

## WHAT DO WE DO?

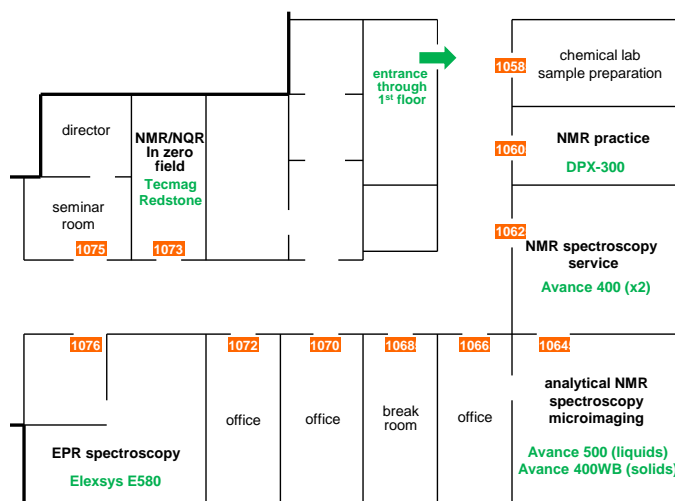
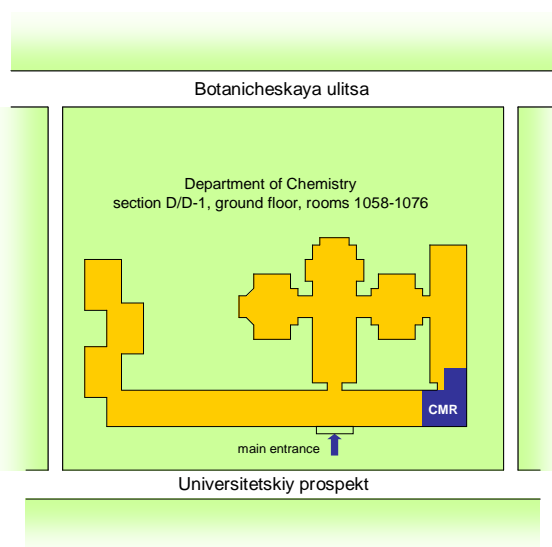
The Center for Magnetic Resonance provides access to the instrumentation, expertise, and infrastructure to carry out and support fundamental, applied and innovative research projects utilizing NMR, EPR and NQR spectroscopy as well as magnetic resonance microimaging. On commercial basis, all services of the Center could be provided to external users, such as chemical engineering, pharmacological and medical organisations, as well as industry. Cooperation aimed for publications in peer-reviewed journals with academic research institutes and universities is possible as pro bono work.

## HOW TO FIND US?

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Room	Phone nr.	Local phone nr.
1058	Chemical lab	
1060	NMR Service	... 428-43-25 4325
1062	NMR Service	... 428-95-63 9563
1064	Analytical NMR	
1066	Office	... 363-69-25 5915 (IP phones only)
1068	Break room	5662 (IP phones only)
1070	Office	5916 (IP phones only)
1072	Office	5917 (IP phones only)
1073	zero-field NMR + NQR	... 428-95-64 9564
1075	Director	... 363-68-99 5661 (IP phones only)
1076	EPR spectroscopy	... 428-95-65 9565

# STAFF



**Ass. Prof. Dr. Peter Tolstoy**, director  
NMR of liquids, solutions and solids

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Research interests: hydrogen bonding, intermolecular interactions, cryospectroscopy, combined NMR/UV



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NMR of liquids and solutions, NMR-service

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Research interests: elucidation of structure and tautomerism of organic compounds and complexes.



**Sergey Smirnov**, lead specialist  
Liquid-state NMR spectroscopy, NMR-service

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Research interests: high-resolution NMR, study of H-bonds by low-temperature NMR in liquified Freons.



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Research interests: structure elucidation of organic compounds using modern NMR spectroscopy techniques

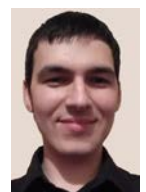


**Mikhail Vovk**  
Liquid-state NMR, relaxation, diffusion measurements

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Research interests: NMR relaxation, hydration of organic molecules in aqueous solutions



**Artem Grevtsev**  
Liquid-state NMR spectroscopy

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Research interests: organic-inorganic composites, thin film solar cells, chalcopyrite nanoparticles



**Roman Belykh**  
NQR spectroscopy

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nanostuctured materials, deposited metallic particles for catalysis



**Dr. Anton Mazur**  
NMR spectroscopy of solids

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NMR of magnetic ordered systems, spin echo method, nanostructured materials, NMR relaxation in solids.



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NMR spectroscopy of solids

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carbon nanotube based composite materials, nanostructured materials.



**Dr. Anna Shmyreva**  
NMR of magnetically ordered systems, NQR spectroscopy

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Research interests: NMR of magnetic ordered systems, nanostructured materials, NQR



**Dr. Stanislav Sukharzhetskii**  
EPR spectroscopy

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Research interests: EPR, application of MR in natural sciences, spectroscopic methods in geology and ecology



**Ekaterina Grebenyuk**  
EPR spectroscopy

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Research interests: spectroscopic methods in chemistry, sol-gel process, nanocomposites.



