

# SupramolChem2023

## VI. SIMPOZIJ SUPRAMOLEKULSKE KEMIJE Supramolecular Chemistry 2023

# KNJIGA SAŽETAKA Book of Abstracts

Knjižnica HAZU  
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# IMPRESSUM

## ORGANIZATORI

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Kemijski odsjek Prirodoslovno-matematičkog fakulteta Sveučilišta u Zagrebu

Institut Ruđer Bošković

Hrvatsko kemijsko društvo

## IZDAVAČ

Institut Ruđer Bošković, Zagreb

## UREDNICI

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## GRAFIČKA PRIPREMA

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## VI. simpozij supramolekulske kemije – *Supramolecular Chemistry 2023*

VI. simpozij supramolekulske kemije (*Supramolecular Chemistry 2023*) održan je 6. prosinca 2023. godine u predavaonici Knjižnice HAZU, u organizaciji Razreda za matematičke, fizičke i kemijske znanosti Hrvatske akademije znanosti i umjetnosti, Kemijskog odsjeka Prirodoslovno-matematičkog fakulteta Sveučilišta u Zagrebu, Instituta Ruđer Bošković i Hrvatskog kemijskog društva.

Prvi simpozij „Supramolekulska kemija u Hrvatskoj – dosezi i pogled u budućnost“, posvećen supramolekularnoj kemiji u Hrvatskoj, održan je 2017. godine kao minisimpozij koji je obilježio 50. godišnjicu otkrića krunastih etera, 30. godišnjicu dodjele Nobelove nagrade za supramolekulsku kemiju i četiri desetljeća sustavnog istraživanja u području supramolekulske kemije u Hrvatskoj.

### Područje i znanstveni program simpozija

Ovogodišnji VI. simpozij supramolekulske kemije sadržajem prati prethodne. Posvećen je tekućim istraživanjima iz područja makrocikličke kemije, molekulskog samoudruživanja, kemije funkcionalnih materijala, molekulske samoorganizacije, supramolekulskih vrsta u čvrstom stanju i sinteze kompleksnih supramolekulskih sustava, kao i istraživanjima u drugim područjima povezanim sa supramolekulskom kemijom.

## ORGANIZATORI

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## ZNANSTVENO-ORGANIZACIJSKI ODBOR

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## ZAHVALE

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VI. simpozij supramolekulske kemije (*Supramolecular Chemistry 2023*) potpomognut je sredstvima Zaklade hrvatske akademije znanosti i umjetnosti (Natječaj Zaklade HAZU za potpomaganje Zakladnih namjena u 2023. godini), sredstvima Instituta Ruđer Bošković iz Fonda za mobilnost istraživača (2023) i Hrvatskog kemijskog društva.



# PROGRAM

8:00 – 9:00	<b>Registracija sudionika</b>
9:00 – 9:10	<b>Otvaranje konferencije</b> <b>Marko Tadić</b> , tajnik Razreda za matematičke, fizičke i kemijske znanosti HAZU <b>David Matthew Smith</b> , ravnatelj Instituta Ruđer Bošković <b>Mirko Planinić</b> , dekan Prirodoslovno-matematičkog fakulteta <b>Leo Frkanec</b> , Institut Ruđer Bošković Predsjedavajući sekcije: <b>Leo Frkanec</b>
9:10 – 9:55	<b>Sijbren Otto</b> (University of Groningen, The Netherlands), Steps Towards the <i>De-Novo</i> Synthesis of Life
9:55 – 10:25	<b>Josip Požar</b> (PMF), The Hydrophobically Driven Inclusion Revisited; the Complexation of Simple Aliphatic and Aromatic Compounds with Cyclodextrins and Cucurbiturils
10:25 – 10:55	<b>Stanka za kavu</b> Predsjedavajući sekcije: <b>Vladimir Stilinović</b>
10:55 – 11:25	<b>Marijana Radić Stojković</b> (IRB), Molecular recognition of DNA: RNA hybrid and multistranded structures
11:25 – 11:55	<b>Ivona Jasprica</b> (Xellia Pharmaceuticals), Strategies for the development of stable liquid formulations, focusing on interactions between components
11:55 – 12:25	<b>Zlatko Smole</b> (Xellia Pharmaceuticals), Data Science methods and their application in pharmaceutical industry
12:25 – 12:35	<b>Lidija Čakanić</b> (Altium), <i>Sponzorsko predavanje</i>
12:35 – 13:45	<b>Stanka za ručak</b> Predsjedavajući sekcije: <b>Dražen Vikić-Topić</b>
13:45 – 14:30	<b>Janez Plavec</b> (National Institute of Chemistry, Slovenia), NMR Revealing the Dynamic Structural Characteristics of DNA
14:30 – 15:00	<b>Ivan Kodrin</b> (PMF), Periodic DFT Calculations in the Design of Functional Materials
15:00 – 15:15	<b>Laura Nuić</b> (PMF), From self-assembled monolayers and bilayers of aromatic C-nitroso derivatives to azodioxy polymer films on gold surface
15:15 – 15:30	<b>Ivona Čipor</b> (IRB), Supramolecular Hydrogels Based on Amino Acids Derivatives for Biomedical Applications
15:30 – 16:00	<b>Stanka za kavu</b> Predsjedavajući sekcije: <b>Dominik Cinić</b>
16:00 – 16:30	<b>Nikolina Vidović</b> (UniRi), Non-covalent interactions in (cyclo)peptides
16:30 – 16:45	<b>Matija Modrušan</b> (PMF) Effect of chain length on the affinities of the short linear homopeptides towards ions in solution
16:45 – 17:00	<b>Marcela Šišić</b> (UniZg) Glycoliposomes functionalized with peptidoglycan monomer as supramolecular structures for probing sugar-lectin interactions
15:00 – 16:55	<b>Posterska sekcija</b> (predsjedavajući sekcije: <b>Vladimir Stilinović</b> , <b>Leo Frkanec</b> )
17:00	<b>Zatvaranje konferencije</b> <b>Leo Frkanec</b> , Institut Ruđer Bošković

## PLENARNA PREDAVANJA

- PL1** **Sijbren Otto** (University of Groningen, The Netherlands): *Steps Towards the De-Novo Synthesis of Life*
- PL2** **Janez Plavec** (National Institute of Chemistry, Slovenia): *NMR Revealing the Dynamic Structural Characteristics of DNA*

# Steps Towards the De-Novo Synthesis of Life

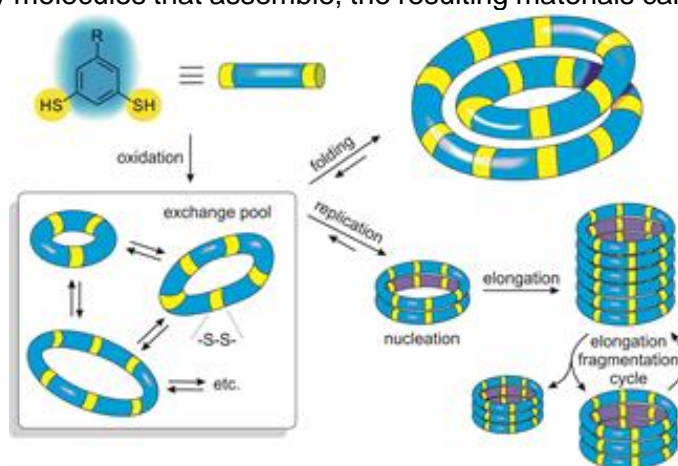
Sjibren Otto

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How the immense complexity of living organisms has arisen is one of the most intriguing questions in contemporary science. We have started to explore experimentally how organization and function can emerge from complex molecular networks in aqueous solution. We focus on networks of molecules that can interconvert, to give mixtures that can change their composition in response to external or internal stimuli. Molecular recognition within or between molecules in such mixtures leads to their mutual stabilization, which drives the synthesis of more of the privileged structures (see Figure). As the assembly process drives the synthesis of the very molecules that assemble, the resulting materials can be considered to be self-synthesizing. Intriguingly, in this process the assembling molecules are replicating themselves, where replication is driven by self-recognition of these molecules in the dynamic network.<sup>1</sup> When such systems are operated under far-from-equilibrium flow conditions, adaptation of the replicators to a changing environment can occur.<sup>2</sup>

