SupramolChem2019

III. SIMPOZIJ SUPRAMOLEKULSKE KEMIJE

Supramolecular Chemistry 2019

KNJIGA SAŽETAKA

Book of Abstracts

Knjižnica HAZU

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Pod pokroviteljstvom Hrvatskog kemijskog društva

IZDAVAČ

Institut Ruđer Bošković, Zagreb

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GRAFIČKA PRIPREMA

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III. simpozij supramolekulske kemije – Supramolecular Chemistry 2019

Prvi simpozij „Supramolekulska kemija u Hrvatskoj – dosezi i pogled u budućnost" posvećen supramolekulskoj kemiji u Hrvatskoj održan je 2017. godine povodom 70. godišnjice rođenja akademika Mladena Žinića, 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.

Minisimpozij je bio izuzetno dobro posjećen i pobudio je velik interes u znanstvenoj javnosti. Stoga je odlučeno da se nastavi s redovitim godišnjim okupljanima. Slijedio je II. simpozij supramolekulske kemije (*Supramolecular Chemistry 2018*), koji je sadržajem pratio prethodni simpozij, ali je bio ponešto drugačije strukturiran. Pored pozvanih predavanja uvedena su kratka usmena priopćenja i posterska sekcija. Skup su obilježile inspirativne prezentacije i diskusije iz raznih područja supramolekulske kemije.

Knjige sažetaka I. i II. Simpozija dostupne su u elektronskom obliku na **https://supramolchem2019.irb.hr/**

Ove godine održat će se III. simpozij supramolekulske kemije (*Supramolecular Chemistry 2019*), kojim nastavljamo ovaj niz sastanaka supramolekulskih kemičara Hrvatske. Sudionici će svoje znanstvene rezultate prezentirati u formi pozvanih predavanja, kratkih usmenih i posterskih priopćenja. U ovogodišnji Simpozij osim akademske zajednice bit će uključeni i zapaženi rezultati iz privrede ostvareni primjenom načela supramolekulske kemije.

Područje i znanstveni program simpozija

III. simpozij supramolekulske kemije bavit će se raznovrsnim temama iz tog područja kemije. Tijekom Simpozija prezentirat će se različiti aspekti tekućih istraživanja iz područja makrocikličke kemije, molekulskog samoudruživanja, kemije funkcionalnih materijala, samoorganizacije, supramolekulskih vrsta u čvrstom stanju i sinteze kompleksnih supramolekulskih sustava te istraživanja u drugim područjima supramolekulske kemije.

ZNANSTVENO-ORGANIZACIJSKI ODBOR

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ZAHVALE

III. simpozij supramolekulske kemije (*Supramolecular Chemistry 2019*) organiziran je u okviru projekta Hrvatske zaklade za znanost Sinteza supramolekulskih samo-udruženih nanostruktura za izgradnju naprednih funkcionalnih materijala (IP-2018-01-6910).

Organizacija skupa potpomognuta je sredstvima Zaklade hrvatske akademije znanosti i umjetnosti i Ministarstva znanosti i obrazovanja Republike Hrvatske.

PROGRAM

08:00 **Registracija sudionika**

09:00 **Otvaranje simpozija – Uvodne riječi**
tajnik Razreda za matematičke, fizičke i kemijske znanosti HAZU akademik Goran Pichler, ravnatelj IRB David Matthew Smith, dekanica PMF Aleksandra Čižmešija, predsjednik Odbora za kemiju HAZU akademik Mladen Žinić, Leo Frkanec

Predsjedavajući sekcije / Chairman: **Dražen Vikić Topić**

09:30 **Tomislav Friščić** (McGill University): *Stabilnost koordinacijskih mreža*

10:00 **Nikola Bregović** (PMF): *Complex equilibrium systems in supramolecular chemistry – "A blessing or a curse?"*

STANKA ZA KAVU

Predsjedavajući sekcije / Chairman: **Leo Frkanec**

11:00 **Aleksandar Danilovski** (Xellia Pharmaceuticals): *Inovativni proizvod (Vankomicin RTU) – kreativna vs. reaktivna vibracija istraživanja*

11:30 **Ivan Halasz** (IRB): *Molekulsko prepoznavanje i selektivnost u reakcijama u čvrstom stanju mljevenjem*

12:00 **Marina Tranfić Bakić** (University of Bologna): *Light Effected Autonomous Molecular Pumps and Reservoirs*

12:15 **Zoran Kokan** (Masaryk University): *Hypervalent Iodine-based Reversible Covalent Bond in Rotaxane Synthesis*

STANKA ZA RUČAK

Predsjedavajući sekcije / Chairman: **Dominik Cinčić**

14:00 **Krešimir Molčanov** (IRB): *Jake međumolekulske interakcije: kovalentne ili nekovalentne?*

14:30 **Nikola Bedeković** (PMF): *Kokristalizacija perhalogeniranih benzenâ s jednostavnim derivatima piridina – usporedba klasičnih donora halogenske veze*

14:45 **Mateja Pisačić** (PMF): *Mechanically adaptable crystals: Impact of supramolecular connectivity on crystal flexibility*

STANKA ZA KAVU

Predsjedavajući sekcije / Chairman: **Vladislav Tomišić**

15:30 **Mirta Rubčić** (PMF): *Polioksomolibdati {Mo132} (Keplerati): funkcionalni supramolekulski receptori*

16:00 **Mario Gabričević** (FBF): *Utjecaj glikozilacije alfa-1-kiselog glikoproteina (AGP) na vezanje lijekova*

16:30 **Dajana Barišić** (IRB): *Protonation and Anion Binding Properties of Urea Derivatives - Comprehending the Proton Transfer*

16:45 **Tomislav Gregorić** (IRB): *Samoudruživanje i polimerizacija bis(aminokiselinskih) fumarata inducirana gama i UV zrakama*

17:00 **Posterska sekcija** (Predsjedavajući sekcije / Chairmen: Vladislav Tomišić, Leo Frkanec)

18:00 **Zatvaranje konferencije – završne riječi**
Leo Frkanec, akademik Mladen Žinić

POZVANA PREDAVANJA

P1 **Tomislav Friščić** (McGill University): *Stabilnost koordinacijskih mreža*

P2 **Nikola Bregović** (PMF): *Complex equilibrium systems in supramolecular chemistry – "A blessing or a curse?"*

P3 **Aleksandar Danilovski** (Xellia Pharmaceuticals): *Inovativni proizvod (Vankomicin RTU) – kreativna vs. reaktivna vibracija istraživanja*

P4 **Ivan Halasz** (IRB): *Molekulsko prepoznavanje i selektivnost u reakcijama u čvrstom stanju mljevenjem*

P5 **Krešimir Molčanov** (IRB): *Jake međumolekulske interakcije: kovalentne ili nekovalentne?*

P6 **Mirta Rubčić** (PMF): *Polioksomolibdati {Mo132} (Keplerati): funkcionalni supramolekulski receptori*

P7 **Mario Gabričević** (FBF): *Utjecaj glikozilacije alfa-1-kiselog glikoproteina (AGP) na vezanje lijekova*

Stabilnost koordinacijskih mreža

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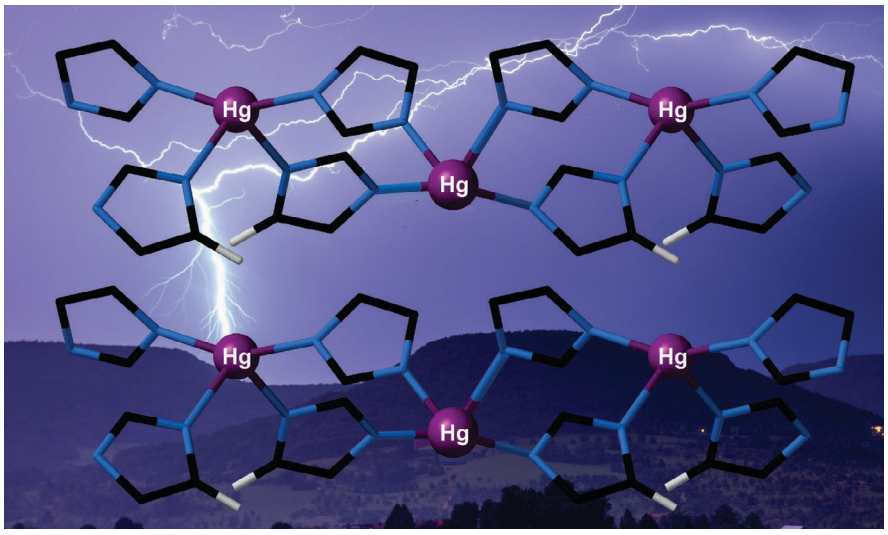
Jedno od najaktivnijih područja moderne znanosti o materijalima su koordinacijske mreže, materijali nastali povezivanjem metalnih iona i organskih liganada u dvije ili tri dimenzije. Takve koordinacijske mreže, koje mogu ali i ne moraju biti stalno porozni materijali, se lako mogu sintetizirati reakcijama u otopini ili u čvrstom stanju, na primjer mehanokemijski[1] ili reakcijama ubrzanog starenja.[2] Općeniti dizajn koordinacijskih mreža temelji se na kombiniranju različitih metalnih iona s raznojako supstituiranim ligandima, što dopušta jednostavan i učinkovit pristup sintezi materijala s raznoraznim naprednim svojstvima, poput absorpcije i razdvajanja plinova, protonske ili elektronske vodljivosti, itd.[3] Iako je već veliki broj znanstvenih radova posvećen razvoju novih koordinacijskih mreža, razumijevanje njihovih energijskih svojstava i stabilnosti je još uvijek na vrlo niskoj razini. Na primjer, termodinamički parametri jedne od najpopularnijih koordinacijskim mreža, cinkovog 2-metilimidazolata (takozvani ZIF-8 ili MAF-4) su tek nedavno izmjereni.[4]

Ovo će predavanje predstaviti rezultate rada naše grupe u eksperimentalnom i teorijskom razumijevanju stabilnosti koordinacijskih mreža, te odnosa izmedu kemijske strukture, mrežne strukture (topologije mreže) te stabilnosti materijala. Predavanje će uključiti istraživanja u smjeru predviđanja topologija i struktura novih, prethodno neistraženih koordinacijskih mreža,[5] te razumijevanja polimorfije koordinacijskih mreža. Također, biti će prikazani naši najnoviji rezultati u mjerenju energetskog učinka koordinacijskih mreža, te nove mogućnosti njihove uporabe u raketnim gorivima.[6]



Slika 1. Umjetnički prikaz fragmenata strukture novog polimorfa dvodimenzijske koordinacijske mreže živinog(II) imidazolata. Autor: I. R. Speight.

