ONLINE EVENT

BOOK OF ABSTRACTS

ECS6 BUDAPEST

6th European Crystallographic School

4–10 July 2021 / Budapest, Hungary

ECS6
6th European Crystallographic School
July 4–10, 2021
Budapest, Hungary

AKCongress
P.O. Box 245, H-1519 Budapest, Hungary
E-mail: ecs6@akcongress.com
https://akcongress.com/ecs6/

Please be aware that certain changes introduced in the Conference programme after editing has been closed may not be included in this Book of Abstracts due to the publishing deadline.

P.O. Box 245, H-1519 Budapest, Hungary
Phone: +36 1 464 8240
E-mail: ak@akademiai.hu
www.akjournals.com / www.akademiai.hu

ISBN 978-963-454-703-7

Contents

ECS6 Programme overview

4–10 July 2021 / Budapest, Hungary (Online event)

	Sun 04.07	Mon 05.07	Tue 06.07	Wed 07.07	Thu 08.07	Fri 09.07	Sat 10.07
08:40–10:10		Opening: ECS6 5′, ECA 5′ IUCr role cryst *McMahon10′* Databases CSD *Ward / Gimondi* 30′ PDB *Armstrong 25′*	Instrumentation, X-ray sources, detectors *Helliwell 25′,* *Šišak Jung 50′*	Macromolec 1 *Weiss*	Disorder, twin: *Fábián 25′* Abs config: *Bényei 25′* Str from powder: *Fábián 25′*	COVID-19 *Fülöp*	20:45–21:40 Virtual bike tour
10:10–10:30		*Coffee break*	*Coffee break*	*Coffee break*	*Coffee break*	*Coffee break*	
10:30–12:00		Diffraction physics Development of X-ray sources *Faigel*	Syncr, neutr, electron *Helliwell 40′* EuXFEL *Feidenhans'l 35′*	Macromolec 2 *Weiss*	Polymorph *Bényei 45′* Isostruct *Bombicz 45′*	Thermodynamics non-ambient *Katrusiak*	
12:00–13:00		*Lunch break*	*Lunch break*	*Lunch break*	*Lunch break*	*Lunch break*	
13:00–14:30		Symmetry, Int Tabl *Lehmann*	Crystallizat small *Báthori 25′* Crystallizat macro *Harmat 25′* Completing anal methods Massera *25′*	Enzymes *Vértessy 38′* E-density maps *Harmat 38′*	Polymorph, MOF, bio-MOF *Duarte*	Cryst eng Supramolec chem Non-covalent interact *Terraneo*	
14:30–16:00	Speakers' information	Theory and Lab: SAXS	LAB: SXRD	LAB: Macromol1	Olex2	LAB: Macromol2	
16:00–16:20		*Coffee break*	*Coffee break*	*Coffee break*	*Coffee break*	*Coffee break*	
16:20–17:10		Reciprocal space *Bortel*	Small molec data correct, str solution, refinement, analysis *Lehmann*	Data validation *Lehmann*: small 15′ *Helliwell 15′* *Weiss:* macro 15′	Powder Diffraction *Schürmann*	Electron Diffraction *Mugnaioli*	
17:10–18:10		Data coll, starting in practice *Stürzer*	Poster 1	Data quality, preservation *Helliwell 30′* Solution *Enyedy 30′*	Poster 2	How to publish *Andrews*	
18:10–19:10		*Networking* *Welcome drink & chat*	*Networking* *Virtual sightseeing of the Buda Castle*	*Networking* *Concert of Chemical Singers*	*Networking* *Quiz & chat*	*Closing ceremony* *Poster prizes* *Goodbye drink & chat*	

6th EUROPEAN CRYSTALLOGRAPHIC SCHOOL ECS6

4–10 July 2021 / online from Budapest, Hungary

Programme in details (All times are in the GMT +2 time zone)

Sunday / 4 July 2021				
14:30	16:00	**Speakers' information**		

Monday / 5 July 2021				
		Monday session 1		
8:40	8:45	**Opening of ECS6, welcome and technical information**	**Petra Bombicz** *Chair of ECS6*	Chemical Crystallography Research Laboratory Research Centre for Natural Sciences Budapest, Hungary
8:45	8:50	**Opening remarks**	**Udo Heinemann** *President of the ECA*	Max-Delbrück-Centrum für Molekulare Medizin and Institut für Chemie und Biochemie Freie Universität Berlin Berlin, Germany
8:50	9:00	**The role of the IUCr in crystallography**	**Brian McMahon**	International Union of Crystallography Chester, United Kingdom
9:00	9:30	**The Cambridge Structural Database – Learning from one million crystal structures**	**Suzanna Ward and Ilaria Gimondi**	Cambridge Crystallographic Data Centre Cambridge, United Kingdom
9:30	9:55	**The Protein Data Bank – 50 years and counting**	**David Armstrong**	Protein Data Bank in Europe Hinxton, United Kingdom
9:55	10:10	**Questions & answers (Udo Heinemann, Brian McMahon, Suzanne Ward and Ilaria Gimondi, David Armstrong)**		
10:10	10:30	**Coffee break**		
		Monday session 2		
10:30	11:45	**Diffraction physics**	**Gyula Faigel**	Wigner Research Centre for Physics Budapest, Hungary
11:45	12:00	**Questions & answers (Gyula Faigel)**		
12:00	13:00	**Lunch break**		
		Monday session 3		
13:00	14:15	**Crystals and symmetry – How to use the International Tables for Crystallography (Volume A)**	**Christian W. Lehmann**	Max-Planck-Institut für Kristallographie Mülheim an der Ruhr, Germany
14:15	14.30	**Questions & answers (Christian Lehmann)**		
14:30	15:30	**Theory and laboratory practice (SAXS): András Wacha: Small-Angle X-ray Scattering: A complementary technique to diffraction**		
15:30	16:00	**Question & answers (Theory and Laboratory practice (SAXS))**		
16:00	16:20	**Coffee break**		

		Monday session 4		
16:20	17:00	**Reciprocal space**	**Gábor Bortel**	Wigner Research Centre for Physics Budapest, Hungary
17:00	17:10	**Questions & answers (Gábor Bortel)**		
17:10	17:55	**Data collection strategy**	**Tobias Stürzer**	Bruker AXS GmbH Karlsruhe, Germany
17:55	18:10	**Questions & answers (Tobias Stürzer)**		
18:10	19:00	**Networking / Welcome drink & chat**		

Tuesday / 6 July 2021				
		Tuesday session 1		
8:40	9:05	**Instrumentation, sources and detectors**	**John R. Helliwell**	University of Manchester Faculty of Science and Engineering Manchester, United Kingdom
9:05	9:55	**Why should you know about X-ray detectors?**	**Dubravka Šišak Jung**	Dectris Ltd. Baden, Switzerland
9:55	10:10	**Questions & answers (John R. Helliwell, Dubravka Šišak Jung)**		
10:10	10:30	**Coffee break**		
		Tuesday session 2		
10:30	11:10	**Overview lecture of the probes of the structure of matter; X-rays, neutrons and electrons**	**John R. Helliwell**	University of Manchester Faculty of Science and Engineering Manchester, United Kingdom
11:10	11:45	**X-ray Free Electron Lasers: A new paradigm in science**	**Robert Feidenhans'l**	European XFEL GmbH Schenefeld, Germany
11:45	12:00	**Questions & answers (John R. Helliwell, Robert Feidenhans'l)**		
12:00	13:00	**Lunch break**		
		Tuesday session 3		
13:00	13:25	**Crystallisation - A very practical guide to getting that perfect single crystal**	**Nikoletta Báthori**	Cape Peninsula University of Technology Cape Town, South Africa
13:25	13:50	**Protein crystallization**	**Veronika Harmat**	Laboratory of Structural Chemistry and Biology Institute of Chemistry Eötvös Loránd University Budapest, Hungary
13:50	14:15	**"With a little help from my friends": complementary techniques to get to know your crystal structure better**	**Chiara Massera**	Department of Chemistry University of Parma Parma, Italy
14:15	14:30	**Questions & answers (Nikoletta Báthori, Veronika Harmat, Chiara Massera)**		
14:30	15:30	**Laboratory practice (SXRD) / Tamás Holczbauer, Gábor Bortel, Nóra V. May, Laura Bereczki, Éva Kováts, Sourav De, Petra Bombicz: Small molecule X-ray diffraction**		
15:30	16:00	**Question & answers (Laboratory practice (SXRD))**		
16.00	16:20	**Coffee break**		

		Tuesday session 4		
16:20	17:00	**From raw diffraction data to refined single crystal structures**	**Christian Lehmann**	Max-Planck-Institut für Kristallographie Mülheim an der Ruhr, Germany
17:00	17:10	**Questions & answers (Christian Lehmann)**		
17:10	18:10	**Poster session and flash presentations I.**		
18:15	19:15	**Networking / Virtual sightseeing of the Buda Castle**		

Wednesday / 7 July 2021				
		Wednesday session 1		
8:40	9:55	**Macromolecular structure determination by X-ray crystallography (Part I)**	**Manfred S. Weiss**	Helmholtz-Zentrum Berlin Berlin, Germany
9:55	10:10	**Questions & answers (Manfred S. Weiss)**		
10:10	10:30	**Coffee break**		
		Wednesday session 2		
10:30	11:45	**Macromolecular structure determination by X-ray crystallography (Part II)**	**Manfred S. Weiss**	Helmholtz-Zentrum Berlin Berlin, Germany
11:45	12:00	**Questions & answers (Manfred S. Weiss)**		
12:00	13:00	**Lunch break**		
		Wednesday session 3		
13:00	13:38	**Enzymes involved in key biomedical processes**	**Beáta Vértessy**	Department of Applied Biotechnology and Food Science Budapest University of Technology and Economics and Laboratory of Genome Metabolism and Repair Institute of Enzimology Budapest, Hungary
13:38	14:15	**Model building and electron density maps – howtos in protein crystallography**	**Veronika Harmat**	Laboratory of Structural Chemistry and Biology Institute of Chemistry Eötvös Loránd University Budapest, Hungary
14:15	14:30	**Questions & answers (Beáta Vértessy, Veronika Harmat)**		
14:30	15:30	**Laboratory practice (Macromol 1) / Ibolya Leveles, Veronika Harmat: Protein crystallization and data collection**		
15:30	16:00	**Question & answers (Laboratory practice (Macromol 1))**		
16:00	16:20	**Coffee break**		
		Wednesday session 4		
16:20	16:35	**Validating the results of small molecule single crystal structure analysis**	**Christian W. Lehmann**	Max-Planck-Institut für Kristallographie Mülheim an der Ruhr, Germany
16:35	16:50	**Validating the results of macromolecule single crystal structure analysis**	**Manfred S. Weiss**	Helmholtz-Zentrum Berlin Berlin, Germany

16:50	17:05	**Data validation**	**John R. Helliwell**	University of Manchester Faculty of Science and Engineering Manchester, United Kingdom
17:05	17:10	**Questions & answers (Christian W. Lehmann, Manfred S. Weiss, John R. Helliwell)**		
17:10	17:35	**Data preservation and quality: FAIR and FACT in crystallography**	**John R. Helliwell**	University of Manchester Faculty of Science and Engineering Manchester, United Kingdom
17:35	18:00	**Equilibrium studies to reveal stability, composition and structure in solution**	**Éva A. Enyedy**	Department of Inorganic and Analytical Chemistry University of Szeged Szeged, Hungary
18:00	18:10	**Question & answers (John R. Helliwell, Éva A. Enyedy)**		
18:10	19:15	**Networking / Concert of Chemical Singers**		

Thursday / 8 July 2021				
		Thursday session 1		
8:40	9:05	**Disorder and twinning**	**László Fábián**	School of Pharmacy University of East Anglia Norwich, United Kingdom
9:05	9:30	**X-ray diffraction as absolute method to determine absolute configuration**	**Attila Bényei**	University of Debrecen Institute of Chemistry Debrecen, Hungary
9:30	9:55	**Structure determination from powder diffraction data**	**László Fábián**	School of Pharmacy University of East Anglia Norwich, United Kingdom
9:55	10:10	**Question & answers (László Fábián, Attila Bényei)**		
10:10	10:30	**Coffee break**		
		Thursday session 2		
10:30	11:08	**Polymorphism of solid state structures and its consequences**	**Attila Bényei**	University of Debrecen Institute of Chemistry Debrecen, Hungary
11:08	11:45	**Polymorphism and isostructurality**	**Petra Bombicz**	Chemical Crystallography Research Laboratory Research Centre for Natural Sciences Budapest, Hungary
11:45	12:00	**Questions & answers (Attila Bényei, Petra Bombicz)**		
12:00	13:00	**Lunch break**		
		Thursday session 3		
13:00	14:15	**Is structural characterization important in the study of Metal Organic Frameworks, bio-MOFs and polymorphs? No doubt about that!**	**Teresa Duarte**	Instituto Superior Técnico Universidade de Lisboa Lisbon, Portugal
14:15	14:30	**Questions & answers (Teresa Duarte)**		
14:30	15:30	**Laboratory practice (Olex2): Horst Puschmann: Solving and refining small-molecule structures using Olex2**		
15:30	16:00	**Question & answers (Laboratory practice (Olex2))**		
16:00	16:20	**Coffee break**		

		Thursday session 4		
16:20	17:00	**Powder Diffraction with single-crystal instruments**	**Christian J. Schürmann**	Rigaku Europe SE Göttingen, Germany
17:00	17:10	**Questions & answers (Christian J. Schürmann)**		
17:10	18:10	**Poster session and flash presentations II.**		
18:10	19:00	**Networking / Quiz & chat**		

Friday / 9 July 2021				
		Friday session 1		
8:40	9:55	**Stuctural aspects of COVID-19**	**Vilmos Fülöp**	University of Warwick Coventry, United Kingdom
9:55	10:10	**Question & answers (Vilmos Fülöp)**		
10:10	10:30	**Coffee break**		
		Friday session 2		
10:30	11:45	**Crystallography in extreme conditions**	**Andrzej Katrusiak**	Faculty of Chemistry Adam Mickiewicz University Poznan, Poland
11:45	12:00	**Questions & answers (Andrzej Katrusiak)**		
12:00	13:00	**Lunch break**		
		Friday session 3		
13:00	14:15	**Noncovalent interactions at work**	**Giancarlo Terraneo**	Politecnico di Milano Milan, Italy
14:15	14:30	**Questions & answers (Giancarlo Terraneo)**		
14:30	15:30	**Laboratory practice (Macromol 2): Veronika Harmat, Ibolya Leveles: Solving protein structures with X-ray crystallography**		
15:30	16:00	**Question & answers (Laboratory practice (Macromol 2))**		
16:00	16:20	**Coffee break**		
		Friday session 4		
16:20	17:00	**Electron crystallograph**	**Enrico Mugnaioli**	Center for Nanotechnology Innovation@NEST Istituto Italiano di Tecnologia Pisa, Italy
17:00	17:10	**Questions & answers (Enrico Mugnaioli)**		
17:10	17:50	**How to publish your research**	**Mike Andrews**	CrystEngComm Royal Society of Chemistry London, United Kingdom
17:50	18:00	**Question & answers (Mike Andrews)**		
18:00	18:10	**Break**		
18:10	19:00	**Closing ceremony / Poster prizes / Goodbye drink & chat**		

Saturday / 10 July 2021		
20:45	21:40	**Virtual sunset bike tour in Budapest**

ECS6 International Programme Committee

Udo Heinemann ECA President
Max-Delbrück-Centrum für Molekulare Medizin and Institut für Chemie und Biochemie
Freie Universität Berlin
Berlin, Germany

Alessia Bacchi ECA Past-President
Dipartimento di Chimica Generale ed Inorganica
Chimica Analitica e Chimica Fisica
Università di Parma
Parma, Italy

Consiglia Tedesco ECA Education Coordinator
Department of Chemistry
University of Salerno
Fisciano, Italy

Annalisa Guerri GIG3 representative
Chemistry Department
University of Florence
Florence, Italy

Petra Bombicz ECS6 chair
Chemical Crystallography Research Laboratory
Research Centre for Natural Sciences
Budapest, Hungary

Kinga Suwinska ECS4 chair
Faculty of Mathematics and Natural Sciences
Cardinal Stefan Wyszynski University in Warsaw
Warsaw, Poland

Catharine Esterhuisen ECS5 chair
Department of Chemistry
Stellenbosch University
Stellenbosch, South Africa

Teresa Duarte ECS7 chair
Centro de Química Estrutural
Instituto Superior Técnico
Lisbon, Portugal

