glycoproteins, but also for other carbohydrate-containing biological molecules.

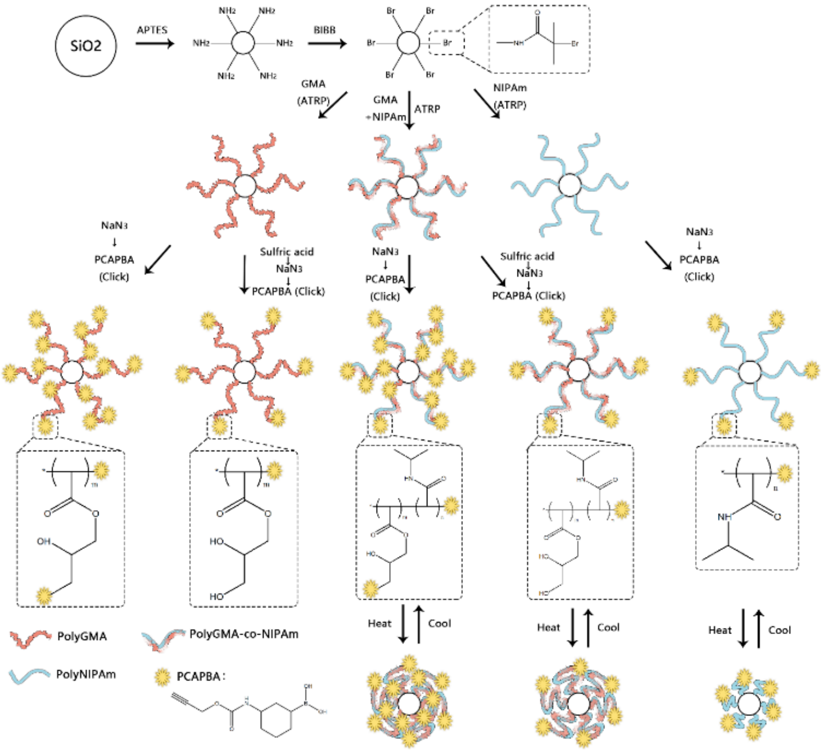

Figure 1. Synthesis of boronic acid-functionalized polymer brushes on silica nanoparticles.

OC37

ANALYSIS OF BIOPOLYMERS BY ION MOBILITY-MASS SPECTROMETRY (IM-MS): A STRUCTURAL STUDY TOWARDS THE CHARACTERISATION OF POLYMER-DRUG CONJUGATES

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Polymers are complex molecules with a wide range of physicochemical properties. They are developed for use in many industrially relevant areas including biotechnology, nanotechnology, materials science, petrochemicals and as biomaterials for the pharmaceutical industry. The development of polymer-drug conjugates (PDCs) is experiencing a significant increase with the primary aim of improving drug delivery. Some of these conjugates include the use of nanoparticles such as polypeptides that can increase the solubility of PDCs for a given route of drug administration. Carefully designed conjugates allow control over drug loading and can enhance the ability of the conjugate to cross a cell wall. Direct infusion electrospray ionisation mass spectrometry is a potentially useful approach with which to separate heterogenic polymers and the related hyphenated technique of ion mobility-mass spectrometry (IM-MS) can provide even more discrimination as it adds an orthogonal dimension of separation.

Mass spectral data along with collision induced dissociation (CID) experiments were acquired on a Waters Synapt G2-S instrument for a variety of polypeptides and synthetic polymers including poly-DL-alanine as the main product of interest. Two different ionisation techniques were used in the scope of this study, namely nanoelectrospray ionisation (nESI) and matrix-assisted laser desorption ionisation (MALDI) to produce multiply and singly charged ions respectively. Multiply charged polymer ions were observed with a variety of polymeric families presenting in charge states 1+ and 2+. Various IM-MS instruments were then used to further separate these ions and obtain collision cross section (CCS) values and distributions as a function of degree of polymerisation including a home-made variable temperature IM-QToF-MS instrument. The change in structure of the gas-phase polymeric ions was also investigated as a function of the buffer conditions along with the amount of activation energy supplied to the system.[1] This work provides an exemplar analytical strategy which could then be applied to a wide range of PDCs and more specifically to PDCs that include polypeptides as structuring polymers.

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OC38

CORE-SHELL SWITCHABLE THERMORESONSIVE POLYURETHANE BASED COLLODIAL PARTICLES WITH INTRINSIC ANTIBACTERIAL PROPERTIES

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Polymer colloids that have unique ability to switch their core and shell in response to temperature are interesting candidates for potential biomedical applications[1]. Herein, we report for the first time core-shell switchable thermoresponsive colloidal particles based on polyurethane grafted (poly(N-isopropylacrylamide)-b-polyionicliquid) [NHP407-g-(PNIPAM-b-PIL)] copolymers.

N-isopropylacrylamide was grafted from an amphiphilic thermoresponsive polyurethane backbone (NHP407)[2] via redox initiated aqueous heterophase polymerization and a hydrophilic ionic liquid monomer was sequentially added and polymerized. ^{1}H-NMR spectra of NHP407-g-(PNIPAM-b-PIL) (Fig. 1) recorded in D_2O as function of temperature revealed interesting insights regarding the molecular mechanism of lower critical solution temperature (LCST) and upper critical solution temperature (UCST) phase behaviour of the respective blocks and mechanism of self-assembly in water.

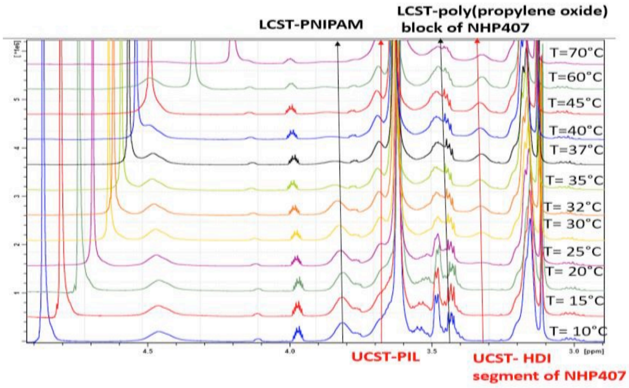

Fig. 1: ^{1}H-NMR spectra of NHP407-g-(PNIPAM-b-PIL) as function of temperature, recorded in D_2O

At 25°C, the appearance of the narrow peak signals at 3.68 ppm highlighted the UCST phase behaviour of the cationic hydrophilic PIL block. The intensity of the chemical shifts at 3.68 and 3.18 ppm increased with temperature, whereas the chemical shifts at 1.79 ppm and 2.4 ppm from the vinyl backbone of PIL block remained constant. This indicated that below 25°C, the PIL block remained buried in the aggregated micelles due to the electrostatic interactions with the carbonyl group of the PNIPAM block.

The onset of the LCST phase behaviour at 30°C of the poly(propylene oxide) block of NHP407 was evident from broadening of the hyperfine splitting in 3.5 to 3.45 ppm region caused by its reduced mobility. The disappearance of the chemical shift at 3.82 ppm associated with the (CH_3- C$\underline{H}$-CH_3) of the grafted PNIPAM block at 37°C indicated the collapse of the polymer chains as result of the LCST transition. Moreover, at 37°C, due to the synergistic effects of the LCST and UCST phase behaviour of the respective blocks, there was a rearrangement of the core-shell structure of NHP407-g- (PNIPAM-b-PIL), where the hydrophilic PIL block migrated to the surface of the aggregates forming the shell. The uniqueness of the NHP407-g-(PNIPAM-b-PIL) colloidal particles lies in its intrinsic bactericidal properties. In fact, the UCST phase transition of the cationic hydrophilic PIL block paved the way for electrostatic interactions with the negatively charged teichoic acid surface groups of Gram- positive bacteria, whereas the hydrophobic part of the aggregates disintegrated the structural integrity of the bacterial membrane. The Minimum Bactericidal Concentration was determined to be as low as
16 µg/mL and 31.25 µg/mL against *S. epidermidis* and *S. aureus*, respectively.

Acknowledgment: HyMedPoly received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 643050.

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OC39

BIO-SORBENTS FOR PHOSPHATE REMOVAL AND RECYCLING

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Abstract

Phosphorus is an essential element for all living organisms and an important nutrient used in fertilisers. However, its sources are limited to only few places in the world, resulting in issues around food security in Europe, that depends almost exclusively on phosphate rock imports to cover its needs.

On the other hand, excessive use of fertilisers results in eutrophication of surface water bodies with vast environmental and financial impacts.

Bio-polymer based sorbents for phosphate capture have been previously reported,[1,2] however, there is a single crosslinked hydrogel-based sorbent reported to date.[3] Here, we will present a new method of bio-sorbents preparation, improving cross-linking density and facilitating their chemical post-modification. The new technique is simpler and faster than the conventional one and thus amenable to scale-up and industrial applications. We will report on the preparation of three generations of polymers, differing in cross-linker type, percentage and post-modification, and their effectiveness in phosphate capture and recycling.

Our method resulted in phosphate adsorption capacity vastly superior to previous reports, even when compared to methods using metal ions, which prohibit reuse of the sorbent and recovered phosphate (Fig. 1). The sorbents were tested in batch and flow system and the effect of solution pH and concentration will be presented. Phosphate recovery of up to 99% and sorbent reusability of at least 10 adsorption-desorption cycles will also be demonstrated.

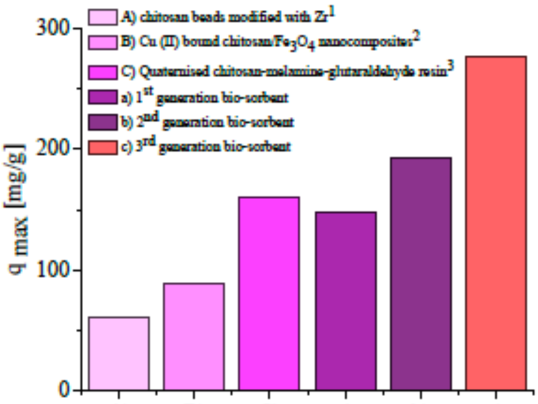

Figure 1. Maximum phosphate adsorption capacity calculated for: A)-C) literature data, a)-c) bio- sorbents prepared in this study.

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OC40

SELF-PERFORATED HYDROGEL NANOMEMBRANES (SPHyNs) FACILITATE STRUCTURAL ANALYSIS OF PROTEINS BY ELECTRON CRYO-MICROSCOPY

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Abstract

Here we present a method to improve the specimen preparation of membrane proteins for electron cryo-microscopy (cryo-EM) by polymeric nanomembranes.[1] To determine the structure of specimens by cryo-EM, the samples are embedded in a thin layer of ice spanning the holes of a holey carbon film. The preparation of vitrified specimens from detergent-solubilized membrane proteins is particularly challenging. The detergent reduces the surface tension of the aqueous solution, which results in the depletion of the biomolecules from the thin water film (Figure 1, A).

We fabricate polyglycerol nanomembranes by cross-linking of thiolated polyglycerol dendrimer films on gold which self-perforate upon transfer to a regular holey carbon transmission electron microscopy grid. The self- perforated hydrogel nanomembranes (SPHyNs) stabilize the thin layer of ice spanning the holes of the carbon film and at the same time prevent the depletion of the proteins from the hole. The hydrogel membrane interacts minimally with the proteins whereby the covering of the carbon film prevents the adsorption of proteins on the carbon substrate (Figure 1, B).

We used two eukaryotic membrane protein complexes to show the impact of the modified substrate on specimen preparation. SPHyN modified holey carbon substrates made it possible to calculate a 3D reconstruction of complex I from *Y. lipolytica* and *Polytomella* ATP synthase from considerably less particles than previously reported.[2]

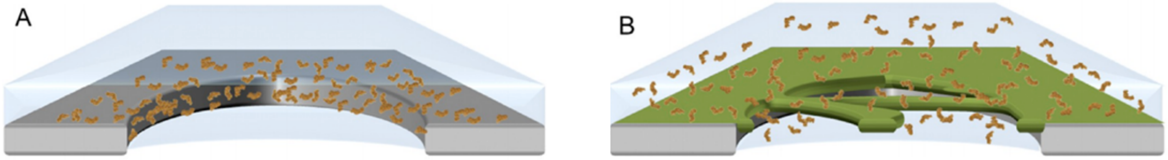

Figure 1: Distribution of membrane proteins on holey carbon film without (A) and with SPHyNs (B). SPHyNs stabilize the thin water layer and cover the carbon film, which prevents the depletion of the proteins from the holes and minimizes the adsorption to the carbon substrate.