**Irina Alisova**  
EPR spectroscopy

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Nanostructured materials, photochemistry, spectroscopy.

# EQUIPMENT

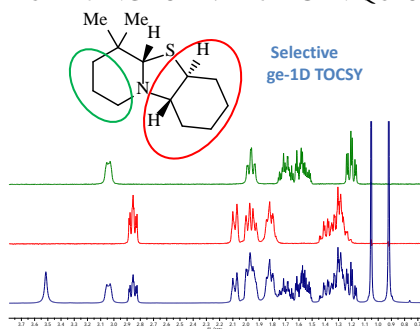
## 2X BRUKER 400 MHZ AVANCE AND BRUKER 300 MHZ DPX



These instruments are dedicated to service routine measurements of 1D and 2D NMR spectra of liquids and solutions.

- Direct and inverse detection probes.
- Observed nuclei range from  $^1\text{H}$  to  $^{109}\text{Ag}$ .
- Possible  $^1\text{H}\{^{19}\text{F}\}$  and  $^{19}\text{F}\{^1\text{H}\}$  measurements.
- Possible  $^2\text{H}$  measurements with  $^{19}\text{F}$  lock.

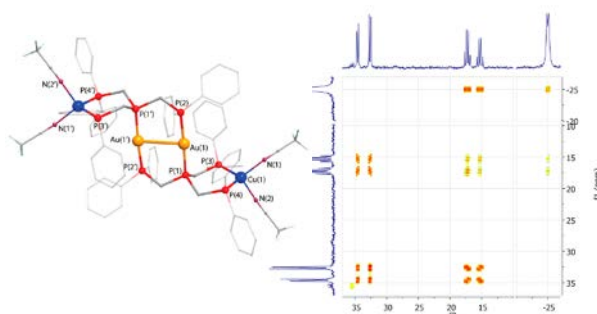
### FULL RANGE OF NMR TECHNIQUES



Selective NMR experiments used to obtain sub-spectra of individual spin systems in order to establish the stereo-chemical structure of a complex molecule.

V.V. Sokolov, A.Yu. Ivanov, M.S. Avdontseva, A.A. Zolotarev, *Chem. Heterocycl. Compd.* 2014, 50, 550-556.

### STRUCTURE BY 2D, 3D ETC. NMR



Homonuclear correlations such as  $^{31}\text{P}$ - $^{31}\text{P}$  COSY and other multi-dimensional techniques allow one to interpret long-range spin-spin couplings and determine structure of organometallic complexes.

M.T. Dau, J.R. Shakirova, A.J. Karttunen, E.V. Grachova, S.P. Tunik et al., *Inorg. Chem.*, 2014, 53, 4705-4715.

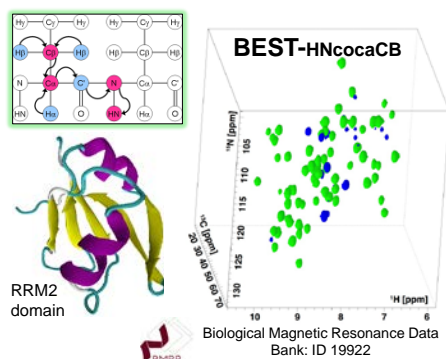
## BRUKER 500 MHZ AVANCE



The spectrometer is suited for measurements of 1D, 2D and 3D NMR spectra of liquids and solutions.

- Long measurements at low temperature (down to 110 K).
- Three-channel architecture (from  $^1\text{H}$  to  $^{109}\text{Ag}$ ).
- Diffusion measurements at temperatures up to 470 K.
- Combined NMR/UV-vis spectroscopy

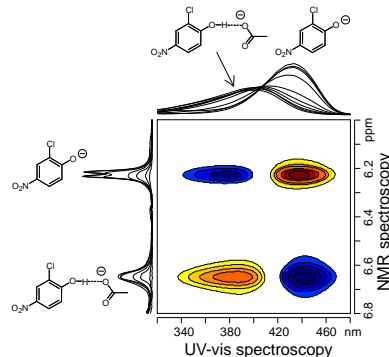
### STRUCTURE DETERMINATION OF PROTEINS



Structure of RNA-recognition motif RRM2 in TDP-43 protein has been established using liquid state multi-dimensional NMR. TDP-43 constitutes a major component of the inclusion bodies formed in the brains of the patients with frontotemporal lobar degeneration.

N.R. Skrynnikov, S.O. Rabdano, I.S. Podkorytov et al., 2014, *unpublished*.