ECS6 Local Organizing Committee

Petra Bombicz
Chair
Chemical Crystallography Research Laboratory
Research Centre for Natural Sciences
Budapest, Hungary

Nóra V. May
Secretary
Chemical Crystallography Research Laboratory
Research Centre for Natural Sciences
Budapest, Hungary

Tamás Holczbauer
Posters, exhibitors
Chemical Crystallography Research Laboratory
Research Centre for Natural Sciences
Budapest, Hungary

Laura Bereczki
Treasurer
Chemical Crystallography Research Laboratory
Research Centre for Natural Sciences
Budapest, Hungary

Péter Németh
Member
Chemical Crystallography Research Laboratory
Research Centre for Natural Sciences
Budapest, Hungary

András Wacha
Member
Biological Nanochemistry Research Group
Institute of Materials and Environmental Chemistry
RCNS HAS
Budapest, Hungary

Beáta Vértessy
Member
Department of Applied Biotechnology and Food Science
Budapest University of Technology and Economics and Laboratory of Genome Metabolism and Repair
Institute of Enzimology
RCNS HAS
Budapest, Hungary

Ibolya Leveles
Member
Budapest University of Technology and Economics
Budapest, Hungary

Kinga Nyíri
Member
Department of Applied Biotechnology and Food Science
Budapest University of Technology and Economics and Laboratory of Genome Metabolism and Repair
Institute of Enzimology
RCNS HAS
Budapest, Hungary

Veronika Harmat
Member
Laboratory of Structural Chemistry and Biology
Institute of Chemistry
Eötvös Loránd University
Budapest, Hungary

Valéria Bugris
Member
X-Ray Crystallography Laboratory
Biological Research Centre, HAS
Budapest, Hungary

Sándor Brockhauser
Member
X-Ray Crystallography Laboratory
Biological Research Centre, HAS
Budapest, Hungary

Attila Bényei
Member
Department of Physical Chemistry
University of Debrecen
Debrecen, Hungary

Gyula Faigel
Member
Department of Experimental Solid State Physics
Wigner Research Centre for Physics
Budapest, Hungary

Éva Kováts
Member
Wigner Research Centre for Physics
Budapest, Hungary

Gábor Bortel
Member
Wigner Research Centre for Physics
Budapest, Hungary

Lecturers

Christian W. Lehmann
Max-Planck-Institut für Kohlenforschung
Mülheim an der Ruhr, Germany

John R. Helliwell
School of Chemistry
University of Manchester
Manchester, United Kingdom

Manfred S. Weiss
Helmholtz-Zentrum Berlin
Berlin, Germany

Brian McMahon
International Union of Crystallography
Chester, United Kingdom

Suzanna Ward
Cambridge Crystallographic Data Centre
Cambridge, United Kingdom

Ilaria Gimondi
Cambridge Crystallographic Data Centre
Cambridge, United Kingdom

David Armstrong
Protein Data Bank in Europe
United Kingdom

Gyula Faigel
Department of Experimental Solid State Physics Wigner RCP
of the Hungarian Academy of Sciences
Budapest, Hungary

Gábor Bortel
Department of Experimental Solid State Physics
Wigner Research Centre for Physics Budapest, Hungary

Tobias Stürzer
Bruker AXS GmbH
Karlsruhe, Germany

Dubravka Šišak Jung
XRD Application Scientist
DECTRIS Ltd.
Baden, Switzerland

Robert Feidenhans'l
European XFEL GmbH
Schenefeld, Germany

Nikoletta Báthori
Chemistry Department
Cape Peninsula University of Technology
Cape Town, South Africa

Veronika Harmat
Laboratory of Structural Chemistry and Biology
Institute of Chemistry
Eötvös Loránd University
Budapest, Hungary

Chiara Massera
Department of Chemistry
University of Parma
Parma, Italy

Beáta Vértessy
Department of Applied Biotechnology and Food Science
Budapest University of Technology and Economics
Laboratory of Genome Metabolism and Repair Institute of Enzimology
Budapest, Hungary

Éva Anna Enyedy
Department of Inorganic and Analytical Chemistry
University of Szeged
Szeged, Hungary

László Fábián
School of Pharmacy
University of East Anglia
Norwich, United Kingdom

Attila Bényei
Department of Physical Chemistry
University of Debrecen
Debrecen, Hungary

Petra Bombicz
Chemical Crystallography Research Laboratory
Research Centre for Natural Sciences
Budapest, Hungary

Teresa Duarte
Instituto Superior Técnico
Universidade de Lisboa
Lisbon, Portugal

Christian J. Schürmann
Rigaku Europe SE
Neu-Isenburg, Germany

Vilmos Fülöp
University of Warwick
Coventry, United Kingdom

Andrzej Katrusiak
Faculty of Chemistry
Adam Mickiewicz University
Poznan, Poland

Giancarlo Terraneo
Politecnico di Milano
Milan, Italy

Enrico Mugnaioli
Center for Nanotechnology Innovation@NEST
Istituto Italiano di Tecnologia
Pisa, Italy

Mike Andrews
CrystEngComm
Royal Society of Chemistry
London, United Kingdom

Teachers of hands-on tutorial and laboratory practices

Horst Puschmann
Durham University
Durham, United Kingdom

András Wacha
Research Centre for Natural Sciences
Budapest, Hungary

Gábor Bortel
Wigner Research Centre for Physics
Budapest, Hungary

Éva Kováts
Wigner Research Centre for Physics
Budapest, Hungary

Tamás Holczbauer
Chemical Crystallography Research Laboratory
Research Centre for Natural Sciences
Budapest, Hungary

Nóra V. May
Chemical Crystallography Research Laboratory
Research Centre for Natural Sciences
Budapest, Hungary

Laura Bereczki
Chemical Crystallography Research Laboratory
Research Centre for Natural Sciences
Budapest, Hungary

Sourav De
Chemical Crystallography Research Laboratory
Research Centre for Natural Sciences
Budapest, Hungary

Petra Bombicz
Chemical Crystallography Research Laboratory
Research Centre for Natural Sciences
Budapest, Hungary

Veronika Harmat
Laboratory of Structural Chemistry and Biology
Institute of Chemistry
Eötvös Loránd University
Budapest, Hungary

Ibolya Leveles
Budapest University of Technology and Economics
Budapest, Hungary

ABSTRACTS

Instrumentation and experimental techniques

Accelerated design of new electrode materials for Li-ion and Na-ion batteries

Iciar Monterrubio[1,3*], *Marine Reynaud*[1], *Agnieszka Wizner*[1,2], *Nebil A. Katcho*[1,4], *Juan Rodríguez-Carvajal*[4], *Amaia Saracibar*[5], *Javier Carrasco*[1], *Montse Casas-Cabanas*[1]

[1]Centre for Cooperative Research on Alternative Energies (CIC energiGUNE), Basque Research and Technology Alliance (BRTA), Alava Technology Park, Albert Einstein 48, 01510 Vitoria-Gasteiz, Spain, [2]Dpto. de Física de la Materia Condensada, UPV/EHU, Campus de Leioa, Bilbao, Spain, [3]Inorganic Chemistry Department, Science and Technology Faculty, Basque Country University (UPV/EHU), 48940 Leioa, Bilbao, Spain, [4]Institute Laue-Langevin, Grenoble, France, [5]Physical Chemistry Department, Pharmacy Faculty, Basque Country University (UPV/EHU), 01006 Vitoria-Gasteiz, Álava Spain
[*]E-mail: imonterrubio@cicenergigune.com

Keywords: Li-ion batteries, Na-ion batteries, high-throughput, bond-valance

A salient aspect of research in batteries is the discovery of new materials or novel properties of existing compounds. The traditional approach is to focus on archetype compounds in which a desirable property was first observed, stimulating further investigations. This has been the innovation pathway of many battery materials ($LiCoO_2$, $LiFePO_4$) which are found in commercial Li-ion batteries. Yet the trial-and-error exploration of the materials space is costly in terms of synthesis and characterization times, which hinders the emergence of new, disruptive materials.

In this contribution, we will present the strategy that have allowed us to develop new high-voltage materials for Li-ion and Na-ion batteries based on the analysis of structural descriptors and on chemical design. This approach consists in spotting, among families of compounds previously studied in other research fields, the ones that can be turned into electrode materials. It is interesting to note that many electrode materials studied for Li-ion and Na-ion batteries crystallizes in mineral structures (e.g. rock salts, spinels, olivines, etc.). Then a mineral compound, selected for the presence in its structure of possible alkali-ion diffusion pathways, and after relevant chemical modifications, can lead to new electrode materials [1].

Screening the structural databases in quest for structures presenting attractive features is, however, an unachievable task if it has to be done by hand, but also using costly DFT-based computational calculations. To tackle this issue, we have developed an efficient computational analysis tool based on the bond-valence theory that enables to carry out a high-throughput analysis of the available ionic diffusion pathways in thousands of structures in a short time [2].

Following this approach, we identified the attractive structural framework of the nitridophosphates $Na_3M(PO_3)_3N$, in which two of the three sodium ions are expected to be mobile. Within this family, $Na_3V(PO_3)_3N$ has been found to be the Na-ion cathode material with the highest operation voltage for the VIV+/VIII+ redox couple together with $Na_7V_3(P_2O_7)_4$ [3]. The associated reaction mechanism occurs with a small voltage hysteresis and a near-zero volume change between the reduced and charged states, which is pretty uncommon among sodium-ion electrode materials.

However, the experimental validation stage remains the limiting step of the process. High-throughput experimental synthesis approaches that are reproducible and scalable are thus required [2, 4]. Then, we are developing an AI-aided autonomous experimental lab which includes a closed-loop experimentation process to integrate the feedback from theoretical calculations, synthesis results, and characterization data.

Acknowledgement:
MCIU for the financial support through the projects ION-STORE, AffINIty and ION-SELF [ENE2016-81020-R, ENE2016-75242-R], to MCIU, AEI, FEDER within the Programme Retos de investigación 2019 for the project ION-SELF [PID2019-106519RB-I00] and fellowship Ayudas Juan de la Cierva-Formación [FJCI-2014-19990]; Basque Government through the program ELKARTEK CICE17.

References:
1. Reynaud et al., *J. Mater. Chem. A.* 2014, 2.
2. Katcho et al., *J. Appl. Cryst.* 2019, 52.
3. Reynaud et al., *Electrochem. Commun.* 2017, 84, 14–18.
4. Carey at al., *Comb. Sci.* 2011, 13, 186.

Mineral and inorganic crystallography

The effect of sodium and silicon on microstructure and crystallography for HAC

Marco Cantaluppi[1*], *Nicoletta Marinoni*[1], *Fernando Cámara*[1]

[1]Earth Science Department "Ardito Desio", University of Milan, Via Botticelli 23, 20133, Milan, Italy
[*]E-mail: marco.cantaluppi@unimi.it

Keywords: high alumina cement, microstructure, synchrotron powder diffraction, minor elements

Calcium Aluminate Cements (CACs) are special type of hydraulic binder which are classified into low alumina (CAC) and high alumina cement based (HAC) and are a specialty class of cements with higher Al_2O_3 % wt. in comparison to OPC [1,2]. HACs represent the most important CACs mainly for refractory castables and typical starting raw materials are pure limestone and synthetic alumina; principal reactive phases are krotite (CA, $CaAl_2O_4$) and grossite (CA_2, $CaAl_4O_7$) [3]. Minor elements are commonly added by raw materials and can enter only in slight amount in aluminate structures and/or promote the growth of unwanted phases. The effects of some minor elements have been broadly studied but the influence of Na_2O and SiO_2 has not been studied, despite they represent most common impurities in synthetic alumina.

In the present research we aim to clarify the effect of Na_2O and SiO_2 on HACs manufacture (mineralogy, crystallography and microstructure) by studying four industrial HACs with different amounts of Na_2O and similar SiO_2 and one highly Na_2O doped HAC by means of laboratory and synchrotron X-Ray Powder Diffraction, Electron Microprobe MicroAnalyser (EMPA) and Scanning Electron Microprobe (SEM).

Results highlighted that: (i) all HACs prepared are characterised by CA and CA_2 and no evidences of common accessory phases; (ii) Na_2O and SiO_2 appeared mainly concentrated in a Na-bearing phase with an empirical formula equal to $Na_2CaAl_{3.9}Si_{0.1}O_8$ and criptocrystallite features; (iii) minor elements do not enter preferably in the crystal structure of CA and CA_2.

References:

1. Stöber S., Prokhnenko O., Schorr S., Döring T., Pöllmann H., Synthesis and crystal chemistry of manganese containing perovskites: phases with brownmillerite structures, Calcium Aluminate Cements: *Proceedings of the Centenary Conference* (2008) 197–206.
2. Pöllmann, H., Calcium Aluminate Cements – Raw Materials, Differences, Hydration and Properties: *Reviews in Mineralogy and Geochemistry* 74 (2012) 1 82. https://doi.org/10.2138/rmg.2012.74.1
3. Zapata, J.F., Maryory, G., Colorado, H.A. Characterization of two calcium aluminate cement pastes, in Advances in high temperature ceramic matrix composites and materials for sustainable development: *Ceramic Transactions* 263 (2017) 493–504.

Search of new rare earth borates prototyped by carbonate minerals

A.B. Kuznetsov[1*], *K.A. Kokh*[1], *N.G. Kononova*[1], *B. Uralbekov*[2], *V.A. Svetlichnyi*[3], *A.E. Kokh*[1]

[1]Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk 630090, Russia,
[2]Al-Farabi Kazakh National University, Almaty 050040, Kazakhstan, [3]Tomsk State University, Tomsk 634050, Russia
[*]E-mail: ku.artemy@igm.nsc.ru

Keywords: crystal structure, crystal growth, rare earth borates, luminescence

At present, many research projects are related to the development of more environmentally friendly light sources and luminophores. These projects have focused on borates due to their high chemical stability, thermal and radiation stability, wide transparency region and high laser threshold. In addition, borate compounds have diverse chemical compositions and crystal structures due to the ability of boron to form anionic BO_3 group. According to the anionic group theory, the compounds with isolated boron groups BO_3 exhibit strong potential for use in the range of VIS to deep UV range. As a rule, compounds with three coordinated boron atoms crystallize in structure similar to carbonate minerals. One of the prominent examples include $YAl_3(BO_3)_4$ (YAB) ((UV cut-off - 160 nm) [1], which crystallizes in huntite ($CaMg_3(CO_3)_4$) structure. Alkali and/or alkali earth borates with a high concentration of rare earth elements were synthesized and proposed to be efficient phosphor materials. As an example, $RNa_3(BO_3)_2$ (R = Y, La, Nd, Gd) [2] crystallizing with buetschliite-type structure ($K_2Ca(CO_3)_2$ $R\bar{3}$ space group) have a low concentration quenching of rare earth atoms. The existence of these multication borates suggests new complex compounds by replacing part of the Na^+ by Ba^{2+}cations, as well as the REE variation. Novel rare earth borates, such as $NaBaSc(BO_3)_2$ and $NaBaY(BO_3)_2$, have been discovered in the system R_2O_3–BaO–Na_2O–B_2O_3 [3]. The consequent substitution of Na→K and of Ba→Sr results in obtaining two new compound families of $KBaR(BO_3)_2$ and $KSrR(BO_3)_2$, which crystallize in the $R\bar{3}$ and $C2/c$ space groups, respectively [4].

In this study, by substituting the cationic part in $KBaR(BO_3)_2$ and $YAl_3(BO_3)_4$ the new rare earth borates ($SmSc_3(BO_3)_4$, $KCaR(BO_3)_2$ and $Li_3Ba_4Sc_3B_8O_{22}$) crystalized with carbonate type structure were obtained. The crystal structure, thermal properties and the phase transformations were discussed. Also, some optical properties are presented, including the Raman spectra and UV-vis-NIR diffuse reflectance spectra (DRS) of the crystal.

Acknowledgement:
This work was supported by RFBR project # 18-32-20001 and 19-33-90012, project GF MES RK IRN P05130794, and state contract of IGM SB RAS.

References:

1. X. Yu, Y. Yue, J. Yao, Z. Hu, *Journal of Crystal Growth* 312, 20, 2010, 3029–3033.
2. Y. Zhang, X.L. Chen, J.K. Liang, T. Xu, *Journal of Alloys and Compounds* 333(1) (2002) 72–75.
3. T.N. Svetlyakova, A.E. Kokh, N.G. Kononova, P.P. Fedorov, S.V. Rashchenko, A. Maillard, *Crystallography Reports* 58(1) (2013) 54–60.
4. V.S. Shevchenko, N.G. Kononova, A.E. Kokh, A.K. Bolatov, B.M. Uralbekov, M.M. Burkitbaev, *Russian Journal of Inorganic Chemistry* 62(9) (2017).