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OC41

SIMPLE UV-VIS STUDY OF POLYMER-MOLECULE SUPRAMOLECULAR INTERACTIONS: ASSESSMENT OF DIFFUSION COEFFICIENTS AND CRYSTALLINITY IN POLYMER FILMS

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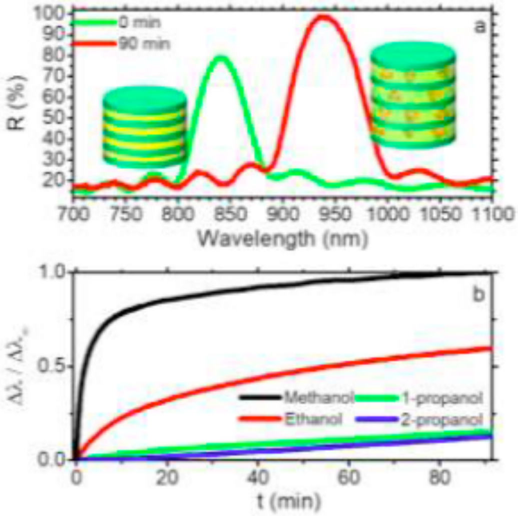
Abstract

Polymer distributed Bragg reflectors (DBRs) are multilayered structures made of transparent media having different refractive index. The interaction between light and these dielectric lattices provides diffraction patterns, which can be visible even by the naked eye as bright iridescent color. In this work we demonstrate that when a small molecule intercalates within such structures, it is possible to describe the interaction occurring between the polymers and the small molecule from a simple analysis of the UV-VIS optical response of the DBRs.

To demonstrate this capability, we use DBRs made of commodity polymers such as polystyrene and cellulose acetate to evaluate molecular diffusion coefficients in the polymer matrices. As an example, Fig.1a displays the reflectance of a DBR before and after exposure to methanol vapors, which shows a maximum assigned to the DBR diffraction peak at 840 nm (green), which shift to ~940 nm after 90 min of exposure (red). From the dynamics of the shift, it is possible to retrieve the optical sorption-curves reported in Fig.1b for methanol and other alcohols, which deliver information on the analyte diffusivity within the polymers, and in turn depends on free-volume, polarity, weak-bonding, and molecular size.[1-2] Then, we can retrieve, for instance, diffusivity values of ~10^{-8} cm^2/min for methanol, in full agreement with gravimetric data.[3-4] Moreover, the DBR response allows label-free selectivity, which nowadays requires long time sampling, separation processes and analyses.



We will also show that when poly (p-phenylene oxide), which is well known to form crystalline clathrates when guest molecules intercalate in the amorphous phase,[5] is used as active medium in the DBRs, it is possible to esteem its crystallinity degree via simple UV-VIS spectroscopy.

Because of the available DBR mass-scale fabrications and integration with packaging,[6] we believe that this method will be industrially relevant for the *in-situ* assessment of diffusive processes of degradation by-products, humidity or even oxygen in smart packaging systems for foods and optoelectronic devices

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OC42

BIOINSPIRED THIOL-TETHERED POLYMER FOR WATER APPLICATION

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Abstract

Easy detection of pollutants (Hg^{2+}, As, F^- etc.) in groundwater via naked-eye has become a global concern as it plays a significant role in health and environmental issues. In view of that, herein, we propose a highly selective and sensitive chemosensors with thiol structure for geogenic pollutants recognition/detection in practical application. The addition of pollutant ion to the receptor causes a dramatically observable colour change instantaneously in aqueous medium. The proposed sulfur based chemosensor has apparent advantages over other methods, such as high sensitivity, selectivity over other ions, operational simplicity, on-site detection, economical method, greener approach and response within a fraction of second. The process has also proved its utility for the practical purpose of detection in real-life and practical applications via visible colour change. The sensor is extremely easy to apply, as it involves just addition of preserved sample solution to observe the colour inference and is applicable for anyone, whether skilled or not.

POSTER CONTRIBUTIONS

P1

SYNTHESIS AND STRUCTURE OPTIMIZATION OF BIOCOMPATIBLE STAR CO-POLYMERS USED AS EFFECTIVE NANOPARTICLE PLATFORM FOR VACCINE DELIVERY

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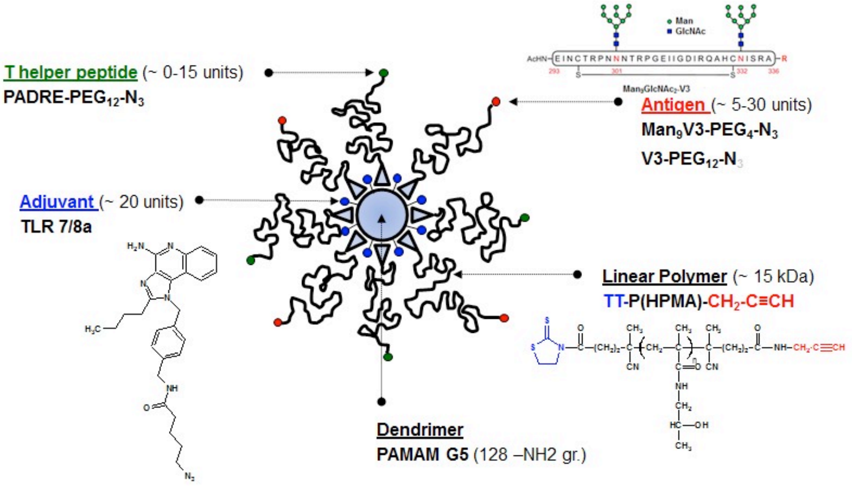
Abstract

Active immunization by means of minimal peptide immunogens represents a promising vaccination strategy in the treatment of numerous infectious diseases. However, direct application of low-molecular-weight peptide immunogens elicits only low level responses as they are often poorly soluble in aqueous solutions and show a relatively low avidity to surface receptors of immune cells. To overcome these issues, we have developed a nanoparticle delivery platform based on biocompatible star co-polymer enabling covalent attachment of multiple copies of peptide immunogens. The star co-polymers, designed and synthesized in this work, were composed of poly[*N*-(2-hydroxypropyl)methacrylamide] (PHPMA) hydrophilic arms extending from a poly(amidoamine) (PAMAM) dendrimer core. Number of PAMAM primary amino groups (i.e. dendrimer generation) as well as the length of PHPMA polymer chains have been optimized to achieve the star co-polymer with an appropriate hydrodynamic size (~ 10-20 nm in radius), maximal possible number of PHPMA grafts and acceptable recovery (> 50%). The PHPMA arms were terminated with the propargyl groups enabling well-defined attachment of azide group-containing peptide immunogen (HIV-1 V3 loop peptide sequence) as well as azide group-modified T cell helper epitope (PADRE peptide). Furthermore, unreacted primary amino groups on the dendrimer core were used for the conjugation with the imidazoquinoline-based immuno-stimulant (Toll-like receptor 7/8 agonist). We hope that our study will contribute to the development of universal and chemicaly tunable nanoparticle platform enabling site-specific delivery of peptide antigens.



This work was financially supported by the Czech Science Foundation (project 16-14957Y) and by the Ministry of Education, Youth and Sports of the Czech Republic within the National Sustainability Program II (project BIOCEV-FAR LQ1604).

P2

BIOBASED GRAPHENE OXIDE/POLYBENZOXAZINE AEROGELS FOR HARD TISSUE SCAFFOLD

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Abstract

Graphene aerogel with high porosity and ultra-light weight has been prepared to exploit its wide applications as hard tissue scaffold. In this study, a new approach to synthesize highly porous graphene based aerogel was developed. The graphene oxide with a lot of carboxylic groups was crosslinked by hydrothermal method with amino functionalized reduced graphene oxide. The morphology and structure of obtained samples were observed by scanning electron microscopy (SEM) and micro-tomography (μCT). Functional groups and chemical bonds were investigated by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Brunauer− Emmett− Teller (BET) surface areas of the samples were measured by nitrogen adsorption-desorption isotherms.

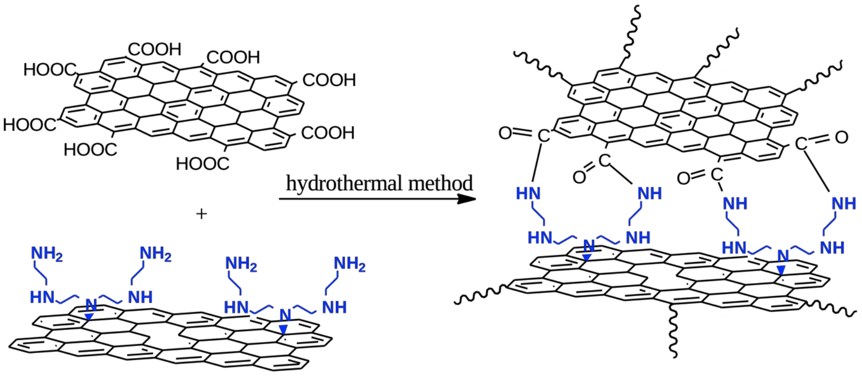

Fig. 1 Synthesis of graphene oxide aerogel

Bio-based polybenzoxazine (PBO) was synthesized from eugenol, aniline and formaldehyde using the solventless method. The bio-based PBO was characterized by proton Nuclear Magnetic Resonance spectroscopy (^{1}H-NMR), FTIR and UV-VIS.

The new idea of this study is to investigate the biocompatibility of novel biobased PBO-graphene aerogel by evaluating their effect on bone cell proliferation and function. Furthermore, the physical and mechanical properties were investigated in order to evaluate the usage of this new material for a bone tissue engineering scaffold.

This work was supported by a grant of Ministery of Research and Innovation, CNCS - UEFISCDI, project number PN-III-P4-ID-PCE-2016-0818, within PNCDI III.

P3

POLYSACCHARIDE-BASED NANOHYDROGELS AS DRUG CARRIERS

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Abstract

Natural and biocompatible polysaccharides, hyaluronic acid (HA) and gellan gum (Ge), were derivatized with hydrophobic moieties (cholesterol or riboflavin) in order to obtain amphiphilic polymers able to self-assemble in water leading to the formation of nanosized structures, named nanohydrogels[1-3] (NHs) (Fig. 1).

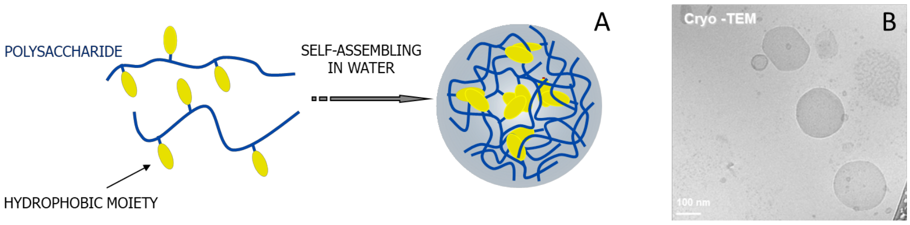

Fig. 1: Self-assembling of derivatized polysaccharides leading to the formation of NHs (A); Cryo-TEM images of HA-based NHs (B)

These systems couple the features of both nanoparticles, as nano-dimensions, and hydrogels, such as soft consistency, high amount of water, and biocompatibility. Moreover, all developed systems showed a high capability to load model drugs, both hydrophilic[4] and hydrophobic ones[5], and also proteins[2], without losing their activity. In the case of hydrophobic molecules, NHs act as solubility enhancers, increasing the apparent water solubility and allowing to obtain water-based formulations. Several derivatives were synthesized and characterized, and a new method to obtain simultaneously the formation, the sterilization and the drug loading into NHs was developed and patented[6].