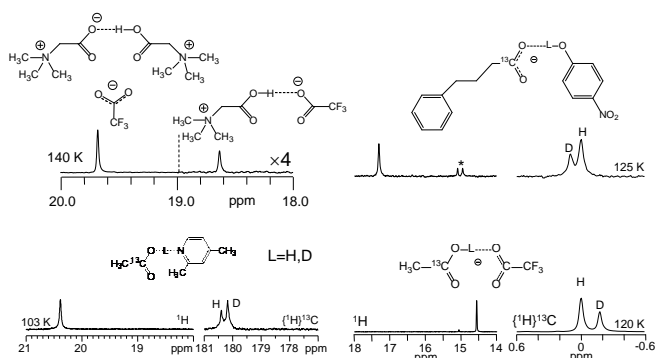
### COMBINED NMR/UV-VIS SPECTROSCOPY



UV-Vis spectrometer build within the magnet of an NMR spectrometer allows one to obtain simultaneously NMR and UV-vis spectra and analyze the consistent set of spectroscopic data by 2D cross-correlation methods.

B. Koepppe, P.M. Tolstoy, E.T. J. Nibbering, T. Elsaesser, *J. Phys. Chem. Lett.*, 2011, 2, 1106-1110.

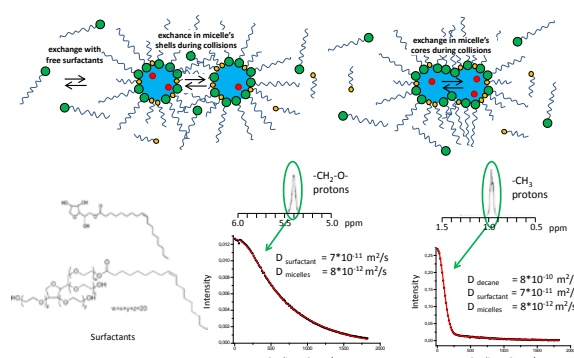
## LOW TEMPERATURE NMR



Extra-low temperature NMR in liquefied gases as solvents ( $\text{CDF}_3/\text{CDF}_2\text{Cl}$ ) allows to reach slow molecular and proton exchange regimes and resolve signals of H-bonded complexes of various stoichiometry & isotope composition.

B. Koeppel, J. Guo, P.M. Tolstoy, G.S. Denisov, H.-H. Limbach, *J. Am. Chem. Soc.* 2013, 135, 7553-7566.

## DIFFUSION-ORDERED NMR SPECTROSCOPY



Diffusion ordered NMR spectroscopy (DOSY) can be used to study sizes of micelles, their mobility and chemical exchange processes in complex microemulsions.

A.S. Koneva, E.A. Safonova, P.S. Kondrakhina, et al., *Colloids and Surfaces A* 2017, 518, 273-282.

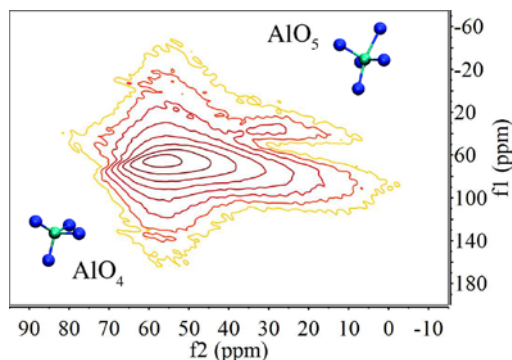
## BRUKER 400 MHZ WB AVANCE



This NMR spectrometer is dedicated to the studies of samples in solid state: crystallines, powders, weakly ordered materials, gels, liquid crystals, amorphous compounds, nanostructures (zeolites, silicates) etc. The spectrometer allows one to study diffusion processes and obtain micro-tomographic image

- Long measurements at temperatures from 130 K to 870 K.
- Microtomography of objects up to 30 mm in linear size.
- Magic angle spinning up to 30 kHz.
- Diffusion measurements (gradients up to 3000 G/cm).

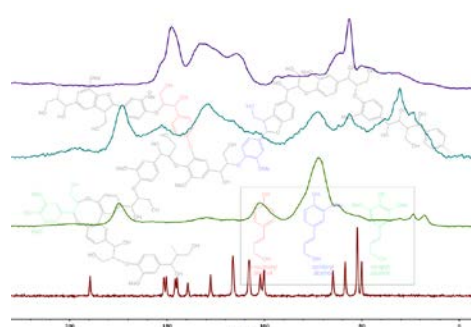
## STRUCTURAL STUDIES OF DISORDERED MATERIALS



The study of the structural composition of the multicomponent glasses by MQ MAS and other methods allows one to create materials with predetermined physical and chemical properties

A. Osipov, V.E. Eremyashev, A.S. Mazur, P.M. Tolstoy, L.M. Osipova, *Glass Phys. Chem.* 2016, 42(3), 230-237.

## STUDIES OF COMPLEX MIXTURES OF NATURAL COMPOUNDS



$^{13}\text{C}$  NMR spectral analysis of complex mixtures of macromolecules of natural origin allows one to track the processes of decomposition (for example of lignins and its derivatives) and soil formation.

E.L. Evstigneyev, A.V. Kalugina, A.Yu. Ivanov et al., *J. Wood Chem. Technol.* 2017, 1-13.