Replicators that are able to catalyse reactions other than their own formation have also been obtained, representing a first step towards metabolism.<sup>3</sup> Rudimentary Darwinian evolution of these systems has been achieved<sup>2</sup> and the prospect of synthesizing life de-novo is becoming increasingly realistic.<sup>4</sup>



**Figure 1.** Molecular recognition within molecules yields foldamers and between molecules drives self-replication.

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# NMR Revealing the Dynamic Structural Characteristics of DNA

Janez Plavec

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Noncanonical DNA structures differ from the typical double helix, which is maintained by Watson-Crick base pairs. These structures tend to emerge in specific circumstances and can be influenced by alterations in the nucleotide sequence, environmental variables, or the presence of ligands. It's worth noting that noncanonical DNA structures can exert functional effects, such as impacting gene expression. One distinctive example of a noncanonical DNA structure is the quadruplex DNA arrangement, which arises when guanine or other nucleobases are stacked in a planar fashion to form four-stranded motifs known as quartets. DNA sequences rich in guanine, which lead to the formation of G- and AGCGA-quadruplex structures, are commonly found in telomeres and specific regulatory regions of the genome.

In addition to variations in their length, telomeric DNA repeats can also display structural diversity. One common form of structural diversity in telomeric DNA involves the formation of different G-quadruplex structures, which can vary in their folding patterns, loop lengths, and the factors that stabilize them. To investigate the structure and stability of G-quadruplexes, our research group employs Nuclear Magnetic Resonance (NMR) spectroscopy as our preferred method.<sup>1-9</sup> The G-quartet and other quartet structures within quadruplex DNA enable interactions with specific small molecules through precise recognition. Notably, Phen-DC<sub>3</sub>, a well-known G-quadruplex ligand, induces a remarkable transformation in the folding of d[TAGGG(TTAGGG)<sub>3</sub>] in a KCl solution from a hybrid-1 to an antiparallel chair-type structure, wherein the ligand inserts itself between two G-quartets (pdb id: 7Z9L).<sup>10</sup> This high-resolution NMR structure provides unprecedented evidence of true ligand intercalation within an intramolecular G-quadruplex.

The oxidation of a guanine nucleotide within DNA results in the formation of an 8-oxoguanine nucleotide (<sup>oxo</sup>G), which represents a mutagenic event within the genome. <sup>oxo</sup>G, due to its distinct configuration of hydrogen-bond donors and acceptors, can have an impact on the secondary structure of nucleic acids. We have demonstrated that <sup>oxo</sup>G can entirely replace G-quartets to form an <sup>oxo</sup>G-quartet with a reconfigured hydrogen-bonding pattern.<sup>11</sup> The increased size of the central cavity does alter the localization and exchange properties of cations.

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## POZVANA PREDAVANJA

- PO1** **J. Požar, A. Usenik, M. Šekutor, K. Leko, M. Alešković, R. Ribić, V. Petrović Peroković, Ž. Car, K. Pičuljan, S. Roca, M. Hanževački, and Z. Brkljača:** *The Hydrophobically Driven Inclusion Revisited, the Complexation of Simple Aliphatic and Aromatic Compounds with Cyclodextrins and Cucurbiturils*
- PO2** **Marijana Radić Stojković:** *Molecular recognition of DNA:RNA hybrid and multistranded structures*
- PO3** **Ivona Jasprica:** *Strategies for the development of stable liquid formulations, focusing on interactions between components*
- PO4** **Zlatko Smole:** *Data Science methods and their application in pharmaceutical industry*
- PO5** **Ivan Kodrin, Ivana Biljan, and Marijana Đaković:** *Periodic DFT Calculations in the Design of Functional Materials*
- PO6** **N. Vidović, G. Horvat, D. Riva, T. Rinkovec, T. Recca, P. Francescato, N. Cindro, V. Tomišić, and G. Speranza:** *Non-covalent Interactions in (Cyclo)peptides*

# The Hydrophobically Driven Inclusion Revisited, the Complexation of Simple Aliphatic and Aromatic Compounds with Cyclodextrins and Cucurbiturils

J. Požar,<sup>a</sup> A. Usenik,<sup>a</sup> M. Šekutor,<sup>b</sup> K. Leko,<sup>a</sup> M. Alešković,<sup>b</sup> R. Ribić,<sup>a</sup> V. Petrović Peroković,<sup>a</sup> Ž. Car,<sup>a</sup> K. Pičuljan,<sup>a</sup> S. Roca,<sup>b</sup> M. Hanževački,<sup>c</sup> and Z. Brkljača<sup>b</sup>

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Understanding the thermodynamics of inclusion reactions involving cyclodextrins and cucurbiturils provides a path for design of new hosts, enables their wider industrial application, and offers insights into the hydration of non-polar surfaces. To examine the influence of host and guest structure, their size, and hydration on the binding equilibrium the complexation of aliphatic and aromatic compounds with cyclodextrins and cucurbiturils was investigated microcalorimetrically over 278–338 K temperature range. The thermodynamic studies were aided by ROESY NMR and computational investigations of the complexes formed.

The affinity of cucurbiturils towards studied guests was significantly higher compared to cyclodextrins comprised of equal number of subunits due to the more exothermic inclusion within the former receptors. The comparative calorimetric studies also revealed that the dehydration of cucurbituril cavities is accompanied with lower entropy changes than the analogous process involving cyclodextrins. Apart from the familiar host-guest size compatibility, the binding thermodynamics could be further rationalized by considering the differences in the structure and related hydration of non-polar guest moieties. A pronounced temperature dependence of  $\Delta_r H^\circ$  (hence  $\Delta_r S^\circ$ ) unaccompanied by changes in complex structure was observed for most of the studied systems. The effect was primarily due to temperature-induced disordering of the guest-hydrating water, *i.e.*, gradual change from classical- towards non-classical hydration of the non-polar moieties. This significantly affected the thermodynamic forces governing the cyclodextrin complexation reactions which were often entropically controlled at 278 K and predominantly enthalpy-driven in high-temperature water. Conversely, due to particularly poor organization of cucurbituril-confined solvent, the binding remained in line with the non-classical rationale over the explored temperature range.

The obtained results indicate that closer examination of the guest structure and the temperature influence on the corresponding complexation reactions could further enhance the utilization of the thermodynamic potential of hydrophobically driven association and result in a better understanding of water hydration properties.

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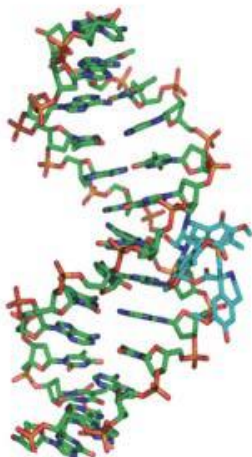
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## Molecular recognition of DNA:RNA hybrid and multistranded structures

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All processes in living organisms are determined by biomolecular interactions such as the interactions of ligands with proteins, nucleic acids, and protein-protein interactions. Molecular recognition between small organic molecules and functional biomacromolecules like nucleic acids can provide insights into the complex molecular mechanisms of biological systems and enable the development of molecular markers, tools, and new active compounds that can efficiently regulate specific cellular pathways and biological processes.