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Complex equilibrium systems in supramolecular chemistry – „A blessing or a curse?”

Nikola Bregović,[a,*] Dajana Barišić,[b] Nikola Cindro,[a] Krunoslav Užarević,[b] and Vladislav Tomišić*,[a]

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As the field of supramolecular chemistry evolves, the systems based on non-covalent interactions find their application in various technologies as chemical sensors, transport systems etc. Consequently, it is of paramount importance to understand the thermodynamics of supramolecular reactions, which enables fine-tuning the properties of the corresponding supramolecules. To this end, the processes leading to their formation should be fully characterised and ever-new interactions stabilising the corresponding systems ought to be discovered.

The reactions yielding supramolecular complexes in solution are often coupled with other processes, *e.g.* proton transfer, aggregation, homoassociation and ion pairing, especially in organic media. These reactions have rarely been taken into account in the course of complex characterisation, although ignoring them could lead to incomplete conclusions and erroneous interpretation of the results. In order to avoid this, it is necessary to carry out systematic identification and characterisation of all processes taking place in the solution. This often demands significant efforts, including innovative use of experimental techniques and elaborate data processing.

In this lecture, several classes of anion binding hosts (urea, amine and amide derivatives) will be presented with a thorough overview of the methodology used for a complete characterisation of multiple equilibria occurring in the solutions containing the hosts and their anionic guests. With this respect, special emphasis will be on acid-base equilibria of the aforementioned ligands and several common, and biologically important anions (*e.g.* chloride, dihydrogen phosphate, acetate). Moreover, the aim of the lecture is to demonstrate that the extra work and time invested in such integrated approach is worthwhile, as it can provide invaluable insight in the behaviour of supramolecular systems, possibly leading to original approach of their further design.

ACKNOWLEDGMENT

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Innovative anti-infective therapies based on supramolecular chemistry

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On 15 February 2019, the U.S. Food and Drug Administration (FDA) approved the innovative pharmaceutical preparation Premixed Vancomycin Injection in a Ready-To-Use (RTU) Infusion Bag intended for the treatment of serious hospital infections. This is a new and patented (two U.S. patents have already been granted) antibiotic pharmaceutical preparation which achieves Vancomycin solution stability at room temperature for as long as 16 months and was entirely discovered at our Innovation Excellence Center in Zagreb.

Two major challenges were resolved, which have numerous researchers across the world unsuccessfully endeavored to resolve, ie. Vancomycin stability at room temperature and in a highly diluted infusion solution for over 16 months (the pharmaceutical preparations of Vancomycin are currently available only in the form of powder injections and remain stable at room temperature for no more than 12 to 24 hours). One of the most important lever in achieving this was applying supramolecular understanding and principles to the world on non-covalent interactions in an aqueous environment.

The importance of this is supported by the fact that the FDA granted it a QIDP (Qualified Infectious Disease Product) designation, which is normally only assigned to new products expected to significantly improve the treatment of serious infections, i.e. products offering solutions to what are presently the greatest medical needs in the critical area of anti-infective treatments.

Xellia Pharmaceuticals is a specialty pharmaceutical company focused on providing important anti-infective treatments against serious and often life-threatening infections. Our anti-infective treatments are generics that combat serious bacterial and antibiotic resistant infections as well as certain fungal diseases. We are a world leader in the development, manufacturing and supply of fermented anti-infectives sold as active pharmaceutical ingredients and finished dosage forms to key pharmaceutical industry companies. Headquartered in Copenhagen, Denmark and owned by Novo Holdings A/S, Xellia Pharmaceuticals has more than 1500 employees globally. From state-of-the-art manufacturing sites in the U.S., China, Denmark and Hungary to R&D sites in Norway and Croatia; Xellia Pharmaceuticals excels within innovative product development to deliver high quality products to its customers.

Our product portfolio of anti-bacterial and anti-fungal products used for the treatment of severe infections, including infections caused by multi-resistant bacteria and fungi, is the foundation for our growth strategy within the antibiotics sector. Xellia is the leading supplier of important anti-infectives Vancomycin and Colistimethate Sodium (CMS). Our success and strong market position is built on more than 100 years experience in the pharmaceutical industry. Xellia Pharmaceuticals' focus its R&D investments within inhalable and injectable product technologies as we are committed to researching solutions, which not only improve patients' quality of life, but will also save lives. Based on our long-term expertise, we bring value for our stakeholders and signify a patient-centric mindset through an embedded corporate motivation of integrating science and innovation to save lives.

Molecular recognition and selectivity in solid-state reactions by mechanochemical milling

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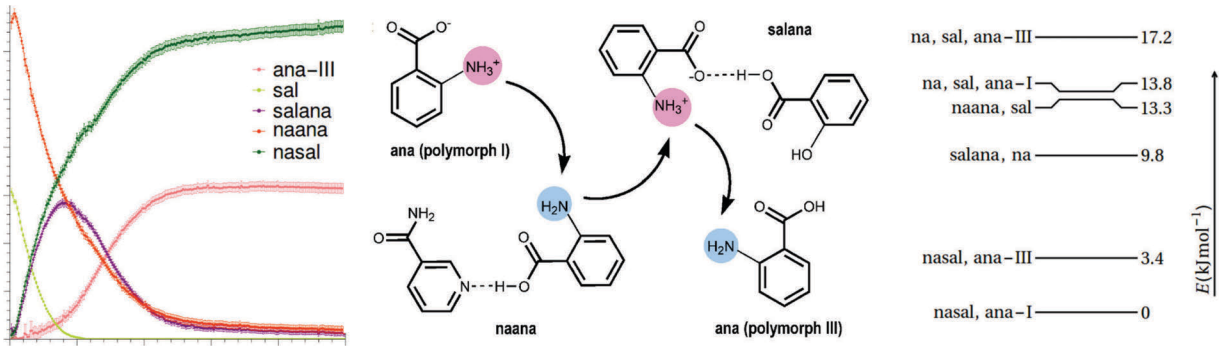
Use of mechanochemistry in achieving supramolecular recognition in the solid state has largely contributed to the expansion of mechanochemistry in all branches of chemistry. In paticular, mechanochemsitry is now well established in screening for cocrystals, even in pharmaceutical industrial applications. Here, we have studied cocrystal formation from binary mixtures of cocrystal coformers, but also in multicomponent mixtures where we have found that selectivity and sequence of formation of cocrystal phases during mechanochemical milling follows their order of stability.[1]



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Jake međumolekulske interakcije: kovalentne ili nekovalentne?

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Tri najznačajnije međumolekulske interakcije, vodikova veza, halogenska veza i π-interakcija pokrivaju široki raspon energijâ od <1 kcal mol^{-1} do >20 kcal mol^{-1}. Prema tome, najjače međumolekulske interakcije su po jačini slične slabim kovalentnim vezama. Kristalografskim određivanjem elektronske gustoće potvrdili smo kovalentnu prirodu u modelnim sustavima s jakim vodikovim i halogenskim vezama te π-interakcijama.

Prototip sustava s jakom vodikovom vezom je Zundelov ion, protonirani dimer molekulâ vode ($H_2O\cdots H^+\cdots OH_2$).[1,2] Poznato je da središnji fragment O···H···O ovoga dimera sadržava dvoelektronsku trocentričnu kovalentnu vezu (2e/3c), tj. da je riječ o dvjema slabim kovalentnim vezama O–H reda 0,5. Naš je rad[1] pokazao da se proton-donor i proton-akceptor ovdje ne razlikuju. U objema je vezama maksimum elektronske gustoće oko 1 e Å^{-3}, do negativna vrijednost Laplacijana ukazuje na dominantno kovalentnu interakciju.

Poznato je da su vodikove i halogenske veze slične; nedavno je pokazano da su i podjednako jake.[3] U halogenskoj vezi *D*–X···*A* kovalentna je veza *D*–X izdužena te je halogeni atom pomaknut prema akceptoru. Proučavali smo tri sustava s različitim jačinama halogenskih veza. *N*-bromsukcinimid smo uzeli kao standard da bismo odredili elektronsku gustoću u tek neznatno perturbiranoj vezi N–Br. U kokristalu *N*-bromsukcinimida s 3,5-dimetilpiridinom bromov je atom pomaknut prema akceptoru za gotovo 0,4 Å, a maksimalna elektronska gustoća u "međumolekulskom" kontaktu je oko 0,4 e Å^{-3}, što ukazuje na znatan kovalentni karakter.[4] Najjaču halogensku vezu proučavali smo na bromonijevom ionu, čiji središnji fragment N···Br···N predstavlja dvoelektronsku trocentričnu kovalentnu vezu sličnu onoj u Zundelovom ionu.[4]

π-interakcije planarnih radikalâ uključuju sparivanje spinova i miješanje SOMO-orbitalâ, pa prema tome također imaju značajan kovalentni karakter. Proučavali smo tri tipa interakcija između semikinonskih radikalâ: blisko vezane dimere (poznate kao '*pancake bonding*'),[5] trimere djelomično nabijenih radikalâ[6] i stupce ekvidistantnih radikalâ.[5] Eksperimentalno određene elektronske gustoće i kvantno-kemijski modeli ukazuju na značajan kovalentni karakter. Prema tome, π-interakcije planarnih radikalâ možemo smatrati dvoelektronskim multicentričnim kovalentnim vezama.[7,8]

Prirodu dvoelektronskih multicentričnih veza također smo proučavali kristalografijom pri ekstremnim uvjetima: u temperaturnom rasponu 80 – 400 K te pri visokom tlaku (do 20-ak GPa). Temperaturna ovisnost međumolekulskih kontakata daje nam podatke o jačini interakcije (procijenjena je na ≥ 15 kcal mol^{-1}) i njezinoj dinamici. Kristalografijom pri visokom tlaku dobivamo podatke o kompresibilnosti i promjeni geometrijskih parametara, iz kojih se pak mogu izvesti dodatni zaključci o prirodi i ponašanju međumolekulske interakcije pri ekstremnim uvjetima.