Investigating corrosion processes of Ag-Cu alloys

Erik Lübke[1*], *Klaudia Hradil*[1]

[1]X-ray Center, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria
[*]E-mail: erik.luebke@tuwien.ac.at

Keywords: metallurgy, in-situ XRD, Rietveld-refinement, inorganic crystallography, silver inks

Copper-silver alloys are among the most ancient alloys and have been used by humans since prehistoric times. Even today they are paramount in a wide array of fields, ranging from art to electronics and heavy industry. However, quite some time has passed since this system has been investigated thoroughly by XRD and new techniques and improved methods have been developed since then. [1]

The motivation of our studies comes from the study of corrosion phenomena of silver inks on historic parchments. Within these investigations we analysed the silver inks of the Viennese Genesis [2]. Furthermore, in-situ X-ray diffraction using lab instruments was performed on Ag-Cu alloys that is in agreement with the original ink composition up to 325 °C.

In our studies of these alloys we found intriguing phenomena [Fig. 1] in this elementary system while developing an approach to perform corrosion studies with in-situ XRD. This effect was further investigated using Rietveld-refinement, which led to the formulation of a hypothesis about the origin of this behaviour and its applications in other fields of research dependent on Ag-Cu Systems.

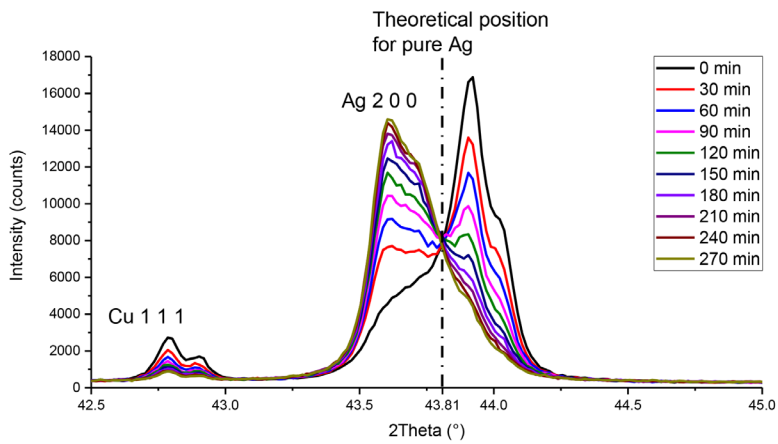


Figure 1. Peak-shift observed during the corrosion of Ag-Cu-alloys at 275°C with Cu-Kα_1/Kα_2 radiation

Acknowledgement:
Austrian Science Fund (FWF) under the contract number P27302-G21

References:

1. Linde R., *Journal of Applied Physics* 1966, 37, 934; https://doi.org/10.1063/1.1708298
2. Hofmann, C. (2020). *The Vienna Genesis.* Vienna, Austria: Böhlau Verlag. ISBN: 978-3-205-21058-0

$[Pd(NH_3)_4]XO_4$(*X*= Cr, Mo): structure and thermal decomposition products

P.S. Serebrennikova[1,2*], *S.A. Gromilov*[2], *V.Yu. Komarov*[2]

[1]Novosibirsk State University, [2]Nikolaev Institute of Inorganic Chemistry
[*]E-mail: polina.buneeva2015@yandex.ru

Keywords: complex salt, co-crystallization, thermal decomposition

Complex salts of the series $[Pd(NH_3)_4]XO_4$ (*X* = Cr, Mo) are promising precursors of metal alloys-catalysts. The possibility of obtaining of the Pd-Cr-Mo system alloys is expected during the thermolysis of the co-crystallization product (CCP) of these salts. However, a fundamental understanding of the structure of the precursor salt is necessary to make right conclusion about the conditions for obtaining a specific alloy, so the aim of the work is the x-ray structural characterization of these salts and their thermolysis products. In addition, it is known from the literature that salts of isostructural series (with Pt instead of Pd) exhibit the effect of negative thermal expansion. Therefore, it would also be interesting to test the presence of this effect on the example of our salts.

The analysis of two CCP obtained as a result of the co-crystallization of the initial salts at the ratios of *X*-metal molar fractions Mo : Cr = 1 : 1 and 1 : 3 was carried out. X-ray diffraction analysis (XRD) of ~10 single crystals showed that in both cases the synthesis products are heterogeneous in composition and are solid solutions of $[Pd(NH_3)_4]Mo_xCr_{1-x}O_4$ (x from 0.02 to 0.88). Moreover, in the case of the product Mo : Cr = 1 : 1 crystals with x≈0.8 were predominantly formed and in the case of the product Mo : Cr = 1 : 3 the crystals could be divided into two groups: large crystals at the edges of the watch glass (x≈0.2) and small crystals in the center (x≈0.05). It is shown that the dependence of the unit cell parameters (UCP) on x is close to linear. A previously developed UCP refinement technique based on the extraction of Kα1 components was tested on the example of a single crystal $[Pd(NH_3)_4]Mo_xCr_{1-x}O_4$ (x=0.02). It is shown that the UCP values (*a*≈7.3, *c*≈15.4, sp. gr. $I4_1/amd$) determined by this method on two different devices (Bruker D8 Venture and Bruker X8 Apex) differ by no more than 0.001 Å while the UCP defined at the routine XRD data reduction differ in the second decimal place. The dependence of the UCP of $[Pd(NH_3)_4]Mo_xCr_{1-x}O_4$ salts on x was refined using the same method. This technique was also used to check the presence of the effect of negative thermal expansion of a single crystal $[Pd(NH_3)_4]CrO_4$ in the temperature range from -173 to +127 °C.

Thermolysis of CCP was carried out in the He and in the H_2 (with presence of LiH) atmosphere at the temperatures from 910 to 1330 °C. X-ray phase analysis showed the formation of a solid solution based on the Pd FCC lattice at temperatures below 1000 °C and the Mo BCC lattice above. The UCP values of the obtained metal phases determined by the method of full-profile analysis allow us to assume the formation of ternary solid solutions of the Pd-Cr-Mo system.

Acknowledgement:
The authors express their gratitude to the S.P. Khranenko for conducting the synthesis, A.V. Zadesenec and P.E. Nikolaev for conducting the thermal decomposition of the samples.

Acid activated muscovite/kaolinite clay: An effective adsorbent for the removal of Pb(II), Cr(II) and Cu(II) from aqueous media

Samuel Tetteh[1*]

[1]Department of Chemistry, School of Physical Sciences, College of Agriculture and Natural Sciences, University of Cape Coast, Ghana
[*]E-mail: samuel.tetteh@ucc.edu.gh

Keywords: powder X-ray diffraction, kaolinite, muscovite, adsorption studies

Clay minerals have been largely explored as important, cheap, readily available adsorbents for the removal of waste materials from domestic and industrial effluents [1,2]. Important characteristics such as pore size, surface charge and ion exchange properties have been the utmost parameters which have been at the centre of continuous research to fine tune the application of clay minerals for various uses. In our earlier work on the extraction and purification of clay minerals [3,4], powder X-ray diffraction studies revealed that most of the samples were muscovite clay and these minerals had high adsorptivity for phenolphthalein and methyl orange dyes. In a current work, diffraction studies have shown that acid activation greatly affect the morphology and surface characteristics of a series of kaolinite/muscovite clay which significantly enhances the thermodynamic and kinetic properties of these minerals for the adsorption of Pb(II), Cr(II) and Cu(II) from aqueous media.

References:

1. I. Feddal, A. Ramdani, S. Taleb, E. M. Gaigneaux, N. Batis, N. Ghaffour, *Desalination and Water Treatment* 2014, 52, 2654–2661.
2. F. Li, M. Rosen, *Journal of Colloid and Interface Science* 2000, 224, 265–271.
3. S. Tetteh, A. Quashie, M. A. Anang, *Journal of Chemistry* 2018.
4. S. Tetteh, R. Zugle, A. Ofori, J. P. K. Adotey, *Frontiers in Chemical Research* 2020, 2, 33–37.

Structural chemistry

$(C_2N_2H_{10})[M(H_2O)_6](HPO_3)_2$ (M= Co, Ni and Mg): Synthesis and crystal structure

Mohamed Akouibaa[1*], *Rachid Ouarsal*[1], *Najlaa Hamdi*[1], *Souâd Rakib*[1], *Mohammed Lachkar*[1], *and Brahim El Bali*[2]

[1]Engineering Laboratory of Organometallic, Molecular Materials, and Environment, Faculty of Sciences, University Sidi Mohamed Ben Abdellah, 30000 Fez, Morocco,
[2]Independent scientist, Oujda, Morocco; ORCID: 0000-0001-6926-6286, e-mail: b_elbali@yahoo.com
[*]E-mail: mohamed.akouibaa@usmba.ac.ma

The present work deals with the preparation in solution, and the structural determination of three new hybrid phosphites: $(C_2N_2H_{10})[Co(H_2O)_6](HPO_3)_2$ (**1**), $(C_2N_2H_{10})[Mg(H_2O)_6](HPO_3)_2$ (**2**) and $(C_2N_2H_{10})[Ni(H_2O)_6](HPO_3)_2$ **(3)**. They are isostructural, crystallizing in the orthorhombic system (S. G. Pbca), $Z = 4$, with the cell parameters: a = 11.1797 (3) Å, b = 9.7394 (2) Å, c = 13.4466 (3) Å, V = 1464.11 (6) Å^3 for **1**; a = 11.1850 (8), b = 9.7739 (6), c = 13.4462 (12), V = 1469.95 (19) Å^3 for **2**; and a= 11.1518 (9), b= 9.8014 (8), c= 13.3782 (8) Å, V= 1462.28(19) Å^3 for **3**. Their crystal structures (Fig.1) exhibit layers, stacked along the b-axis, trapping the ethylenediammonium cations $(H_2en)^{2+}$ in the interlayer space. The FTIR spectroscopy analysis showed the expected bands of ethylenediamine, water molecules and hydrogenphosphite oxoanion groups. The thermal analysis revealed mainly the loss of H_2O and ethylenediamine moieties leading to the formation of an anhydrous metal phosphite compounds. The three compounds were tested and were found to be significantly efficient as catalysts in the reduction of nitrophenols isomers to their corresponding aminophenols by $NaBH_4$.

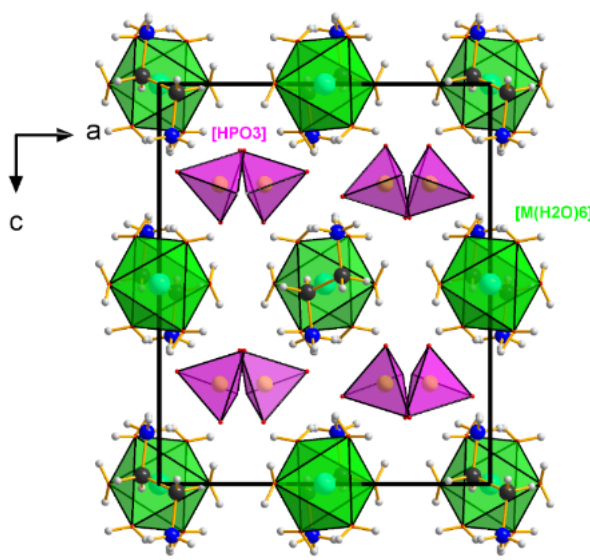


Figure 1. Projection along b-axis of the crystal structures of $(C_2N_2H_{10})[M(H_2O)_6](HPO_3)_2$, M = Co (**1**), Mg (**2**) and Ni (**3**).

A new ICCs based on copper 2,2'-Bipyiridine and DDS structural, DFT and magnetic study

Amani Hind Benahsene[1*], *Lamia Bendjeddou*[1], *Carlos J. Gómez García*[2], *Bachir Zouchoune*[1,3]

[1]Unité de Recherche Chimie de l'Environnement et Moléculaire, Structurale 'CHEMS', Faculté des Sciences Exactes, Campus Chaabet Ersas, Université Frères Mentouri Constantine 1, 25000 Constantine, Algeria, [2]Catedrático de Química Inorgánica Instituto de Ciencia Molecular Parque Científico. Universidad de Valencia C/José Beltrán,2 46980 Paterna (Valencia) Spain, [3]Laboratoire de Chimie Appliquée et Technologie des Matériaux, Université Larbi Ben M'Hidi – Oum El Bouaghi, 04000 Oum El Bouaghi, Algeria
[*]E-mail: amani.benahsene@hotmail.com

Keywords: ionic co-crystals, antiferromagnetic, 2,2'-Bipyridine, Dapson (DDS)

Utilization of noncovalent interactions to develop designed self-assembly of individual molecules is a frontier research area[1]. Formation of multicomponent crystals, which are known as cocrystals, of complexes especially Ionic cocrystals (ICCs) [1], is difficult to understand in most cases[1]. Again, most of the reported cocrystals are two component systems having different ratios of the individual moieties. In contrast, cocrystals containing more than two components are rare and have been observed in organic systems[1]. In this study, we report the ICCs of copper bipyridine nitrate with (4,4'-diaminodiphenyl sulfone (DDS). The ICCs compound is constituted by two crystallographically independent cationic [Cu(2,2'-Bipy)2 (O_2NO)] entities, two free nitrate anions, two neutral DDS molecule and three solvate water molecule.

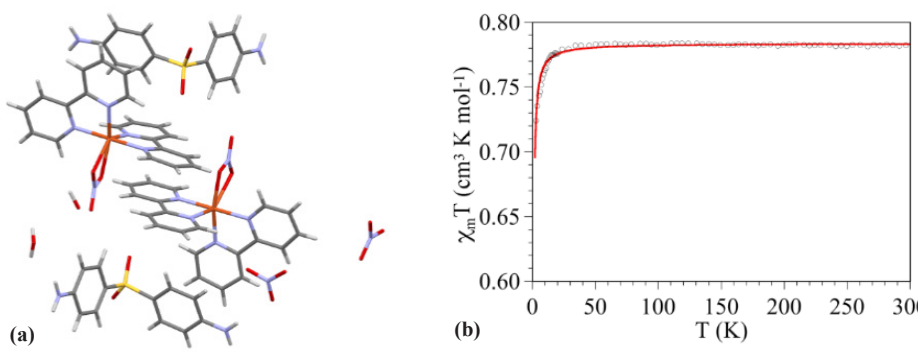


Figure 1. **(a)** Asymetric Unit of [Cu(2,2'-Bipy)2 (O_2NO)]$^+$(NO_3)$^-$(DDS)(H_2O), **(b)** The plots of magnetic susceptibilities χm vs. T in the temperature region of 0-300 K.

References:

1. F. Nouar, J. F. Eubank, T. Bousquet, L. Wojtas, M. J. Zaworotko and M. Eddaoudi, *J. Am. Chem. Soc.* 2008, 130, 1833.

Photocrystallographic studies of novel nitro complexes

P. Borowski[1*], *S.E. Kutniewska*[1], *R. Kamiński*[1], *K.N. Jarzembska*[1]

[1]Department of Chemistry, University of Warsaw, Zwirki i Wigury 101, 02-089 Warsaw, Poland
[*]E-mail: pz.borowski2@student.uw.edu.pl

Keywords: photocrystallography, photoswitchable compounds, photoisomerisation

The importance of solid-state materials of real-life application is constantly increasing. Hence, the current study was devotem to a series of newly designed and synthesized photoactive complexes which contain the NO_2 group bound to the metallic centre. The nitro group may undergo a photoisomerisation reaction in the solid state under certain conditions – upon light irradiation or/and temperature changes. The primary aim of the project was to examine the photoreactivity of the obtained crystal systems and understand the nitro-nitrito linkage isomerization mechanism. For that purpose, multi-temperature and spectroscopic experiments were conducted. Additionally, the XRD experiments with our self-designed light-delivery device for in situ photocrystallographic experiments [1] were conducted. To thoroughly understand the photoisomerisation reaction process the reaction cavity volumes, intermolecular contacts, linkage isomers' stability and crystal packing were thoroughly investigated.

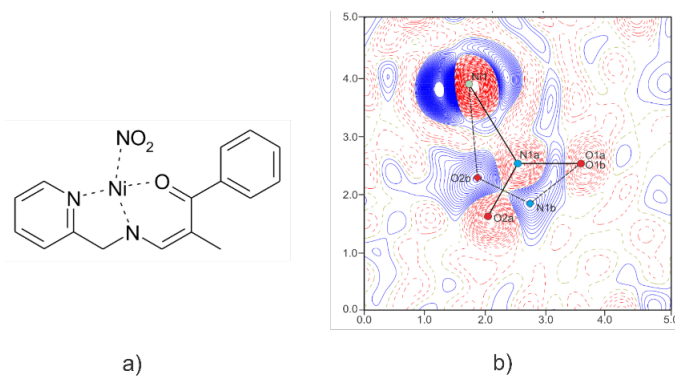


Figure 1. The photodifference map showing the coexsistence of both nitro and exo-nitrito linkage isomers.