A. Lupachev, E. Abakumov, S. Gubin, *Geosciences*, 2017, 7, 24.

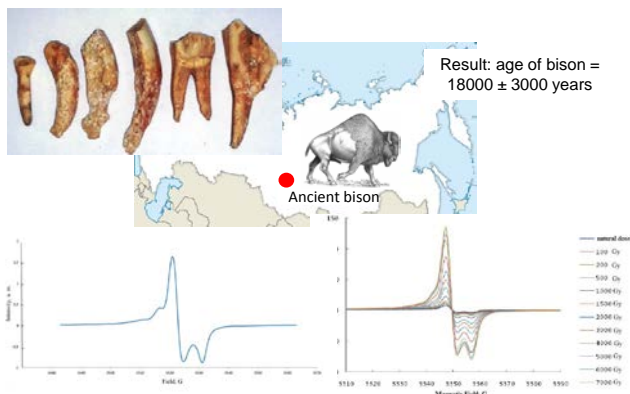
## EPR SPECTROMETER BRUKER ELEXSYS E580



EPR spectrometer ( $\lambda = 3.2$  cm, X-band) for studies of paramagnetic centers in solids, liquids, solutions, including aqueous solutions, and gases. Spectrometer is capable of measurements in CW-mode as well as in FT-mode.

- UV-irradiation of the samples (100 W, 200-2000 nm).
- Temperature range from 3.7 K to 500 K.
- ENDOR/TRIPLE measurements.

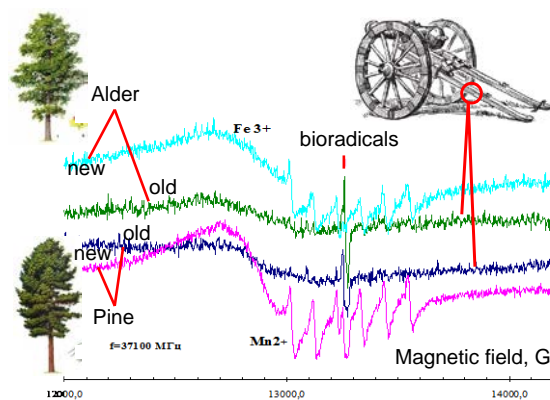
### EPR-DATING OF TOOTH ENAMEL



EPR spectra of radiation defects in tooth enamel of ancient bison. The nature of the paramagnetic centers and their development with time allows one to date such paleontological samples.

A.I. Antipov, A.Yu. Kul'taeva, S.M. Sukharzhevski et al., 2014, *unpublished*

### EPR-STUDY OF WOOD DEGRADATION



EPR spectra of old and new wood samples from the digs at Borodino battlefield. Signals of bioradicals and of  $Mn^{2+}$  and  $Fe^{3+}$  ions can be identified. These data can be used in historical reconstruction of the events in the year 1812.

S.M. Sukharzhevski et al., *unpublished*

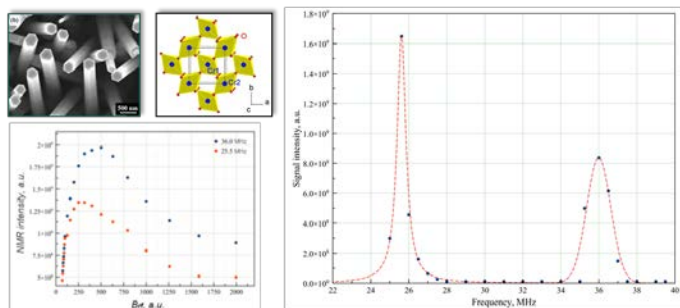
## TECMAG REDSTONE NMR/NQR 1-500 MHz



This spectrometer allows one to obtain spectral and relaxation NMR and NQR parameters for solids, polymers, metals, glass and magnetically ordered systems.

- Observed frequencies in a zero external magn. field 20-120 MHz.
- Temperature range from 4 K to 500 K.
- Acquisition of weak NQR signals by multiple scans
- NQR spectra of  ${}^7Li$ ,  ${}^{27}Al$ ,  ${}^{35}Cl$ ,  ${}^{63,65}Cu$ ,  ${}^{75}As$ ,  ${}^{93}Nb$ ,  ${}^{183}Ta$  etc nuclei.
- NMR of  ${}^{11}B$ ,  ${}^{57}Fe$ ,  ${}^{59}Co$ ,  ${}^{61}Ni$  etc. nuclei.
- Investigation of orientation dependence for monocrystals.

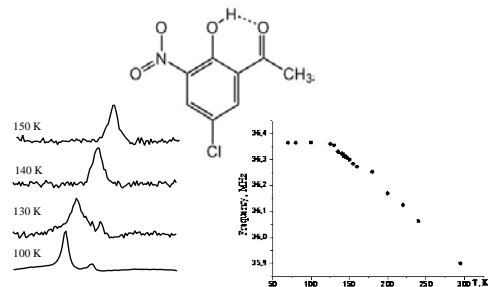
### NMR OF MAGNETICALLY ORDERED NANOPARTICLES



Two lines in the NMR spectrum of  $CrO_2$  nano-rods with the structure of rutile show that there are two non-equivalent types of Cr ions instead of monovalent  $Cr^{4+}$ .

A.A. Shmyreva, O.M. Osmolowskaya et al., 2015, *unpublished*.