DNA:RNA hybrid and multistranded structures represent attractive targets for small molecules due to their significance in many biological processes. Therefore, this presentation will showcase the results of the quest for new structural motifs/compounds with preferential binding to DNA:RNA hybrid and multistranded structures. The method of competitive dialysis was employed for the selection of such compounds as a high-throughput method. Additionally, the binding modes of selected ligand complexes and nucleic acid structures were investigated through spectroscopic methods (fluorescence, UV/vis, circular

dichroism), calorimetric techniques, and computational methods (molecular modeling). The correlation between the high binding potential of selected compounds and their antiproliferative activity in cell culture was explored, along with cellular entry via confocal microscopy.

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## **Strategies for the development of stable liquid formulations, focusing on interactions between components**

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The lecture aims to present different strategies for liquid formulation development, focusing on their strengths and drawbacks and proposing the optimal formulation development process. Various aspects of drug product development will be presented, with particular attention paid to studying the interactions between formulation components. Namely, studying the interactions between excipients and active pharmaceutical ingredients (API) is essential to understanding excipients' effects on the API.

An illustrative example of the stabilizing effect of magnesium on beta-lactam antibiotic ceftriaxone, explained through interactions between these two formulation components, will be presented and discussed.

## **Data Science methods and their application in pharmaceutical industry**

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This lecture will present data science methods as computational methods used for pattern discovery in diverse industries including the pharmaceutical industry. In the last few decades, the number of practical applications of data science methods has steadily increased at an exponential rate, especially in the field of drug discovery and drug development.

Examples of such methods are from the straightforward similarity search and design of experiments methods to the complex machine learning algorithms such as convolutional neural networks. All these techniques have one thing in common - the identification of the hit molecules based on specific patterns.

## Periodic DFT Calculations in the Design of Functional Materials

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Computational chemistry relies on mathematical algorithms to simulate molecular behaviour. Based on quantum and molecular mechanics, scientists perform complex simulations to predict the electronic and thermodynamic properties of numerous chemical systems. Periodic density functional theory (DFT) allows us not only to study different geometries of periodic systems but also to investigate and predict the properties of functional materials accurately and rapidly in a more cost-effective way than experimentally. The practical use of periodic DFT calculations will be demonstrated in designing two types of new functional materials. Porous organic polymers are proven to be promising materials for capturing CO<sub>2</sub> from the atmosphere. Our preliminary study focused on several building units connected by three nitrogen-nitrogen linkages (azo, azoxy and azodioxy). We investigated the effect of different topologies on the CO<sub>2</sub> adsorption properties of porous materials. Calculated electrostatic potential (ESP) values helped us predict the CO<sub>2</sub> adsorption properties of newly designed porous organic polymers and to locate the most relevant binding sites for CO<sub>2</sub>/framework interactions.<sup>1,2</sup> A similar approach can help us predict the most probable interactions from the calculated ESP values in the co-crystals of one-dimensional (1-D) cadmium(II)-based coordination polymers with the small symmetric cofomers.<sup>3</sup> Crystals of similar 1-D coordination polymers also exhibit elastic flexibility and show a different extent of elasticity in response to applied mechanical force.<sup>4</sup> The periodic DFT calculations proved an important tool for better understanding intermolecular interactions and their impact on the bulk properties of mechanically flexible materials. Together with the experimental findings, the periodic DFT approach provides a solid background for studying structure-property relationships.

**Acknowledgements.** This work has been supported by the Croatian Science Foundation under the projects IP-2020-02-4467 and IP-2019-04-1242.

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## Non-covalent Interactions in (Cyclo)peptides

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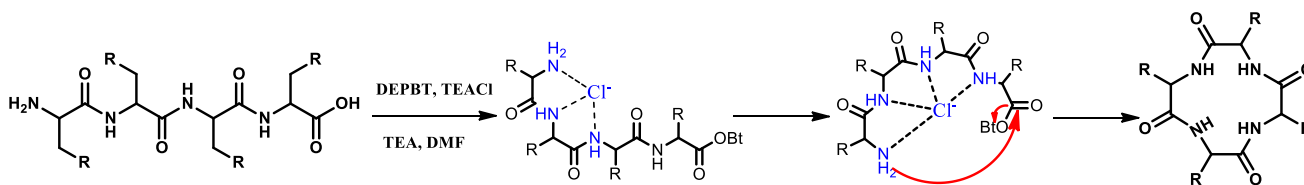
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Since the synthesis of insulin in 1921, peptides have attracted a great interest due to their unique chemical and biological properties. Currently there are more than 100 peptide drugs approved for treating a variety of diseases including diabetes, cancer, multiple myeloma, osteoporosis, cardiovascular disease and many others, being another approximately 140 peptide drugs currently in clinical trials and more than 500 therapeutic peptides in preclinical development.<sup>1</sup> Despite high affinity and specificity, peptide-based drugs have two main intrinsic drawbacks: low membrane permeability and poor *in vivo* stability. Structure optimization, including cyclization and backbone optimization, is required to improve activity and physicochemical properties of peptides. In both cases non-covalent interactions play a crucial role.

Cyclic peptides generally exhibit improved proteolytic stability, bioavailability, enhanced binding affinity and selectivity toward receptors when compared to their more-flexible linear analogues. These properties make cyclic peptides promising candidates for drug discovery. However, the synthesis of cyclopeptides continues to represent a significant synthetic challenge. The main factor that affects the success of a ring closure reaction is the conformational preorganization, that is the ability of a linear precursor to bring its *N*- and *C*-termini in close spatial proximity. A favorable conformation facilitating the intramolecular cyclization process may be achieved by using an external template such as ions.

Backbone optimization, among other things, includes substitution of particular amino acid(s) or switching their position in the primary structure which can improve the physicochemical properties of a given peptide affecting also the stabilization of the secondary structure.

In this presentation, the impact of non-covalent binding on efficiency of peptide macrocyclization as well as on physicochemical properties of cyclic peptides will be discussed.<sup>2,3</sup>



**Scheme 1.** Template-induced preorganization of linear peptide's reactive termini.

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## KRATKA USMENA PRIOPĆENJA

- KP1** Laura Nuić, Barbara Panić, Iva Šrut Rakić, Marko Kralj, Ivana Biljan: *From self-assembled monolayers and bilayers of aromatic C-nitroso derivatives to azodioxy polymer films on gold surface*
- KP2** Ivona Čipor, Ivo Piantanida, Leo Frkanec: *Supramolecular Hydrogels Based on Amino Acids Derivatives for Biomedical Applications*
- KP3** Matija Modrušan: *Effect of chain length on the affinities of the short linear homopeptides towards ions in solution*
- KP4** M. Šišić, L. Frkanec, and R. Frkanec: *Glycoliposomes Functionalized with Peptidoglycan Monomer as Supramolecular Structures for Probing Sugar–Lectin Interactions*



# From self-assembled monolayers and bilayers of aromatic C-nitroso derivatives to azodioxy polymer films on gold surface

Laura Nuić,<sup>a</sup> Barbara Panić,<sup>a</sup> Iva Šrut Rakić,<sup>b</sup> Marko Kralj,<sup>b</sup> Ivana Biljan<sup>a</sup>

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An interesting class for the design of new functional materials with potential application in molecular electronics are aromatic C-nitroso compounds. Adsorption of nitrosobenzene derivatives functionalized with sulfur-containing group on Au(111) surface results in the formation of ordered self-assembled monolayers and bilayers.<sup>1-4</sup> High-resolution scanning tunneling microscopy (STM) revealed that within monolayers and bilayers, molecules are arranged into hexagonal structures.<sup>1</sup> The ability of aromatic C-nitroso compounds to form azodioxides provides the possibility for controlled fabrication of bilayer or multilayer films by interactions of nitroso groups exposed at the monolayer interface and nitroso groups free in solution through azodioxy bonds. Recently, it has been shown that compounds containing aromatic dinitroso moiety have interesting electronic properties,<sup>5</sup> so their incorporation into azodioxy films could be used for the construction of organic electronic devices.<sup>6</sup>