Acknowledgement:
The authors thank the PRELUDIUM grant (2017/25/N/ST4/02440) of the National Science Centre in Poland and the Inter-Faculty of Individual Studies in Mathematics and Natural Sciences, University of Warsaw, for financial support. The Wrocław Centre for Networking and Supercomputing (grant No. 285) is gratefully acknowledged for providing computational facilities. The in-house X-ray diffraction experiments were carried out at the Department of Physics, University of Warsaw, on Rigaku Oxford Diffraction SuperNova diffractometer, which was co-financed by the European Union within the European Regional Development Fund (POIG.02.01.00-14.122/09)

References:

1. Kamiński, R, Jarzembska, K. N., Kutyła, S. E. & Kamiński, M., *J.Appl.Cryst.* 2016, 49, 1383.
2. Hatcher, L. E., Skelton, J. M., Warren, M. R. & Raithby, P. R., *Acc. Chem. Res.* 2019, 52, 4, 1079.

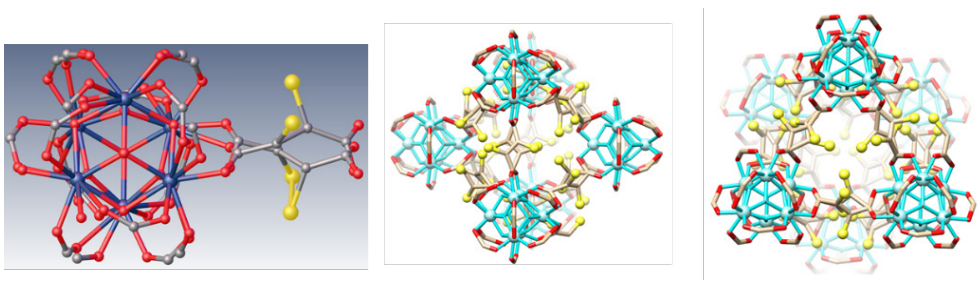
Green synthesis of the zirconium mercaptosuccinate Metal-Organic Framework

Leire Celaya Azcoaga[1,2*], *Ainara Valverde*[1,3], *Bárbara Gonzalez-Navarrete*[4], *Oscar Castillo*[2], *Andreina García*[4], *Roberto Fernández de Luis*[1]

[1]BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain, [2]Department of Inorganic Chemistry and [3]Department of Physical Chemistry, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), Barrio Sarriena s/n 48940 Leioa, Spain, [4]Advanced Mining Technology Center (AMTC), Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Av. Tupper 2007, 8370451, Santiago, Chile
[*]E-mail: leire.celaya@bcmaterials.net

Keywords: Metal-Organic Frameworks, crystallization, green synthesis

Metal-Organic Frameworks (MOFs) are a class of porous hybrid materials produced by a coordination reaction between metal clusters and organic ligands. The great flexibility upon which constituents can be varied endow each MOF different physical-chemical properties that can be further adapted to specific applications [1]. Taking advantage of the great stability shown by zirconium-based MOFs and the increasing applicability of mercaptosuccinic acid in biochemical research, this work presents the green synthesis and crystallization conditions of the cubic (F23) zirconium mercaptosuccinate (BCM-01) isomorphous to previously synthesized MOF-801 and MIP-203-F/S/M [2][3]. BCM-01 was crystallized from water aqueous solution by using formic acid as modulator. An screening of the synthesis temperature, the reagents´ concentration and the modulator´s addition was explored in order to found the best crystallization conditions, as well as the paths to modulate the BCM-01 particle size down to the nanometer regime.



(a) (b) (c)

Figure 1. (a) Local structure of the zirconium hexanuclear clusters in BCM-01, (b) View of the octhadral pores of BCM-01 and (c) View or the pore window entrance to the octhahedral pore system decorated with disordered thiol groups (yellow spheres).

Acknowledgement:
The authors thank the Basque Government (BG) Industry and Education Departments under the ELKARTEK, HAZITEK AND PIBA (PIBA-2018-06) programs, and European H2020-MSCA-RISE-2017 (Ref: 778412) INDESMOF project. Ainara Valverde acknowledges the BG (Education Department) for her PhD grant (PREB_2018_1_004).

References:
1. V. K. Sharma, M. Feng, *J. Hazard. Mater.* 2017.
2. S. Kai, Y. Hu, Y. Liu et al, *Fluid Phase Equilibria*, 2014, 361, 282–288.
3. S. Wang, N. Xhaferaj, M. Wahiduzzaman et. al., *J. Am. Chem. Soc.* 2019, 141 (43), 17207–17216.

Hierarchy of intermolecular interactions for crystal engineering

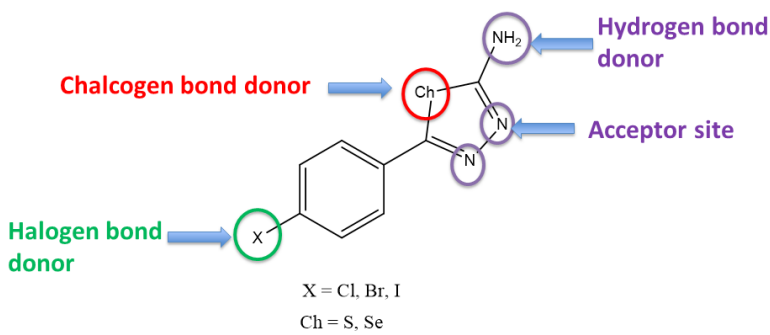
Viraj De Silva[1*], *Abhijeeth S. Sinha*[1], *Victor Day*[2], *Boris Averkiev*[1], *Christer B. Aakeröy*[1]

[1]Kansas State University, [2]University of Kansas
[*]E-mail: slvdesilva@ksu.edu

Keywords: chalcogen bonding, halogen bonding, hydrogen bonding, intermolecular interactions, sigma hole

Crystal engineering utilizes intermolecular interactions for preparing crystalline materials with desired structural features and physiochemical properties. In order to accomplish this task it is necessary to have a good understanding of the balance and competition between many different non-covalent forces. Hydrogen bonding have been the most used intermolecular interaction for synthetic crystal engineering but recent developments in halogen and chalcogen bonding have shown the potential of such interactions to compete with hydrogen bonding. In pharmaceutical industry, where there are multiple functional groups in a single drug molecule, competition between intermolecular interactions can lead to unexpected conditions such as polymorphism. The study of how these interactions compete and co-exit can be utilized to predict and prevent such adverse conditions.

This study focuses on molecules with multiple donor and acceptor sites capable of forming not only hydrogen bonding but also halogen and chalcogen bonding, Scheme 1. Activation of halogen atoms through the addition of strong electron withdrawing groups and chalcogen by changing it from S, Se leads to stronger halogen and chalcogen sigma hole type interactions creating a competition.



Scheme 1. Molecule containing multiple donor acceptor sites.

Acknowledgement:
We are thankful for support from the Johnson Cancer Research Center, Kansas State University. We acknowledge the NSF-MRI grant CHE-2018414, which was used to purchase a single-crystal X-ray diffractometer and associated software employed in this study.

References:

1. C. B. Aakeröy, J. Desper, M. Baldrighi, P. Metrangolo, G. Resnati, *Chem. Eur. J.* 2013, 19, 16240–16247.

Physical and catalytic studies of a new coordination polymer

Najlaa Hamdi[1*], *Safaa Hidaoui*[1], *Mohamed Akouibaa*[1], *Brahim El Bali*[2], *Mohammed Lachkar*[1]

[1]Engineering Laboratory of Organometallic and Molecular Materials, Faculty of Sciences, University Sidi Mohamed Ben Abdellah, Po. Box 1796 (Atlas), 30000 Fez, Morocco, [2]Independent scientist
[*]E-mail: hamdi.najlae@gmail.com

Keywords: crystal structure, slow evaporation, catalytic oxidation

A new one-dimensional cobalt phosphate $[(N_2H_5)_2Co(HPO_4)_2]$ was synthesized by wet chemistry and characterized by means of single-crystal X-ray diffraction, Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric Analysis (TGA). Its catalytic activity was tested using UV-visible absorption measurements [1]. The Compound crystallizes in the monoclinic system (S.G: $P2_1/c$) with the following cell parameters (Å,°): a = 5.3665(3), b = 11.1271(6), c = 7.7017(4), β = 104.843(4), V = 444.55(4) Å3 and Z = 2. The crystal structure, depicted in Figure 1 and consisting of a linear chain, is made of rings of $[CoN_2O_4]$ octahedra and [PO3(OH)] tetrahedra sharing vertices via oxygen atoms coordinated to cobalt centers. The rings are linked to chains running along [001] and form thereby polymeric chains that are connected by hydrogen bonds in a three-dimensional arrangement. The phosphate complex exhibits efficiency in catalytic oxidation and degradation of methylene blue dye. The ac magnetic susceptibility shows a peak indicating antiferromagnetic order with a Neel temperature of 5.5 K. fitting the Curie-Weiss equation to the ac magnetic susceptibility above 50K gives the average Curie-Weiss Constant to be –11.8K.

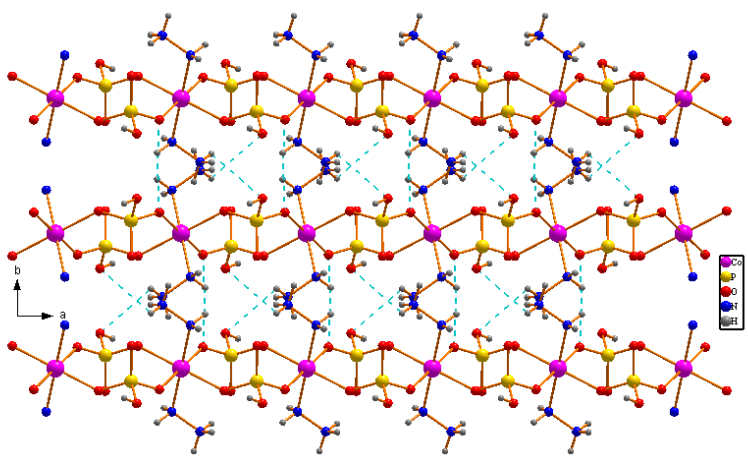


Figure 1. The crystal structure of $[(N_2H_5)_2Co(HPO_4)_2]$ in a projection along [001] emphasizing the hydrogen bonding (Dashed line) between the chains.

References:

1. N. Hamdi, S. Hidaoui, H. O. Hassani, M. Lachkar, M. Dusek, N. Morley, B. El Bali, *Journal of Molecular Structur* 2020, 1217, 128317.

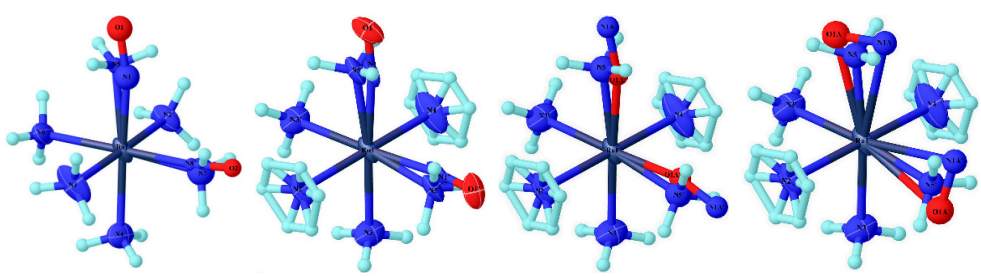
Photocrystallography on a disordered ruthenium nitrosyl complex

Asma Hasil[1*], *Sébastien Pillet*[1], *Emmanuel Wenger*[1], *Dominik Schaniel*[1]

[1]Universite de Lorraine, CNRS, CRM2, Nancy, France
[*]E-mail: asma.hasil@univ-lorraine.fr

Keywords: nitrosyl disorder, inversion twin, centric or acentric, light-induced isomerism, photocrystallography

Photoinduced linkage isomers (PLI) in nitrosyl complexes have been extensively studied using photocrystallography for the determination of the light-induced structural changes. Generally, in order to get the best possible structural information on PLI in nitrosyl complexes, the molecular compound is preferred to be 'disorder free' particularly at 'nitrosyl' position before excitation. It is always difficult to locate the light induced structural changes, and even more so if the position of nitrosyl is itself disordered in the ground state (GS). The present research effort highlights the idea of choosing a centrosymmetric *P*nma space group [1] over the acentric polar space group $Pna2_1$ with an inversion twin, in order to properly locate the structural configuration of the PLI with X-ray crystallography even at the disordered nitrosyl position. We redetermined the crystal structure of $[Ru(NH_3)_5(NO)]Cl_3.H_2O$, reported in $Pna2_1$ [2], but discovered a disorder of NH_3 and NO groups over two positions, with additionnally an inversion twin of ~0.5 in GS. Refining the structure is possible, but needs the application of several constraints and thus limits severely the study of the PLI. Solving the same structure in *P*nma allows for structure determination of the PLI. We have generated PLI1 by laser irradiation at 422nm and PLI2 by subsequent irradiation at 1064nm, yielding populations of 45 and 10.6% respectively. The PLI configurations were first identified on photodifference maps. Subequent refinement using isonitrosyl and side-on configuration of the NO ligand for PLI1 and PLI2 converged and allowed for determining a structural model for these two states in Pnma space group. This result indicates that in some cases when encoutering disordered molecules at nitrosyl position, refinement of the structure using a higher symmetery would reduce/resolve the problem.



(a) (b) (c) (d)

Figure 1. (a) GS crystal structure solved in $Pna2_1$ with N1O1 N7(H_3)=0.66, N8O2 N5(H_3)=0.34, inversion twin 0.5 (b) GS crystal structure solved in *P*nma (c) MS1 in *P*nma (d) MS2 in *P*nma

Acknowledgement:
A. H. thanks the Region Grand Est for PhD grant. We thank the PMD²X X-ray diffraction facility of the Institut Jean Barriol, Université de Lorraine for X-ray diffraction measurements. We thank K. W. Krämer from the University of Bern for providing beautiful single crystals.

References:
1. Abrahams, S. C. et al., *Acta Crystallographica Section B: Structural Science* 1998, 54(4), 399–416.
2. Bottomley, F., *Journal of the Chemical Society, Dalton Transactions* 1974 (15), 1600–1605.

Investigating influences of interactions on the self-assembly of pillarplexes

Alexandra A. Heidecker[1*], *Alexander Pöthig*[1]

[1]Faculty of Chemistry, Technical University Munich, Lichtenbergstraße 4, 85784 Garching
[*]E-mail: alexandra.heidecker@tum.de

Keywords: organometallocavitands, self-assembly, functional building blocks

The implementation of pillarplexes as functional building blocks is investigated towards the formation of porous materials. The class of supramolecular organometallic complexes (SOCs) includes the pillarplexes.[1] The complexes bear macrocyclic NHC ligands and eight metal centers forming a tubular cavity, where exclusive shape selective encapsulation of linear molecules is possible. By simple anion exchange reactions the solubility of the pillarplex salts is tuned. The (Au(I)-pillarplexes show intrinsic photoluminescence.[2][3][4] The structural self-assembly is expected to be governed by the shape, charge and size of employed anions based on their interactions with the anisotropic pillarplex cations.

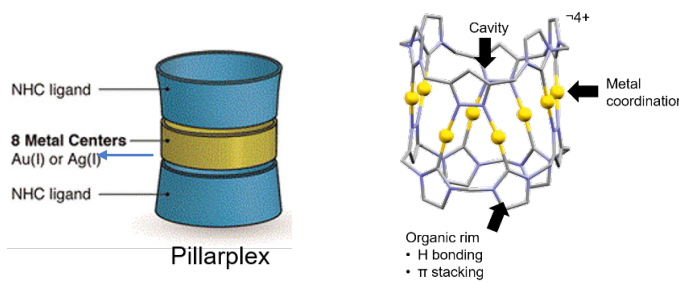


Figure 1. Schematic presentation of the pillarplex anion interactions sites.

Consequently, a series of pillarplex salts with various anions is targeted to synthesized and characterized towards the structure and crystal packing to fulfill the aim of identification of the structure-dictating interactions. The pillarplex salts are synthesized by simple anion exchange reaction and crystalized under solvothermal conditions. The salts are characterized by solid-state analysis (PXRD, SC-XRD, TGA) following porosity measurements (BET) and selected examples are presented and discussed.