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Polioksomolibdati {Mo_{132}} (Keplerati): funkcionalni supramolekulski receptori

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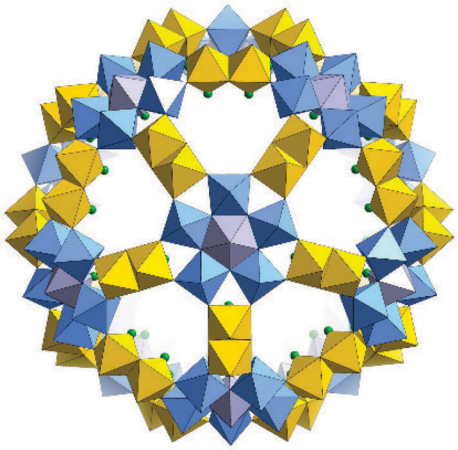
Polioksometalati tipa {{(Mo)Mo_5}$_{12}${Mo^V_2}$_{30}$ ≡ Mo_{132}}, odnosno Keplerati, klasteri su nanometarskih dimenzija.[1] Radi se o jedinstvenim anionskim sustavima koje je moguće vrlo jednostavno sintetizirati i/ili derivatizirati. Zbog svoje specifične strukture, koja uključuje 20 {Mo_9O_9} pora kroz koje mogu prolaziti jedinke odgovarajuće velčine, te svojih impresivnih dimenzija, ovi sustavi omogućuju istraživanja različitih supramolekulskih fenomena pri čemu su mnogi od interdisciplinarnog značaja. Tako primjerice ovi sustavi mogu djelovati kao nanokromatografi za različite (akva)katione, ovisno o njihovoj veličini, odnosno radijusu.[2] S druge strane, relativno jednostavna izmjena koordiniranih aniona, koji se vežu s unutrašnje strane Keplerata, omogućuje fino podešavanje svojstva ovih klastera, poput promjene hidrofilnosti/hidrofobnosti njihove unutrašnjosti.[3,4]



Slika 1. Keplerat {Mo_{132}}

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Utjecaj glikozilacije alfa-1-kiselog glikoproteina (AGP) na vezanje lijekova

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Nakon aplikacije lijeka u krv, lijek se u određenoj mjeri veže na proteine plazme. Vezanje ovisi je o afinitetu koji je određen strukturom lijeka i karakteristikama proteina prisutnih u plazmi. Udio vezanja pri ravnotežnim uvjetima određuje koncentraciju slobodnog lijeka. Slobodni (nevezani) udio lijeka je najčešće onaj koja je raspoloživ za aktivnost ili difuziju u okolna tkiva te se stoga samo slobodna odnosno nevezana frakcija lijeka smatra aktivnim oblikom, u skladu s “free drug principle”.[1] Kao posljedica njihove visoke koncentracije, proteini plazme kontroliraju koncentraciju slobodnog lijeka u plazmi, kao i u biološkim odjeljcima koji su s njom u ravnoteži, utječući na taj način na djelotvornost *in vivo*.[1]

Izrazito glikozilirani alfa kiseli glikoprotein (AGP) je jedan od dva proteina u plazmi koji vežu veliki broj različitih lijekova i općenito utječu na njihovu djelotvornost. Promjene u njegovoj koncentraciji, isto kao i visoki stupanj prirodne (strukturalne) varijabilnostiima ima utjecaja na vezanje lijekova, posebice u patološkim stanjima. Vezanje lijekova za AGP može biti promijenjeno u brojnim patološkim i fiziološkim stanjima kao rezultat promijene u glikozilacijskom uzorku; i to u sialinizaciji, fukozilaciji i razgranatosti oligosaharidnog lanca.

Ukupno gledajući, tri glavna faktora utječu na vezanje lijekova kod AGP-a:

a) Koncentracija AGP-a

b) Omjer različitih genetičkih varijanti

c) Promjene u glikozilacijskom uzorku.

Poznavanje ovih parametara omogućuje eventualnu korekciju aplicirane doze nekih lijekova ovisno o vrijednostima parametara kod te osobe u skladu s principom individualizirane terapije.

Prikazat će se utjecaj promjene glikozilacije i koncentracije AGP-a na koncentraciju slobodnog lijeka u slučaju citostatika Imatiniba (Glivec) i antikoagulansa Dipiridamola.

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KRATKA USMENA PRIOPĆENJA

KP1 **Marina Tranfić Bakić** (University of Bologna): *Light Effected Autonomous Molecular Pumps and Reservoirs*

KP2 **Zoran Kokan** (Masaryk University): *Hypervalent Iodine-based Reversible Covalent Bond in Rotaxane Synthesis*

KP3 **Nikola Bedeković** (PMF): *Kokristalizacija perhalogeniranih benzenâ s jednostavnim derivatima piridina – usporedba klasičnih donora halogenske veze*

KP4 **Mateja Pisačić** (PMF): *Mechanically adaptable crystals: Impact of supramolecular connectivity on crystal flexibility*

KP5 **Dajana Barišić** (IRB): *Protonation and Anion Binding Properties of Urea Derivatives - Comprehending the Proton Transfer*

KP6 **Tomislav Gregorić** (IRB): *Samoudruživanje i polimerizacija bis(aminokiselinskih) fumarata inducirana gama i UV zrakama*

Light Effected Autonomous Molecular Pumps and Reservoirs

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The control of motion on the molecular scale is of fundamental importance for living organisms, but the construction of synthetic molecular machines able to operate autonomously and perform a specific task remains one of the most intriguing challenges in supramolecular chemistry and nanoscience.[1,2]

Here, we present a dissipative self-assembling pseudorotaxane system that utilizes light as external source of energy needed to perform directed molecular motion in a cyclic manner away from chemical equilibrium.[3] Upon light irradiation, macrocycles are transported through the thread unidirectionally, making the system behave as a molecular pump. It operates by dissipating irradiation energy in an autonomous fashion and in accordance to both energy and information ratchet mechanisms.[4]

The described light-powered molecular pump can further be modified and expanded to a more complex architecture comprising a reservoir. In this way, in addition to pumping, the macrocycles can be trapped in the reservoir, in a higher energy state, once light of appropriate wavelength is shined on the system.

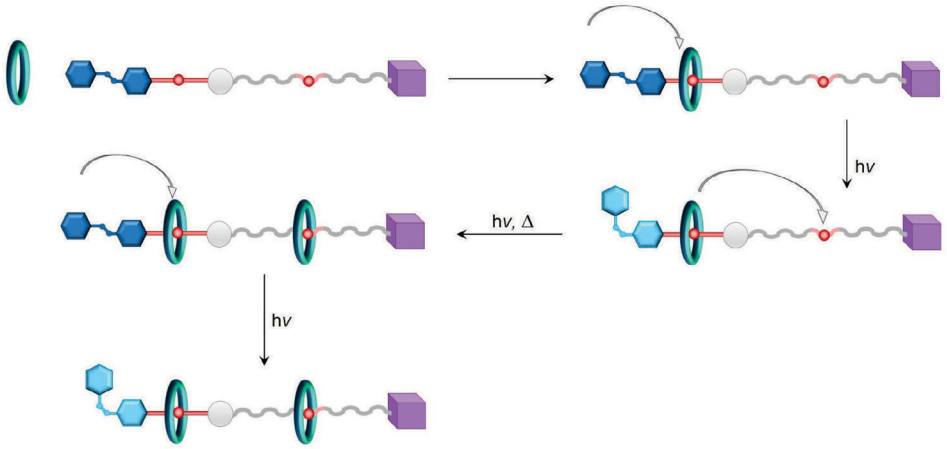

Figure 1. Pump-reservoir model and its operation mode.

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ACKNOWLEDGMENT

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Hypervalent Iodine Based Reversible Covalent Bond in Rotaxane Synthesis

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Successful design of chemical systems with targeted functions/properties relies heavily on novel approaches for governing the molecular assembly. Alongside non-covalent interactions, reversible covalent bonds[1] have been frequently utilized in the design and synthesis of numerous functional molecules. Due to their dynamic nature, reversible covalent bonds facilitate the high-yielding synthesis of mechanically interlocked molecules. Despite this synthetic advantage, a limited number of reversible covalent bonds have been utilized in this manner.

Herein, we introduce a novel approach for the fast and simple preparation of mechanically interlocked molecules, combining the dynamic bond character of reactive bis(acyloxy)iodate(I) anions[2] with macrocyclic bambusuril[3] anion receptors (Figure 1).[4] The rotaxane formation was confirmed in the solid state and solution by the X-ray and NMR studies, respectively. The reactivity of the compounds in the reaction with 3,4-dihydro-2*H*-pyran could be modulated by the chemical stimuli in terms of anion competition reactions. The dynamic behavior of the rotaxanes was successfully shown in the component exchange experiments using either the mixture of the axles, carboxylic acids, or tetrabutylammonium salts thereof. Our novel approach could be utilized in the fields of dynamic combinatorial chemistry, supramolecular polymers, or molecular machines, as well inspire further research on molecules that exhibit dynamic behavior, but due to their high reactivity, have not been considered as constituents of more elaborate supramolecular structures.

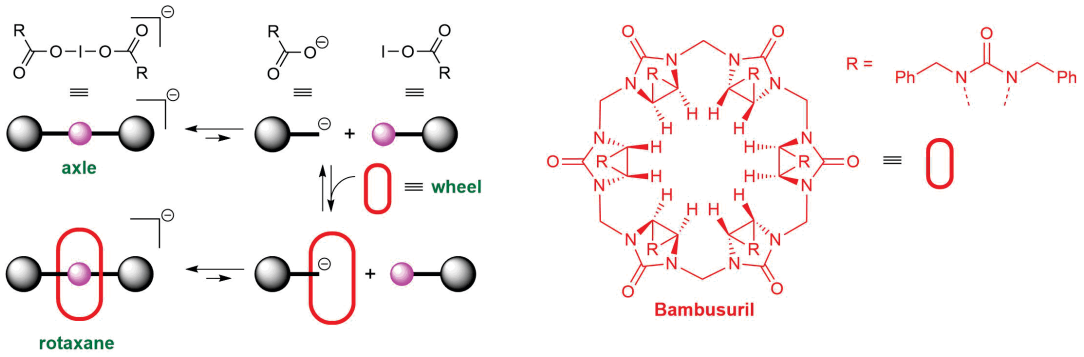

Figure 1. The proposed mechanism of rotaxane formation via the bis(acyloxy)iodate(I) dynamic bond dissociation and stabilization thereof by the bambusuril macrocycle.