All NHs were tested for their cytocompatibility on a series of cell lines, showing a complete safety up to 0.5 mg/ml. Several NHs formulations obtained with model drugs, such as antibiotics[4], anti-inflammatory[3] and anticancer drugs[5], were prepared and optimized; their activities were tested in vitro and in vivo, and in all cases an improvement of the therapeutic activity was observed. In Fig. 2, the results obtained on HeLa intracellular infections caused by S. Aureus and P. Aeruginosa treated with free levofloxacin (LVF) or NHs-loaded levofloxacin (LVF-NH) are reported.

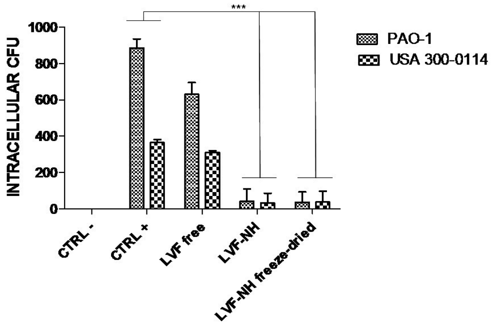

Fig. 2: Activity data of LVF and LVF-NH against intracellular P. aeruginosa (PAO-1) and S. aureus (USA 300-0114)[4] infections.

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P4

BIOMIMETIC PLATFORMS FOR SELECTIVE ELECTROCHEMICAL DETECTION OF COCAINE IN STREET SAMPLES

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Abstract

Electrochemical methods have gained increasing interest for the detection of illicit drugs, due to their rapidity, simplicity and low cost[1]. The development of sensing systems based on the combination of molecular imprinted polymers (MIP) with electrochemical transduction represents a promising approach for sensitive and selective detection of drugs in complex matrices[2]. Among the preparation methods for MIP, electropolymerization is a simple and convenient way, allowing to easily control film thickness and obtain thin, adherent films in one-step, directly on the surface of the transducer.

We present the development of the first amperometric sensor based on MIP for direct detection of cocaine in street samples. Monomers with high recognition ability for cocaine were selected by computational modelling and deposited directly on the surface of graphene-modified electrodes via electropolymerization. Firstly, poly(*p*-aminobenzoic acid) and poly(*o*-phenylenediamine) layers were employed in voltammetry studies and compared in terms of binding affinity and electrochemical response towards cocaine. Based on these results, *p*-aminobenzoic acid was further selected as monomer for MIP synthesis.

It was shown that the integration of nanoparticles in MIP materials has the benefit of enhancing the number of accessible complementary cavities and the fast equilibration with the analyte[3]. Thus, palladium nanoparticles (PdNPs) were employed and electrodeposited on the surface of graphene-electrodes prior to monomer polymerization by applying a fixed potential for 60s. Afterwards, MIP layers were prepared by cyclic voltammetry in a solution containing *p*-aminophenolic acid and cocaine in PBS pH 7. After extraction cavities were obtain with recognition ability for cocaine. Experimental parameters related to ratio and concentration of monomer and template, PdNPs deposition time, extraction solution and time, rebinding time have been optimized.

Acknowledgements:
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P5

TGA-GC-MS CHARACTERIZATION OF MAGNETIC POLYMERIC NANOPARTICLES FOR PHOSPHOPEPTIDE ENRICHMENT

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Abstract

Protein phosphorylation investigation currently represents an important field of method development. Direct analysis of phosphopeptides in a complex mixture is not feasible, due to the low abundance of phosphopeptides and the suppression caused by the more abundant non-phosphorylated peptides during the MS analysis. Accordingly suitable enrichment and selective systems is highly required. In this frame, IMAC (Immobilized Metal Affinity Chromatography)[1] still represents the most frequently used technique to enrich phosphopeptides. Positively charged metal ions can be immobilized by different chelators, such as the traditional chelating agents nitrilotriacetic acid and iminodiacetic acid (IDA), among others.

In this context, a new functional multishell magnetic material for IMAC enrichment of phosphopeptides was produced by a multistep procedure (Fig. 1) employing the "grafting from" approach by the activator regenerated by electron transfer−atom transfer radical polymerization (ARGET-ATRP) technique, to obtain Fe_3O_4@silica@GMA nanoparticles.

The prepared material was extensively characterized both from the structural point of view by SEM analysis and for the compositional point of view by thermogravimetry alone and coupled with a gas chromatographic separation and a mass spectrometric detection (TGA-GC-MS). Classical techniques require the detachment from the substrate of the organic part causing major structural modifications.

On the contrary, by TGA-GC-MS each step of the organic decoration of the silica particles was characterized directly on the sample without any pre-treatment of detachment from the substrate. Fe_3O_4@silica@GMA nanoparticles were successfully tested for the enrichment of a bovine serum albumin in mixture with casein.

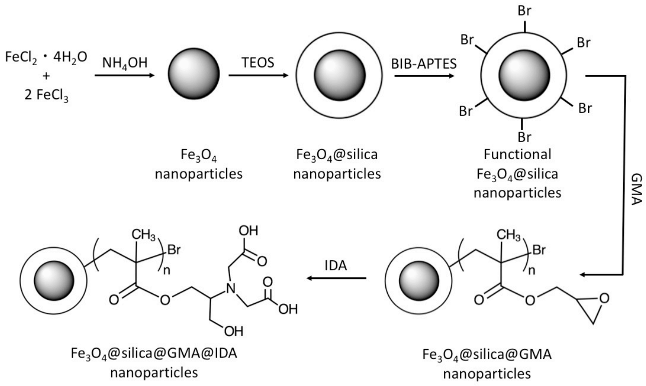

Figure 1. Magnetic polymeric nanoparticles preparation scheme.

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P6

NANOCARRIERS MODIFIED WITH POLYETHYLENE GLYCOL FOR ANTICANCER DRUG DELIVERY

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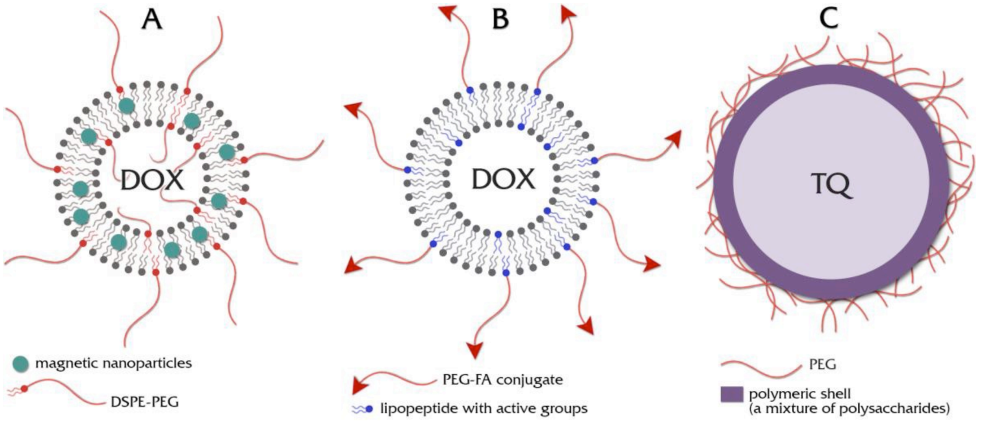
The design of antitumor drug delivery systems (DDS) is a challenge of biomedicine. Conventional DDS have a number of disadvantages, including low stability in the blood stream. Recently, to enhance DDS longevity, various modifications have been proposed. Polyethylene glycol (PEG) is known as one of the most frequently used polymers for DDS stabilization due to its biocompatibility, solubility, hydrophilicity and high chain flexibility. The aim of the current study was to develop nanocarriers (NCs) modified with PEG and to evaluate their *in vitro* cytotoxicity in 2D (monolayer culture) and 3D (tumor spheroids) models.

Three types of NCs have been modified with PEG by different techniques. Doxorubicine (DOX)-loaded magnetic liposomes (A) were developed to provide controlled drug release under a low-frequency magnetic field. To modify the liposome surface, PEG was added at the thin film formation stage by mixing lipids with DSPE (1,2-Distearoyl-sn-glycero-3-phosphoethanolamine)-PEG conjugates. For active targeted drug delivery, DOX-loaded cationic liposomes associated with folic acid (FA) vector molecules (B) have been developed. In this case, to provide covalent PEG binding to FA and orientation of the obtained PEG-FA complex only at the liposome outer surface, an original "click"-chemistry approach has been proposed. Finally, polymer NCs based on polyelectrolyte complex of oppositely charged polysaccharides, namely xanthan gum and DEAE-dextran (C), have been proposed for encapsulation of lipophilic drug thymoquinone (TQ). For this purpose, previously prepared NCs were coated with PEG by adsorption. All NCs were characterized in terms of their physical-chemical properties (mean size, ζ-potential, storage stability etc.) and in vitro cytotoxicity. In this study, MCF-7 (human breast adenocarcinoma), U-87 MG (human brain glioma) and C6 (rat brain glioma) cells were used. The NCs accumulation and localization in 2D and 3D models were evaluated by confocal microscopy and flow cytometry, while MTT-test was used for cytotoxicity assay. Thus, three different NCs were successfully modified with PEG and their cytotoxicity was evaluated *in vitro*.



This study was supported by RFBR (grant 18-34-00919 in part of folate-associated liposomes, grant 17-54-33027 in part of magnetic liposomes and grant 18-04-01087 in part of tumor spheroids) and RSF (grant 18-19-00718 in part of polymeric nanocontainers).

P7

FAST CAPTURE AND EFFECTIVE DEACTIVATION OF BACTERIA BASED ON AG AND POLYETHYLENIMINE MODIFIED NANOPARTICLES

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Abstract

Bacterial infection is one of the major problems for human health. To prevent outbreak of bacteria-caused diseases, early diagnosis of bacterial pathogen and effective deactivation of pathogenic microorganisms are in urgent need. In this work, we developed a new method that can effectively deactivate bacteria captured by Ag and polyethylenimine (PEI) functionalized particles. The nanoparticles were synthesized using micro-emulsion polymerization of glycidyl methacrylate (GMA).[1] The epoxide groups on the surface of the PGMA were reacted with high molecular weighted PEI to introduce cationic amine groups. The amine groups on the nanoparticle surface enhanced the stability of particle suspension (Fig. 1a). The PEI moieties in the particle shell were used as a complexation agent for the deposition of Ag nanoparticles.[2] Thus, the Ag modified PEI shell supported on PGMA nanoparticles could be used to capture and deactivate negatively charged bacteria (Fig. 1b, c). In addition to deactivation of bacteria, the Ag-polymer nanocomposite are also being developed as surface enhanced Raman scattering probes to detect pathogenic bacteria.

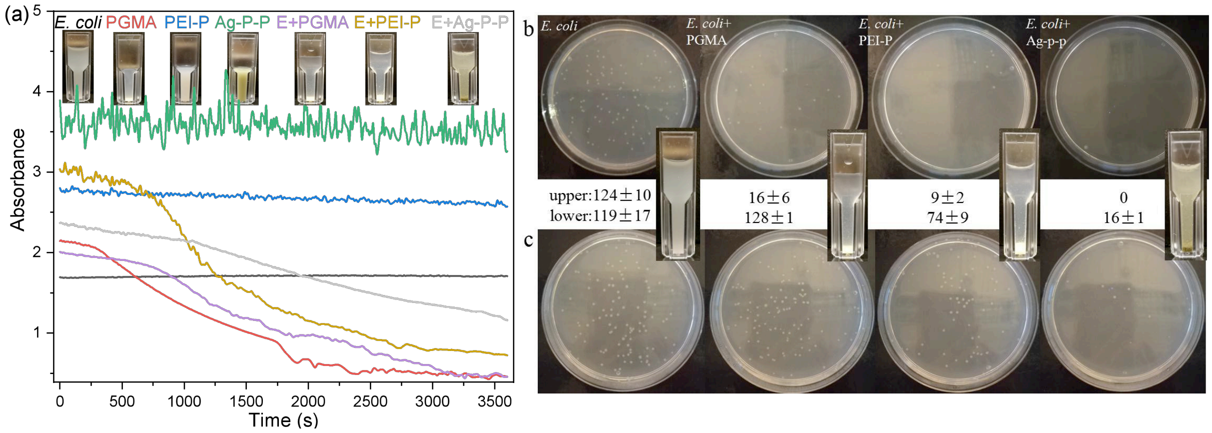

Figure 1. (a) Stability of *E. coli*, particles and a mixture of *E. coli* and particles monitored by measurement of absorbance of visible light at 600 nm. After standing for 1 h, 1 mL of the upper (a) or the lower phase (c) was diluted 10^6 times. The diluted phases (200 µL) were then cultured at 37°C overnight.