Acknowledgement:
We thank the Deutsche Forschungsgemeinschaft (DFG Projekt: SPP 1928, Coornets) for financial support as well as the TUM Graduate School and FCI. A thanks to the LRZ for the high-performance computing capacity.

References:

1. A. Pöthig, A. Casini, *Theranostics* 2019, *9*, 3150–3169.
2. P. J. Altmann, A. Pöthig, *J. Am. Chem. Soc.* 2016, *138*, 13171–13174.
3. P. J. Altmann, C. Jandl, A. Pöthig, *Dalt. Trans.* 2015, *44*, 11278–11281.
4. P. J. Altmann, A. Pöthig, *Angew. Chemie - Int. Ed.* 2017, *56*, 15733–15736.

Crystal structure of dinuclear complexes based on Schiff base ligand *o-van-en*

Lenka Krešáková[1*], *Juraj Kuchár*[1], *Anna Vráblová*[1], *Juraj Černák*[1]

[1]Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, P. J. Šafárik University in Košice, SK-041 54 Košice, Slovakia (juraj.cernak@upjs.sk)
[*]E-mail: lenka.kresakova@student.upjs.sk

Keywords: Schiff base ligand, heterodinuclear complexes, crystal structure

There is a great potential of the Schiff bases generated from *o*-vanillin and diamino precursors in coordination chemistry due to their ability to incorporate in their two compartments a variety of chemical species, e.g. a pair of 3d and 4f atoms. Thus formed dinuclear 3d/4f complexes exhibit interesting properties including magnetism, luminescence, catalysis or cytotoxicity [1], [2]. Previously, we have studied heterodinuclear Ni/Ln (Ln = Ce, Gd, Dy) complexes [Ni(*o-van-en*)Ln(H_2O)Cl_3] based on *o-van-en*, Schiff base formed by condensation of *o*-vanillin and ethylenediamine, and chlorido co-ligands [3]. All three complexes behave as field induced SMMs including the nominally isotropic Gd(III) complex. As a continuation of our research we have prepared and characterized novel complexes using bromide co-ligands, namely [Ni(*o-van-en*)GdBr(H_2O)$_3$]Br_2·EtOH (**1**), [Ni(*o-van-en*)DyBr(H_2O)$_3$]Br_2·EtOH (**2**) and [Ni(*o-van-en*)$CeBr_2$(CH_3OH)(H_2O)$_2$]Br·H_2O (**3**). The results of the crystal structure analysis of the Ce(III) compound, stable at room temperature, comfirmed the formation of the expected molecular structure with nona-coordinated Ce(III) atom and successful incorporation of two bromido ligands in the coordination sphere of Ce(III) atom (see Figure 1.).

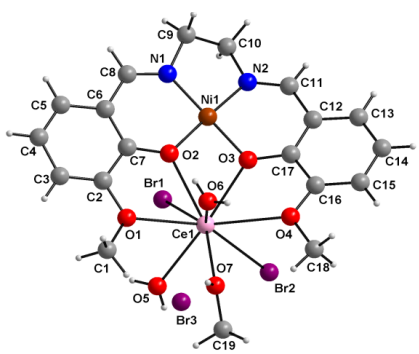


Figure 1. Molecular structure of [Ni(*o-van-en*)$CeBr_2$(CH_3OH)(H_2O)$_2$]Br·H_2O (**3**).

Acknowledgement:
Slovak grant agencies APVV-18-0016, vvgs-2020-1657 are acknowledges for finatial support.

References:

1. M. Andruh, *Dalton Trans.* 2015, 44, 16633–16653.
2. J. P. Costes, S. Mallet-Ladeira, L. Vendier, R. Maurice, W. Wernsdorfer, *Dalton Trans.* 2019, 48, 3404.
3. A. Vráblová, M. Tomás, L. R. Falvello, Ľ. Dlháň, J. Titiš, J. Černák, R. Boča, *Dalton Trans.* 2019, 48, 13943.

Polymorphic control using co-sublimation

S.G. Le Roux[1*], *D.A. Haynes*[1]

[1]Department of Chemistry and Polymer Science, University of Stellenbosch, P. Bag X1, Matieland, 7602, South Africa
[*]E-mail: 21289603@sun.ac.za

Keywords: polymorphs, co-sublimation, dithiadiazolyl

Dithiadiazolyl radicals have been investigated as molecular magnets [1]. The compound 4′-(4-cyano-2,3,5,6-tetrafluorophenyl)-1,2,3,5-dithiadiazolyl (radical **1**) has received much attention due to the interesting magnetic properties of its two polymorphs. The α-polymorph of **1** shows Curie-Weiss behavior above 50 K indicating weak antiferromagnetic interactions but due to its elusive nature it has been termed a "disappearing polymorph" [2]. The β-polymorph crystallises as long needles, and orders as a ferromagnet at 36 K under ambient pressure [2]. **1α** exhibits anti-parallel alignment of chains in the solid state while **1β** has co-parallel alignment of chains in the solid state (Figure 1). This study aimed to identify how we could achieve polymorphic control of **1** using another DTDA, 4′-(2,6-difluorophenyl)-1,2,3,5-dithiadiazolyl (radical **2**), as an additive during sublimation crystallisation. We found that the control over the morphology of the crystals of **1β** is achieved by co-sublimation with **2**. Polymorphic control of **1** using **2** as an additive is also achievable when using dichloromethane to mix the two radicals prior to sublimation. An explanation for the effect of the presence of **2** on the crystals of **1** is proposed. This study confirms the feasibility of using co-sublimation of DTDAs as a technique for achieving polymorphic control provided suitable sublimation conditions have been chosen.

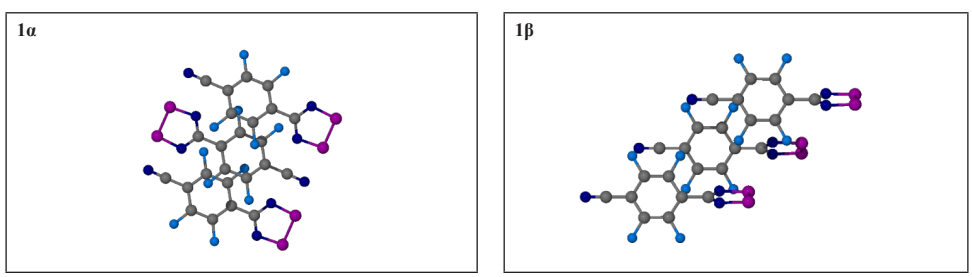


Figure 1. The anti-parallel (left) and co-parallel (right) alignment of chains in polymorphs of **1** dictate the magnetic behavior observed.

Acknowledgement:
We are grateful to Stellenbosch University and Sasol South Africa for financial support.

References:

1. J. M. Rawson, A. Alberola, A. Whalley, "Thiazyl radicals: Old materials for new molecular devices," *J. Mater. Chem.*, 16, 2560.
2. Y. Beldjoudi, A. Arauzo, F. Palacio, M. Pilkington, J. M. Rawson, "Studies on a 'Disappearing Polymorph': Thermal and Magnetic Characterization of α-*p*-NCC_6F_4CNSSN•," *J. Am. Chem. Soc.*, 138, 16779, 2016.

Connecting solution stability of half-sandwich complexes with their structure

János P. Mészáros[1], Tamás Holczbauer[2,3], Nóra V. May[2], Alexander Roller[4], Éva A. Enyedy[1]*

[1]Department of Inorganic and Analytical Chemistry & MTA-SZTE Lendület Functional Metal Complexes Research Group, Interdisciplinary Excellence Centre, University of Szeged, Dóm tér 7, H-6720 Szeged, Hungary, [2]Centre for Structural Science, Research Centre for Natural Sciences, Magyar tudósok körútja 2, H-1117 Budapest, Hungary, [3]Institute of Organic Chemistry, Research Centre for Natural Sciences, Magyar tudósok körútja 2, H-1117 Budapest, Hungary, [4]Institute of Inorganic Chemistry, Faculty of Chemistry, University of Vienna, Währinger Str. 42, A-1090, Vienna, Austria
[*]E-mail: meszaros.janos@chem.u-szeged.hu

Keywords: anticancer, stability, single-crystal, metal complex

In this poster I would like to introduce in some examples how the single-crystal X-ray diffraction can support the results obtained from aqueous solution stability of half-sandwich Rh(III) and Ru(II) complexes. Most of these complexes show anticancer activity [1] and in the preclinical studies the solution stability and reactions under physiological conditions are crucial [2]. In this research area a plethora of complex structures were determined by single-crystal X-ray diffraction. Most of these structures proved the coordination mode of ligands. However, there are cases when di- or trinuclear complexes were found in the solid phase although in solution the mononuclear complex is present [3].

I will show examples how we can extract more information which can support the results obtained from aqueous stability measurements and structure-activity relationship studies. Steric congestion resulted in lower complex stability in the case of the N,N,N',N'-tetramethylethylenediamine ligand [4]. Another example proved the decomposition of half-sandwich Ru(arene) complexes of 2,2'-bipyridine-like ligands [5]. Finally, I will present a predictive model for the chloride ion affinity of various half-sandwich Rh(C_5Me_5) complexes based on structural parameters e.g. bond angles [4].

Acknowledgement:
This work was supported by the National Research, Development and Innovation Office-NKFIA through projects GINOP-2.3.2-15-2016-00038, FK 124240 and Ministry of Human Capacities, Hungary grant, TKP-2020, and a Momentum Grant of the Hungarian Academy of Sciences.

References:

1. a) M. Malecka, A. Skoczynska, D. M. Goodman, C. G. Hartinger, E. Budzisz, *Coord. Chem. Rev.* 2021, 436, nr.: 213849 b) S. Thota, D. A. Rodrigues, D. C. Crans, E. J. Barreiro, *J. Med. Chem.* 2018, 61, 5805–5821.
2. T. Kiss, É. A. Enyedy, T. Jakusch, *Coord. Chem. Rev.* 2017, 352, 401–423.
3. a) P. Buglyó, E. Farkas, *Dalton Trans.* 2009, 8063–8070. b) J. P. Mészáros, G. Németi, J. M. Poljarevic, T. Holczbauer, N. V. May, É. A. Enyedy, *Eur. J. Inorg. Chem.* 2021, 19, 1858–1868.
4. J. P. Mészáros, O. Dömötör, C. M. Hackl, A. Roller, B. K. Keppler, W. Kandioller, É. A. Enyedy, *New. J. Chem.* 2018, 42, 11174–11184.
5. J. P. Mészáros, V. F. S. Pape, G. Szakács, G. Németi, M. Dénes, T. Holczbauer, N. V. May, É. A. Enyedy, *Dalton Trans.* in press, doi: 10.1039/D1DT00808K

Core-modified s-Confused Porphycenes

Vishnu Mishra[1*], *Venkataramanarao G. Anand*[1]

[1]Department of Chemistry, Indian Institute of Science Education and Research,
Dr. Homi Bhabha Road, Pune-411008, Maharashtra, India
[*]E-mail: vishnu.mishra@students.iiserpune.ac.in

Keywords: sulphur bridged annulenes, Confused Porphycene, aromatic, antiaromatic

Synthesizing new constitutional isomers of thiophene derived annulenes [1] were always a challenging task in organic synthesis. The most popular ones are porphycene and Confused(inverted) porphyrin. There are many reports for the "Confused" Porphyrin and Porphycenes but till now there is no report in the literature for "Confused" Porphycene. Herein we'll report first time the synthesis of the 20π as well as two different types of 30π Confused Porphycenes (inverted Porphycene), Which was confirmed by X-Ray diffraction analysis. X-Ray diffraction analysis suggests clearly about non planner nature of these Porphycenes, due to which They do not display any kind of ring current effects which was confirmed by its 1H NMR spectrum. NICS calculations reveal the non-(anti)aromatic as well non-aromatic behaviour for the Porphycenes.

The reason behind exploring the chemistry of these molecules is the unique structural and electronic features of these compounds which can give rise to interesting physical and optical properties with applications in biomedicine and materials science. [2]

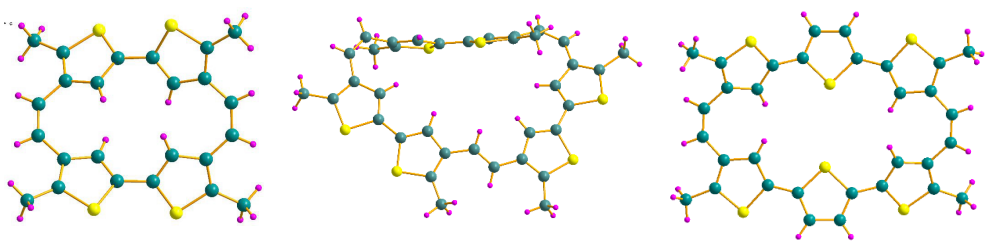


Figure 1. Molecular structure of 20π, 30π and 30π porphycenes as determined from single crystal X-ray diffraction analysis

Acknowledgement:
IISER PUNE for the financial Support

References:

1. Zhongying Hu, Jerry L. Atwood, and Michael P. Cava, *J. Org. Chem.* 1994, 59, 8071–8075.
2. Gonzalo Anguera and David Sanchez-García, *Chem. Rev.*

'Triple activation' of σ-hole donors: Structure and theory

Vinu V. Panikkattu[1*], *Abhijeet S. Sinha*[1], *Boris Averkiev*[1], *Christer B. Aakeröy*[1]

[1]Department of Chemistry, Kansas State University, USA
[*]E-mail: vinu@ksu.edu

Keywords: halogen bond, crystal engineering, σ-hole, triple activation

Halogen bonding is an indispensable tool for chemists, used in a wide variety of applications ranging from design and synthesis of liquid crystalline, phosphorescent and non-linear optical materials, to resolution of racemic mixtures, and pharmaceutical property modulation through co-crystal formation.[1] Many structural features of these materials are a direct result of the high directionality and tunability of these σ-hole interactions, and the magnitude of the σ-hole potential is often used as a yardstick to measure the strength of its halogen-bond donor ability. A stronger interaction results in synthon robustness which is desriable in terms of molecular recognition, structural prediction, self-assembly and design strategy.[2] A double activation strategy has previously been demonstrated to produce effective and powerful halogen bond donors with very high σ-hole potentials.[3] In this work, we attempt to push the boundaries of activation even further in triply activated halogen-bond donors. Here we present a library of triply activated 3-iodo-1-phenylprop-2-yn-1-ones, substituted with -F, -C≡N and -NO_2 groups which display the highest known σ-hole potentials to date. We compute interaction energies between synthesized targets and ammonia as a model acceptor to predict the most stable interaction from within this series. We also compare the targets explored herein with other previously studied molecules exhibiting strong halogen bonds with favorable σ-hole potentials.[4]

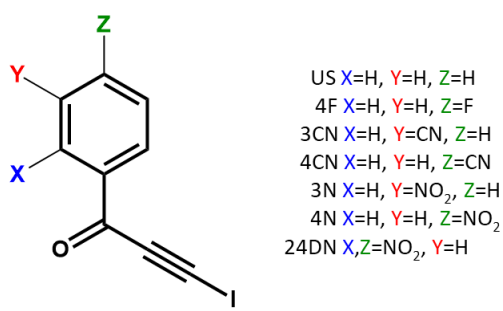


Figure 1. Targets explored in this study

Acknowledgement:
Department of Chemistry, Kansas State University.

References:

1. A. Legon, *Phys. Chem. Chem. Phys* 2010, 12 (28), 7736–7747.
2. J. Y. C. Lim, P. D. Beer, *Chem* 2018, 4 (4), 731–783.
3. C. B. Aakeröy, T. K. Wijethunga, J. Desper, M. Đaković, *Cryst. Growth Des.* 2015, 15 (8), 3853–3861.
4. N. R. Goud, O. Bolton, E. C. Burgess, A. J. Matzger, *Cryst. Growth Des.* 2016, 16 (3), 1765–1771.

Tunning magnetic properties of copper(II) polymers via functional group effect

N. Penić[1,2*], *M. Đaković*[2], *D. Pajić*[1]

[1]Department of Physics, Faculty of Science, University of Zagreb, [2]Department of Chemistry, Faculty of Science, University of Zagreb
[*]E-mail: penic@phy.hr

Keywords: supramolecular assemblies of copper(II) complexes, antifferomagnetic spin chains

In field of molecular magnetism, often investigated systems are miscellaneous copper compounds because of its spin simplicity S=1/2 and using copper oxides as catalysts. Because of its dynamic nature, metal-organic systems are not even approximately investigated as oxide compounds, especially compounds with pyrazine and pyridine based ligands in which copper is bridged by halogen element. So far it is known that pyrazine and pyrazine derivates can be mediators of magnetic exchange within dimers, linear chains and two-dimensional lattices, and they are used in preparation of low-dimensional magnetic materials. However, some insight in functional group effects on magnetic exchange of these systems in literature is not observed. [1] In order to understand the magnetic behaviour of crystalline coordination compounds and correlate structural features (in particular, functional groups, chemical linkages, bond length and angles) we prepared a series of 1-D halide coordination polymers of copper(II) with halogen derivatives of pyridine.