ACKNOWLEDGMENT

This work was supported by the Czech Science Foundation (18-21801S), and by the RECETOX Research Infrastructure (LM2015051 and CZ.02.1.01/0.0/0.0/16_013/0001761). We acknowledge the CF X-ray diffraction and Bio-SAXS and CF Proteomic supported by the CIISB research infrastructure (LM2015043 funded by MEYS CR). We thank Pia Jurček for the valuable remarks and discussions.

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Kokristalizacija perhalogeniranih benzena s jednostavnim derivatima piridina – usporedba klasičnih donora halogenske veze

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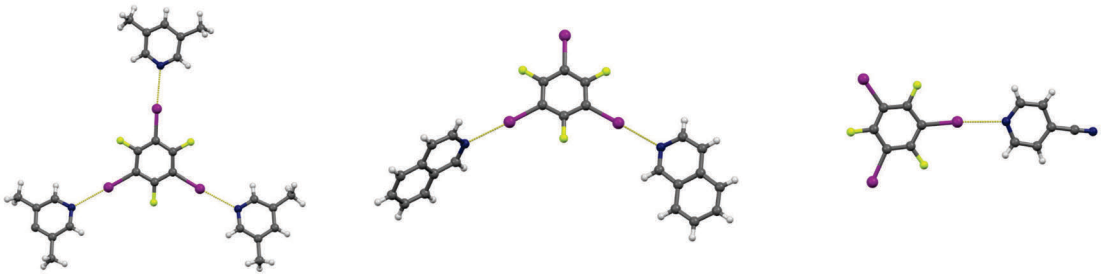
Perhalogenirani jodbenzeni su skupina donora halogenske veze koja obuhvaća niz spojeva s različitim brojem i razmještajem donorskih atoma joda u molekuli, a koriste se za sintezu organskih[1] i metaloorganskih[2] kokristala sa željenim stehiometrijskim omjerima i točno određenim motivima povezivanja molekula u kristalu. U kristalografskoj bazi podataka CSD[3] prisutno je najviše strukturnih podataka s 1,4-dijodtetrafluorbenzenom (**14tfib**; njih 387) a slijede ga *orto* (**12tfib)** i *meta* (**13tfib**)[3] izomeri dijodtetrafluorbenzena te 1,3,5-trifluor-2,4,6-trijodbenzen (**135tftib**). Pomnijom analizom dostupnih kristalnih struktura može se zaključiti da je većina višekomponentnih krutina sa spomenutim donorima pripravljena iz strukturno složenijih višetopičnih akceptora, a poznato je iznimno malo spojeva čiju strukturu čine jednostavniji monotopični akceptori. Nadalje, stehiometrijski omjeri molekula u kokristalima te motivi njihovog pakiranja u kristalu su različiti i ovise o korištenim donorima i akceptorima. Unatoč tome što je poznato da na stehiometriju kokristala i pakiranje molekula ponajviše utječe razmještaj donornih atoma u molekuli donora, veličina σ-šupljine na donornim atomima, bazičnost akceptora te sterička ograničenja donora i akceptora, sveobuhvatne usporedne studije u kojima se detaljnije istražuju navedeni utjecaji do danas nisu provedene. U ovom istraživanju su pripravljene te strukturno i termički okarakterizirane 34 binarne krutine donorâ halogenske veze, **12tfib**, **13tfib**, **14tfib** i **135tftib** s monotopičnim derivatima piridina različitih bazičnosti. Najmanji broj spojeva (njih pet) pripravljen je s **12tfib**, od kojih su tri spoja stehiometrije 1:1, dok je s **13tfib** pripravljeno sedam kokristala, od kojih su njih šest stehiometrije 1:1. Očekivano najveći broj kokristala dobiven je s **14tfib** (12), od kojih njih jedanaest kristalizira s omjerom donora i akceptora 1:2, čime nastaju diskretni molekulski kompleksi. S tritopičnim donorom **135tftib** pripravljeno je jedanaest spojeva od kojih četiri kristaliziraju s omjerom 1:3, tri s omjerom 1:2, dok su ostali stehiometrije 1:1. Strukturna raznolikost dobivenih kokristala (s obzirom na uočene stehiometrije, motive povezivanja molekula u kristalu te geometrije ostvarenih halogenskih veza) može se djelomično objasniti suodnosom bazičnosti akceptora, steričkih ograničenja donora i akceptora halogenske veze te gustoćom kristalnog pakiranja nastalih formulskih jedinki u kristalu.



Slika 1. Različiti ishodi kokristalizacije **135tftib** s monotopičnim akceptorima u ovisnosti o njihovoj bazičnosti.

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Mechanically Adaptable Crystals: Impact of Supramolecular Connectivity on Crystal Flexibility

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There is a constant need for specific devices with improved performances, what in turn requires simultaneous development of new configurable materials. Materials that display dynamic characteristics similar to those of living beings, i.e. having the ability to change shape or move, along with fast and efficient energy transfer, are highly desired and among the top targeted ones in current materials design. Recently, it has been found that some crystalline materials are capable of responding mechanically to the application of a variety of external stimuli, such as light, thermal energy or mechanical pressure,[1] what makes them excellent candidates for usage in the design of new smart devices.[2] So far, a number of organic crystals that respond flexibly upon the application of mechanical force have been reported,[3] but only two reports on elastically bendable metal-organic compounds could be found in the literature.[4,5]

Since the insertion of a metal centre in organic systems opens a whole new spectrum of possible applications, we decided to systematically explore metal-organic systems with the aim to fully understand the structural features that endue the metal-organic crystals with mechanical flexibility. For that purpose several coordination polymers of cadmium(II) halides with pyrazine based ligands were synthesized, and the adaptability of those crystals to external mechanical stress was tested. For crystals that displayed elastic behaviour, the responses were quantified and correlated with structural features, primarily the strength and geometry of supramolecular interactions, but also with the mechanical behaviour of analogous metal-containing systems.

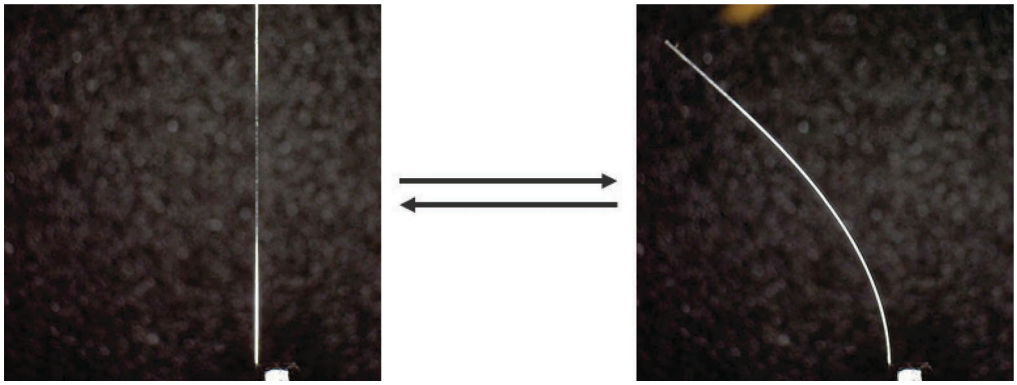

Figure 1. Elastic bending of $[CdBr_2(CONH_2pz)_2]_n$ crystal.

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Protonation and Anion Binding Properties of Urea Derivatives – Comprehending the Proton Transfer

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Knowledge regarding the acid-base behaviour in non-aqueous media has remained relatively scarce in spite of its importance for many aspects of chemistry. Recently, we reported on a detailed study of acid-base properties of dihydrogen phosphate and acetate in aprotic organic solvents (acetonitrile, dimethyl sulfoxide, and dimethylformamide).[1] It was found that several processes, i.e. protonation, homoassociation, and dimerisation play important roles in defining the basicity of these widely important anions. A comprehensive thermodynamic characterisation of the corresponding processes was carried out which provided valuable information for the advancement of host-guest chemistry focusing on highly basic anions.

In this field, urea derivatives have been among the most studied receptors, and numerous studies of their complexation with diverse anionic species have been reported. To gather reliable thermodynamic information about the anion binding processes, it is of great importance to identify and characterise the coupled reactions. In the case of anion receptors bearing urea moieties, one of the most commonly encountered side reactions is deprotonation of the NH group, accompanied by protonation of the anion, that is, receptor to anion proton transfer. This process is especially favorable in aprotic organic solvents of lower polarity owing to the drastic increase in basicity of the commonly used anions (e.g., F^-, AcO^- or $H_2PO_4^-$) with respect to aqueous medium.

As a continuation of our work, a series of aromatic bis-urea derivatives was prepared and their proton dissociation, as well as anion binding properties in DMSO were investigated revealing remarkably high acidities of the compounds (log $K_1^H \approx 14$).[2] Studied receptors were selective for acetate and dihydrogen phosphate among several anions forming complexes of 1:1 and 1:2 (ligand:anion) stoichiometries. Proton transfer was taken into account in the course of data analysis, which was especially important in the case of AcO^-. Knowledge regarding protonation properties proved to be essential for reliable quantitative determination of anion binding affinities.

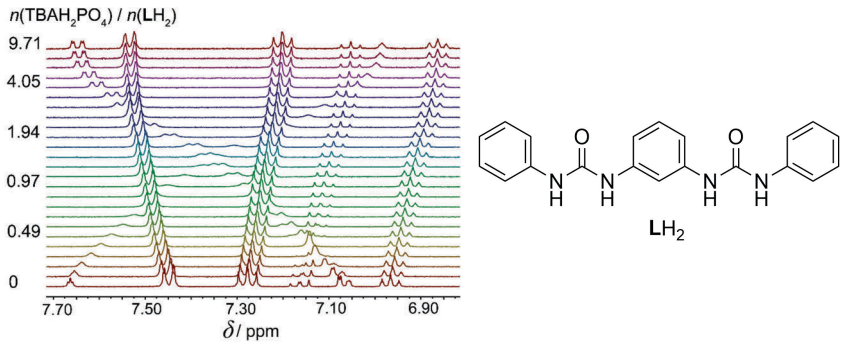

Figure 1. ^{1}H NMR titration of **L**H_2 with $TBAH_2PO_4$ in DMSO-d_6 at 25.0 °C.