The first part of this study deals with the synthesis and self-assembly of new disulfide-containing aromatic C-nitroso compounds with or without an alkyl side chain. We investigated the self-assembly behavior of the synthesized compounds on gold surface by AFM and STM. The obtained results suggested the existence of the interrelationship between the molecular and surface structures. Self-assembly of structurally different new nitroso derivatives resulted in distinct surface morphologies, especially regarding the formation of defects. Additionally, we examined the influence of thermal annealing. In the second part of this study, we investigated the polymerization of various aromatic dinitroso compounds initiated by nitroso-terminated monolayer on a gold surface by ellipsometry, AFM and nano-FTIR spectroscopy. The collected results indicated the formation of azodioxy oligomer films composed of only a few monomeric subunits or the possible tilting and intertwining of the oligomeric chains within the films resulting in poorly organized surface structures.<sup>6</sup>

**Acknowledgments.** This work has been fully supported by the Croatian Science Foundation under the project IP-2020-02-4467.

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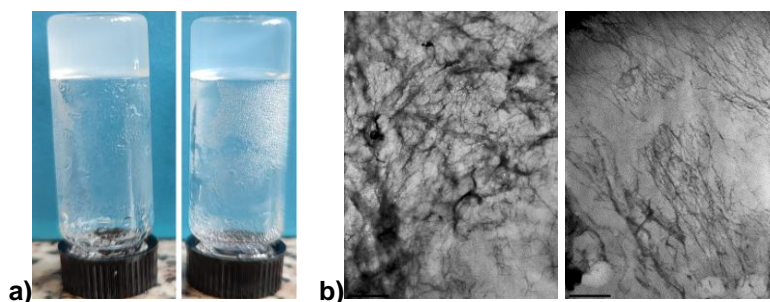
# Supramolecular Hydrogels Based on Amino Acids Derivatives for Biomedical Applications

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Supramolecular hydrogels are soft materials that are often stimuli-responsive and biocompatible due to their dynamic nature. Owing to these properties, they have seen a rise in scientific and industrial interest in the last few decades, with some hydrogels becoming commercially available medicinal products<sup>1,2,3</sup>. In this study, hydrogelator molecules based on amino acids, long alkyl chains, and different pH-sensitive end groups, particularly 4-picolyl amine and 2,2-dipicolyl amine were synthesized, characterized, and studied for their drug delivery or biosensing applicability. To enhance their properties, formulations with additive polymer molecules, namely PVA, were also studied. Fluorescent derivatives were explored for their potential as new probes for biomolecule sensing by analyzing the interactions of these hydrogelators with biomolecules such as DNA and RNA.



**Figure 1.** a) Images of hydrogels of a phenylglycine derivative (1% w/V) with 1% PVA (left) and without PVA (right), b) transmission electron micrographs of both gels (scale bar = 1  $\mu\text{m}$ ).

The results indicate enhanced thermal stability in PVA gels, with more entangled networks in the PVA formulations. The main proposed mode of self-assembly for these gels is hydrogen bonding as determined through spectroscopic measurements. In model drug delivery measurements, formulations with PVA exhibited a faster release whereas pure hydrogels displayed a more sustained release profile. A derivative based on tryptophane and 4-picolyl amine group showed a binding affinity for DNA in the micromolar range. The mentioned cases provide evidence of potential biomedical applications, either as drug delivery systems or sensors for biomolecules.

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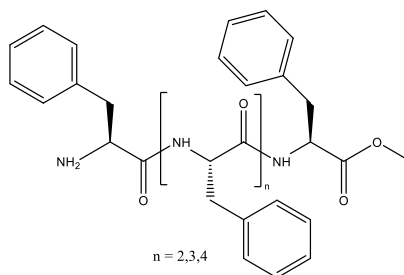
# Effect of chain length on the affinities of the short linear homopeptides towards ions in solution

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In the past few decades cyclic peptides have attracted interest as versatile receptors of cations and anions.<sup>[1,2]</sup> These compounds also exhibit enhanced binding affinity towards ions compared to their more flexible linear analogues.<sup>[2,3]</sup> The most challenging step in their synthesis is macrocyclization, i.e. the ability of a linear precursor to bring its reactive termini in close spatial proximity. This reaction step requires templating species amongst which the most frequently used are simple inorganic ions. In this work we studied the complexation of several templating ions by linear homopeptide methyl esters comprised of various number of phenylalanine subunits in acetonitrile and DMF by means of <sup>1</sup>H NMR, CD, and fluorimetric titrations. The obtained results clearly indicate the existence of the chelate effect of peptides in the binding of simple charged species. Further insight into the structural and energetic characteristics of peptide–ion complexes was obtained by MD simulations.



**Figure 1.** Structure of peptides investigated in this work.

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## Glycoliposomes Functionalized with Peptidoglycan Monomer as Supramolecular Structures for Probing Sugar–Lectin Interactions

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Recognition of glycans by sugar-recognizing proteins, known as lectins, plays a crucial role in various aspects of cell physiology. Carbohydrate-protein interactions typically exhibit weak affinities when observed in isolated and purified forms. However, in natural processes, the low affinities are surpassed by the simultaneous interactions of multiple receptor-binding sites with multiple ligands. The increased binding affinity resulting from these multiple, simultaneous ligand-receptor interactions is called the multivalent effect. Liposomes are artificial vesicles, in which an aqueous inner compartment is enclosed by a spherical bilayer of phospholipids, which spatially separates the interior from its environment. Liposomes have been extensively investigated as drug delivery systems and liposomes have also served as simple cell membrane models for supramolecular chemists. More recently, molecular recognition events in the confined environment of the lipid bilayer membrane or on the membrane surface have received increasing attention. Glycoliposomes are particularly useful in research on the interactions between carbohydrates and lectins due to the fact that liposomes provide the possibility of multivalent ligand presentation at the surface that improves the affinity of lectins for monosaccharides. Most of the lectins are multivalent and they can mediate agglutination of the glycosylated vesicles, so the agglutination assay is a convenient first method to employ for the study of carbohydrate-protein interactions. In our study, we were primarily interested in the study of interactions between fragments of bacterial peptidoglycan, peptidoglycan monomer (PGM), with GlcNAc-specific lectins. We designed and prepared glycosylated liposomes whose surfaces were decorated with PGM, the disaccharide pentapeptide,  $\beta$ -D-GlcNAc-(1 $\rightarrow$ 4)-D-MurNAc-L-Ala-D-isoGlu-*meso*A<sub>2</sub>pm-( $\epsilon$ NH<sub>2</sub>)-D-Ala-D-Ala. To incorporate the PGM into the lipid bilayer, a lipophilic derivative, PGM-oleyl was synthesized. The agglutination method was used to study the interaction of glycan moiety of PGM on the surface of glycoliposomes with Wheat Germ Agglutinin (WGA), Ulex Europaeus Agglutinin II (UEA-II) and Griffonia Simplicifolia Lectin (GS-II). After the formation of aggregates, transmission electron microscopy was used to visualize them. Preliminary results showed that WGA has the strongest binding affinity for GlcNAc among three tested lectins. Further investigation of interactions between GlcNAc-specific lectins and PGM will provide new perspectives on the molecular recognition mechanisms involving biologically active carbohydrates and model lectins. Additionally, the obtained data could be useful in the development of the next generation of functional glyconanomaterials with potential applications in diagnostics and targeted therapeutics.