For all obtained coordination compounds ($[CuX_2(3\text{-}Spy)_2]_n$ (X=Cl, Br; S=Cl, Br, I)temperature dependence of magnetization M(T) was measured using SQUID magnetometer in the temperature range 2–300 K. Linear dependence between magnetization and magnetic field allows usage of the linear magnetic susceptibility, χ. In accordance with crystal structure, we applied approach of Bonner–Fischer and modelled entire M(T) curves for all obtained compounds using spin chain of antiferromagnetically interacting neighbouring Cu2+ ions along structural chains where impact of the counter ion and Cu–X···Cu angles on superexchange interaction J is observed.

References:

1. O. Kahn, Molecular magnetism, Wiley-VCH, 1992.

Tuning the release of active molecules through cocrystallization

Michele Prencipe[1*], *Paolo P. Mazzeo*[1], *Fabio Montisci*[1], *Alessia Bacchi*[1]

[1]Università degli Studi di Parma, Dip. SCVSA, Parma, Italy
[*]E-mail: michele.prencipe@unipr.it

Keywords: cocrystals, crystal engineering, mechanochemistry

Cocrystals are multi-component crystalline materials obtained by the interaction of at least two different molecules in a defined stoichiometric ratio. The choice of suitable coformers and the final physical properties still represent the main challenges in predicting cocrystal formation. Crystal engineering is therefore a useful tool providing a heuristic approach based on the complementarity among molecules functionalities and their recurrence in the crystal structures. Nowadays pharmaceutical and agrochemical industry largely use cocrystals to tune physical properties of the active components, such as solubility or volatility, without altering their chemical structure [1]. The coformers thus play a rule of "co-builders" of a new crystalline scaffold, but their molecular properties often remain untapped.

The purpose of this work is thus to exploit cocrystalisation to drive the release of active molecules and control their availability. We here report about cocrystals examples where the release of the active components is triggered by external stimuli as a function of the coformer used. In addition, it is worth noting that all cocrystals proposed are synthesized through mechanochemical methods (grinding, ball milling).

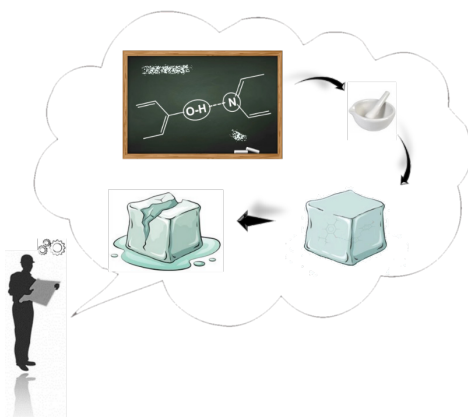


Figure 1. Design of cocrystals for driving the release of active molecules.

Acknowledgement:
We acknowledge the COMP-HUB Initiative, funded by the 'Departments of Excellence' program of the Italian Ministry for Education, University and Research (MIUR, 2018-2022). We also acknowledge COST Action CA18112 – Mechanochemistry for Sustainable Industry.

References:
1. P. P. Mazzeo et al, *ACS Sustainable Chem. Eng.* 2019, 7, 17929−17940.

Charge transfer chemistry of novel strong electron acceptor – 5,6-diciano-1,2,5-selenadiazolo[3,4-*b*]pyrazine

Ekaterina A. Radiush[1*], *Nikolay A. Semenov*[1], *Andrey V. Zibarev*[1]

[1]Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, 630090 Novosibirsk, Russia
[*]E-mail: iokimaru@nioch.nsc.ru

Keywords: 1,2,5-chalcogenadiazoles, radical anions, charge transfer complexes, XRD structure

1,2,5-Chalcogenadiazoles are of interest to the fundamental chemistry and its applications in materials science. Their common property is high positive electron affinity (EA) making them effective electron acceptors. The transfer of electron density onto the heterocycle may be complete, leading to the thermodynamically stable radical anions (RAs), or partial one leading to charge transfer complexes (CTC) [1]. The present contribution covers several examples of the above reactivity of 5,6-Dicyano-1,2,5-selenadiazolo[3,4-b]pyrazine **1** - a novel strong acceptor with reversible single-electron reduction at –0.022 V vs. SCE (cyclic voltammetry). Reaction of **1** with potassium thiophenolate or $Na_2S_2O_4$ gives RA salts [K(18-crown-6)][**1**] (**2**) and [Na(18-crown-6)][**1**] (**3**) respectively. **2** and **3** have remarkably different crystal structures, despite very little difference between compositions, which affects their magnetic properties [2]. Interaction of **1** with Ph_4PCl, KBr or KI gives chalcogen bonded anionic complexes **4, 5** and **6** respectively, which were isolated and structurally characterized by XRD. The length of the Se-X bond in the anions **4, 5** and **6** is by 1 Å longer than the sum of the covalent radii, but by 0.4 Å shorter than the sum of Van Der Waals radii, indicating that these are rather weak complexes. Complexes **4**, **5**, and **6** are the new examples of the family of chalcogen bonded anionic complexes, previously obtained only for 3,4-dicyano-1,2,5-chalcogenadiazoles [1].

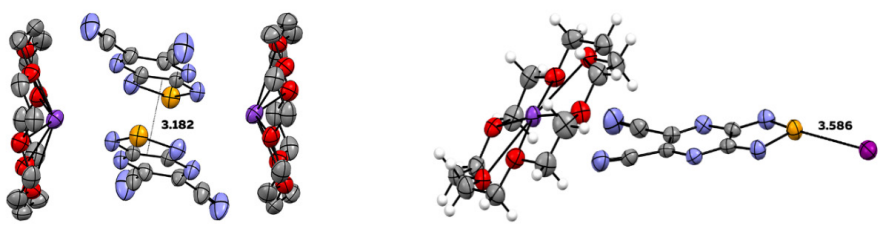


Figure 1. XRD structures of RA salt **2** (left) and CT complex **6** (right)

Acknowledgement:
The authors are grateful to the Russian Foundation for Basic Research (projects 20-33-90232 and 20-43-543016) for the financial support.

References:

1. E.A. Chulanova, N. A. Semenov, N.A. Pushkarevsky, N. P. Gritsan, A. V. Zibarev, *Mend. Comm.* 2018, 28 (5), 453–460.
2. N.A. Semenov, E.A. Radiush, E.A. Chulanova, A.M.Z. Slawin, J.D. Woollins, E.M. Kadilenko, I.Yu. Bagryanskaya, I.G. Irtegova, A.S. Bogomyakov, L.A. Shundrin, N.P. Gritsan and A.V. Zibarev, *New J. Chem*. 2019, 43, 16331–16337.

Synthesis of hydrogen-bonded organic frameworks containing N-heterocyclic carbene precursors

Jennifer Robertson[1*], *Georiga Orton*[1] *and Neil R. Champness*[1]

[1]School of Chemistry, University of Birmingham, UK
[*]E-mail: jhr046@student.bham.ac.uk

Keywords: framework, hydrogen-bonding

Hydrogen-bonded organic frameworks (HOFs) are a relatively new class of crystalline porous material. They are formed from organic compounds which self-assemble into porous crystalline frameworks solely through hydrogen bonding interactions [1]. Our early results cocrystallising N,N'-bis(isophthalate) functionalised imidazolium with amidinium linkers led to the formation of large single crystals of HOFs, permitting detailed structural analysis with X-ray crystallography. The imidazolium moiety serves as a precursor to N-heterocyclic carbenes (NHCs), able to be deprotonated at the N-CH-N carbon and subsequently coordinated to metal complexes. Two-coordinate metal complexes of N-heterocyclic carbenes can be photoluminescent and have potential for use in optoelectronic devices [2]. Our studies work towards the encapsulation of these NHC-complexes within the pores of the HOFs in order to study how the enclosed environment influences this fluorescence. The HOF will be used as a scaffold, with the NHC compounds serving the dual purpose of a linker in the framework and a ligand in the complex.

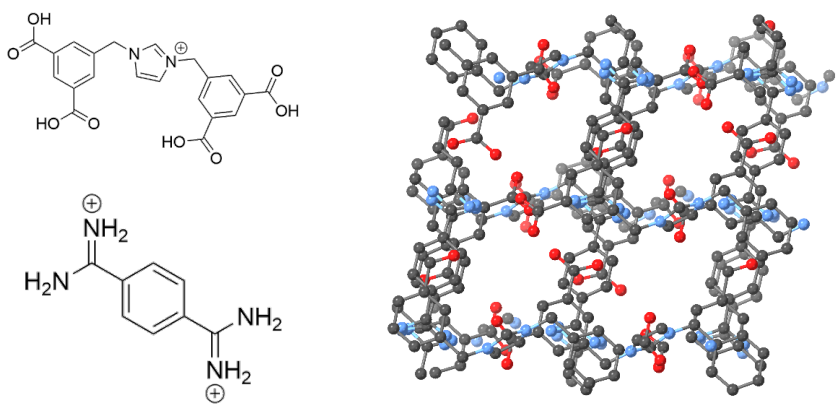


Figure 1. Left: Chemical structures of linkers used in this work; Right: Crystal structure of a HOF containing these linkers.

Acknowledgement:
This project is funded by the EPSRC.

References:

1. B. Wang, R. Lin, Z. Zhang, S. Xiang, B. Chen, *J. Am. Chem. Soc.* 2020, 142, 34, 14399–14416.
2. R. Visbala, M. Concepción Gimeno, *Chem. Soc. Rev.* 2014, 43, 3551–3574.

Testing the robustness of molecular organic crystals for atomic substitutions

Elin Sødahl[1*], *Carl Henrik Gørbitz*[2], *Kristian Berland*[1]

[1]Norwegian University of Life Sciences, [2]Universty of Oslo
[*]E-mail: elin.dypvik.sodahl@nmbu.no

Replacing inorganic materials for organic molecular crystals can reduce cost and toxicity related to production and processing in many applications. The functional properties of these materials, such as thermal and electronic conductivity, optical transparency and ferroelectricity, can be tuned by substitution of atoms or functional groups.

If the structure after substitution is similar to that of the initial compound, this can be an indication of tunable functional properties. This work is carried out as a case study, with the goal of finding substitutions that can preserve or yield a polar structure, as materials with a polar structure can exhibit ferroelectric properties.

There are reports in literature of promising substitutions yielding isostructural compounds, indicating possibility of tuning material properties as well as preserving a desired structure [1]. Further, there are reports of substitution that can lower symmetry from a non-polar to a polar space group [2,3]. Both these types of substitutions are investigated to find what substitutions can be used for tuning material properties in general, and what substitutions that can be suited to achieve a ferroelectric molecular crystal.

In this work, searches in the Cambridge Structural Database are used to find compounds only differing by an atom or a functional group. The structures associated with a substitution are compared to determine if the structure is preserved or if the substitution yields a whole new material. By screening the CSD, trends in the effect of substitution on the structure of molecular crystals is investigated.

This will aid design of new molecular crystals as well as guide attempts to tune the material properties of organic molecular crystals.

Acknowledgement:
This work is part of the FOX project (Project No. 302362) supported by the Research Council of Norway.

References:

1. M. K. Corpinot, D.-K. Bučar, *CrystalGrowth & Design* 2019, 19, 1426–1453.
2. H.-Y. Liu, *American Chemical Society* 2020, 142, 15205–15218.
3. Q. Pan, *Materials Chemistry Frontiers* 2021, 5, 44-59.

Structure determination of new peroxidomolybdenum hybrid compounds

Adrianna Sławińska[1*], *Paweł Serda*[2], *Marcin Oszajca*[2], *Wiesław Łasocha*[1,2]

[1]Jerzy Haber Institute of Catalysis and Surface Chemistry,Laboratory of XRD and Thermoanalysis, Polish Academy of Sciences,Krakow, Poland, [2]Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Krakow, Poland
[*]E-mail: adrianna.slawinska@ikifp.edu.pl

Keywords: peroxidomolybdates, polyoxocompounds, X-ray crystal structure analysis, thermal decomposition

Peroxido compounds belong to polyoxocompounds which are a wide and diverse group, characterizing by various structures, properties and applications: catalytic oxidation of cyclic hydrocarbons, alcohols and sulfides, epoxidation, effluent treatment, pyrotechnics, hydrometallurgy and medicine. Peroxido compounds are built of MO_X clusters, where M is transition metal in the highest oxidation state and O is oxygen. Moreover, peroxide compounds characterize by the presence of low strength of -O-O- bonds. It is possible to observe one, two or four peroxo-bonds connected with one metallic center.

Peroxidomoliybtate are synthesized in our group since 2013 [1,2,3]. This study show crystal structure of ten oxidodiperoxidocompounds with various derivates of pyridine carboxylic nicotinic acid, nicotinic acid N-oxide, picolinic acid N-oxide, isonicotinic acid N-oxide, 2,6-dicarboxypyridene acid and 3,5-dicarboxypyridene acid. The newest four compounds contain 2,6-dicarboxypyridine acid or 3,5-dicarboxypyridine acid as an organic part. Picture 1 shows two newest hybrids of potassium oxidodiperoxido molybdate(VI).

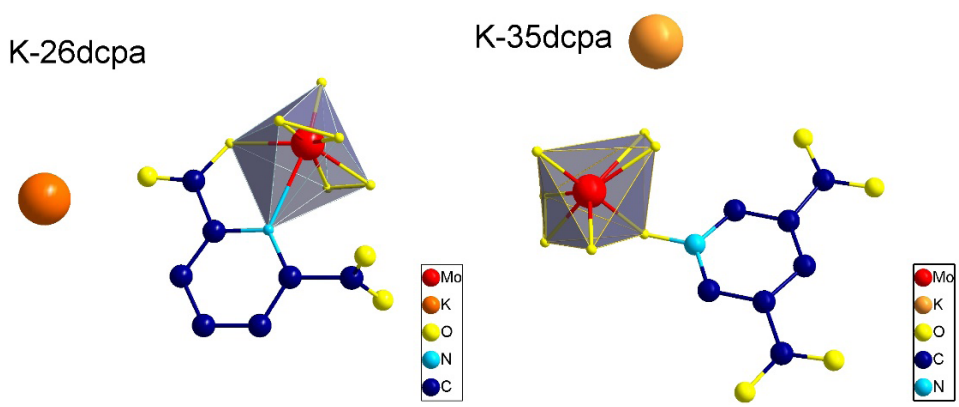


Figure 1. Visualisation of an asymetric unit of K-26dcpa and K-35dcpa[4]

Acknowledgement:
Adrianna Sławińska acknowledges the support of InterDokMed project no. POWR.03.02.00-00-I013/16.

References:
1. A. Szymańska, W. Nitek, D. Mucha, R. Karcz, K. Pamin, J. Połtowicz, W. Łasocha, *Polyhedron* 2013, 60, 39–46.
2. A. Sławińska, P. Serda, K. Pamin, J. Poltowicz, W. Łasocha *Polyhedron* 2017, 121, 191–198.
3. A. Sławińska, P. Serda, M. Oszajca, K. Pamin, J. Połtowicz, W. Łasocha, *Polyhedron* 2020, 183.
4. K. Brandenburg, Diamond version 3.2g, Crystal Impact GbR, Bonn, Germany, 1997–2001.

Redox induced structural dynamics of core modified hexaphyrin

Pragati Shukla[1*], *Venkataramanarao G. Anand*[1]

[1]Department of Chemistry, Indian Institute of Science Education & Research, Pune, India
[*]E-mail: pragati.shukla@students.iiserpune.ac.in

Keywords: hexaphyrin, redox properties, conformation

Porphyrins and its derivatives have been attracting significant importance ranging from its applications in the biological field to material. Its unique properties such as redox, metalation and structural dynamics makes them a promising class of molecules. Expanded form of porphyrin[1] is expected to have more diverse applications. But due to its structural dynamics, aggregation, π-π interactions, it becomes challenging to characterize these class of molecules in the solution state. Therefore, X-ray crystallography provides a strapping evidence for exploring this chemistry. Hence, this workshop will be very useful for my research to establish fruitful porphyrinoid chemistry.