ACKNOWLEDGMENT

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Samoudruživanje i polimerizacija bis(aminokiselinskih) fumarata inducirana gama i UV zrakama

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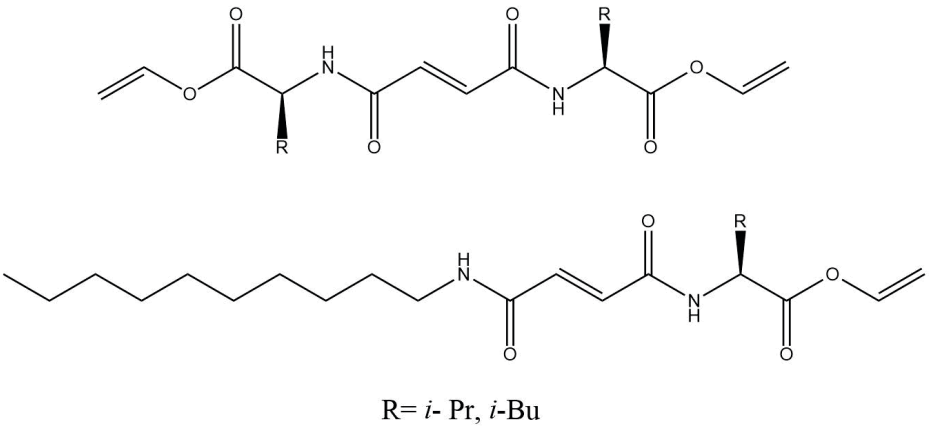
Vrlo zanimljivo područje u supramolekulskoj kemiji je sinteza novih materijala koji sa svojim svojstvima naći će primjenu za razne svrhe u medicinskoj znanosti, razvoj novih biomaterijala, senzora i mnogim drugim[1]. Glavna prednost supramolekularne kemije za sintezu novih materijala su širok spektar mogućnosti sinteze samoorganiziranih nanomaterijala koristeći nekovalentne interakcije kao što su vodikove veze, π-π slaganje ili Van der Waalsove sile. U tu svrhu razvijani su novi aminokiselinski derivati fumarne kiseline, kao što su mono i bis amidni vinilni esteri aminokiselina. Sintetizirani se novi supramolekulski gelatori male molekularne mase (Slika 1.). Ovi spojevi putem molekulskog samo-udruživanja u mogućnosti su formirati gelske mreže s različitim organskim otapalima. Nadalje, istražena je mogućnost reakcija polimerizacije u pripremljenim gelovima inducirane pomoću UV i gama zraka. Rezultati istraživanja su pokazali da male promjene u specifičnoj samoorganizaciji znatno utječu na ishod polimerizacije. Sintetizirani derivati i priređeni supramolekulski gelovi karakterizirali su pomoću ^{1}H, ^{13}C NMR i FT-IR spektroskopijom, a morfologija gelske mreže i polimera određena je TEM, SEM i AFM mikroskopijom.



R= *i*- Pr, *i*-Bu

Slika 1. Strukturne formule fumaramidnih gelatora

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POSTERSKA PRIOPĆENJA

PP1 **Gordan Horvat** (PMF): *Anion Binding Properties of Homocyclopeptides in Acetonitrile and Dimethyl Sulfoxide*

PP2 **Vinko Nemec** (PMF): *Kokristali tautomera imina izvedenog iz 2-hidroksi-1-naftaldehida i 3-aminopiridina s 1,3-dijodtetrafluorbenzenom*

PP3 **Jakov Slade** (IRB): *Utjecaj supramolekulske strukture na difuziju radikala u alkoholima*

PP4 **Nikola Jakupec, Erik Uran** (PMF): *Raznovrsnost intermolekulskih interakcija u solima heksacijanoželjezove(iii) kiseline i nekih supstituiranih piridina*

PP5 **Katarina Lisac** (PMF): *In situ PXRD monitoring the mechanosynthesis of metal-organic halogen-bonded cocrystals*

PP6 **Nika Gazdek** (IRB): *Solid-state study of the structure and host–guest chemistry of α- and β-cyclodextrin-ferrocene inclusion complexes*

PP7 **Luka Fotović** (PMF): *Halogen and hydrogen bonds with halogenide ions – database survey and crystal structure analysis of o-, m- and p-iodopyridinium halogenides*

PP8 **Adela Štimac** (CRKTB-UNIZG): *Self-assembled Hybrid Bilayer Membrane Functionalized by Bacterial Peptidoglycan as Biosensor for Lectin Recognition*

PP9 **Andrea Usenik** (PMF): *Termodinamika kompleksiranja kationa zemnoalkalijskih metala s fluorescentnim derivatom kaliks[4]arena*

PP10 **Darko Vušak** (PMF): *1D porozni koordinacijski polimeri kompleksa bakra s glicinom i L-homoserinom*

PP11 **Silvia Pšeničnik** (IRB): *New cyanine-piperazine derivatives as fluorescent sensors for DNA/RNA secondary structures*

PP12 **Iva Zonjić** (IRB): *DNA and RNA interactions of benzimidazole amidines with antitrypanosomal activity*

PP13 **Ivana Furač** (MEF): *A Novel Nitroprusside Association Complex with the Pharmacologically Important Ligand: Crystal Structure and Supramolecular Assembly*

Anion Binding Properties of Homocyclopeptides in Acetonitrile and Dimethyl Sulfoxide

Gordan Horvat,[a] Tamara Rinkovec,[a] Siniša Tarana,[a] Nikolina Vidović,[b] Nikola Cindro,[a] Giovanna Speranza,[b] and Vladislav Tomišić[a]

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The anion interactions with various natural and synthetic receptors are subject of an intensive and quickly-developing research field of supramolecular chemistry.[1] Modern studies of anionic receptors often use the basic coordination and recognition principles taken from the receptors observed in natural systems.[1–4]

A class of macrocyclic compounds that contains amide groups in their backbone and can be used as selective receptors of anionic species are cyclopeptides.[2–4] Rather good complexation properties of these compounds can be attributed to the remarkable hydrogen-bonding donor properties of the amide groups. In addition, the well-structured, yet sufficiently flexible structure of the cyclopeptides, as well as the presence of multiple functional groups oriented in the appropriate direction, with the additional possibility of modifying the peptide backbone and/or the side chains, contribute to the high efficiency and selectivity for anion binding of these receptors.[2–4]

Here we present the studies of halides and oxoanions binding with several homocyclopeptide ligands (Figure 1) in acetonitrile and dymethylsulfoxide carried out by NMR and microcalorimetric titrations as well as molecular dynamics simulations. The aim of the investigation was to obtain as detailed as possible insight into the thermodynamic and structural characteristics of the receptors and their complexation reactions, and to rationalize the relation between structure and reactivity of the investigated cyclopeptides. The solvent effect on equilibria of the studied reactions was particularly addressed.

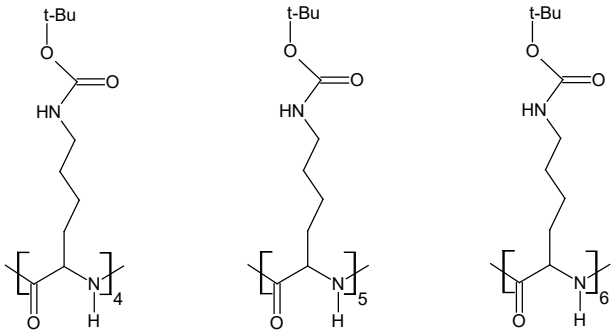

Figure 1. Structures of cyclopeptide ligands.

ACKNOWLEDGMENTS

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Kokristali tautomera imina izvedenog iz 2-hidroksi-1-naftaldehida i 3-aminopiridina s 1,3-dijodtetrafluorbenzenom

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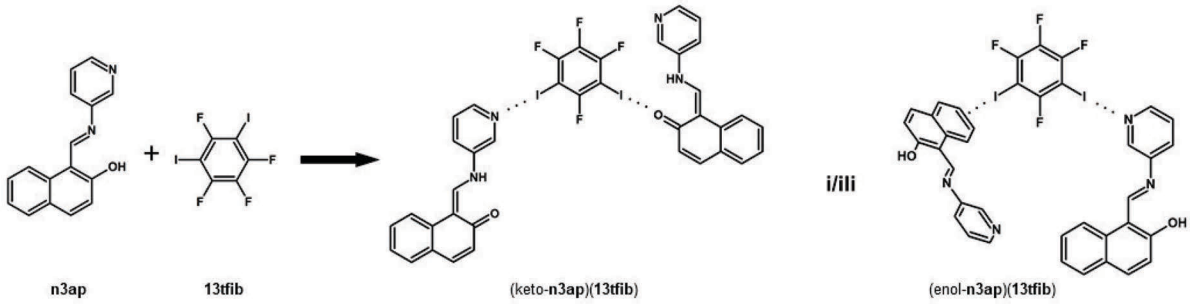
Imini su spojevi od interesa u kristalnom inženjerstvu i izučavanju međumolekulskih interakcija zato što se variranjem vrste karbonilnog spoja i amina mogu pripraviti imini s različitim funkcijskim skupinama, koje su potencijalni donori ili akceptori halogenskih ili vodikovih veza. Nadalje, imini koji u *o*- položaju u odnosu na ugljik C=N veze sadrže hidroksilni kisikov atom također pokazuju svojstvo keto-enolne tautomerije,[1] pri čemu je u čvrstom stanju u većini slučajeva moguće izolirati samo jedan tautomer imina.[2]

U ovom radu po prvi put su izolirani i izučavani kokristali imina **n3ap**, izvedenog iz 2-hidroksi-1-naftaldehida i 3-aminopiridina, s donorom halogenske veze, 1,3-dijodtetrafluorbenzenom, **13tfib**, koji su identičnog sastava ali s različitim tautomerima. U sintezi su korištene mehanokemijska metoda i kristalizacija iz otopine, a dobiveni produkti karakterizirani su difrakcijom rentgenskog zračenja u jediničnom kristalu i polikristalnom uzorku, te razlikovnom pretražnom kalorimetrijom. Prema literaturi je za imin **n3ap** utvrđeno da kristalizira kao enol-imino tautomer.[3] Kokristalizacijom **n3ap** s **13tfib** u otopini konkomitantno su dobivena dva kokristala s različitim tautiomerima imina, (keto-**n3ap**)(**13tfib**) i (enol-**n3ap**)(**13tfib**). Pokusi mljevenja imina i donora rezultirali su nastajanjem samo kokristala (keto-**n3ap**)(**13tfib**). Strukturnom analizom utvrđeni su geometrijski parametri karakteristični za oba tautomera: za keto-amino tautomer *d*(C=O) = 1,28 Å, *d*(C–N) = 1,32 Å, te za enol-imino tautomer *d*(C–O) = 1,321 Å, *d*(C=N) = 1,300 Å. U kokristalu (keto-**n3ap**)(**13tfib**) halogenske veze ostvaruju se s dušikovim atomom piridilnog fragmenta kao i karbonilnim kisikovim atomom, čime nastaje motiv uzvojnice, dok se u (enol-**n3ap**)(**13tfib**) halogenske veze ostvaruju s dušikovim atomom piridilnog fragmenta i *π*-sustavom naftaldehidnog fragmenta, čime nastaju diskretni četveročlani supramolekulski motivi. Kvantno-kemijski izračuni energije različitih halogenskih veza između molekula **13tfib** i **n3ap** *in vacuo* pokazali su da relativna jakost akceptorskih mjesta prati trend $N_{piridil} \approx O_{keto} > O_{enol} > \pi$-sustav. Navedeno je u skladu s opažanjem C–I···O_{keto}, ali ne i C–I···O_{enol} veze u kokristalima te sugerira da je tautomerija **n3ap** u ovim kokristalima uvjetovana različitim motivima halogenske veze.