## POSTERSKA PRIOPĆENJA

- PP1** Ivica Cvrtila and Ivan Halasz: *2-Formylpyridine Blue Out of the Blue*
- PP2** Maria Kolympadi Markovic, Nikolina Vidović, Lucijana Svetić, Davor Šakić, Valerije Vrček, and Dean Marković: *Three-component carboxylative C-C coupling reactions for the synthesis of cyclic carbonates*
- PP3** Karla Kukina Gradečak, Katarina Leko, Andrea Usenik, Nikola Cindro and Vladislav Tomišić: *Thermodynamics of Cation-Binding Reactions of Tertiary-Amide Calix[6]arene Derivative*
- PP4** K. Lisac, M. Klacsova, D. Uhrikova, T. Mišić Radić, and N. Ivošević DeNardis: *Nanomorphological Characterization of Self-assembled Algal Nanovesicles*
- PP5** Krešimir Molčanov, Petra Stanić, and Valentina Milašinović: *Two-electron Multicentre Bonding (Pancake Bonding): an Unusual Interaction Bordering Intra- and Intermolecular*
- PP6** Tea Ostojić, and Luca Grisanti: *Interactions in nucleobase assemblies in water: a methodological study on uracil dimer*
- PP7** K. Petrić and A. Knežević: *Synthesis of Amphiphilic Nonionic Surfactants and Properties of their Supramolecular Aggregates*
- PP8** M. Razum, M. Rosenwinkel, C. Mönich, T. Portada, L. Frkanec, M. Schönhoff, A. Šantić: *Unleashing the Power of Supramolecular Ionogels for Battery Technology*
- PP9** Petra Stanić, Petar Štrbac and Krešimir Molčanov: *Quantum crystallography study of intermolecular interactions in salts of unusual organic cyano-anions*
- PP10** L. Svetić, N. Vidović, M. Kolympadi Markovic, D. Marković: *Sinteza cikličkih karbamata iz ugljikovog dioksida*
- PP11** L.-M. Tumir, I. Zonjić, L. Racané, L. Ptiček, K. Gunčević, and M. Radić Stojković: *Interactions of Amidino-Substituted Bis-Benzothiazole, Bis-Benzoxazole and Bis-Benzimidazole Ligands with Double-Stranded, Triple-Stranded and Hybrid DNA:RNA Polynucleotides*
- PP12** M. Kraševac Sakač, D. Madunić-Čačić, D. Marković, N. Sakač, and M. Jozanović: *Potentiometric Sensor for Nonionic Surfactants*

## 2-Formylpyridine Blue Out of the Blue

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During research in acyl hydrazone photoswitching and dynamic exchange<sup>1</sup>, in the broader context of dynamic combinatorial chemistry,<sup>2</sup> some of the stock solutions unexpectedly started showing blue discoloration after prolonged standing. In particular, blue color had always appeared in solutions of 2-formylpyridine in aqueous ammonium acetate buffered to pH = 4.0. On longer standing dark-blue globular and fibrillar aggregates would form (Figure 1). Such behavior was not only unexpected, but, up to our knowledge, has also been undocumented, up to the point of there being only a single mentioning of a similar product appearing in a similar context, as “black and insoluble tar side products”.<sup>3</sup> Since the formation context and visual properties suggest the possibility of a polyconjugated polymeric product, with prospects of a new organic (semi)conductor, pigment, or a dynamic self-assembled material, we are highly motivated to elucidate its structure, find optimal approach to its synthesis and isolation, as well as to study its physical and chemical properties. In this report we present the current status of our ongoing research on this material.



**Figure 1.** Globular and fibrillar aggregates formed by condensation of 2-formylpyridine.

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## Three-component carboxylative C-C coupling reactions for the synthesis of cyclic carbonates

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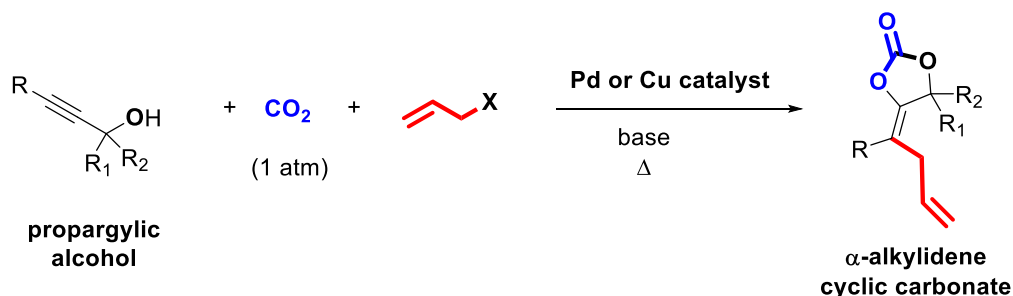
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Capture of carbon dioxide (CO<sub>2</sub>) and transformation to highly valued organic compounds are particularly challenging due to its increased kinetic and thermodynamic inertness. However, the direct use of CO<sub>2</sub> as a C1 synthon represents an attractive approach in modern organic synthesis for the valorization of this atmospheric gas responsible for the greenhouse effect.<sup>1</sup>

Catalytic capture of CO<sub>2</sub> by propargylic substrates -alcohols or amines- affords α-alkylidene cyclic carbonates or carbamates, respectively, which are structural motifs often found in pharmaceuticals, polymers, chiral auxiliaries, etc.<sup>2</sup> Combination of CO<sub>2</sub> capture with C-C cross-coupling reactions may give direct access to complex products that otherwise require multistep syntheses.<sup>3</sup>

We report three-component carboxylative C-C cross-coupling reactions catalyzed by palladium or copper salts. Our efforts are focused on allylation reactions employing allyl halides, propargylic alcohols, and CO<sub>2</sub> under atmospheric pressure (Figure 1.). Optimization of the reaction conditions are currently in progress, as well as elucidation of the reaction mechanism by the combination of experimental and computational methods, i.e., control experiments, *in situ* NMR monitoring and density functional theory (DFT) calculations.



**Figure 1.** Three-component carboxylative C-C cross-coupling allylation reactions.

**Acknowledgements.** Croatian Science Foundation (INDICATOR, IP-2019-04-8846); University of Rijeka (uniri-prirod-18-102-1237).

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## Thermodynamics of Cation-Binding Reactions of Tertiary-Amide Calix[6]arene Derivative

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Calix[ $n$ ]arenes are macrocyclic oligomers consisted of phenolic residues ( $n \geq 4$ ) linked by methylene bridges in the *ortho* position.<sup>1</sup> Depending on the size and functionalization of their upper and/or lower rim, these compounds can be very efficient and even selective receptors for various neutral and ionic chemical species.<sup>1–3</sup> Although calixarenes have been widely used as receptors in supramolecular chemistry for the past few decades, most of the investigations have been oriented towards calix[4]arene derivatives, whereas thermodynamics of complexation reactions of calix[6]arenes has remained rather unexplored.

In the scope of this work, the fluorescence properties of tertiary-amide calix[6]arene derivative **L** (Figure 1) were investigated, as well as its binding affinities towards alkali and alkaline earth metal cations in acetonitrile. Thermodynamic parameters of the reactions yielding complexes of 1:1 and 2:1 (cation:ligand) stoichiometries were determined by means of spectrophotometry, NMR spectroscopy, isothermal titration calorimetry, and fluorimetry. The obtained results were discussed regarding the structural characteristics of the ligand as well size and charge density of the cations.

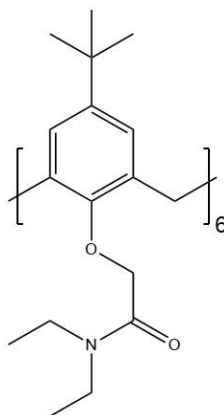


Figure 1. Structure of calix[6]arene derivative **L**.