### ${}^{35}Cl$ NQR SPECTRA OF ORGANIC COMPOUNDS



Molecule of 2-hydroxy-3-nitro-5-chloroacetophenone undergoes a phase transition at ca. 120 K, which can be detected by the  ${}^{35}Cl$  NQR spectroscopy.

E.V. Kukushkina, A.I. Filarowski, P.M. Tolstoy et al., 2015, *unpublished*.

# RESEARCH COOPERATION PARTNERS

## IN RUSSIA



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Institute of Inorganic Chemistry, Siberian branch of Russ. Acad. Sci., Novosibirsk  
A.N. Nesmeyanov Institute of Organoelement Compounds of Russ. Acad. Sci., Moscow  
Immanuel Kant Baltic Federal University, Kaliningrad  
Kazan Federal University, Kazan  
Southern Federal University, Rostov-on-Don  
Murmansk State Technical University  
Jaroslavl State University, Jaroslavl  
Kuban State University, Krasnodar  
Irkutsk Institute of Chemistry SB RAN, Irkutsk  
South Ural State University, Cheljabinsk

## AROUND THE WORLD



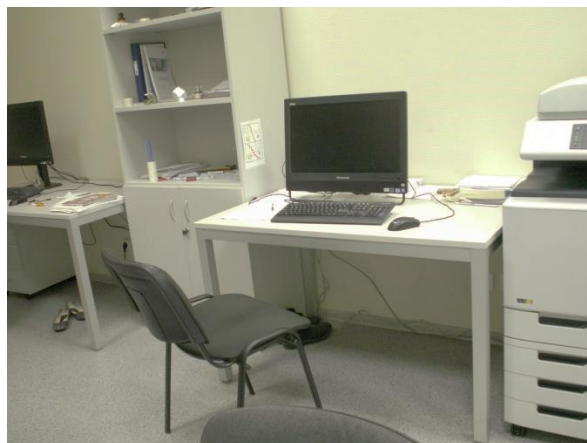
Institute of Biochemistry, Ernst-Moritz-Arndt University of Greifswald, Germany  
Institute of Chemistry and Pharmacology, University of Regensburg, Germany  
Institute of Chemistry and Biochemistry, Free University of Berlin, Germany  
Max-Born Institute of Non-Linear Optics and Short Pulse Spectroscopy, Berlin, Germany  
Martin-Luther University, Halle-Wittenberg, Germany  
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Exact Sciences and Engineering Center, University of Guadalajara, Mexico  
Department of Chemistry, University of Wroclaw, Poland  
Wroclaw University of Technology, Poland  
Ben-Gurion University in Negev, Beer-Sheva, Israel  
Free State University, Bloemfontein, South Africa