Slika 1. Mogući ishodi kokristalizacije **n3ap** i **13tfib**.

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Utjecaj supramolekulske strukture na difuziju radikala u alkoholima

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Pojava supramolekulske strukture u tekućim monohidroksilnim alkoholima, kao i njena statička i dinamička svojstva, predmet su znanstvenog istraživanja već više od sto godina.[1] Uzrok te pojave je agregacija molekula alkohola putem vodikovih veza koje nastaju između njihovih hidroksilnih skupina. Razumijevanje mehanizama nastanka suprastrukture i s njom povezane dinamike u jednostavnim sustavima alkohola mogu pružiti bolji uvid u prirodu kompleksnijih supramolekulskih sustava kao i u ponašanje ostalih tekućina s vodikovim vezama. Zanimljivo pitanje, koje je otvoreno nedavnim istraživanjima ionske vodljivosti i katalitičkih reakcija u alkoholima, jest koliko suprastruktura u alkoholima utječe na raspored i transport stranih molekula u njima.[2,3]

Ukoliko je strana molekula otopljena u tekućini dugoživući radikal, odnosno paramagnetska molekula, njena transportna svojstva moguće je proučavati spektroskopijom elektronske paramagnetske rezonancije (EPR). Difuzija radikala u tekućini mijenja jačinu magnetskih interakcija između spinova njihovih nesparenih elektrona i tako utječe na oblik spektra EPR-a radikala. To nam omogućava da analizom ovisnosti spektra EPR-a o koncentraciji radikala odredimo njihov difuzijski koeficijent (difuzivnost). Unapređenje te metode prikazano je u nedavno objavljenom članku, zajedno s mjerenim rezultatima temperaturnih ovisnosti difuzivnosti komercijalnih nitroksilnih radikala u tri različite viskozne tekućine.[4]

U ovom istraživanju, metodom EPR-a određivali smo difuzivnost deuteriranog nitroksilnog radikala Tempon (2,2,6,6-tetrametil-4-oksopiperidin-1-oksil) i ovisnost difuzivnosti o temperaturi u dvije skupine tekućina. Prva skupina su primarni dugolančani nerazgranani alkoholi koji pokazuju superstrukturu, a druga su dugolančani nerazgranani alkani koji su primjer homogenih tekućina bez suprastrukture.[5] Dobivene rezultate za difuzivnost Tempona u tim tekućinama usporedili smo s onima za koeficijente samodifuzije izmjerene tehnikom pulsnog NMR-a.[6,7] Razlike u odnosima difuzije Tempona i samodifuzije u tim dvjema skupinama tekućina ukazuju na mogući utjecaj supramolekulske strukture u alkoholima na transport strane molekule.

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Raznovrsnost intermolekulskih interakcija u solima heksacijanoželjezove(iii) kiseline i nekih supstituiranih piridina

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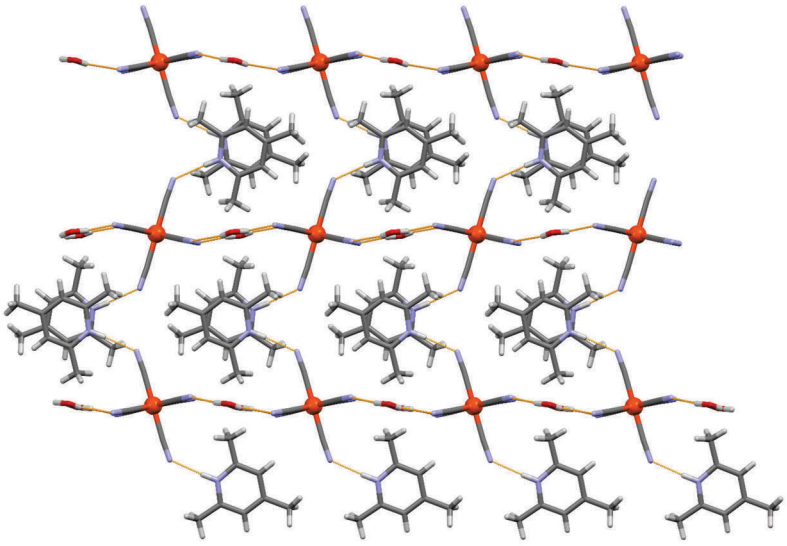
Heksacijanoferati su najstariji predstavnici policijanometalata, koordinacijskih spojeva poznatih već više od 300 godina. Na njima su provedena brojna istraživanja, a istraživaju se i danas. Usprkos tome, tek su početkom 21. stoljeća dobili veću pažnju u vidu kristalnog inženjerstva kao dobri akceptori vodikove i halogenske veze, gdje su se kao polazni reagensi koristile soli alkalijskih metala.[1,2] Heksacijanoželjezova(II) kiselina, $H_4[Fe(CN)_6]$ tek je nedavno korištena u sličnim istraživanjima.[3,4] S druge strane, heksacijanoželjezova(iii) kiselina, $H_3[Fe(CN)_6]$, dosad nije upotrebljena u kontekstima kristalnog inženjerstva.

Kako bi ispitali raznovrsnost intermolekulskih interakcija s heksacijanoferatnim(III) anionom, pripremljene su soli supstituiranih piridina koji sadrže razne funkcionalne skupine (metilne, aminske i halogenske): 2,4,6-kolidinom (**col**), 4-aminopiridinom (**4-amp**), 2-klorpiridinom (**2-Clpy**) i 3-brompiridinom (**3-Brpy**) s heksacijanoželjezovom(iii) kiselinom (**H_3hcf**). U svim dobivenim spojevima prisutna je dvodimenzionalna mreža **hcf**$^{3-}$ aniona. Analizom kristalne strukture soli s **col** primjećeno je kako se povezivanje ostvaruje isključivo pomoću vodikovih veza između molekula vode i protoniranih piridinskih dušika te policijanometalata. Uz to, primjećena je delokalizacija protona između dvije molekule **col** i četiri molekule vode. U slučaju s **4-amp** aminska skupina protoniranog piridina sudjeluje u premoštenju **hcf**$^{3-}$ aniona zajedno s vodom, dok u solima s **2-Clpy** i **3-Brpy** dolazi do povezivanja slojeva **hcf**$^{3-}$ aniona vodikovim i halogenskim vezama između protoniranog piridina i dva **hcf**$^{3-}$ aniona dok su oni sami premošteni $H_5O_2^+$ (Zundelovim) kationima.



Slika 1. Kristalno pakiranje u (H_3O^+)(H**col**)$_2$(**col**)$_2(H_2O)_4$**hcf**

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In situ PXRD monitoring the mechanosynthesis of metal-organic halogen-bonded cocrystals

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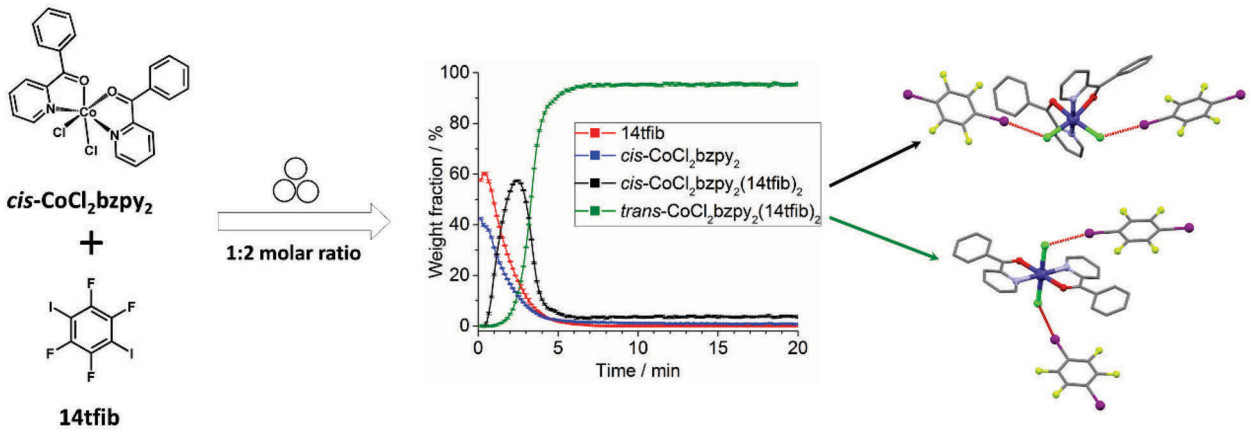
In the last decade, *in situ* powder X-ray diffraction (PXRD) monitoring of mechanochemical reactions has become a prominent technique for studying the course and mechanisms of organic and metal-organic solid formation.[1] Following our previous study on mechanochemical syntheses of metal-organic halogen-bonded cocrystals,[2] in this work we have investigated mechanosynthesis of cocrystals containing $CoCl_2$**bzpy**$_2$ (**bzpy** = 2-benzoylpyridine) and a halogen bond donor, 1,4-diiodotetrafluorobenzene (**14tfib**), by *in situ* PXRD. First, we performed experiments in solution, and have unexpectedly obtained three different products: two cocrystals with different metal-organic unit isomers, *trans*-($CoCl_2$**bzpy**$_2$)(**14tfib**)$_2$ and *cis*-($CoCl_2$**bzpy**$_2$)(**14tfib**)$_2$, and a cocrystal of 1:1 stoichiometry, *cis*-($CoCl_2$**bzpy**$_2$)(**14tfib**). In order to determine whether single phases could be prepared, mechanosynthesis of obtained cocrystals was studied by *in situ* PXRD using synchrotron X-ray radiation. Three different liquid-assisted grinding experiments were monitored: grinding of $CoCl_2$**bzpy**$_2$ and **14tfib** in the 1:2 molar ratio, one-pot grinding of $CoCl_2 \cdot 6H_2O$, **bzpy** and **14tfib** in the 1:2:2 molar ratio and grinding of $CoCl_2$**bzpy**$_2$ and **14tfib** in the 1:1 molar ratio. All three monitored reactions revealed presence of a cocrystal with *cis* isomer as an intermediate and fast conversions to a final, thermodynamically more stable product, *trans*-($CoCl_2$**bzpy**$_2$)(**14tfib**)$_2$, in less than 20 min. Single crystal X-ray diffraction experiments reveal that dominant supramolecular interactions in all obtained solids are I···Cl halogen bonds. In the *trans*- cocrystal halogen bonds form 2D networks while in *cis*- cocrystals 1D chains are formed.