Our current studies of expanded form of porphyrin, a core modified hexaphyrin, shows various structural transformations of a macrocycle upon addition of suitable oxidising and reducing agent. Its 26π, 28π, 30π conjugated system have different conformation and all these three states of macrocycle is redox interconvertible. Because of its wide range of redox properties these can be promising candidates for future organic electronics[2].

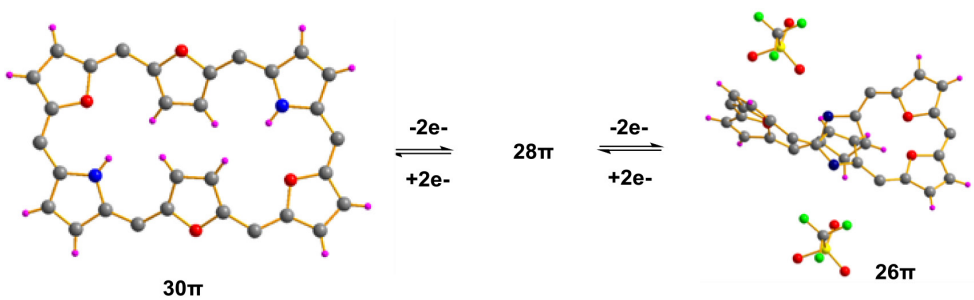


Figure 1. Interconvertible redox stages of core-modified hexaphyrin

Acknowledgement:
Thanks to IISER Pune for funding and research opportunities.

References:

1. Takayuki Tanaka and Atsuhiro Osuka, *Chem. Rev*. 2017, 117, 2584−2640.
2. Ji-Young Shin, Zhongyue Zhang, Kunio Awaga and Hiroshi Shinokubo, *Molecules* 2019, 24, 2433.

Crystal structure of fluorinated furan-phenylene co-oligomers

Alina A. Sonina[1*], *Christina S. Becker*[1], *Anatoly D. Kuimov*[1], *Inna K. Shundrina*[1], *Maxim S. Kazantsev*[1]

[1]N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS
[*]E-mail: belalina04@gmail.com

Keywords: crystal packing, intermolecular interaction, organic optoelectronics

Furan-phenylene co-oligomers are considered as promising materials for organic optoelectronics due to superior solubility (compared to their thiophene analogues), high photoluminescence quantum yields and charge mobility [1]. However, the systematic study of their substituted derivatives, in particular with electron-withdrawing groups is still lacking [2].

In this work a series of fluorinated furan-phenylenes (Figure 1, F-FP5s) were crystallized and studied. The structures of fluorinated FP5s differ by x-slip (shift along the long molecular axis) and inclination angle (δ_{tilt}) against the basal crystal facet. All structures are formed by π-π-stacking, C-H···F interactions and F···F close contacts, in turn C-H···π interactions were found only for FP_F5. The direction of π-π-stacking corresponds to the direction of crystal growth for elongated-shaped crystals. Upon the fluorintation, the solubility in toluene increases for central fluorinated phenylene ring (FP_F5) and decreases at fluorination of the terminal phenyl rings as compared with FP5. All compounds have high luminescence efficiency in THF solution (~80%) and in crystals (~50%), the highest PL QY has FP_F5 (61%) due to the greatest inclination of molecules with respect to the main crystal facet.

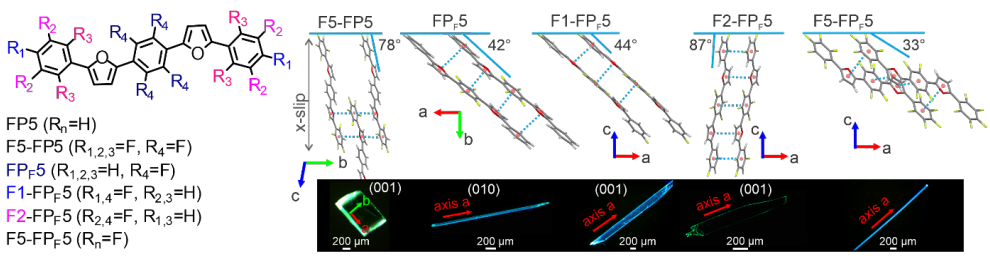


Figure 1. The chemical scheme, fragments of crystal structures in respect to the main crystal facet and single crystals under blue laser irradiation (405 nm) of fluorintated furan-phenylenes.

In summary, we have demonstrated a series of highly-emissive single crystals based on fluorine-substituted furan-phenylenes. The crystal packing and optical properties of linear conjugated oligomers can be effectively tuned by the selective introduction of fluorine substituents.

Acknowledgement:
This work was supported by RSF project №20-73-10090.

References:

1. Kazantsev M.S. el al., *RSC Adv.* 2016, 6, 92325–92329.
2. Sonina A.A. et al., *Acta Cryst. B.* 2018, 75 (5), 450–457.

Determination of the structure of zeolite A by electron diffraction tomography

Juan I. Tirado[1*], *Jose L. Jorda*[1], *Partha Pratim Das*[2]

[1]Instituto de Tecnología Química (UPV-CSIC), Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas, Avenida de los Naranjos s/n, 46022, Valencia, Spain, [2]NanoMEGAS SPRL, Blvd Edmond Machtens 79, B-1080 Brussels, Belgium
[*]E-mail: juaticas@itq.upv.es

Keywords: Electron Diffraction Tomography, Precession Electron Diffraction, zeolites

Microporous materials like zeolites have great academic and industrial applications in catalysis because of their varying properties which are strongly related to their crystalline structure. While single crystal X-ray diffraction and powder X-ray diffraction are the main techniques for structure solution, they are limited by the small crystal sizes usually obtained during the synthesis and by strong peak overlapping, respectively. Thus, in last decades a novel method called Electron Diffraction Tomography (EDT) or 3D Electron Diffraction (3D ED) has been developed allowing crystalline structure determination of nano-sized crystals performed in standard transmission electron microscopes.[1][2][3] This method can be assisted by Precession Electron Diffraction (PED) which minimizes dynamical effects and also provides reduction of excitation error.[4] Both techniques in combination with a continuous tilt of the crystal during acquisition of diffraction patterns can result on an almost complete reconstruction of reciprocal space. Thus, the unit cell and space group of zeolites, as well as intensities of reflections can be obtained from ED patterns, allowing the complete estrucure determination of the material.[5]

In this work, we have determined the complete structure of pure silica zeolite A, a material synthetized in our institute,[6] using a combination of EDT and PED.

Acknowledgement:
This research was supported by projects RTI2018-101784-B-I00 and SEV-2016-0683-18-3 and grant PRE2018-083623 from the Spanish government.

References:

1. Kolb, U., Gorelik, T., Mugnaioli, E., *MRS Proceedings* 2009, 1184, 1184-GG01-05.
2. Gemmi, M., Nicolopoulos, S., *Ultramicroscopy* 2007, Volume 107, Issues 6–7, 483–494.
3. Gemmi, M., Mugnaioli, E., Gorelik, T. E., Kolb, U., Palatinus, L., Boullay, P., Hovmöller, S., Abrahams, J. P., *ACS Cent. Sci*. 2019, 5, 1315−1329.
4. Vincent, R., Midgley, P.A., *Ultramicroscopy* 1994, 53, 271–282.
5. Bieseki, L., Simancas, R. Jordá, J. L., Bereciartua, P. J., Cantín, Á., Simancas, J., Pergher, S. B., Valencia, S., Rey, F., Corma, A., *Chem. Commun*. 2018, 54, 2122–2125.
6. Corma, A., Rey, F., Rius, J., Sabater, M.J., Valencia, S., *Nature* 2004, 431, 287–290.

Amino acid encoded Metal-Organic Framework adsorbents for heavy metals

Ainara Valverde[1,2*], *Gabriel I. Tovar-Jiménez*[3], *Dimas Torres*[3], *Maria I. Arriortua*[1,2], *Guillermo Copello*[3], *José M. Laza*[2], *José Luis Vilas-Vilela*[2], *Roberto Fernández de Luis*[1]

[1]BCMaterials, Basque Center for Materials, Applications and Nanostructures, Leioa, Spain, [2]University of the Basque Country (UPV/EHU), Leioa, Spain, [3]Universidad de Buenos Aires (UBA), Buenos Aires, Argentina
[*]E-mail: ainara.valverde@bcmaterials.net

Keywords: Metal-Organic Framework, heavy metal, adsorption, post-synthetic functionalization

Metal-Organic Frameworks (MOFs) have emerged as highly promising porous and crystalline materials to address heavy metal pollution, overcoming the adsorbing capacities and kinetics of classic adsorbents [1]. MOFs are formed by easily tunable inorganic and organic building blocks arranged in a porous and ordered fashion, creating a crystalline structure with large surface areas. Among all the broad variety of MOFs, Zr (IV) based ones, like MOF-808, have attracted the attention of the scientific community because of their great water stability, even in acidic conditions. However, the majority of Zr-MOFs show little selectivity towards heavy metal ion capture [2], which can be overcome encoding –SH, $–NH_2$ or –COOH functionalities into their structures. In these work, cysteine, histidine and citric acid have been post-synthetically anchored to the uncoordinated positions of Zr hexanuclear clusters of MOF-808, in order to increase its adsorption affinity over metal cations with different acidities. In fact, MOF-808 has six uncoordinated positions per cluster where formate molecules are found. Amino acids and natural acids can easily replace formate anions mimicking their binding mechanism to the cluster through the carboxyl groups [3]. Final encoding provides the pores of MOF-808 with amino acid residual groups able to act as metal-adsorption sites (Fig. 1) similar to the ones found in many metalloproteins active cores.

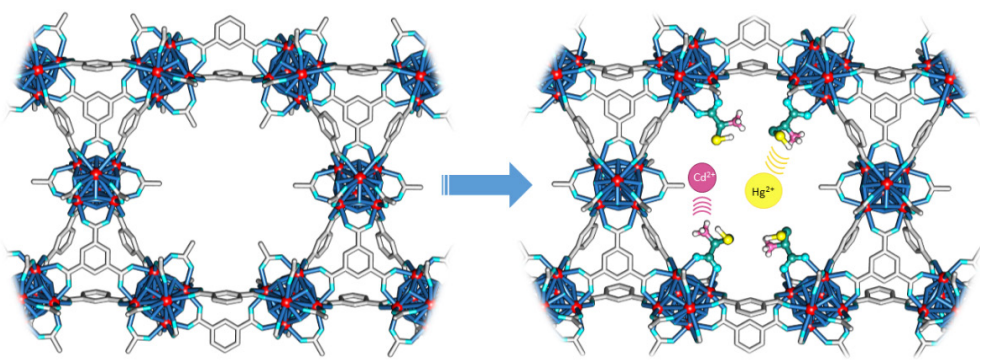


Figure 1. Post-synthetic functionalization of MOF-808 with cysteine and possible metal adsorbing sites.

Acknowledgement:
The authors thank Spanish Ministry of Economy and Competitiveness (MINECO) for financial support through projects MAT2016-76739-R (AEI/FEDER, UE). To the Basque Government Industry and Education Departments under the ELKARTEK, HAZITEK AND PIBA (PIBA-2018-06) programs H2020-MSCA-RISE-2017 (Ref: 778412) INDESMOF project. Ainara Valverde acknowledges the Basque Government (Education Department) for her PhD grant (PREB_2018_1_004) that made this work possible.

References:
1. P. Kumar, A. Pournar, K. Kim, *Progress in Materials Science* 2017, 86, 25–74.
2. Y. Peng, H. Huang, Y. Zhang, *Nature Communications* 2018, 9, 1–9.
3. S. S. Dhankhar, C. M. Nagaraja, *New J. Chem* 2019, 43, 2163–2170.

CO adsorption-induced spin transition in MOFs with unsaturated Fe^{2+} sites

Marco Vandone[1*], *Luca Braglia*[2], *Martina Fracchia*[3], *Silvia Mauri*[2], *Toni Grell*[1], *Paolo Ghigna*[3], *Piero Torelli*[2], *Valentina Colombo*[1]

[1]Dipartimento di Chimica, Università degli Studi di Milano, Italy, [2]IOM-CNR, Istituto Officina dei Materiali, Elettra Synchrotron, Italy, [3]Dipartimento di Chimica, Università di Pavia, Italy
[*]E-mail: marco.vandone@studenti.unimi.it

Keywords: SOFT-XAS, metal-organic frameworks, cooperative adsorption processes

Metal–organic frameworks are a class of permanently porous materials exhibiting impressive chemical tunability and high internal surface areas.[1] An important subset of MOFs features high densities of exposed metal cation sites that typically act as Lewis acids, able to accept electron density from easily polarized gas molecules, such as CO_2.[2] This electrostatic interaction is at the basis for a wide variety of potential applications in gas storage and separations.[3] Moreover, MOFs featuring π-donating exposed metal sites acids can display unprecedented selectivity in separations with gas molecules that can behave as π-acids, such as CO and other small molecules with low-lying π* orbitals. Exceptional adsorption performances have been indeed observed in MOFs with coordinatively unsaturated Fe^{2+} sites that undergo a transition from high to low spin upon binding CO. The framework Fe-BTTri (H_3BTTri = 1,3,5-tris(1H-1,2,3-triazol-5-yl)benzene) exhibits extremely steep yet reversible CO uptake.[3] Moreover, a cooperative spin transition mechanism for CO uptake on Fe^{2+} sites has been reported for Fe_2Cl_2(btdd) (H_2btdd = bis(1H-1,2,3-triazolo[4,5-b],[4′,5′-i]) dibenzo[1,4]dioxin).[4] In this contribution we report our work on the characterization of these adsorption processes with X-ray absorption spectroscopy (XAS) experiments in *operando* conditions (Figure 1). These experiments are able to provide a direct and highly sensitive measure of the electronic processes behind the CO adsorption induced spin transition, providing valuable electronic structure details about the underlying mechanism.

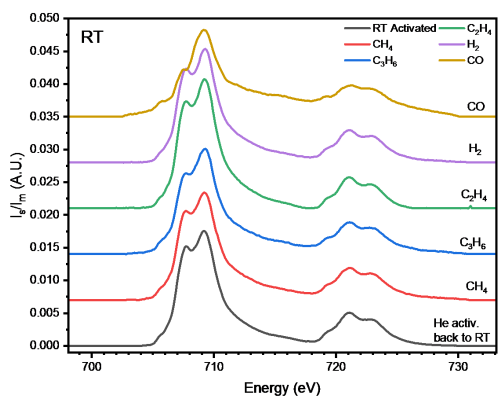


Figure 1. Fe $L_{2,3}$-edge spectra for FeBTTri under different gas atmosphere, showing the CO-induced spin-transition (orange line).

Acknowledgement:
The Italian Ministry MIUR is acknowledged for funding through the project PRIN 2017 “MOSCATo”.

References:

1. Zhou, H. C., Long, J. R. & Yaghi, O. M., *Chem. Rev*. 2012, 112, 673–674.
2. Caskey, S. R., Wong-Foy, A. G., Matzger, A. J., *J. Am. Chem. Soc.* 2008, 130, 10870–10871.
3. D.A. Reed, D.J. Xiao, M.I. Gonzalez, L.E. Darago, Z.R. Herm, F. Grandjean, J.R. Long, *J. Am. Chem. Soc.* 2016, 138, 17, 5594–5602.
4. D.A. Reed et al., *Nature* 2017, 55, 0, 7674, 96–100.

Structural biology

XRD study of the formation of cubic ice in monoolein/hemoglobin based system

I. Baranova[1,2], A. Angelova[3], W. Shepard[4], J. Andreasson[1], B. Angelov[1]*

[1]Institute of Physics, ELI Beamlines, Academy of Sciences of the Czech Republic, CZ-18221 Prague, Czech Republic, [2]MFF, Charles University, Prague, Czech Republic, [3]Institut Galien Paris-Sud, CNRS UMR 8612, Université Paris-Sud, Université Paris-Saclay, F-92296 Châtenay-Malabry, France, [4]Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin, BP 48, F-91192 Gif-sur-Yvette, France
[*]E-mail: iuliia.baranova@eli-beams.eu

Keywords: X-ray powder diffraction, cubic ice, monoolein, hemoglobin

The study of lipid/protein/salt/water systems is important and interesting from several points of view: understanding the factors influencing the conformational changes of lipid structures; control and understanding of the organization of protein crystals in lipid media; and the behavior of water in a multicomponent mixture under different conditions. In the present work we investigated the kinetics of ice formation in self-assembled hemoglobin/monoolein/salt/water system by X-ray diffraction (XRD) under continuous flow of liquid nitrogen (cryo-streaming). We show that the confined water molecules in the liquid crystalline system may form crystals of cubic and hexagonal symmetries during the freezing process. The rate constants for every diffraction peak of cubic phase of water were calculated from the obtained XRD data.