FACILITIES AVAILABLE FOR VISITORS WORKING ON JOINT RESEARCH PROJECTS

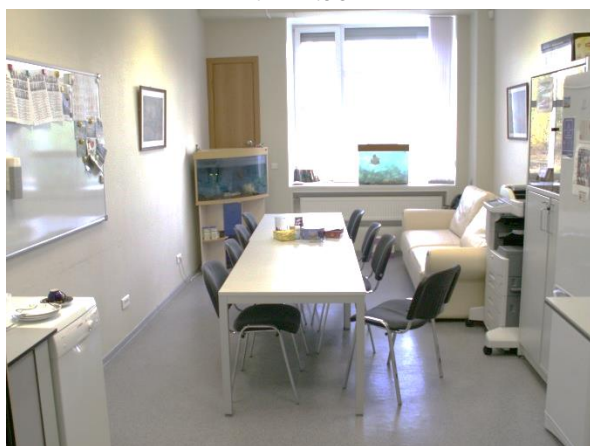
OFFICE ROOMS



PERSONAL DESK SPACE FOR VISITORS



BREAK ROOM



COMMON SPACE



CHEMICAL LAB FOR SAMPLE PREPARATION



HOODS



ROTARY EVAPORATOR



HIGH VACUUM LINE

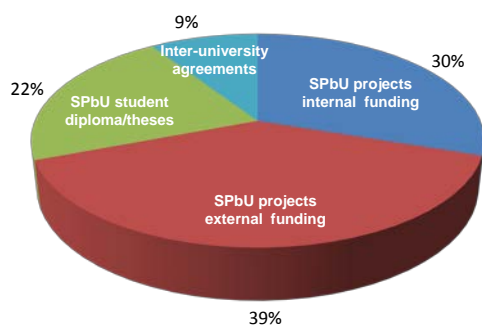


SCALES

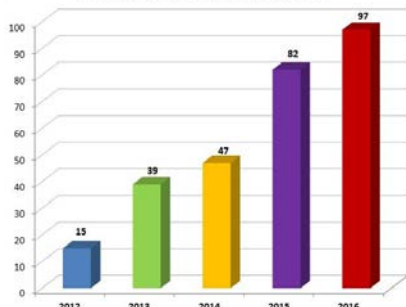


## WORKLOAD AND PUBLICATION STATISTICS 2013-2015

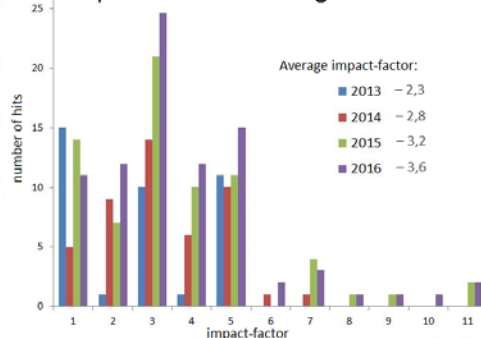
### Measurement time distribution



### Papers published per year



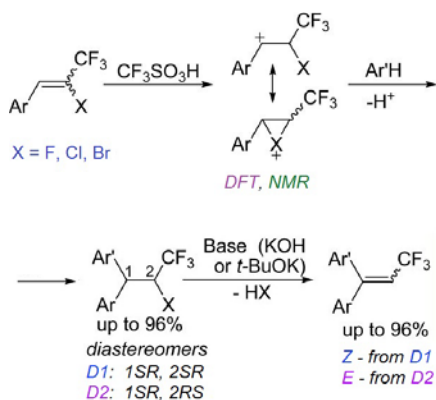
### Papers with acknowledgement to CMR



### Users and projects:

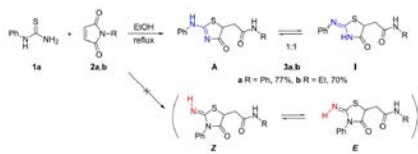
- ~350 primary users: 75% chemists, 15% physicists, 10% other (biologists and geologists)
- ~100 projects: ca. 1 projects per week, av. duration 1.5 yrs
- ~80-100 requests per day: 90% routine, 10% other

## SELECTED PUBLICATIONS 2016-2017



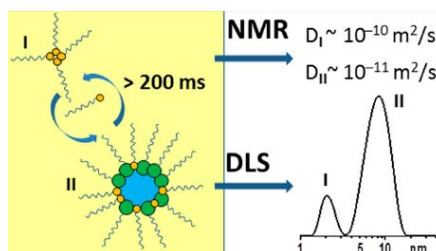
The formation of the benzyl cations  $[\text{ArHC}^+-\text{CH}(\text{X})\text{CF}_3]$  takes place under protonation of E-/Z-2-halogeno-2- $\text{CF}_3$  styrenes  $[\text{ArCH}=\text{C}(\text{X})\text{CF}_3]$ , X = F, Cl, Br in superacids. The structures of these new electrophiles were studied by means of NMR and theoretical DFT calculations. According to these data, in the case of bromo derivatives, the formed cations, most probably, exist as cyclic bromonium ions; however, in the cases of chloro and fluoro derivatives, open forms are more preferable. Subsequent reaction of these benzyl cations with arenes proceeds as Friedel-Crafts alkylation to afford 1,1-diaryl-2-halo-3,3,3-trifluoropropanes  $[\text{Ar}(\text{Ar}')\text{CH}-\text{CH}(\text{X})\text{CF}_3]$  in high yields (up to 96%) as a mixture of two diastereomers. The prepared halogenopropanes were easily converted into the corresponding mixtures of E-/Z-trifluoromethylated diarylethenes  $[\text{Ar}(\text{Ar}')\text{C}=\text{CCF}_3]$  (in yields up to 96%) by dehydrohalogenation with base (KOH or t-BuOK). The mechanism of elimination ( $\text{E}_2$  and Ecb) depends on the nature of the leaving group and reaction conditions.

The structure of the product was confirmed by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^1\text{H}-^{13}\text{C}$  HSQC NMR (**Bruker 400 WB Avance III**). E/Z stereochemistry was determined by  $^1\text{H}-^{19}\text{F}$  NOESY. M.A. Sandzhieva, A.N. Kazakova, I.A. Boyarskaya, A. Yu. Ivanov, V.G. Nenajdenko, A.V. Vasilyev "Friedel-Crafts Alkylation of Arenes with 2-Halogeno-2- $\text{CF}_3$ -styrenes under Supercritical Conditions. Access to Trifluoromethylated Ethanes and Ethenes", *J. Org. Chem.* 2016, 81, 5032-5045, DOI: 10.1021/acs.joc.6b00419



2-(Alkyl(aryl)amino)thiazol-4(5H)-ones can regioselectively be prepared from monoalkyl(aryl)thioureas and maleimides. In solution, the former heterocycles exist in a tautomeric equilibrium with 2-(alkyl(aryl)imino)thiazolidin-4-ones and the substituent on the exocyclic nitrogen atom governs the ratio of these tautomers. Isomers with the alkyl group in the endocyclic position can be obtained from N-methyl(ethyl)thioureas. 2D NMR spectroscopy and DFT calculations rationalize experimental results.