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Solid-state study of the structure and host–guest chemistry of α- and β-cyclodextrin-ferrocene inclusion complexes

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It has been recently shown that N-alkylated ferrocene quinoline conjugates exhibited inhibitory effects on selected tumor cell lines.[1] Similar biological activity has been demonstrated by ferrocene thymine conjugates. However, their application is limited, due to the high lipophilicity of these compounds and the poor solubility in water. Therefore, to solve these obstacle inclusion complexes with cyclodextrin have proved to be useful because they allow better solubility in water, and thus better bio-distribution and pharmacokinetic properties of some drugs.[2,3]

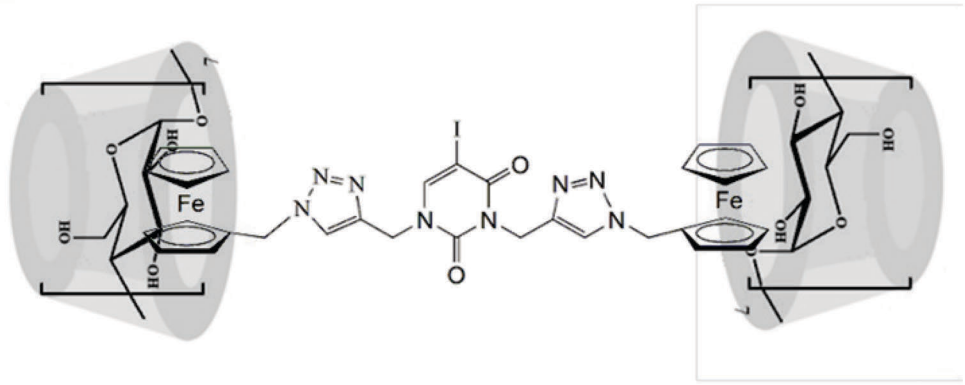

Figure 1. β-cyclodextrin ferrocene thymine conjugate complex

The formation of inclusion complex of ferrocene derivatives with α- and β-cyclodextrin was carried out mechanochemical by ball-milling (Figure 1). The solid-state grinding approach to preparing complexes is a newer method within green chemistry approach that draws great attention. Host-guest complexation in the solid state was studied and characterized by NMR spectroscopy, IR and X-ray powder diffraction.

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Halogen and hydrogen bonds with halogenide ions – database survey and crystal structure analysis of *o*-, *m*- and *p*-iodopyridinium halogenides

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Halogen and hydrogen bonds, two valuable tools for supramolecular chemistry and crystal engineering, are almost equal due to their strength and directionality as well as in trends in which they change.[1] Due to their negative charge and electron richness, halide ions can act as both halogen and hydrogen bond acceptors. Hydrogen bond strength increases from larger to smaller halide anions. There is, however, no clearly established trend in strengths of halogen bonds with halide anions as acceptors to date; some studies report smaller halide anions are weaker halogen bond acceptors, while others report the opposite trend.[2,3]

A possible way to study the difference in hydrogen and halogen bond proclivity as a function of the halogenide size is constructing materials in which the halogenide ions act simultaneously as halogen and hydrogen bond acceptors. However, very few systematic studies of such systems have been published to date.[4,5] Therefore, we have undertaken a combined data-mining (Cambridge Structure Database)[6] and an experimental study of halogenide salts containing simultaneous halogen and hydrogen bonds. Specifically, we have studied chlorides, bromides and iodides of *o-, m- and p-* iodopyridine, which has allowed as a detailed investigation of the interrelationship between the hydrogen and halogen bonding with the studied halogenide acceptors.

In all prepared salts, the halogenide ions and iodopyridine cations were connected through both C–I···X^- halogen and N–H···X^- hydrogen bonds. The hydrogen bond was found to be more sensitive to the change of the halide anion as an acceptor than the halogen bond. Although it was not possible to establish any significant trend of halogen bond strengths within the system, the preference of lighter halogenide anions to hydrogen bond and heavier halogenide anions to halogen bond has been observed from crystal structure of double salt, *o*-iodopyridinium chloride iodide.

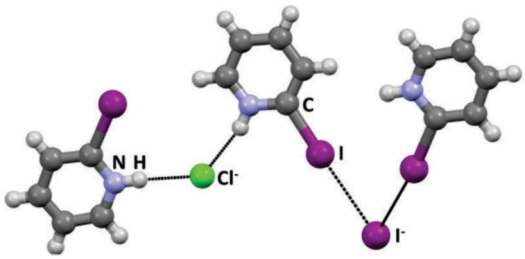

Figure 1. Halogen and hydrogen bonding in double salt of di-2-iodopyridinum iodide chloride

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Self-assembled Hybrid Bilayer Membrane Functionalized by Bacterial Peptidoglycan as Biosensor for Lectin Recognition

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Peptidoglycan is the major component of bacterial cell walls which is recognized by the innate immune system through a series of pattern recognition receptors (PRR), which play a key role in first-line defense of the body.[1] Lectins, naturally occurring carbohydrate-binding proteins, are involved in numerous biological processes and some of them act as PRR and bind significantly to PGN.[2] In this study we were primarily interested to test interaction of peptidoglycan monomer (GlcNAc-MurNac-L-Ala-D-isoGln-mesoDAP(εNH_2)-DAla-D-Ala, PGM),[3] disaccharide pentapeptide isolated from B. divaricatum with model plant lectin, wheat germ agglutinin (WGA), by quartz crystal microbalance (QCM) method (Figure 1). WGA has a high binding affinity for N-acetyl-glucosamine (GlcNAc), one of the essential components of PG glycan strands. In order to study interactions of PGM with lectins, lipophilic derivative, PGM-oleyl was synthesized and was used for preparation of the self-assembled hybrid bilayer membrane (HBM). The results showed that PGM was effectively recognized by WGA and that strength of interactions depend on amount of PGM-oleil used for HBM preparation. The association constant for the binding of WGA to PGM functionalized hybrid bilayers was determined. It was demonstrated that the use of functionalized self-assembled bilayer as a biosensing platform has the potential to become a powerful tool for the study of other glycans by using a greater variety of lectins.

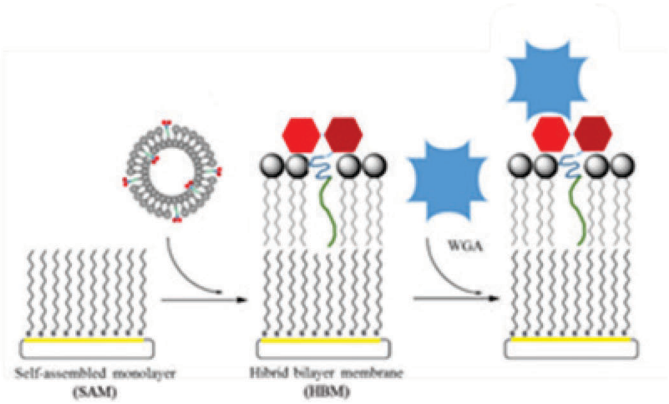

Figure 1. Schematic presentation of WGA lectin interaction with self-assembled hybrid bilayer membrane functionalized with bacterial peptidoglycan

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Termodinamika kompleksiranja kationa zemnoalkalijskih metala s fluorescentnim derivatom kaliks[4]arena

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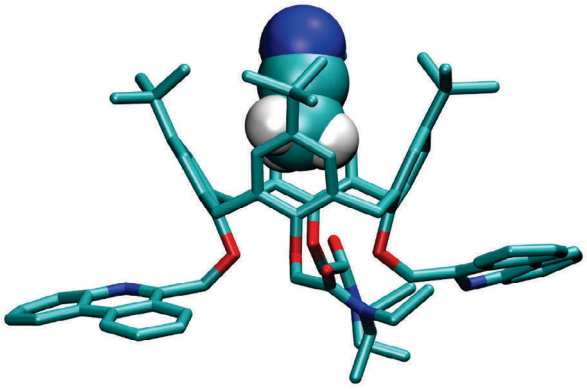
Kaliksareni su makrociklički oligomeri koji se sastoje od četiri ili više fenolnih podjedinica povezanih metilenskim skupinama u *ortho*-položaju fenola. Specifičan oblik i mogućnost njihove funkcionalizacije čine kaliksarene zanimljivim molekulama domaćinima za razne neutralne i nabijene goste. Da bi se povećao afinitet za vezanje kationa, najčešće se na donji obod kaliksarena uvode ketonske, esterske ili amidne skupine. Funkcionalizacijom kaliksarena fluorescentnim supstituentima moguće je prirediti visokoosjetljive senzore za niz kemijskih vrsta, pri čemu ti supstituenti, osim što su zaslužni za fluorescenciju spoja, mogu sudjelovati i u vezanju kationa.[1–4]

U ovom radu proučavana su kompleksacijska svojstva derivata kaliks[4]arena (slika 1) koji, osim tercijarnih amidnih supstituenata, kao dio veznog mjesta posjeduje i fenantridinske fluorofore čija su potencijalna kation-vezujuća svojstva temeljena na prisustvu aromatskih dušikovih atoma. Mikrokalorimetrijskim, spektrofotometrijskim i fluorimetrijskim titracijama istražene su odgovarajuće reakcije kompleksiranja s kationima zemnoalkalijskih metala u više otapala (acetonitril, metanol, etanol). Odabir otapala zasnovan je na topljivosti liganda, solvatacijskim svojstvima i mogućnosti povezivanja vodikovim vezama. Određene su konstante stabilnosti kompleksa te standardne entalpije i entropije reakcija kompleksiranja. Također, istražen je utjecaj otapala i vezanja kationa na intenzitet fluorescencije navedenog kaliksarena te njegova potencijalna primjena kao fluorescentnog kationskog senzora. Da bi se stekao dojam o mogućim strukturama istraživanog spoja i njegovih kompleksa te utjecaj inkluzije molekula otapala u hidrofobnu kaliksarensku šupljinu, provedene su odgovarajuće simulacije molekulske dinamike.