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P8

NEW BUILDING BLOCKS FOR INVESTIGATION OF "BIO-SWITCHABLE" SURFACES

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Abstract

The gylcocalyx, a layer of oligosaccharides which surrounds most of the mammalian cell membranes, plays an important role in the adhesion of pathogenic bacteria. This interaction is enabled by special proteins, so-called lectins, which can selectively bind to sugar epitopes. Biomimetic surfaces like glycoarrays, made *e.g.* by deposition of self-assembled monolayers (SAMs), permit the investigation of this molecular recognition.

In previous work[1] the bacterial adhesion to a glycoarray made of molecules containing a mannose epitope, a photo-switchable azobenzene-unit and a biorepulsive oligoethylene glycol (OEG) joint to the surface (see Figure 1). By irradiation upon light of distinct wavelength the mannosyl moiety was either accessible or sterically shielded, but residual bacterial adhesion of the switched state was observed. The incomplete biorepulsion may be caused by unswitched or re-isomerized SAM-building blocks.

Here we present newly designed SAM-building blocks, which contain an always-locked azobenzene or a stabilization unit to avoid the fast re-isomerization of the photo-switch. Compared to the previously presented system, no or a significantly reduced bacterial adhesion to these new glycoarrays should be observed.

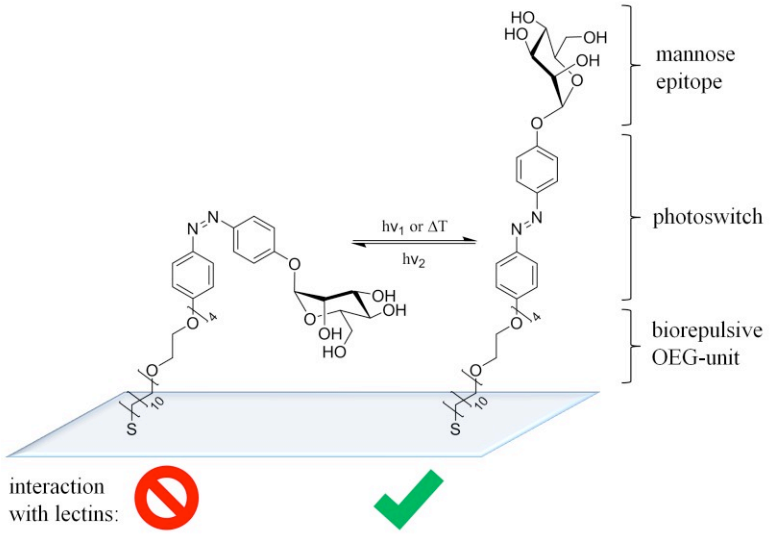

Figure 1: glycoarray published by Weber *et. al.* containing a mannose epitope, a photoswitch for sterical control and an OEG-unit to avoid unspecific adhesion.

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P9

SYNTHESIS OF NOVEL WATER-SOLUBLE STAR-LIKE POLYMER CARRIERS

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Abstract

Nowadays the star-like copolymers based on *N*-(2-hydroxypropyl)methacrylamide (HPMA) represent one of the most intensively studied and most promising systems for efficient passive tumor accumulation and drug delivery. HPMA copolymers are water-soluble, non-toxic and non-immunogenic drug carriers enabling controlled drug delivery. Earlier the synthesis and properties of HPMA based copolymer conjugates, in which the drug is attached via pH sensitive hydrazone bond, was described.[1] The enhanced accumulation of HPMA copolymer conjugates and connected excellent antitumor activity could be explained by EPR (Enhanced Permeability and Retention) effect.[2] Generally, excretion of polymeric carriers from body through renal filtration is limited by its molar mass, i.e. for HPMA copolymers the limit 50 kg/mol was estimated. For high-molecular weight polymer carriers, their degradation to degradation products with molecular weight bellow this renal threshold is crucial. Therefore we designed, synthetized and characterized highly defined biodegradable water-soluble star-like polymer carriers with core based on 2,2-bis(hydroxymethyl)propionic acid (BisMPA). This core is slowly hydrolytically biodegradable at physiological conditions (pH>7). To synthesize star-like copolymers, HPMA copolymers were grafted to this core. (see Figure 1.) HPMA based copolymers were synthetized using controlled polymerization technique, namely Reversible addition−fragmentation chain-transfer (RAFT) polymerization. Semitelechelic HPMA copolymers were grafted to different BisMPA cores by various methods including click chemistry or aminolytic reaction. The molar mass of these star-like carriers can be well controlled in range of 150 to 600 kDa by the changing the ration core to polymers, concentration and time. Cytostatic drug doxorubicin was attached to these carriers via pH-sensitive hydrazone bond and activity of this conjugates was tested *in vitro* and *in vivo*.

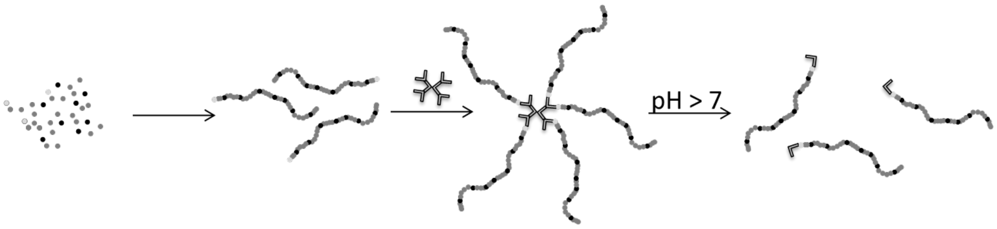

Figure 1. Schematic description of synthesis and degradation of star polymers

Acknowledgment: This work was supported by the Ministry of Education, Youth and Sports of Czech Republic within the National Sustainability Program II, Project BIOCEV-FAR (LQ1604).

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P10

THE TEMPERATURE-RESPONSIVE NANOASSEMBLIES OF AMPHIPHILIC RANDOM COPOLYMERS CARRYING POLY(SILOXANE) AND POLY(OXYETHYLENE) PENDANT CHAINS

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Abstract

Self-assembly of biological macromolecules, such as proteins, is a highly specialized mechanism to produce complex molecular structures with specific functions[1]. Among the synthetic polymers, there has been considerable interest in the possibility of producing nanomaterials through the folding of single polymer chains due to the introduction into the chemical structure of various intramolecular interactions, such as the hydrophobic interactions[2]. Developing a single-chain folding device, as an alternative to common collective aggregates, is beneficial in terms of atom economy and size reduction, both being crucial features in current nanotechnologies. Due to their unique architecture, unimolecular micelles show excellent stability regardless of the high dilution condition and other microenvironment changes, making them particularly attractive for the design of stable nanoassemblies for specific applications[3]. Random amphiphilic copolymers consisting of hydrophilic poly(ethylene glycol) methacrylate (PEGMA) and various hydrophobic (meth)acrylates have been shown to self-fold in water into nanostructures, so-called unimer micelles[4].

We report on novel amphiphilic random copolymers that were synthesized from hydrophilic PEGMA and hydrophobic poly(dimethyl siloxane) methacrylate (SiMA) by atom transfer radical polymerization (ATRP) starting from a fluorescent, julolidine-based initiator (Figure 1). For these copolymers, a reversible transition was observed between two different aggregation states in water at a critical transition temperature T_c. Above the T_c, single-chain self-folded nanoassemblies, ie. unimer micelles, (D_h = 8Ή10 nm by DLS) collapsed into multi-chain aggregates (D_h = 700Ή1400 nm). Covalently linked julolidine terminal and added ethidium bromide were separately used as fluorescent probes to monitor the fluorescence emission of the aggregation state of a confined system. Fluorescence emission measurements with both probes showed a direct dependence between the temperature and the different self-association of the copolymers in water.

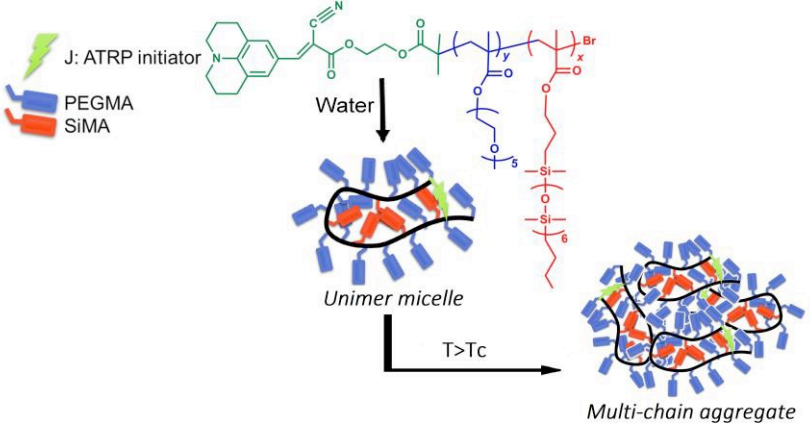

Figure 1: Schematic representation of the unimer micelle in water and multi-chain aggregate formed at $T > T_\mathrm{c}$.

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P11

CONDUCTIVE POLYMER COMPOSITES FOR 3D PRINTING OF BIOSENSORS

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Abstract

3D printing is a unique technology that potentially offers a high degree of freedom for the customization of practical products that incorporate electrical components, such as sensors. The availability of inexpensive, reliable, electrically conductive material will be indispensable in the fabrication of various devices. Due to their unique and fascinating properties, polymer nanocomposites with conductive carbon nanostructures offer high electron conductivity.

Herein, we are developing and fabricating 3D-printable, flexible, and conductive thermoplastic-based material for strain sensing applications. Thermoplastic polymers with conductive additives such as multiwalled carbon nanotube (MWCNT), graphene oxide, metal nanowire are investigated and their mechanical, electrical, and piezoresistivity behaviors will be investigated under monotonous and cyclic loadings. To improve the sensor performance, nanocomposites of various combinations such as conductive polymers with graphene, carbon nanotubes, and metal nanoparticles endow high electrical conductivity, effective surface area, and fast electron transfer rate. MWCNT enabled nanocomposites have received much attention as a highly attractive alternative to conventional composite materials due to their mechanical, electrical, thermal, barrier and chemical properties such as electrical conductivity, increased tensile strength, improved heat deflection temperature, or flame retardancy.

Several conductive polymers are known to interact with biological samples while maintaining good biocompatibility and hence, they qualify as interesting candidates for use in a numerous biological and medical applications as sensors (electrochemical biosensor, tactile sensing 'skins', and thermal sensors) 3D printing can be used to explore experimentally the topology optimization of sensors where their sensitivity is related to their structural parameters.