2D NOESY,  $^{13}\text{C}-^1\text{H}$  HSQC and HMBC,  $^{15}\text{N}-^1\text{H}$  HSQC and HMBC spectra (**Bruker 400 Avance III**, **Bruker 500 Avance III** NMR spectrometers) were used for signals assignment. The ratios of tautomers were obtained from  $^1\text{H}$  NMR spectra. The positions (endocyclic or exocyclic) of parent thiourea's substitute group of thiazol-4-one derivatives were proved by 2D NMR experiments. A.S. Pankova, P.R. Golubev, A.F. Khlebnikov, A. Yu. Ivanov, M.A. Kuznetsov "Thiazol-4-one derivatives from the reaction of monosubstituted thioureas with maleimides: structures and factors determining the selectivity and tautomeric equilibrium in solution", *Beilstein J. Org. Chem.* 2016, 12, 2563-2569 DOI: 10.3762/bjoc.12.251



In the present study, the microstructure and diffusion of the components of water-in-n-decane Winsor IV microemulsions stabilized by a mixture of nonionic surfactants Span 80 (sorbitane monooleate, HLB 4.9) and Tween 80 (polyoxyethylene sorbitan monooleate, HLB15.0) at the weight ratios 49:51 (i.e. at the maximal ability to solubilize water) were investigated by viscosimetry, PGSTE NMR and DLS.

$^1\text{H}$  NMR diffusion experiments were performed on a **Bruker 500 Avance III** spectrometer equipped with GREAT 1/60A gradients and 5 mm MIC DIFF/30 probe with  $^1\text{H}$  insert. Specific for the systems under consideration bimodal distributions of the diffusion coefficients were determined using both DLS and PGSTE NMR methods. The growth of the microemulsion droplets with the increase of water content was found.

A.S. Koneva, E.A. Safonova, P.S. Kondrakhina, M.A. Vovk, A.A. Lezov, Yu. S. Chernyshev, N.A. Smirnova "Effect of water content on structural and phase behavior of water-in-oil (n-decane) microemulsion system stabilized by mixed nonionic surfactants SPAN 80/TWEEN 80", *Colloids and Surfaces A* 2017, 518, 273-282 DOI: 10.1016/j.colsurfa.2017.01.020

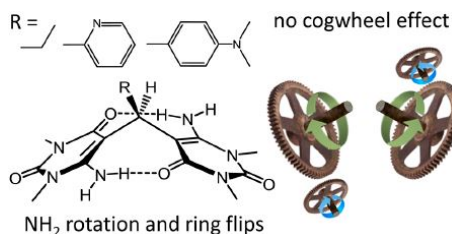




Tris(2-pyridyl)phosphine oxide reacts with CuSCN to form a variety of luminescent complexes, depending on the specified metal-to-ligand ratio and the solvent used, viz. mononuclear  $[\text{Cu}(\text{N},\text{N}',\text{N}''\text{-Py}_3\text{P}=\text{O})(\text{NCS})]$ , dinuclear  $(\text{N},\text{N}'\text{-Py}_3\text{P}=\text{O})\text{Cu}(\text{SCN})\text{Cu}[(\text{N},\text{N}'\text{-Py}_3\text{P}=\text{O})]$ , their co-crystal (2 : 1, correspondingly) and trinuclear  $\{\text{Cu}(\text{NCS})[\text{SCN}\text{Cu}(\text{N},\text{N}',\text{N}''\text{-Py}_3\text{P}=\text{O})]_2\}$ . In the solid state, these complexes feature red-orange emission upon UV photoexcitation. The reaction of tris(2-pyridyl)phosphine with CuSCN quantitatively produces an almost insoluble coordination polymer,  $[\text{Cu}(\text{Py}_3\text{P})\text{NCS}]_n$ , which exhibits bright green emission.

$^{31}\text{P}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$  CPMAS NMR spectra were recorded on a **Bruker 400 WB Avance III** spectrometer. Obtained by solid state NMR data allowed one to conclude that in obtained  $[\text{Cu}(\text{Py}_3\text{P})\text{NCS}]_n$ , the phosphine ligand is coordinated to Cu(I) via the phosphorus atom as well as one or two nitrogen atoms. Taking into account the ability of (2-Py) $_3$ P to act as an  $\text{N},\text{N}_0$ -chelating and P-monodentate ligand, the chain-polymer structure has been assumed.

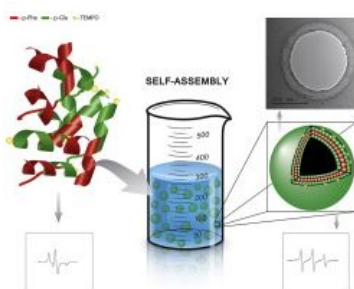
A.V. Artem'ev, E.P. Doronina, M.I. Rakhmanova, A.O. Sutyryna, I.Yu. Bagryanskaya, P.M. Tolstoy, A.L. Gushchin, A.S. Mazur, N.K. Gusarova, B.A. Trofimov "Luminescent Cu thiocyanate complexes based on tris(2-pyridyl)phosphine and its oxide: from mono-, di- and trinuclear species to coordination polymer", *New J. Chem.* 2016, 40, 10028-10040 DOI: 10.1039/C6NJ02087A