Slika 1. Struktura adukta fenantridinskog derivata kaliks[4]arena s acetonitrilom dobivena simulacijom molekulske dinamike.

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1D porozni koordinacijski polimeri kompleksa bakra s glicinom i L-homoserinom

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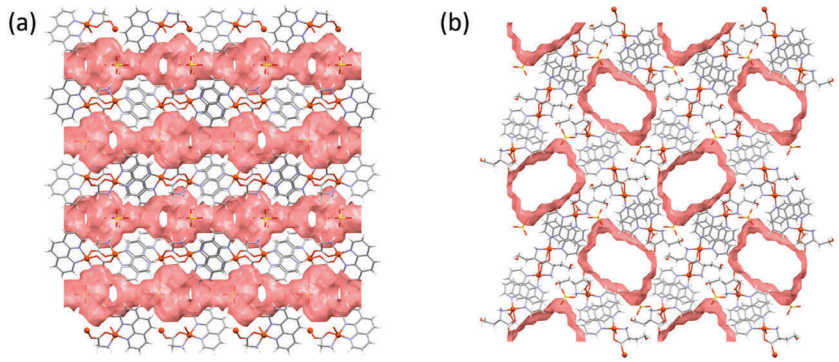
U posljednjih dvadesetak godina, koordinacijski polimeri se intenzivno istražuju kao potencijalni funkcionalni materijali. Bakrovi(ii) kompleksi s aminokiselinama i heterocikličkim bazama, zahvaljujući različitim nekovalentnim interakcijama, poput vodikovih veza i π-interakcija, stvaraju različite supramolekulske arhitekture u čvrstom stanju, a između ostalog i porozne strukture koje mogu naći primjenu u adsorpciji otapala ili plinova te kao katalizatori.[1,2] Također, pokazano je kako se kod takvih spojeva podešavanjem uvjeta (dovođenje mehaničke energije ili kontrola atmosfere – pare otapala, relativna vlažnost zraka) ciljano mogu prirediti određene strukture, ali i izmjeniti otapalo u čvrstom stanju.[1] Osim fizikalno-kemijskih svojstava, pokazalo se kako bakrovi kompleksi s heterocikličkim bazama i aminokiselinama posjeduju i raznovrsna biološka svojstva, između ostalog i antitumorsku aktivnost.[1,3]

U ovom radu bit će prezentirana dva nova porozna koordinacijska polimera bakra s 1,10-fenantrolinom (phen) te glicinom (gly) ili L-homoserinom (hser): $\{[Cu(\mu\text{-gly})(phen)]_2SO_4\cdot 6CH_3OH\}_n$ (**1**) i $\{[Cu(\mu\text{-hser})(phen)][Cu(hser)(CH_3OH)(phen)]SO_4\cdot 7CH_3OH\}_n$ (**2**). Oba spoja tvore 1D beskonačne lance u kojima su bakrovi ioni premošćeni preko karboksilne skupine aminokiseline. U spoju **1** lanci se prostiru duž osi *c* te se međusobno povezuju π-interakcijama čineći supramolekulske slojeve u *a*-*c* ravnini. Između slojeva kompleksa nalaze se sulfatni ioni i 2D porozni kanali u kojima su molekule metanola. U spoju **2** 1D lanci kompleksa prostiru se duž osi *a* te su π-interakcijama naizmjence povezani nepremošćeni $[Cu(hser)(CH_3OH)(phen)]^+$ kompleksni kationi te $[Cu(\mu\text{-hser})(phen)]^+$. 1D beskonačni kanali s molekulama metanola nalaze se između lanaca kompleksa te sačinjavaju 25,3 % volumena jedinične ćelije.



Slika 1. (a) 2D kanali molekula metanola u spoju 1; (b) 1D kanali molekula metanola u spoju 2.

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New cyanine-piperazine derivatives as fluorescent sensors for DNA/RNA secondary structures

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Design of new sensors and/or biologically active molecules often comprises the combination of different structural subunits that sterically and/or electronically influence on binding to polynucleotides. Cyanine dyes are well known fluorescent probes.[1] They exhibit very small or no intrinsic fluorescence, while their fluorescence emission increases dramatically upon binding to polynucleotides.[1–3] N-methyl-piperazine group increases binding selectivity of small molecules toward G-quadruplex structures.[4]

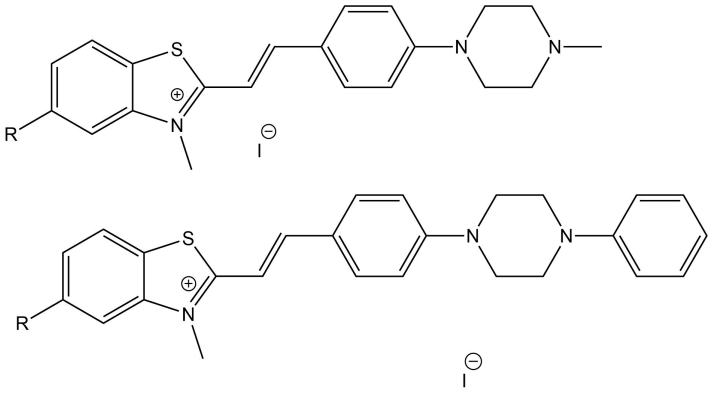

Figure 1. Novel cyanine-piperazine compounds

The newly prepared cyanine-N-methyl- (or N-phenyl)piperazines showed strong binding on different polynucleotides and significant preference on DNA over RNA. Cyanine-N-methyl-piperazines revealed also AT preference over GC sequences. Generally, examined compounds were bound to the polynucleotide minor groove, whereas in case of N-phenyl-piperazine derivatives intercalation into DNA/RNA has been observed. The results of confocal microscopy confirmed the entry of compounds into the cell.

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DNA and RNA interactions of benzimidazole amidines with antitrypanosomal activity

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A series of novel benzimidazole amidines derivatives are synthesized at the Department of Organic Chemistry, Faculty of Chemical Engineering and Technology. They differ only in one substituent (–F vs. –H vs. $–OCH_3$) attached on phenyl ring (Figure 1.). These three compounds were selected for the binding study with DNA and RNA based upon their antitrypanosomal activity. Binding of studied compounds to DNA and RNA polynucleotides (ctDNA, poly(dAdT)$_2$, poly(dGdC)$_2$ and poly A – poly U) was monitored with the fluorescence spectroscopy. CD titrations and ΔT_m experiments were used for a determination of the binding modes (intercalation, groove binding, external binding).

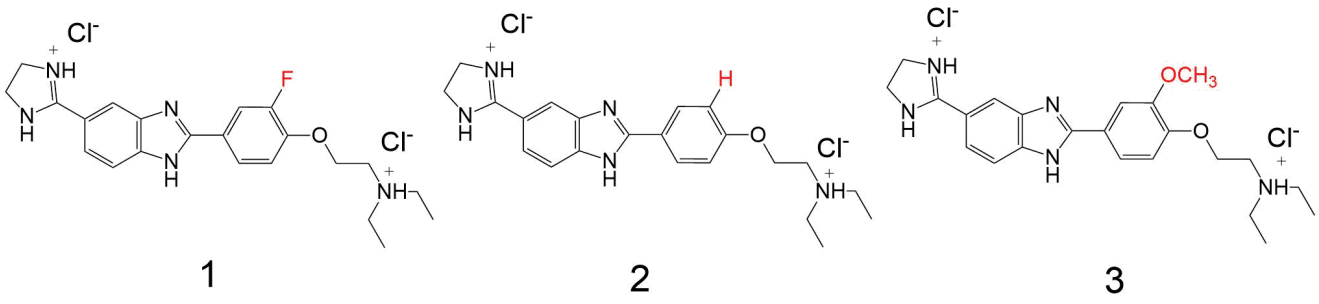

Figure 1. A series of novel benzimidazole amidines derivates which differ only in one substituent on phenyl ring.

Interestingly, despite the fact that even benzimidazole amidines derivatives differ only in one substituent, they caused opposite changes in fluorescence upon interaction with studied polynucleotides. While addition of derivatives 1 and 2 caused a decrease of fluorescence in the presence of DNA/RNA, the addition of any polynucleotide resulted exclusively in strong emission increase of derivate 3 which can probably be ascribed to donor properties of methoxy group.

All three compounds exhibited positive induced CD spectra (ICD) with ctDNA, poly(dAdT)$_2$ and poly A – poly U. Usually, a positive ICD band, with an intensity similar or stronger than CD band of DNA/RNA, strongly supports the minor groove binding to DNA or the major groove binding to ds-RNA.[1] Thus, it can be concluded that studied compounds bind to minor groove of ctDNA and AT-DNA and to major groove of ds-RNA.

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A Novel Nitroprusside Association Complex with the Pharmacologically Important Ligand: Crystal Structure and Supramolecular Assembly

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Nitroprussides (pentacyanonitrosylferrate(II) anions, $[Fe(CN)_5NO]^{2-}$) are emerging as novel materials with promising applications in diverse molecular communication and for storage information devices. Reaction between photochromic nitroprusside anion and the bis-pyridinium-4-oxime cation of Toxogonin (TOXO-2Cl) in the water results in spontaneous formation of association compound. This complex crystallize in the triclinic system, space group *P*-1. The asymmetric unit contains one $TOXO^{2+}$ cation, one $[Fe(CN)_5NO]^{2-}$ anion and water molecules of crystallization. These mutual interactions and the water hydrogen bonding link the ions and molecules into layered 2D structures of formula unit $TOXO[Fe(CN)_5NO]$. Herein, we report the structural, spectroscopic (Mössbauer, FT-IR, solid UV-VIS) and thermal characterization of this novel complex compound.

INDEKS AUTORA

III. SIMPOZIJ SUPRAMOLEKULSKE KEMIJE

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