P12

CONDUCTING POLYMER-BASED BIOELECTRODES TO PRODUCE BIOMIMETIC SYSTEMS

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Abstract

In the last years, conducting polymers have gained great attention in various biomedical studies, in particular to influence cellular and tissue responses. The exciting continuous research for new biomaterials with mimetic chemical properties is focused to the development of electrically conductive devices for a wide range of applications, including bioactuators, biosensors, drug delivery devices, cardiac/neural electrodes, and tissue scaffolds. In this contest, conducting polymers (CPs) play a key role since in aqueous solutions and under flow of electric currents they can behave as soft and wet biomimetic reactors. In fact, the intrinsic conductivity and the good charge-transfer properties of CP allow to mimic several biological functions performed by specialized cells in different organs. Furthermore, CPs can be useful to electrically stimulate various cells, including neurons and cardiomyocytes, and electrically deliver biological molecules to modulate cellular behaviors for potential tissue-engineering applications. The peculiar redox processes of CPs are accompanied by a volume change; such a deformation of the polymer backbone is explained in terms of swelling or deswelling (contraction/expansion) and it is induced by charge-compensating ions displacement into or from the CP. This interesting property mimics the action of muscles and makes CPs suitable materials for producing electrochemomechanical actuators. Among the CPs, polyaniline (PANI) is considered one of the most promising system because of its low cost, easy synthesis, high electrical conductivity, good environmental stability and biocompatibility [1-2].

We present here innovative bioelectrodes made up by a titanium sheets coated with conductive and boron free diamond films onto which thin layers of PANI have been subsequently electrodeposited. Structural and morphological features of the PANI are investigated by Raman spectroscopy, atomic force microscopy (AFM) and scanning electron microscopy (SEM) measurements. Using electrochemical atomic force microscopy (EC-AFM) we study the swelling /deswelling processes of PANI which entails the transition from the fully reduced form, leucoemeraldine, to the fully oxidized one, pernigraniline. EC-AFM allows the "in situ" analysis of the electrochemical reactions occurring at the solid-liquid interfaces; in particular it is possible to monitor the in-situ electrodeposition of PANI [3]. In this research EC-AFM technique is employed to investigate the volume changes as a function of applied potential by cyclic voltammetry (CV) experiments simultaneously to AFM imaging. In this way, it is possible to reveal the re-organization of the polymeric chain during PANI redox reactions and to monitor morphology and thickness changes of the film. The PANI conformational movements upon redox processes make this CP a promising reactive biomimetic material for the realization of new artificial intelligent motor systems. The future research will aim at controlling and optimizing PANI characteristics and performance.

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P13

BIOMIMETIC HYBRID MICROPARTICLES FOR RETENTION/RELEASE OF PESTICIDES IN ORDER TO MINIMIZE SOIL AND WATER POLLUTION

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Abstract

The need for innovative strategies for water and soil protection, able to replace the time-, energy- and resource-consuming remediation processes with other more efficient and environmentally-friendly ones, is becoming more pressing than ever. Environmental issues associated with pesticides, particularly the highly mobile ones, are of worldwide concern because of the increasing presence of these agrochemicals in ground and surface waters[1]. In agriculture, a large quantity of toxic pesticides is used globally, and theycan bioaccumulate in soil and in different water bodies, and finally, reaching dangerous levels in the food chain.

The use of natural zeolites in wastewater remediation is one of the oldest and the most perspective areas of their application. Recent investigations of natural zeolites as adsorbents in water and wastewater treatment, their properties and possible modification of natural zeolites have been a subject of intense research. Modification of natural zeolites can be performed by several methods, such as acid treatment, ion exchange, and surfactant functionalization. The modified zeolites can show enhanced adsorption capacity also for organic matter and anions[2].

In this study, we present a new concept for preparing modified mesoporous zeolite by host-guest molecular imprinting of vinylic monomers in the presence of template pesticide, to create selective cavities for pesticides and hydrophilic branches for the subsequent physical immobilization of silicate particles into a hydrogel matrix. In this regard, new modified biomimetic hybrid microparticles have been prepared by radical polymerization of acrylonitrile or acrylonitrile and pesticide (Dithane M-45) solution in the zeolite pores (expanded perlite).

The modified silicates were characterized using various techniques i.e. Fourier-Transform Infrared Spectroscopy (FTIR), Dynamic Light Scattering (DLS), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and porosity measurements (BET) to prove that final modified materials show enhanced features and elevated sorption capability for organic compounds in dynamic mode.

Acknowledgments. The authors would like to thank the EU and (UEFISCDI) for funding, in the frame of the collaborative international consortium (ProWsper) financed under the ERA-NET Cofund WaterWorks2015 Call. This ERA-NET is an integral part of the 2016 Joint Activities developed by the Water Challenges for a Changing World Joint Programme Initiative (Water JPI).

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P14

NANOGELS – POLY(AMINO ACID)- BASED NANOPARTICLES BY HORSERADISH PEROXIDASE CATALYZED CROSSLINKING IN AN INVERSE MINIEMULSION

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Abstract

The contribution presents an investigation of horseradish peroxidase (HRP)/H_2O_2-mediated crosslinking in an inverse miniemulsion for the successful preparation of nanogels from a poly(amino acid)-based polymer precursors based on biocompatible poly(α,β-*N*-(2-hydroxyethyl)-D,L-aspartamide with tyramine units (PHEA) and biocompatible and biodegradable poly(N^5-2-hydroxypropyl-L-glutamine) with tyramine units (PHEG). Generally, the linear synthetic poly(amino acid)s exist in random coil conformation in aqueous solution. We took advantage of this behavior and pioneered the HRP/H_2O_2-mediated crosslinking in the inverse miniemulsion with emulsifier sorbitane monooleate (SPAN 80) for a preparation of the poly(amino acid) based nanogels. As first, the innovative approach was investigated with various concentrations of PHEA which served as model polymer precursor. The aqueous solutions of PHEA with HRP were emulsified in the presence of cyclohexane and SPAN 80. The addition of an aqueous solution of hydrogen peroxide induced crosslinking between the polymer chains via the tyramine units (Tyr) and targeted formation of nanogels. The size, morphology and architecture of the hydrogel nanoparticles were characterized by dynamic light scattering (DLS), nanoparticle tracking analysis (NTA) and cryogenic transmission electron microscopy (cryo-TEM). The results confirmed that the (HRP)/H2O2-mediated crosslinking in an inverse miniemulsion led to formation of different nanogels with hydrodynamic radii (Rh) ranging approximately from 200 to 400 nm and their morphology was affected by initial concentration of PHEA polymer precursor. The cryo-TEM measurements confirmed that final nanogels were composed of composed of the small ~ 5 nm globules corresponding to the PHEA coils[1]. The developed approach was subsequently applied for preparation of the nanogel from PHEG. The effect of ratio between H2O2 and Tyr, and concentration of HRP on final size and morphology of the nanogels were studied. The application of biocompatible and biodegradable PHEG also resulted in crosslinked soft nanoparticles. In comparison with the previous results, these nanogels were smaller and had R_h in range approximately from 70 to 250 nm. This procedure led to successful formation of nanogel particles based on synthetic poly(amino acid) and it was found out that their nanoparticle radius, morphology, and architecture could be regulated by the initial concentration of the precursor. The colloidal stability of the selected PHEG-based nanogel was finally analysed at different conditions: in water at 25 °C, in water at 37 °C, in PBS buffer with pH 7.4 at 25 °C, in PBS buffer with pH 7.4 at 37 °C and the PHEG-based nanogel maintained their colloidal stability over 168 h under all conditions.

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P15

MODIFICATION OF SURFACE PROPERTIES OF MATERIALS BASED ON EPDM/IIR BY ELECTRON BEAM IRRADIATION

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Abstract

The superhydrophobic effect, discovered in some leaves, such as lotus leaves, is due to the interaction of surface chemistry and topography at macro and nano scale. Superhydrophobic surfaces are of particular interest to the scientific community, due to their self-cleaning properties [1-2].

The purpose of this paper is to study to modify the surface properties of elastomeric materials based on ethylene-propylene-diene terpolymer rubber (EPDM) and butyl rubber or halogenated butyl rubber (IIR-Br and IIR-Cl) by changing the composition and electron beam processing. It is known that electron beam irradiation of elastomeric materials leads to oxidation reactions at the surface of samples, and to a change in the surface roughness, which may induce the self-cleaning property. In addition, irradiation with a high dose leads to their vulcanisation/crosslinking. Electron beam vulcanization has demonstrated extremely positive results compared to the conventional curing system (usual needing high temperature and sulphur and crosslinking agent leading to release of toxic gases) such as: no polymer degradation due to high temperature as electron beam crosslinking occurs at room temperature, no oxidative degeneration in polymers as observed in classical crosslinking, direct crosslinking by C-C linkage by EB, extremely strong bonds, high degree of crosslinking, extremely short curing cycles, zero blooming effects, extremely high tensile strength, extremely high resistance to compression set, extremely high resistance to oils, grease, lubricants, highly improved accelerated ageing properties, very high productivity, perfect for thin products, lower material waste [3-4].

EPDM possesses better general physical properties such as high heat resistance, ozone, cold temperature, and moisture resistances than butyl rubber/ halogenated butyl rubber. Because of the low gas and moisture permeability, good weathering resistance, and high thermal stability of butyl rubber/ halogenated butyl rubber, its blends with EPDM would be attractive. These elastomeric components can be used to obtain consumer goods in the pharmaceutical, food, automobile, etc., where self-cleaning properties are very important [4-5].

For the blends were used EPDM rubber, three types of buthylic rubber (IIR, IIR-Br, IIR-Cl), a polyfunctional monomer and other ingredients. The mixtures were carried out in a Plasti-Corder Brabender mixer at 160–200°C. The test specimen sheets of all compounds were produced using compression moulding at 120°C. Samples were subjected to electron beam at different irradiation doses and chracterized by: contact angle measurements, sol-gel analysis, crosslinking density measurements, microscopic analysis, FTIR and physico- mechanical properties.

Acknowledgment
This work was supported by a grant of the Ministry of National Education and Scientific Research, RDI Programe for Space Technology and Avanced Research - STAR, project number 140/2017.

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P16

POLY(ANILINE-*co*-PHENYLENEDIAMINE)/POLY(VINYL ALCOHOL) CRYOGELS: SPECTROSCOPIC STUDY

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Abstract

Molecular structure of conducting composite cryogels based on poly(aniline-*co*-phenylenediamine) stabilized by poly(vinyl alcohol) was studied by the infrared and Raman spectroscopies. Cryogels were prepared by oxidative copolymerization of aniline hydrochloride and *m*- or *p*-phenylenediamine dihydrochloride with ammonium peroxydisulfate in 5 wt% aqueous solution of poly(vinyl alcohol). The freshly prepared mixture of monomer and oxidant was sucked into plastic syringes, frozen in solid carbon dioxide/ethanol suspension, and left in a freezer at –24 °C for 7 days. After thawing at room temperature, cryogels were removed from the syringes, washed with excess of water and freeze-dried.[1]

Copolymer cryogels and the parent homopolymer cryogels have uniform macroporous structure with pore sizes up to tens of micrometers based on scanning electron microscopy. The increase in *p*-phenylenediamine fraction in polymerization medium led to a decrease of conductivity from 5×10^{-2} to $<10^{-11}$ S cm^{-1} for dry compressed copolymer cryogels. The infrared and Raman spectra proved the conducting form of polyaniline by the presence of polaron bands. A partial deprotonation of the samples was demonstrated by the main band of polyaniline base situated at 1472 cm^{-1} in the Raman spectra recorded using 633 nm excitation laser (Figure 1). Non-toxic, biocompatible and stimuli-responsive polyaniline-based hydrogels are of special interests for biomedical applications.

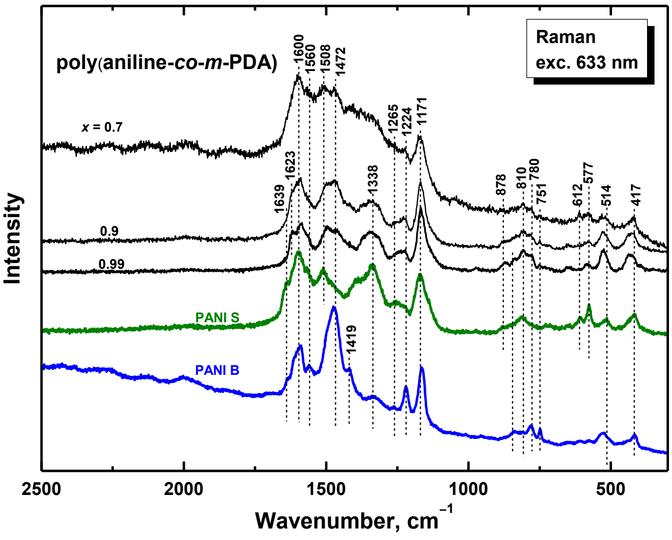

Figure 1. Raman spectra of poly(aniline-*co*-*m*-phenylenediamine)/poly(vinyl alcohol) cryogels for various molar fractions of aniline hydrochloride, *x*. Spectra of standard polyaniline powder in salt (PANI S) and base (PANI B) forms are shown for comparison.