Three bis(6-amino-1,3-dimethyluracil-5-yl)-methane derivatives were studied experimentally by variable-temperature  $^1\text{H}$  NMR in polar aprotic solutions ( $\text{CD}_2\text{Cl}_2$ ,  $\text{C}_5\text{D}_5\text{N}$ ,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) and computationally by DFT. The unusual for diarylmethanes coplanar conformation of dimethyluracil rings of each molecule is held by a pair of unequal intramolecular  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds. We show the presence of two dynamic processes involving breakage/formation of these bonds. First, it is two independent  $\text{NH}_2$  group rotations, each coupled to nitrogen inversion. Second, it is uracil ring rotations (ring flips). The thermodynamic parameters ( $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$ , and  $\Delta G^\ddagger$ ) of both processes were estimated by the full line shape analysis of NMR signals and also by DFT calculations. We demonstrate that, though the ring flips exchange pairs of NH protons, the two processes are not coupled: during the ring flip  $\text{NH}_2$  groups do not rotate, and during the  $\text{NH}_2$  rotation the rings do not necessarily rotate. Unlike in many other diarylmethanes, the ring flips in the studied compounds are happening stepwise; i.e., the configuration when both rings are "in flight" at the same time is energetically unfavorable (small degree of "cog wheel effect"). The signs of the  $\Delta S^\ddagger$  values indicate that the molecular flexibility increases during the  $\text{NH}_2$  rotations, but decreases during the ring flips.

Variable-temperature (300 – 180 K)  $^1\text{H}$  NMR spectra were obtained on a **Bruker 500 Avance III** spectrometer.

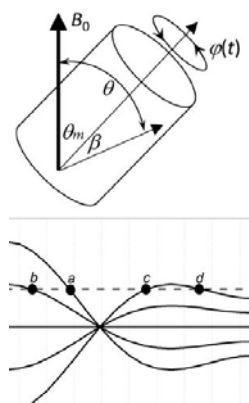
M.V. Sigalov, S.A. Pylaeva, P.M. Tolstoy "Hydrogen Bonding in Bis(6-amino-1,3-dimethyluracil-5-yl)-methane Derivatives: Dynamic NMR and DFT Evaluation", *J. Phys. Chem. A* 2016, 120, 2737–2748 DOI: 10.1021/acs.jpca.6b02184



The development of detectable nanoparticles for controlled drug delivery systems has tremendous practical importance regarding the monitoring of drug pathway in organism. Self-assembly amphiphilic block-copolymer poly(L-glutamic acid)-b-poly(L-phenylalanine) (pGlu-b-pPhe) was chosen for the preparation of discussed nanoparticles. The synthesis of blocks was carried out using ring-opening polymerization (ROP) of N-carboxyanhydrides of mentioned amino acids.

EPR spectra of obtained nanoparticles in solid state and suspensions were obtained on a **Bruker Elexsys E580**. It was proved that in the case of nanoparticles EPR detectable spin labels are located on polymersome surface. The experiments in cell culture demonstrated the absence of cytotoxicity of labeled nanoparticles. Additionally, it was shown that TEMPO-label can be detected inside the cell by EPR method.

A.V. Hubina, A.A. Pogodaev, V.V. Sharoyko, E.G. Vlakh, T.B. Tennikova, "Self-assembled spin-labeled nanoparticles based on poly(amino acids)", *Reactive and Functional Polymers* 2016, 100, 173–180 DOI:10.1016/j.reactfunctpolym.2016.01.018.



Orders of magnitude decrease of  $^{207}\text{Pb}$  and  $^{199}\text{Hg}$  NMR longitudinal relaxation times  $T_1$  upon magic-angle-spinning (MAS) are observed and systematically investigated in solid lead and mercury halides  $\text{MeX}_2$  (Me = Pb, Hg and X = Cl, Br, I). In lead(II) halides, the most dramatic decrease of  $T_1$  relative to that in a static sample is in  $\text{PbI}_2$ , while it is smaller but still significant in  $\text{PbBr}_2$ , and not detectable in  $\text{PbCl}_2$ . The effect is magnetic-field dependent but independent of the spinning speed in the range 200–15 000 Hz. The observed relaxation enhancement is explained by laboratory-frame heteronuclear polarization exchange due to crossing between energy levels of spin-1/2 metal nuclei and adjacent quadrupolar-spin halogen nuclei. The enhancement effect is also present in lead-containing organometal halide perovskites. Our results demonstrate that in affected samples, it is the relaxation data recorded under non-spinning conditions that characterize the local properties at the metal sites. A practical advantage of fast relaxation at slow MAS is that spectral shapes with orientational chemical shift anisotropy information well retained can be acquired within a shorter experimental time.

$^{79}\text{Br}$ ,  $^{81}\text{Br}$  and  $^{127}\text{I}$  NQR spin-echo spectra were recorded on **Tecmaq Redstone** spectrometer. NQR spectra were applied for refinement quadruple parameters obtained from solid state NMR.

A.A. Shmyreva, M. Safdari, I. Furó, S.V. Dvinskikh, "NMR longitudinal relaxation enhancement in metal halides by heteronuclear polarization exchange during magic-angle spinning", *J. Chem. Phys.* 2016, 144, 224201 DOI:10.1063/1.4953540