Acknowledgement:
This work was supported by the projects "Structural dynamics of biomolecular systems" (ELIBIO) (CZ.02.1.01/0.0/0.0/15_003/0000447) and "Advanced research using high-intensity laser produced photons and particles" (CZ.02.1.01/0.0/0.0/16_019/0000789) from the European Regional Development Fund.

Towards molecular movies: Studying protein binding dynamics at SwissFEL

Melissa Carrillo[1*], *John H. Beale*[2], *Celestino Padeste*[1]

[1]Laboratory of Nanoscale Biology, and [2]Photon Science Division, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
[*]E-mail: melissa.carrillo@psi.ch

Keywords: X-ray Free Electron Lasers, fixed-targets, protein dynamics, serial femtosecond crystallography

X-ray Free Electron Laser (XFEL) are a new generation of light sources that provide novel experimental capabilities to study structure and dynamics in biology, chemistry and material sciences due to their short and highly coherent X-ray pulses. Serial femtosecond crystallography (SFX) is a powerful new method at XFELs, providing the ability of collecting many thousands of diffraction patterns from individual protein microcrystals prior to radiation damage and at near physological temperatures. It also enables time-resolved SFX (TR-SFX); the study of protein reaction structural dynamics [1].

Fixed-target SFX sample delivery methods have principally focused on chips microfabricated from silicon wafers that offer an inert support for the immobilized crystals and a precise aperuture array for rapid alignment strategies [2]. These chips are reusable but brittle and prone to fracturing. Furthermore, they can also give strong bragg reflections along the Si(111) axis when misaligned.

Here we present preliminary data on polymer-based fixed-targets being developed for TR-SFX at SwissMX, the SwissFEL end station dedicated to fixed-target SFX. As a model system for time-resolved measurements, streptavidin-biotin binding will be used. We aim at capturing the binding events of photocaged biotin- and Strep-Tag II- derivatives upon photocleavage initiated by an optical laser pulse at defined time-points before probing with the XFEL pulse.

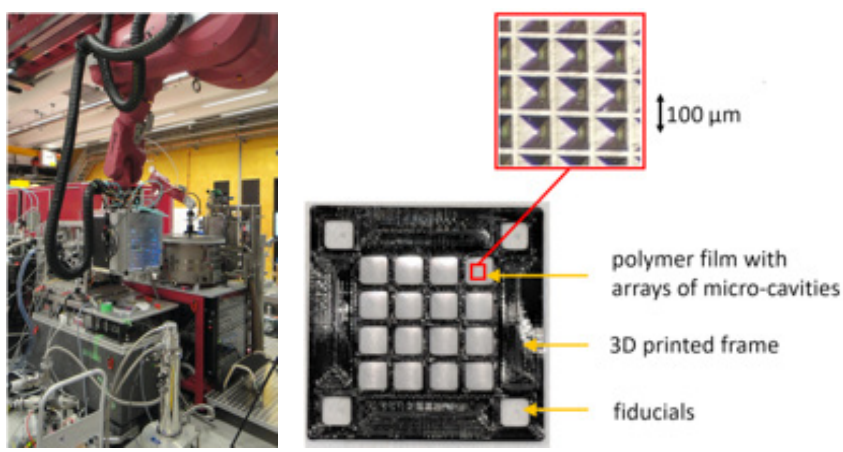


Figure 1. Left: Fixed-target entstation at SwissFEL's Bernina, Right: solid supports for SFX

Acknowledgement:
This project is supported by the Swiss Nanoscience Institute (SNI #1904)

References:

1. Chapman, H. N., et al. (2011). Femtosecond X-ray protein nanocrystallography, *Nature* 470(7332), 73–77.
2. Sherrell, D. A., et al. (2015). "A modular and compact portable mini-endstation for high-precision, high-speed fixed target serial crystallography at FEL and synchrotron sources." *J. Synchrotron Radiation*. 22, 1372–1378.

SAXS structural characterization of full-length murine prion protein

Stefano Da Vela[1], Mohsin Shafiq[2], Ladan Amin[3], Behnam Mohammadi[2], Taisiia Cheremnykh[1], Hermann Altmeppen[2], David A. Harris[3], Markus Glatzel[2], Dmitri I. Svergun[1]*

[1]European Molecular Biology Laboratory (EMBL) Notkestr. 85, 22607 Hamburg, Germany,
[2]University Medical Center Hamburg-Eppendorf (UKE), Martinistr. 52, 20246 Hamburg, Germany,
[3]Boston University School of Medicine, Boston, MA 02118, United States
[*]E-mail: sdavela@embl-hamburg.de

Keywords: SAXS, prion, protein, disorder

The prion protein (PrP) is a key protein in the pathogenesis of several neurodegenerative diseases, such as scrapie, kuru, Creutzfeldt-Jakob disease and bovine spongiform encephalopathy, where it converts to a misfolded aggregation-prone conformational variant (PrP^{Sc}) [1]. Interestingly, PrP has also been shown to modulate the aggregation of amyloid beta (Aβ) fibril aggregation in Alzheimer's disease while retaining its cellular form (PrP^{C}) [2]. We studied murine PrP^{C}, in the solution state, by small-angle X-ray scattering (SAXS). SAXS is a powerful tool for the characterization of proteins featuring disordered regions in quasi-native conditions. We could model the structure of full-length PrP^{C}, including its disordered N-terminal portion [3], and characterize it as a conformational ensemble. Using SAXS and complementary techniques we showed that the aggregation state of PrP^{C} is dependent on the buffer conditions employed even when the cellular conformational variant is maintained.

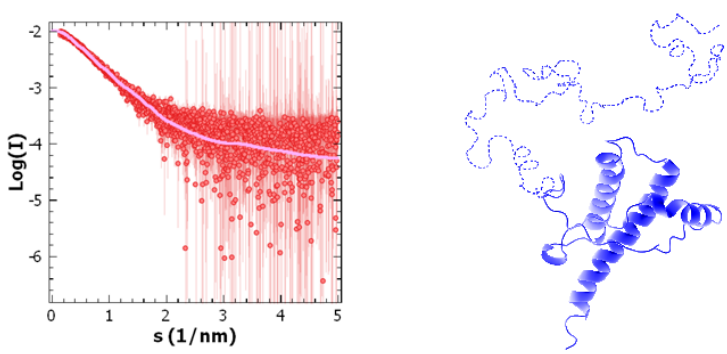


Figure 1. Left, SAXS data (dots) and best model fit (solid line) for murine PrP^{C}. Right, a typical conformation of PrP^{C}, featuring the disordered N-terminus.

Acknowledgement:
We acknowledge funding from the Joachim Herz Stiftung, Hamburg, Germany (Biomedical Physics of Infection)

References:

1. R. Linden et al., *Physiol. Rev.* 2008, 88, 673–728.
2. C. Falker, A. Hartmann et al., *J. Neurochem.* 2016, 137, 88–100.
3. A.D. Gossert et al., *Proc.Natl.Acad.Sci. USA* 2005, 102, 646–650.

Molecular characteristics of S1-P1 nucleases from human pathogens

Blanka Husťáková[1,2], Mária Trundová[1], Kristýna Adámková[1,2], Tomáš Kovaľ[1], Jan Dohnálek[1]*

[1]Laboratory of Structure and Function of Biomolecules, Institute of Biotechnology of the Czech Academy of Sciences, Biocev, Průmyslová 595, 25250 Vestec, Czech Republic,
[2]University of Chemistry and Technology, Technická 5, 166 28 Prague 6 – Dejvice, Czech Republic
[*]E-mail: hustakovab@ibt.cas.cz

Nucleases from S1-P1 family are metal dependent enzymes mostly occurring in fungi, plants, trypanosomatids and bacteria. Structures of some of them have already been solved using crystallographic techniques. S1-P1 nucleases also occur in human pathogens including representatives of genus *Leishmania* or opportunistic bacteria such as *Stenotrophomonas maltophilia* or *Legionella pneumophila.* Regarding the fact that S1-P1 nucleases are not present in human, they may represent potential drug targets. However, their structures and their role in pathogens remain unknown. S1-P1 nuclease from *S. maltophilia* was expressed in *E. coli* and its structure has been solved. Furthermore, its biophysical and catalytical properties were investigated. Following research will be focused on ligand binding into the active site with the aim to gain a better understanding of the specific properties of the enzyme from the multiresistant bacterial strain.

Acknowledgement:
This project was supported by the ERDF fund (CZ.02.1.01/0.0/0.0/16_013/0001776), Czech Science Foundation, project 20-12109S, and financial support from specific university research (MSMT-No-21-SVV/2020).

Determination of the cytochrome P450 structure and function

Ivan Kapranov[1*]

[1]Moscow Institute of Physics and Technology, National Research University
[*]E-mail: kapranov.ia@phystech.edu

Keywords: structural biology, cytochrome P450, tuberculosis

Cytochromes from P450 family are found in most organisms where they are involved in the metabolism and synthesis of steroids, bile acids, unsaturated fatty acids, phenolic metabolites as well as in the neutralization of exogenic chemicals [1]. Drugs targeting cytochromes P450 have been shown to inhibit the growth of Mycobacterium tuberculosis, the causative agent of one of the deadliest diseases – tuberculosis [2]. Thus, inhibition of cytochromes P450 is a promising strategy for the development of new anti-tuberculosis drugs.

In this work the crystal structure of mycobacterial cytochrome P450 was obtained. The crystals diffracted up to 1,6 Å and allow for unambiguously determination of conformations of key aminoacids in the active site as well as important water molecules. Complementary experiments were carried out to access and determine dissociation constants of putative ligands binding to the protein with microscale thermophoresis (MST).

Acknowledgement:
This work was supported by a joint grant received from Belarusian Republican Foundation for Fundamental Research, B20R-061 and Russian Foundation for Basic Research, 20-54-00005.

References:

1. Denisov I.G. [et al.]. Structure and Chemistry of Cytochrome P450 // *Chemical Reviews* 2005. № 6 (105). C. 2253–2278.
2. Ortega Ugalde S. [et al.]. Function, essentiality, and expression of cytochrome P450 enzymes and their cognate redox partners in Mycobacterium tuberculosis: are they drug targets? // *Applied Microbiology and Biotechnology* 2019. T. 103. № 9. 3597–3614 c.

Structural and biochemical investigations of the transcription factor HNF-1A

Laura Kind[1], Arne Raasakka[1], Pål Rasmus Njølstad[3,4], Petri Kursula[1,2], Thomas Arnesen[1,5,6]*

[1]Department of Biomedicine, Faculty of Medicine, University of Bergen, Bergen, Norway, [2]Faculty of Biochemistry and Molecular Medicine & Biocenter Oulu, University of Oulu, Oulu, Finland, [3]KG Jebsen Center for Diabetes Research, Department of Clinical Science, University of Bergen, NO-5020, Bergen, Norway, [4]Department of Pediatrics and Adolescents, Haukeland University Hospital, NO-5021, Bergen, Norway, [5]Department of Biological Sciences, University of Bergen, NO-5020, Bergen, Norway, [6]Department of Surgery, Haukeland University Hospital, NO-5021, Bergen, Norway
[*]E-mail: laura.kind@uib.no

Keywords: MODY3, POU transcription factor, synchrotron radiation

Hepatocyte nuclear factor 1A (HNF-1A) plays a crucial role in pancreatic islet development and β-cell function, making it indispensable for the regulation of blood glucose levels via glucose-stimulated insulin secretion. Mutations in the HNF-1A gene are associated with a monogenic form of diabetes mellitus, Maturity-onset Diabetes of the Young 3 (MODY3) [1]. Mutations affect the dimerization domain, the DNA-binding domain, and the disordered region of the protein [2]. With the aim to understand this enigmatic protein on the molecular level, we set out to study native and pathogenic HNF-1A variants in an *in vitro* environment. Here, we present the development of an efficient protein purification protocol for different HNF-1A constructs, as well as initial data on protein structure. Biophysical methods confirm an alpha-helical fold with the presence of random coil structures and small-angle X-ray scattering (SAXS) data demonstrate a high degree of flexibility in the POU transcription factor. Initial X-ray crystallographic experiments and biochemical DNA binding assays pave the way to understand the binding mode to a promoter region crucial for β-cell function.

Acknowledgement:
University of Bergen (PhD stipend), Meltzer foundation UiB (PhD project fund).

References:

1. F. L. Cardenas-Diaz, C. Osorio-Quintero, M. A. Diaz-Miranda, S. Kishore, K. Leavens, C. Jobaliya, D. Stanescu, X. Ortiz-Gonzalez, C. Yoon, C. S. Chen, R. Haliyur, M. Brissova, A. C. Powers, D. L. French, and P. Gadue, *Cell Stem Cell* 2019, 25, 273–289.
2. S. Ellard, *Hum Mutat* 2000, 16, 377–85.

Microcrystal electron diffraction of the peptide gramicidin

Nicole Hoefer[1*], *David McComb*[1,2]

[1]Center for Electron Microscopy and Analysis, The Ohio State University, Columbus, Ohio, 43212,
[2]Department of Material Science and Engineering, The Ohio State University, Columbus, Ohio, 43210
[*]E-mail: hoefer.3@osu.edu

Keywords: micro-ED, gramicidn, cryo-TEM

Microcrystal electron diffraction (micro-ED) is a cryo-TEM technique that can be used to determine the atomic structure of proteins, peptides, and small molecules [1]. Micro-ED data is obtained by continuously tilting the crystal in the cryo-TEM while recording diffraction information [2]. This method has been successfully used for the structure determination of proteins such as proteinase K, lysozyme, adenosine A_{2A} receptor (G-protein coupled receptor) and peptides such as an Alzheimer associated amyloid-β (20-34), SVQIVY (tau protein fragment) and others [3-7].

Growing diffraction quality crystals of proteins and peptides can be challenging. X-ray diffraction techniques typically require crystals that are at least 1 μm in each direction. Crystals smaller than that could not be utilized in single crystal diffraction studies until the advent of micro-ED. In this technique the ideal thickness of the crystal perpendicular to the incident beam is in the nanometer range [2].

In this contribution we report on our research to determine the structure of gramicidin D, a peptide antibiotic produced non-ribosomally by *Bacillus brevis* [8]. It acts, in part, by creating pores in membranes, rendering them incapable of supporting life-sustaining transmembranal gradients. Gramicidin is a highly apolar pentadecapeptide consisting of alternating D- and L-amino acids. Naturally occurring gramicidin is a mixture of isoforms: gA (80%), gB (6%), and gC (14%). The amino acid sequence of gA is:

Formyl–NH–L–Val–Gly–L–Ala–D–Leu–L–Ala–D–Val–L–Val–D–Val–L–Trp–D–Leu–L–Trp11–D–Leu–L–Trp–D–Leu–L–Trp–CO–NH–CH2–CH2–OH.

In gB and gC, Trp at position 11 is replaced by L-Phe and L-Tyr, respectively. The ion conducting form of gD is generally considered to be a dimer. Gramicidin exists in two major conformations; a head-to-head, single stranded helical dimer and a left- or right-handed intertwined, parallel or antiparallel, double stranded double helix [9].

The peptide was dissolved in a mixture of ethanol / PEG 4000 and crystallized in batch-mode at 4°C. Small plate-like crystals formed. The crystals in the presence of ethanol / PEG 4000 mixture were transferred onto Quantifoil R 2/2 grids and access solvent was removed by vacuum suction. The grids were flash frozen in liquid nitrogen and transferred into a Glacios cryo-TEM equipped with a Ceta-D camera. Datasets from several crystals were successfully collected. We will discuss the data processing in XDS and our progress on solving and refining the structure.

Acknowledgement:
The authors acknowledge funding from the Foundation For A Better World.

References:
1. Nannenga, BL & Gonen, *T, Nat. Methods* 2019, 16, 369–379.
2. Shi D, et al., *Nat Protoc.* 2016 May, 11(5), 895–904.
3. Nannenga BL, et al., *Nat Methods.* 2014 Sep, 11(9), 927–930.
4. Martynowycz MW, et al., *Structure.* 2019 Oct 1;27(10):1594–1600.e2.
5. Martynowycz, MW, et al., *bioRxiv* 2020.09.27.316109 (2020).
6. Warmack RA, et al., *Nat Commun.* 2019 Jul 26;10(1):3357.
7. Seidler PM, et al., *J Biol Chem.* 2019 Nov 1;294(44):16451–16464.
8. Wallace BA, *Annu Rev Biophys Biophys Chem.* 1990, 19, 127–57.
9. Höfer N, et al., *Cryst Growth Des.* 2011 Apr 6;11(4):1182–1192.

Index

Subject index