Acknowledgment. The authors thank the Czech Science Foundation (17-04109S) for financial support.

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P17

PREPARATION AND CHARACTERIZATION OF A NEW ION IMPRINTED POLYMER FOR LEAD(II) RECOGNITION

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Imprinted polymers are designed to recognize the target species that has been used for their preparation. Indeed, they are synthesized by copolymerization of a functional monomer with a crosslinker in the presence of a template ion (Figure 1). This creates a rigid three-dimensional network around this ion whose removal generates the selective binding cavities[1]. The efficiency of IIPs for metal cations extraction is now well established[2,3]. It can be further enhanced by using some functional monomer including groups designed to chelate the target ion. Thus, this creates a synergy effect between the imprinting effect and the own selectivity efficiency of the functional monomer.

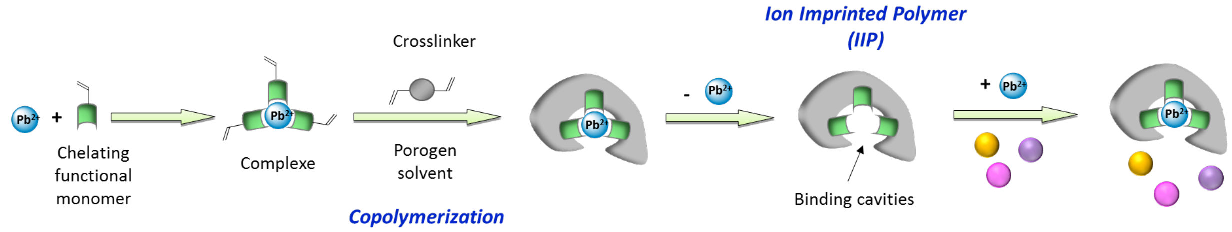

Figure 1. Schematic scheme of IIP synthesis and action.

In this work, we report the synthesis of a new chelating methacrylate monomer for lead(II) ions in a four step synthesis path (Figure 2). IIP was then prepared by precipitation copolymerization of this monomer with ethyleneglycol dimethacrylate in the presence lead(II) ions. The presence of the functional monomer inside the polymers was assessed via FTIR and the polymer microstructure was characterized by SEM. The selective retention of this IIP for lead(II) was compared with a control polymer (prepared in the absence of the target ion). A good selectivity was evidenced in the presence of competing major cations, namely calcium(II) and magnesium(II). The IIP efficiency was also evidenced to extract lead in the presence of organic matter. All these results open interesting perspectives for the use of these polymers in environmental conditions.

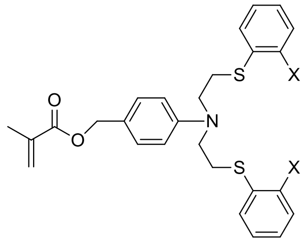

Figure 2. New chelating monomer for lead(II) ions

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P18

NANOPARTICLES FUNCTIONALIZED WITH PROTEINS BY MOLECULAR IMPRINTING POLYMER TECHNIQUE

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Abstract

The creation of functionalized nanoparticles is a subject studied with more enthusiasm during these last years. Besides, a technique that could implement this objective is the Molecular Imprinting technique, which has been successfully used for small molecules such as herbicides or amino acids. In our case, we will focus on functionalized silica nanoparticles with an imprinted core shell based on a vinyl copolymer (MPS copolymerized with certain monomers), for later bind over it a specific protein (Poly-lysine). Indeed, the interesting point to research is create binding sites over the nanoparticle and test the binding specificity and affinity of the imprinted material. Afterwards a comparison of the polymer with and without the protein template is accomplished.

P19

MOLECULARLY IMPRINTED ELEMENTS FOR THE RECOGNITION OF 2,4,6-TRINITROTOLUENE

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Abstract

TNT (2,4,6-trinitrotoluene) is an inexpensive nitro-aromatic explosive compound, commonly used in military and terrorist activities. Its early detection is paramount considering global environmental protection and international security issues. Consequently, it is crucial to employ new effective methods for TNT rapid detection based on state-of-the-art techniques. In principle, molecular imprinting (MI) is a simple, yet effective way to create biomimetic materials with recognition sites for virtually any target species we choose. These materials offer different attractive features, not least their ease and low cost of manufacture and their robust nature. Furthermore, MIT can be combined with various deposition methods for developing efficient and reusable sensitive elements[1].

This study provides a preview to understanding the new self-assembly mechanism of TNT with N-(2-aminoethyl)-3-aminopropyl methyl dimethoxysilane *via* double Meisenheimer complexes. Ultimately, the knowledge is used as a tool for narrowing the specific binding time of TNT, down to 5 minutes, onto molecularly imprinted organosilica films (thin and thick layers). In this context, ellipsometry measurements were performed to reveal the structural changes of TNT-molecularly imprinted films that follow the specific TNT-monomer self-assembly. Batch re-binding experiments indicated that thinner molecularly imprinted organosilica films are more efficient for recognizing TNT; and thus, can further be scaled for developing fast-response sensors, dedicated to on-site specific measurement of nitro-aromatics.

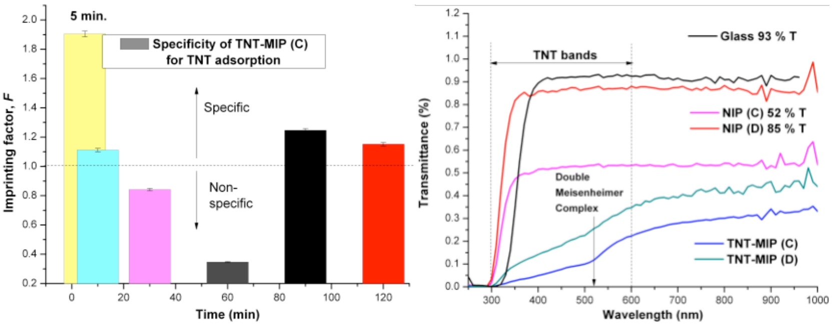

Figure 1. (left) Variation of imprinting factors, F, for TNT-MIP (C) in time (5-120 min) in batch adsorption measurement at 24°C (right graph) Transmittance profiles for TNT-MIP thick (C) and thin (D) films compared to their corresponding NIP (C) and (D) films

Acknowledgments. The work has been funded by the Romanian National Authority UEFISCDI through Project PN-III-70PCCDI-2018 SECURE-NET.

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P20

FLUORESCENT MOLECULARLY IMPRINTED POLYMER FOR CHLOROGENIC ACID (CGA) DETECTION

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Abstract

Chlorogenic acids (CGAs) are a particular class of phenolic compounds present in the plant kingdom, which contribute to health benefits such as antioxidant, anti-inflammatory and antispasmodic activity. In the human diet, coffee is the major source of chlorogenic acids (CGAs) and they are considered an important indicator of quality in coffee[1]. Together with an analytical study of their presence in the coffee matrix, it is also important to develop a reliable, rapid, sensitive and simple method for the quantification of these substances. MIPS based in non-covalent interactions have been mostly used in solid phase extraction and sample concentration for the analysis of CGAs[2]. In the present work, we describe a fluorescent molecularly imprinting polymer (MIP) able to detect 5-caffeoylquinic acid (commonly known as chlorogenic acid). The polymer was prepared in DMSO, using MBA as crosslinker and a fluorescent derivative of naphtalimide as a monomer able to interact with the template by hydrogen bonding, while 4-vynilpiridine was chosen as the co-monomer. The polymer was imprinted with a mimic compound of 5-caffeoylquinic acid (5-CQA) prepared in order to avoid polymerization of the double bond present in the real analyte. Interactions between the monomers and the template were evaluated by ^{1}H NMR titrations and the binding tests were carried out by HPLC analysis showing a good sensitive towards the template with recoveries of 80-90%. An enhancement of the polymer fluorescence was noticed after binding of the template in a range of 300μM-80mM. This MIP represents a valid starting point for the development of an optical sensor.

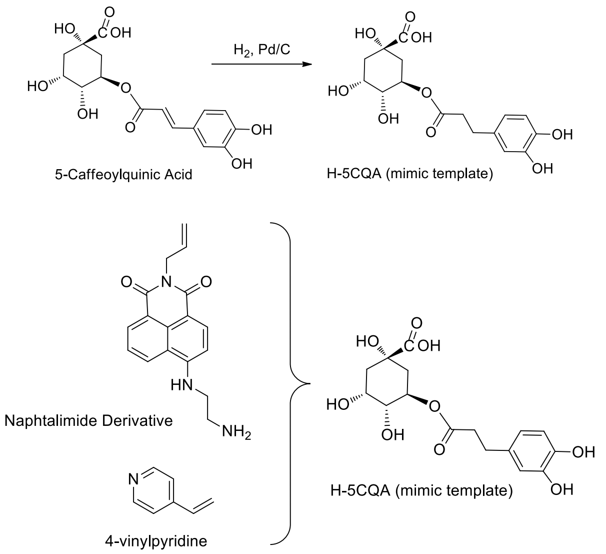

Figure 1. Mimic template and monomers

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P21

RECOGNITION PROPERTIES OF MOLECULARLY IMPRINTED FILMS FOR BISPHENOL A

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Abstract

Extensive efforts have been devoted to the development of effective determination methods, capable of monitoring toxic compounds rapidly. Bisphenol A (BPA) is classified as an endocrine disrupting chemical (EDC) due to its potential to affect not only the human health but also both industrial and agricultural sectors. Until now, it has been found in various kinds of environmental matrices such as surface waters, oil, sediments or air. Thus, efficient and sensitive detection of BPA is essential for human and environmental monitoring. One of the newest methods to prepare sensors rely on using MIP films as receptors for target molecules. Since the sol-gel methods enables tailoring both the specific cavities *via* organic functional groups and the semi-conductive features of the receptor layer all together, the interest in such sol-gel derived methods has increased in the field of detection tools. Molecular Imprinting has been demonstrated to be an operative and versatile technique for the formation of recognition sites able to mimic natural receptors including drugs or pollutant[1].

This work describes the preparation of [N-(2-aminoethyl)-3-aminopropyl trimethoxy silane]and 3-Mercaptopropyl) trimethoxy silanes matrices *via* one-pot sol-gel method in the presence of BPA as target molecule using a previous described procedure[2]. After preliminary investigation of BPA- silanes interaction, imprinted solutions were further deposited onto glass supports as thin films, afterwards washed with different solutions for template removal. The proposed approach is based on easy, rapid and homogenous deposition of BPA-solutions, which are prepared by air-spraying. The non-imprinted polymer (NIP) was also synthesized in the same manner but without BPA. Both MIP and NIP films were characterized by Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Films thickness and roughness determined by ellipsometry were also investigated. Surface measurements confirmed good adhesive behaviour towards BPA and, furthermore, excellent adsorption properties proving that the BPA-films can be used as recognition layers for sensor devices. Optimum adsorption capacity of BPA by the MIP was found to be 16.4 mg g^{-1} after just 1 minute of adsorption, while that of the NIP film was 11.1 mg $_{g^{-1}}$.

Acknowledgments. The work has been funded by the Romanian National Authority UEFISCDI (MCI) through Project No. 10/2016 ERA.NET-RUS Co-funded Call - SNIFF.