**Acknowledgements.** This work has been supported by the Croatian Science Foundation, grant number IP-2019-04-9560 (project MacroSol), and the European Regional Development Fund (infrastructural project CluK, grant number KK.01.1.1.02.0016).

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- 3 J. Požar, I. Nikšić-Franjić, M. Cvetnić, K. Leko, N. Cindro, K. Pičuljan, I. Borilović, L. Frkanec, V. Tomišić, *J. Phys. Chem. B* **2017**, *121*, 8539; N. Cindro, J. Požar, D. Barišić, N. Bregović, K. Pičuljan, R. Tomaš, L. Frkanec, V. Tomišić, *Org. Biomol. Chem.* **2018**, *16*, 904; J. Požar, M. Cvetnić, A. Usenik, N. Cindro, G. Horvat, K. Leko, M. Modrušan, V. Tomišić, *Molecules* **2022**, *27*, 470; K. Leko, A. Usenik, N. Cindro, M. Modrušan, J. Požar, G. Horvat, V. Stilinović, T. Hrenar, V. Tomišić, *ACS Omega* **2023**, *8*, 43074.



## Nanomorphological Characterization of Self-assembled Algal Nanovesicles

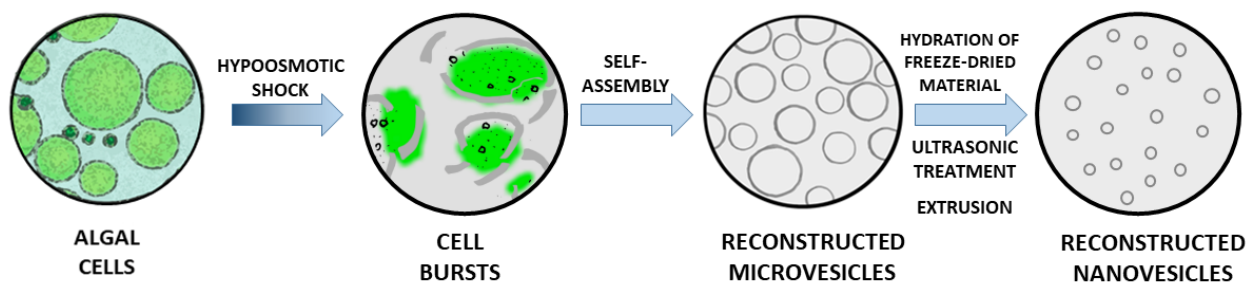
K. Lisac,<sup>\*,a</sup> M. Klacsova,<sup>b</sup> D. Uhríkova,<sup>b</sup> T. Mišić Radić,<sup>a</sup> and N. Ivošević DeNardis<sup>a</sup>

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Although algae are widely used as food, pharmaceutical agents and energy sources, there are still numerous applications that need to be explored due to their immense potential in biotechnology. One of these is undoubtedly the production of drug carriers that mimic natural biological membranes.<sup>1</sup> The unicellular marine microalga *Dunaliella tertiolecta*, which has a thin elastic plasma membrane and a glycocalyx surface layer, has proven to be a suitable cell model for preparation of reconstructed vesicles.<sup>2,3</sup> Following hypoosmotic shock, the soft cells rupture, the intracellular contents are discharged and the remaining membrane fragments self-assemble to spontaneously form membrane vesicles in suspension. Our recent experiments have shown that vesicles can be reconstructed by hydration of freeze-dried material followed by ultrasonication and extrusion through a filter with a pore size of 200 nm. The aim of this study is to prepare reconstructed nanovesicles and perform nanomorphological characterization by atomic force microscopy in liquid. The nanometer-sized vesicles had a spherical shape with an average diameter of  $172.2 \pm 25.9$  nm and an average height of  $32.8 \pm 6.9$  nm.



**Figure 1.** Protocol of a reconstructed membrane vesicle preparation.

**Acknowledgments.** This work is supported by International Visegrad Grant “Research network VF-Croatia for the development of novel drug carriers from algae” (No. 22220115).

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## Two-electron Multicentre Bonding (*Pancake Bonding*): an Unusual Interaction Bordering Intra- and Intermolecular

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Two-electron multicentre bonding ( $2e/mc$  or *pancake bonding*) is a strong interaction between planar organic radicals. Two electrons from contiguous radicals are coupled, forming a HOMO orbital which extends between the radicals, so the interaction has a significant covalent component. Total energy is comparable to the strongest intermolecular (also partially covalent) interactions, hydrogen bonding and halogen bonding. The covalent component often exceeds  $-15 \text{ kcal mol}^{-1}$ . Thus,  $2e/mc$  bonding can be regarded as weak, unlocalised  $\pi$ -bonding. Until recently, majority of studies dealing with  $2e/mc$  bonding were theoretical.

A detailed experimental study of various radical systems by us involves a novel approach by a combination of advanced experimental and theoretical methods: analysis of X-ray charge density (*quantum crystallography*), crystallography under extreme conditions (variable temperature and pressure), characterisation of electrical (by impedance spectroscopy) and magnetic properties (by EPR spectroscopy and SQUID), study of theoretical charge density by periodic DFT methods and *ab initio* study of isolated clusters.

Our work shows that  $2e/mc$  bonding also forms between partially charged radicals (with a formal charge of  $-1/2$  or  $-1/3$ )<sup>1,2</sup> and between electron donors and acceptors in charge transfer compounds.<sup>3</sup> Although a prototype of pancake bonding is a radical dimer sharing an electron pair, weaker  $2e/mc$  bonding also occurs in different oligomers (trimers, tetramers etc.),<sup>1,2</sup> but also extends in 1D<sup>4,5</sup> and also in 2D.<sup>2</sup> This also means bond order lower than 1, i.e. a single electron pair shared by three or more rings. The first high-pressure studies<sup>6,7</sup> showed that application of pressure increases covalent character of the interaction,<sup>8</sup> and may a phase transition may transform  $2e/mc$  bonded dimers into a 1D pancake-bonded polymer.<sup>8</sup>

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## Interactions in nucleobase assemblies in water: a methodological study on uracil dimer

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Aggregates and molecular crystals are an interesting playground to monitor how interactions can affect properties, such as optical properties and photochemical behaviour. We decided here to focus on nucleobases as crucial molecular units whose properties are strongly relevant for life and its chemistry.<sup>1</sup> Besides the interest in photochemistry, the uracil dimer has been largely investigated in the past as model for non-covalent interaction of organic (bio)-molecules.<sup>2</sup>

As the nucleobase association in water is a rare event due to the competition for interactions with water, we started our study by critically choosing the set of collective variables to properly sample the configurational space.<sup>3</sup> We were able to capture all the minima states that have been reported for uracil dimer in vacuum (stacking, 2H-bonded and T-shaped stacking/1H bond) and to compare with results available in literature.<sup>2</sup> Besides, a significant part of the investigation focuses on the decision-making process in selecting the force field and water model. It aims to clarify the methodological intricacies involved in accurately capturing the dynamics of these molecular assemblies. Parameterized AMBER99 with TIP3P water model versus AMBER99 with OPC water are compared.<sup>4,5</sup> After validation of the best force field, additional analysis and runs, including a slightly different Molecular Dynamics methodology, are performed to confirm the obtained results and validate well-tempered metadynamics as an applicable method to this problem.