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P22

PHOTOPOLYMERIZED MOLECULARLY IMPRINTED POLYMER TAILORED FOR ELECTROCHEMICAL DETECTION OF BRAIN-DERIVED NEUROTROPHIC FACTOR ON SCREEN-PRINTED ELECTRODES

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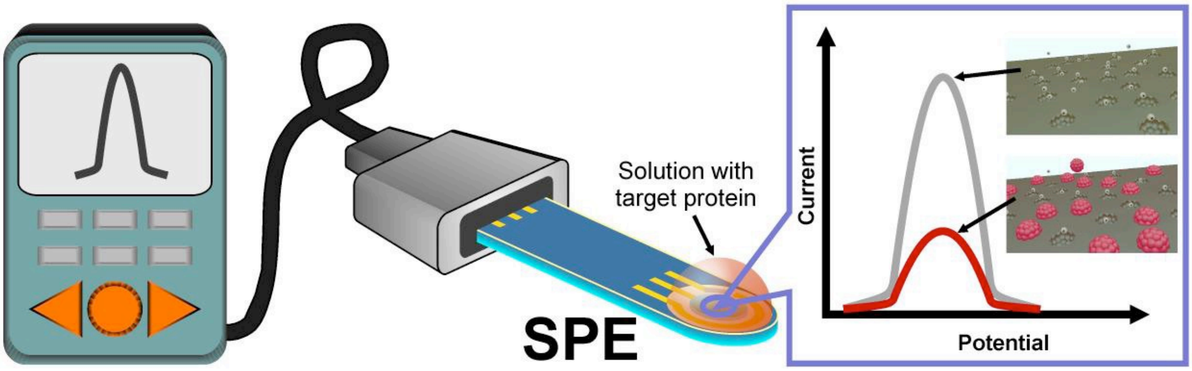
Abstract

Brain-derived neurotrophic factor (BDNF) is a member of the family of protein neurotrophins that selectively affects the development, maintenance and survival of neurons, and its abnormal level in the blood may be associated with a number of neurodegenerative diseases (ND)[1]. Serum concentration of BDNF could be a potential biomarker for the early-stage diagnosis of ND. Molecularly Imprinted Polymer (MIP) based biosensors for BDNF detection might simplify and reduce the cost for the NF detection assays. MIP film synthesized on screen-printed electrodes (SPE) provides a considerable option for obtaining a lab-on-chip analytical device. In this study BDNF-MIP was generated on the gold surface of SPE by surface-initiated controlled/living radical (C/LR) photopolymerization. Bis-acrylamide, 2-(diethylamino)ethyl methacrylate, sodium diethyldithiocarbamate were used as a cross-linker, a functional monomer and a initiator, respectively, to prepare the polymer matrix for the BDNF-MIP film. The initiator was grafted to the gold surface of the SCE via electrophilic substitution reaction with the previously deposited 3,5-dichlorophenyl diazonium tetrafluoroborate. The SCEs were incubated in the template-monomers solution followed by exposition to UV light to induce photopolymerization process on the gold surface. The generated polymeric thin films were treated in NaOH/SDS solution aiming to remove BDNF from the polymer and form BDNF-MIPs. The resulting the BDNF-MIP films were characterized by scanning electron microscopy, IR spectroscopic ellipsometry and contact angle measurements. The binding affinity and selectivity of the BDNF-MIP films toward BDNF were studied by means of electrochemical impedance spectroscopy (EIS) and differential pulse voltammetry (DPV). The electrochemical measurements demonstrated the ability of the prepared BDNF-MIP films to discriminate the target protein among the interferents.



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P23

EXTRACTION OF SERTRALINE BY MOLECULARLY IMPRINTED POROUS COPOLY(ACRYLIC ACID-DIVINYLBENZENE) PREPARED BY TWO-STAGE POLYMERISATION

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Abstract

Sertraline (SER) is known as the most widely prescribed antidepressant and belongs to a class of selective serotonin reuptake inhibitors. Sertraline and many other antidepressants enter wastewaters by human excretion or by discarding unused drugs. There is evidence for bioaccumulation in aquatic organisms that may have negative effects on flora and fauna.[1]

Due to low concentrations of SER in aquatic systems it is challenging to find a method with sufficient selectivity and sensitivity for the detection. For this purpose, molecularly imprinted polymers were used in our study. Molecularly imprinted polymers (MIPs) have an increased affinity and selectivity towards a target molecule. Target molecule is reversibly bound to a functional monomer and copolymerised with a crosslinker to provide a rigid network. Removed target molecule leaves an imprint for the future rebinding of the target molecule.[2]

In our work acrylic acid was used as the functional monomer and divinylbenezene (DVB) as the crosslinker. Sertraline as the target molecule was bound via acid-base interactions to acrylic acid to form a molecularly imprinted polymer. In order to produce porous SER-imprinted copoly(acrylic acid-divinylbenzene) high specific surface area and accessible acrylic acid sites for binding of sertraline have to be obtained. By varying the proportion of crosslinker (DVB) and by adding a porogen (toluene), the formation of pores can be achieved, while higher accessibility of acid functional groups was achieved by using a two-stage polymerisation. In the first stage DVB was polymerised using toluene as the porogen and in the second stage acrylic acid was grafted onto unreacted vinyl groups of swollen polyDVB.

It was found that the two-stage polymerisation procedure improves the imprinting effect of SER compared to a standard polymerisation procedure.

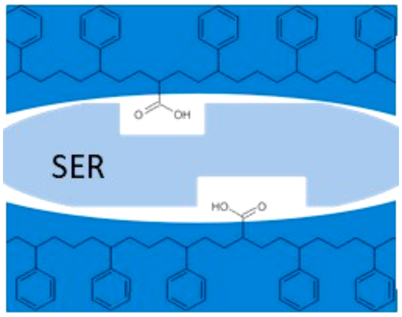

Figure 1: Sertraline imprinted porous copoly(acrylic acid-divinylbenzene)

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P24

CHARACTERIZATION OF MOLECULAR IMPRINTED POLYMERS BY THE SOLID NMR TECHNIQUE

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Abstract

In the field of molecular imprinted polymers, most of the time pre-polymerization techniques are used because of the difficulty to work with polymerized systems. In this work, the NMR HR-MAS is used because allows characterize the material after polymerization, obtaining spectra from semi-solids with some flexibility in their bonds[1]. The results obtained allow distinguishing the bonds of interest and the differences between the MIP, NIP and the polymer after the washing and rebinding processes.

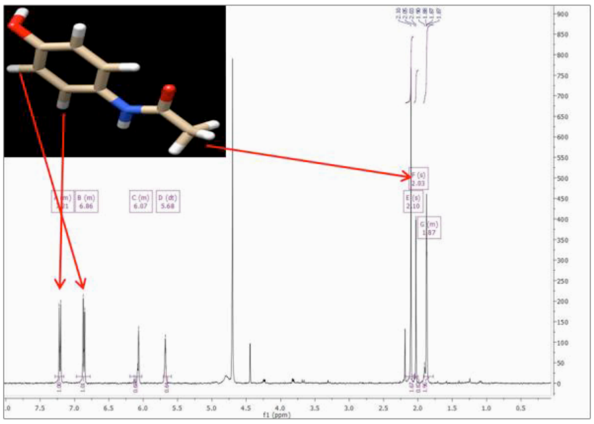

Fig.1. MIP-Acetaminophen spectrum (NMR HR-MAS en D_2O) and its molecule (UCFS Chimera 1.10.2).

Previously, a number of template- functional monomer combinations were selected and analyzed with computational calculations[2] (Acetaminophen- Methacrylic acid, Diclofenac- 2-vinylpyridine, Indomethacin-Itaconic acid y Ibuprofen-Itaconic acid) and finally tested in the laboratory by simple polymerization procedure. In all cases, Acetone-ACN (3:1) is used as solvent and EGDMA as crosslinker. The results obtained in the optimization performed with computational calculations and analyzed by NMR HR-MAS were validated by batch rebinding experiments. These tests were used to evaluate the binding properties and the polymers selectivity[3]. (Table I):

Table 1. Binding sites parameters.

Langmuir isotherm	R_L	$0.01 < R_L < 0.76$	Equilibrium parameter
Freundlich isotherm	m (L/g)	0.74-0.81	Surface heterogeneity
Allosteric isotherm	n	0.8-1.01	Correlated to the number of binding layers
Dubinin-Radushkevich	E (kJ/mol)	259-673	Free energy of adsorption

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P25

EFFECT OF SURFACTANTS ON THE BINDING PROPERTIES AND SELECTIVITY OF MOLECULARLY IMPRINTED POLYMERS

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Abstract

The artificial receptors known as Molecularly Imprinted Polymers (MIPs) represent one of the most successful type of man-made materials developed to mimic the binding properties of natural receptors like antibodies and enzymes. One of the most significant application concerns the use of MIPs as substitutes of natural antibodies in immunoaffinity extraction, in the so-called Molecularly Imprinted Solid Phase Extraction (MISPE). In this technique, the target analyte contained in the sample is loaded onto an imprinted solid phase, and after a washing step, it is recovered to be quantified.

Of consequence, to enhance the MIP's selectivity and to assure high recoveries of the analyte it is of paramount relevance to minimize non-specific interactions between MIP and the sample matrix. Such non-specific interactions are generally based on weak hydrophobic forces between the surface of the MIP and the less hydrophylic components of the sample matrix. Consequently, additives able to interfere with such interactions should be able to significantly reduce any non-specific binding effect. Among the possible additives, surface active agents represent an interesting class of substances as they are cheap, easily available and compatible with the organic solvents commonly used in MISPE technique. Here we report a study about the effect of several surfactants on the binding properties and the selectivity of a trichlorophenoxyacetic acid-imprinted polymer. HPLC columns packed with imprinted and non-imprinted polymers were eluted with mixtures of water/acetonitrile (containing acetic acid 2% v/v) added with variable amounts of three different surfactants: the anionic sodium dodecylsulphate (SDS, 0-0.2% w/v), the cationic cetyltrimethylammonium bromide (CTAB, 0-0.2% w/v) and the non-ionic polyoxyethylene-(20)-sorbitan monolaurate (Tween 20, 0-2.5% w/v). The binding ability of the polymers towards the template 2,4,5-T and two related ligands 2,4-D and 4-M was evaluated by measuring the capacity factors of these ligands and calculating imprinting factors and selectivity.

From the experimental results, it is possible to observe that surfactants are able to increase the imprinting effect by decreasing the non-specific binding. This effect is less marked with the non-ionic surfactant respect to the two ionic ones. This indicates that surfactants act mainly by inhibiting the ionic pair interaction between the acidic ligands and the basic functional monomer 4-vinylpyridine. About selectivity, all the surfactants show no influence, as any increase of selectivity observed can be directly related only to the amount of water present in the mobile phase.

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EFFECT OF TEMPLATE LATE ADDITION ON THE BINDING PROPERTIES OF MOLECULARLY IMPRINTED POLYMERS

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Abstract

In non-covalent molecular imprinting approach, the use of pre-polymerized functional macromonomers – freely dissolved in a porogenic solvent or grafted onto a solid surface – greatly increases the stability of the complex between the template molecule and the forming cross-linked polymer, with a net gain in terms of binding properties. The cross-linking process of such macromonomers can be considered somewhat similar to the change of state from a microgel solution to a solid polymer that happens during the process of bulk polymerization. On this basis, we hypothesized that the late addition of a template molecule to a mixture of functional monomers and cross-linkers during the polymerization process can enhance the binding properties of the final bulk polymer.

To verify this hypothesis we chose to imprint a series of bulk polymers with a well-known template, diclofenac (figure 1), by using a polymerization mixture in acetonitrile (4-vinylpyridine / 2-hydroxyethylmethacrylate / divinylbenzene 2+2+5 mol/mol) previously developed in our laboratory, but adding the template progressively later respect to the beginning of the thermopolymerization process. The experimental conditions were chosen after a preliminary study of the polymerization process, designed to determine the gelling speed according to the polymerization temperature. After the polymerization, the imprinted bulk materials were crushed, sieved and exhaustively washed from the template with MeOH / AcOH 9+1 v/v. The powdered polymers were used to perform batch rebinding experiments in MeCN to measure the binding isotherms with the aim to calculate the dissociative equilibrium constant, K_D, and the binding site density, B_{max} for diclofenac.