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# Synthesis of Amphiphilic Nonionic Surfactants and Properties of their Supramolecular Aggregates

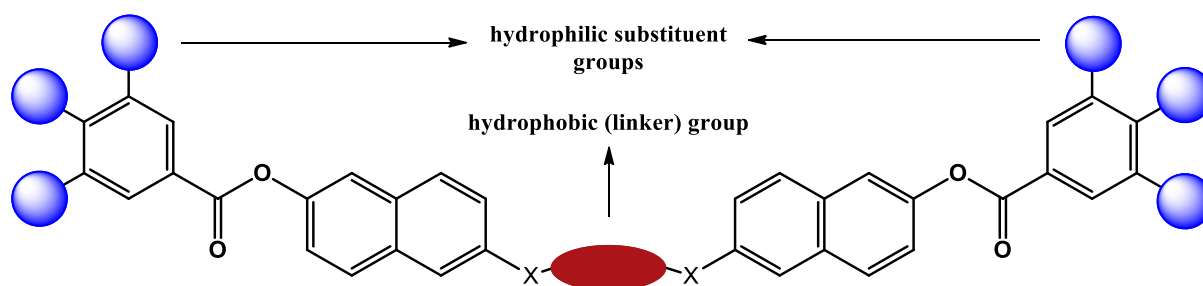
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In modern times, more attention is given to the principles of “green chemistry”, a trend that has also permeated the field of organic synthesis. Therefore, it is important to find ways to reduce harmful waste, from byproducts to the solvents used. The “greenest” solvent is water, which is a reason for the efforts of many researchers to find ways to make organic synthesis in an aqueous medium efficient and usable on a large scale. One approach is the use of organic amphiphilic surfactants that form supramolecular structures with hydrophobic pockets in water, such as micelles. Organic reactions, that are performed in organic solvents by default, now take place in the hydrophobic, non-aqueous environment of supramolecular aggregates. This approach is proven feasible by Lipshutz et. al. with their surfactant TPGS-750-M<sup>1</sup>. Surfactants as such have great potential to catalyze a number of reactions<sup>2</sup>.

Our goal is to develop a surfactant model that could be easily tailored to achieve different properties, such as type, size, and stability of supramolecular structures. In the early stage of this research, the type of linkage group between the hydrophobic and hydrophilic parts of the surfactant molecule was tested in terms of the stability of the supramolecular structure in water. Synthesized surfactants exhibited supramolecular arrangements in water in tests with hydrophobic fluorescent probe – thioflavin T. Furthermore, the supramolecular aggregates were characterized by calorimetry and microscopy techniques. Finally, prepared surfactants were tested in Williamson ether formation reactions, where they showed an increase in yield in the presence of surfactant, in contrast to surfactant-absent reaction mixtures.



**Figure 1.** General design of amphiphilic surfactant molecules and the position of hydrophobic and hydrophilic parts.

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# Unleashing the Power of Supramolecular Ionogels for Battery Technology

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Ionic liquids (IL) have garnered significant attention for their role in advancing novel electrolytes for emerging electrochemical applications<sup>1,2</sup>. One notable application is in lithium-ion batteries, where ILs present an alternative to conventional organic electrolytes, such as ethylene carbonate-dimethyl carbonate (EC-DMC), known for their safety-related drawbacks. Conventional organic electrolytes are prone to issues like high flammability, volatility, and potential leakage from the battery in the event of damage, posing serious risks such as fire or battery explosion<sup>2</sup>. Ionic liquids offer a solution to these challenges due to their low vapor pressure, non-flammability, high ionic conductivity, and good chemical and thermal stability<sup>3,4</sup>. However, as with any other liquid, they always carry a risk of leakage. One effective strategy to mitigate this risk involves immobilizing the ionic liquid within a gel, resulting in what is known as an ionogel. In this configuration, the IL is confined within a gelator matrix, ensuring the preservation of high ionic conductivity while addressing safety concerns.

This research focuses on the preparation and characterization of the Li-ionogels prepared by combining an ionic liquid with lithium salt and an oxalamide-based gelator to induce gelation. Specifically, we studied ionogels composed of an ionic liquid with a pyrrolidinium cation and bis(trifluoromethylsulfonyl) imide anion, using (*S,S*)-bis(phenylalaninol)oxamide as the gelator. Samples with up to 10 wt% of lithium salt (Li- bis(trifluoromethylsulfonyl) imide) were prepared and the minimum concentration of gelator needed to form the Li-ionogels was determined. The ionic conductivity of these ionogels was measured using impedance spectroscopy in a broad temperature and frequency range, from  $-80\text{ }^{\circ}\text{C}$  to  $80\text{ }^{\circ}\text{C}$  and 0.01 Hz to 20 MHz. Remarkably, all studied Li-ionogels retained high ionic conductivity of their parent gelator-free solution of the Li-salt in an ionic liquid indicating that the gelator matrix has no effect on the ion dynamics in these materials. This promising result represents great potential in developing supramolecular ionogels as a new family of electrolytes for Li-batteries.

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## Quantum crystallography study of intermolecular interactions in salts of unusual organic cyano-anions

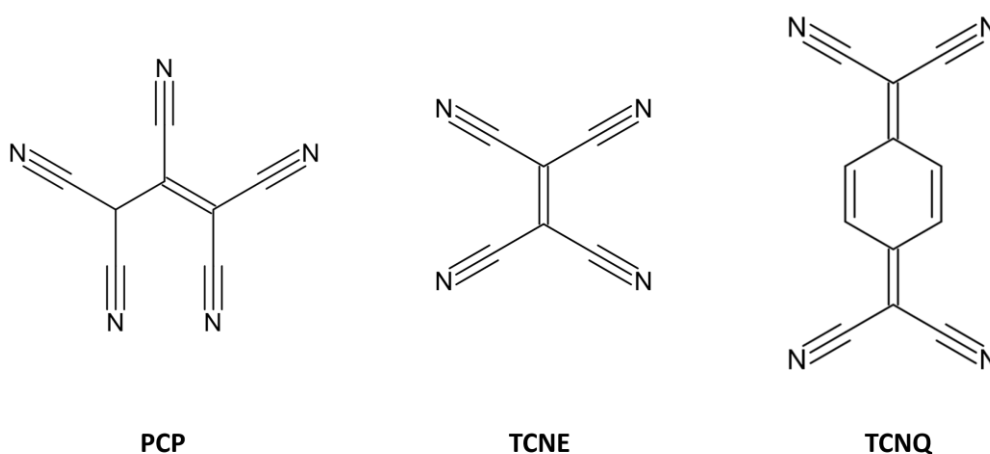
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Three novel salts of unusual cyano-anions, pentacyanopropenide (PCP) carbanion, tetracyanoethylene (TCNE) radical anion and partially charged 7,7,8,8-tetracyanoquinodimethane (TCNQ) radical anion, with organic cations were studied with experimental X-ray charge density. Due to the presence of electron-withdrawing cyano groups at the periphery of anions and consequently delocalisation of the negative charge in the conjugated  $\pi$ -electron system, stability of all three anions is expressed. Partial atomic charges show that the cyano groups have the most negative charge in PCP and the least in TCNQ, which is in agreement with molecular electrostatic potential. Topology of electron density reveals that bond orders in the carbon skeletons correspond to delocalised  $\pi$  bonding: in PCP bond orders in the central C-C-C fragment are 1.45 and 1.63 and in TCNE order of the central C-C bond is 1.61. The six-membered ring in TCNQ is approximately half-way between quinoid and semiquinoid.

In all three studied systems, radical anions form dimers where they are bound by two-electron multicentre bonding ( $2e/mc$ ). In salt with TCNE anion, dimer consists of four centers, and maximum electron density in two bonding critical points between two TCNE moieties is  $0.17 e \text{ \AA}^{-3}$ . TCNQ dimer is formed of 32 centers and there are multiple bonding critical points between the moieties, with maximum electron density of  $0.08 e \text{ \AA}^{-3}$ .



**Figure 1.** Anions precursors used in this research to prepare crystals: pentacyanopropenide (PCP) carbanion, tetracyanoethylene (TCNE) radical anion, 7,7,8,8-tetracyanoquinodimethane (TCNQ) radical anion.

## Sinteza cikličkih karbamata iz ugljikovog dioksida

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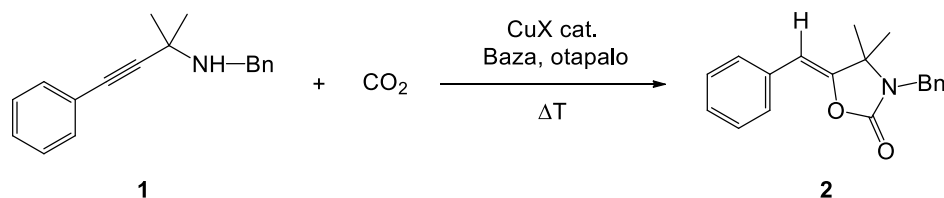
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Ugljični dioksid (CO<sub>2</sub>) je inertan i netoksičan plin. Glavni izvor emisije CO<sub>2</sub> u atmosferu proizlazi iz procesa izgaranja ugljikovodika i drugih fosilnih goriva koji se koriste u sektorima industrije, dobivanja energije i transporta. Njegova prekomjerna emisija ima ozbiljan negativan utjecaj na okoliš, manifestirajući se kroz ekološke poremećaje, globalno zatopljenje i klimatske promjene. Aktualna istraživanja usmjerena su na razvoj novih katalitičkih reakcija i procesa koje omogućavaju pretvorbu CO<sub>2</sub> u proizvode i goriva s dodanom vrijednošću.<sup>1</sup> U sklopu navedenih tijekom proteklog desetljeća, značajno je poraslo zanimanje za iskorištavanje CO<sub>2</sub> kao pristupačnog i ekonomičnog C1-izvora ugljika u svrhu dobivanja karbonata i karbamata, čija važnost dodatno naglašena kroz mogućnost njihove raznovrsne upotrebe.<sup>1</sup>

Primjerice, oksazolidinoni su ciklički karbamati koji imaju značajnu primjenu u farmaceutskoj industriji, a posebice su važni kao ključni sastojci antibiotika.<sup>2</sup> Ovi spojevi mogu se uspješno sintetizirati u kataliziranim reakcijama CO<sub>2</sub> i propagil amina. S ciljem unapređenja ovih procesa CO<sub>2</sub>-fiksacija i važnost oksazolidinona, razvijen je široki spektar organometalnih katalizatora temeljenih na plemenitim metalima, uključujući Ru, Pd, Au i Ag.<sup>3</sup>

U ovom istraživanju opisana je sinteza oksazolidinona **2** iz *N*-benzil-2-metil-1-fenilbut-3-in-2-amina (**1**) u jednom koraku, bez upotrebe skupih katalizatora (Shema 1). U svrhu optimizacije reakcijskih uvjeta, kao katalizator su korištene različite jeftine soli bakra, a također je proučen i utjecaj različitih baza, otapala i temperature na iskorištenje reakcije.



**Shema 1.** Sinteza oksazolidinona **2** iz *N*-benzil-2-metil-1-fenilbut-3-in-2-amina (**1**).

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# Interactions of Amidino-Substituted Bis-Benzothiazole, Bis-Benzoxazole and Bis-Benzimidazole Ligands with Double-Stranded, Triple-Stranded and Hybrid DNA:RNA Polynucleotides

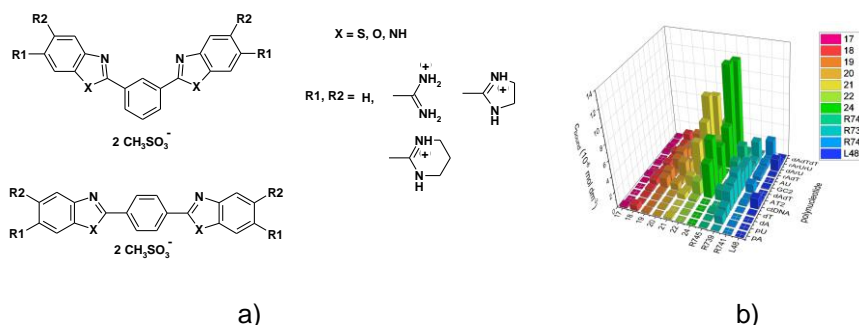
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Combining various structural components that affect binding to polynucleotides sterically and/or electrically is a common step in the design of novel physiologically active compounds.<sup>1</sup> Using the competitive dialysis method, newly synthesized compounds with amidino substituents positioned differently in the bis-benzothiazole, bis-benzoxazole, and bis-benzimidazole core were examined for their affinity toward different polynucleotide structures and sequences.<sup>2</sup>



**Figure 1.** a) Amidino substituted bis-benzothiazole, bis-benzoxazole and bis-benzimidazole ligands; b) Summary of competition dialysis results with ligands binding to 13 nucleic acid structures and sequences (cbound = concentration of ligand bound to each nucleic acid in  $\mu\text{M}$ )

Determined by the competition dialysis method, the amount of bound ligand is directly proportional to the ligand binding affinity. Ligands **21** and **24** showed the highest affinity for double-stranded and triple-stranded polynucleotides and also the best structural selectivity. These complexes were examined further using thermal melting studies, circular dichroism (CD), and fluorescence spectroscopy since they exhibited the greatest binding to dArU, rAdT, and dAdTdT.

The mode of ligand binding to polynucleotides was determined by use of CD spectroscopy. According to negative ICD signals, *meta*-substituted **24** bound to hybrid DNA:RNA polynucleotides via intercalation. At higher ratios **24**/polynucleotide, strong negative ICD signals pointed to aggregation of **24** along the polynucleotide phosphate backbone. Strong positive and/or bisignate ICD signals of *para*-substituted **21** indicated minor groove binding of single and/or dimer form of **21** to the hybrid DNA:RNA. Both compounds bound to the minor groove of triple stranded dAdTdT; **24** showed aggregation at higher molar ratios. Biological activity of compound will be examined.

**Acknowledgments.** Financial support from the Croatian Science Foundation under the project IP-2018-01-4694 is gratefully acknowledged.

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## Potentiometric Sensor for Nonionic Surfactants

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Nonionic surfactants are composed of molecules that lack a charged functional group, unlike their anionic (negatively charged) and cationic (positively charged) counterparts. They are typically formed by combining hydrophilic groups like polyethylene glycol, ethoxylated sorbitan, or ethoxylated fatty alcohols with hydrophobic groups such as long alkyl chains. Nonionic surfactants do not dissociate when dissolved in water and have the broadest range of properties depending upon the ratio of hydrophilic–lipophilic balance. They are widely used in household products, personal care products, pharmaceuticals, agrochemicals, and different industrial processes (inks, paints, coatings, textile manufacturing, etc.) for emulsification, foaming and wetting, solubilization, and stabilization. Nonionic surfactants are generally considered toxic since their biodegradability can vary based on the specific chemical composition.

The classical approach in nonionic surfactant detection is based on chromatography techniques (HPLC, LC, GC), spectroscopic methods (MS, IR, and NMR), electrochemical methods (polarography, voltammetry, and capillary electrophoresis), and other techniques (surface tension measurement and fluorescence spectroscopy). Surfactant sensors represent an interesting alternative for low-cost, sensitive, and simple detection and quantification of nonionic surfactants. We presented the surfactant sensor for nonionic polyethoxylated alcohols (EONS) usually used in commercial product formulations. The PVC-based liquid membrane-type surfactant sensor is used as an end-point indicator in potentiometric titrations of EONS in the form of barium pseudo cationic complexes<sup>1</sup>, using sodium tetraphenylborate as a titrant.

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