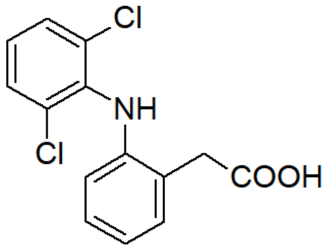

Figure 1: diclofenac

The analysis of the experimental langmuirian binding isotherms showed that the initial hypothesis is fully verified. The imprinted polymers prepared by template late addition (delay time of 5-30 minutes) show a higher binding affinity with respect to the reference polymer (prepared in the presence of template from the beginning), with a maximum at about 5-10 minutes and a decreasing trend with the increase of the delay time. Moreover, a limited effect on the binding site density was observed.

P27

MACROPOROUS CONDUCTING POLYANILINE CRYOGELS: ICE CRYSTALS AS A POLYMERIZATION TEMPLATE

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Abstract

Conducting hydrogels represent new materials with high potential applicability in biomedicine[1] due to their ability to assist in monitoring or stimulation of various biological objects. Among them, polyaniline cryogels supported by poly(vinyl alcohol) (Figure 1) rank among the most prospective materials due to their soft macroporous structure.[2] Such cryogels were prepared by the oxidation of aniline in the frozen aqueous solutions of poly(vinyl alcohol), when ice crystals produced the template that guided the polymerization of aniline. They have good biocompatibility[3] and are suitable, *e.g.*, in the tissue engineering of electrically excitable objects.

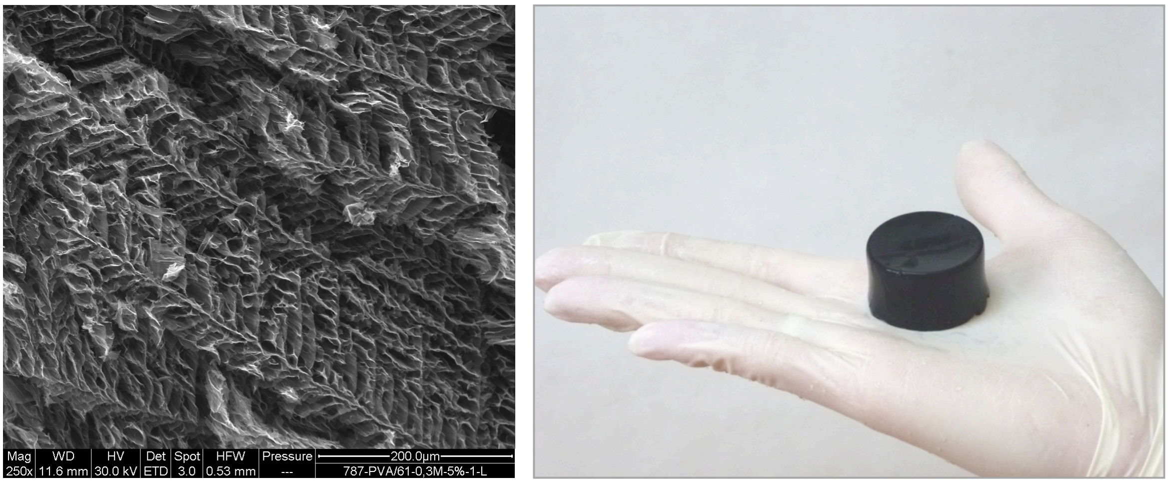

Figure 1: Polyaniline/poly(vinyl alcohol) cryogel (right) and its macroporous structure (left).

A variety of cryogels can be produced by replacing poly(vinyl alcohol) with other water-soluble polymers or by using polypyrrole instead of polyaniline. The cryogels can also be converted by freeze-drying to corresponding aerogels, and by subsequent heating to 600 °C in inert atmosphere to carbogels, *i.e.* to macroporous nitrogen-containing carbons. The latter type of new materials will be tested as adsorbents or organic compounds in water-pollution treatment.

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P28

DETECTION OF PATHOGENS USING MAGNETIC MOLECULARLY IMPRINTED POLYMERS

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Abstract

In this work, a method of molecular imprinted polymers was used for detection of bacteria. A non-covalent imprinting approach was employed due to the simplicity of preparation. Dopamine seems to be an ideal choice of functional monomer because of a simple oxidative polymerization forming the self-assembly monolayer without need addition of any cross-linker. *Staphylococcus aureus* that is one of the most common causes of pyogenic infections was chosen as the target bacteria. Concentration range of $1 \cdot 10^3$ cfu·ml^{-1} to $1 \cdot 10^7$ cfu·ml^{-1} of bacteria was used. The lowest used concentration corresponded to the concentration that is dangerous for healthy individuals. Layer of molecularly imprinted polymer was created on a surface of magnetic particles and bound bacteria were fluorescently labelled by fluorescamine - a reagent for the detection of primary amines. The labelling reaction is very fast and the unreacted dye undergoes hydrolysis and therefore does not influence the fluorescence determination. The products are highly fluorescent after excitation by light with wavelength of 350 nm.

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P29

LIPOPOLYSACCHARIDE-MOLECULARLY IMPRINTED POLYMER LAYERS FOR GRAM-NEGATIVE BACTERIA ISOLATION

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Abstract

One of the current global issues refers to water quality and human and environmental hazards from the exposure to pathogenic bacteria originated from wastewater and its streams, e.g. grey or black waters. Whereas, the contamination of wastewaters by antibiotics or other pollutants leads to the rise of pathogens resistance, these bacteria can be also found in soils, water bodies and even crops. This issue is of high concern as most pathogens responsible for waterborne diseases originate from faecal or food waste contamination caused by insufficient or not treated wastewater. Thus, in order to minimise the hazards and protect public and environmental safety, faecal contamination and food borne pathogens should be detected promptly and reduced efficiently preventing further transmission of pathogenic strains to water bodies. In this direction, we present a new concept for preparing bactericidal surfaces for Gram-negative Bacteria (GNB) inactivation from contaminated wastewaters. For this mater, this study proposes combined methodologies for creating bio-mimetic artificial surfaces that imply both the use of sol-gel techniques and of molecular imprinting technique (MIT). MIT has been developed to such a stage that the synthetic technique can now offer robust materials for challenging caption and isolation applications. Among the different forms of MIPs, MIP films are more suitable for many practical and modern applications. We have previously reported on the succesfull development of trinitrotoluen selective MIPs as thin films via sol-gel technique[1]. The present contribution will address innovative layer-by-layer nano-assembled films against pathogenic GNB via sol-gel and MIT. In this regard, lipopolysaccharide-molecularly imprinted polymer (LPS-MIP) layers have been prepared using (3- Mercaptopropyl)trimetoxysilane and 3-(2-trimethoxysilyl)-propylmethacrilate monomers. The LPS-MIP sensing layers were grafted onto suitable glass slides. Consequently, the hybrid vinyl-LPS-MIP layers will be used as smart tools for improving the wastewater purification technologies with regard to reduction of GNB. Furthermore, to confirm the presence of imprinted sites complementary to LPS, binding studies were performed.

Figure 1. 3D Topography (left) **and** rugosity profile (right graph) of LPS-MIP layer (10x10) µm^2

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P30

LASER ABLATION ICP-MS ANALYSIS OF CdS QUANTUM DOTS-BASED IMMUNOASSAY COMBINED WTH PARTICLE IMPRINTED POLYMER TECHNOLOGY

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Abstract

In this work, for the first time, the combination of molecularly imprinted polymer (MIP) technology with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is presented with focusing on optimization of the LA-ICP-MS parameters such as laser beam diameter, laser beam fluence, and scan speed using CdS quantum dots (QDs)-labelled antibodies as a template and dopamine (DA) as a functional monomer. A non-covalent imprinting approach was employed in this study due to the simplicity of preparation. Simple oxidative polymerization of the dopamine that creates a self-assembly monolayer seems like an ideal choice. The QDs were prepared by UV light irradiation and were stabilized by mercaptosuccinic acid. Prepared QDs were characterised by dynamic light scattering and transmission electron microscopy. Formation of QD-antibody complex and QD-antibody-antigen complex was verified by capillary electrophoresis with laser-induced fluorescence detection. A special peptide linker was used to connect QDs and antibodies. Two types of immunoassay were tested: 1) QD-labelled antibodies coated over MIP layer with extracted antigen, 2) MIP extraction of the whole complex formed by antigen, antibody, and QD. The first approach provided higher sensitivity, however, the second provided higher selectivity.

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P31

DIAZONIUM-BASED ION-IMPRINTED POLYMER/CLAY NANOCOMPOSITE FOR THE SELECTIVE EXTRACTION OF LEAD (II) IONS IN AQUEOUS MEDIA

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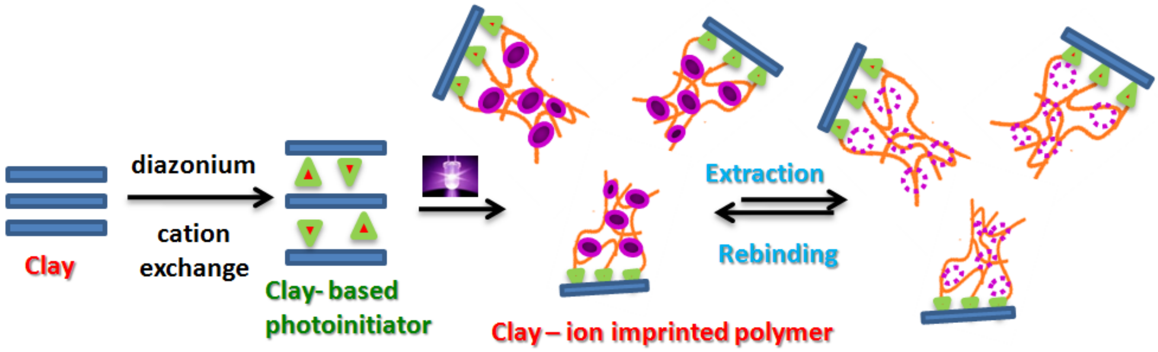
Abstract

Contamination of soils, water and food by heavy metals is a global concern,[1,2] which is tackled world-wide as it can provoke a number of serious health (e.g. liver and kidney damage, denaturation of DNA and enzymes) and environmental problems.[3] To address these issues, researchers spend time and efforts developping ultrasensitive and highly selective adsorbents of heavy metal ions.

In this context, montmorillonite/ion imprinted polymer nanocomposite (MMT/IIP) was prepared by sequential diazonium chemistry and photopolymerization process, and used for the selective removal of Pb(II). Clay was ion exchanged with dimethylaminobenzene diazonium (DMA) to facilitate incorporation of hydrogen donating sites in the layered support. Upon irradiation of the mixture of the intercalated clay, acrylamide, bisacrylamide and Pb(II)–dithizone complex in the presence of benzophenone in DMSO, the copolymerization initiated by the free radicals formed by the hydrogen abstraction of photoexcited benzophenone from the dimethylamino groups of the intercalated clay. The resulting MMT/IIP nanocomposite and the precursors pristine and diazonium cation intercalated clays were thoroughly characterized by FT-IR, XPS, XRD and SEM. Particularly, XRD analysis brought strong supporting evidence for high exfoliation of the clay upon photopolymerization, whereas XPS permitted to demonstrate that the final nanocomposite has polyacrylamide-rich surface. The adsorption and recognition properties of MMT/IIP for Pb(II) were evaluated using atomic absorption technique. The MMT/IIP directed towards Pb(II) exhibits an adsorption capacity as high as 301mg/g. It is also highly selective to Pb(II) relative selectivity coefficients to Zn^{2+} and Fe^{3+} of 9.2 and 93, respectively.[4] Compared with non-imprinted clay/polymer nanocomposite, the MMT/IIP exhibited much higher affinity for Pb(II) therefore stressing the importance of the artificial receptor sites within the nanocomposite. Altogether, the results indicate that the actual MMT/IIP is specific to Pb(II).



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