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Fields of research

- Helicene based chiral stationary phase for HPLC
- Chiral separation of helicenes
- Rearrangement of 1-methylcyclohex-1-ene during hydrodesulfurization of FCC gasoline
- Highly fluorinated cyclopentadienes for application in catalysis
- Peracetylated 3-deoxy-3-fluoro analogs of D-glucosamine and D-galactosamine
- Synthesis of helicene derivatives and [*n*]phenacene derivatives
- Sensors based on laser ablated graphene
- Silicon nanowires grown on metal substrates

Applied research

- Enzymatic optical sensor and optical fiber biosensor of glucose
- Printed optical chemical sensors
- Development of new analytical methods
- Analytical services to the research departments of ICPF
- Highly efficient catalyst and process for degradation of resistant antibiotics
- Macroporous titanium surfaces for enhancing bone osseointegration and adhesion to titanium implants

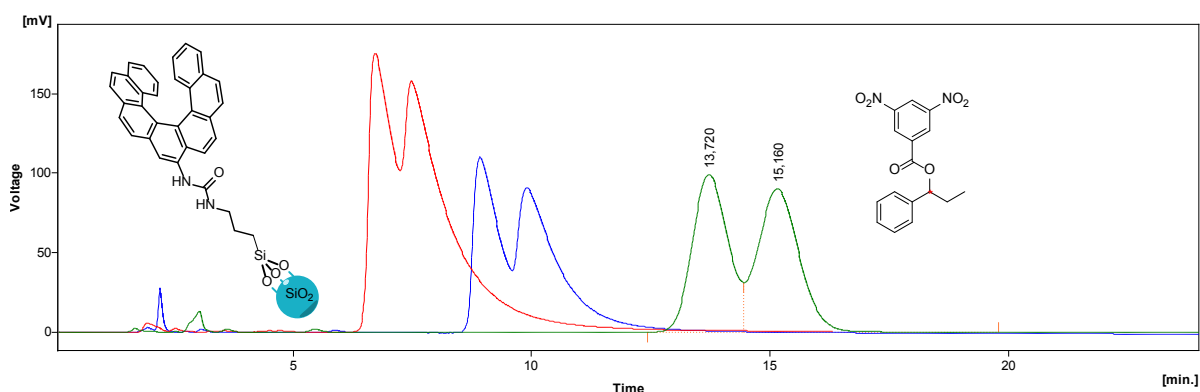
Research projects

Preparation of helicene based chiral stationary phase for HPLC

(J. Sýkora, sykora@icpf.cas.cz; joint project with Watrex Praha, s.r.o.; supported by TACR, project No. TA01010646)

The main aim of the project is to develop a new chiral stationary phase for HPLC which would serve for column manufacturing. During the project the procedure for large scale production of helicene derivatives has been developed and patented. The explored reactivity of 9-bromo[7]helicene was utilized in preparation and subsequent electropolymerization of [7]helicenyl-thiophene. [Ref. 8]

During the fourth year of the project pure enantiomers of 9-amino[7]helicene were isolated, reacted with 3-(triethoxysilyl)propyl isocyanate and finally anchored onto silica. The performance of new chiral stationary phase was then tested on various racemic substrates in order to evaluate the relevancy for possible HPLC column production and sale.



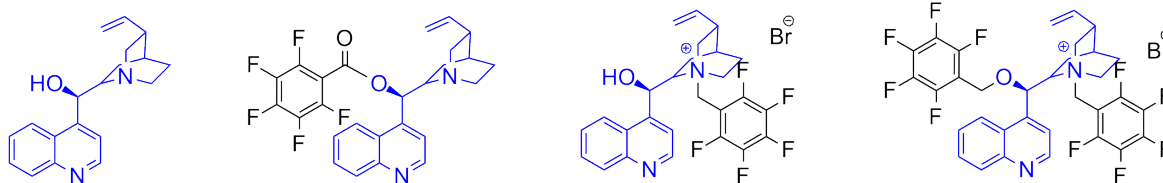
Separation of 1-phenylpropyl ester of dinitrobenzoic acid (red - helicene based phase endcapped, blue - no endcap, green - Kromasil Cellucoat phase), column dimensions 150 x 3 mm, flow 0.5 ml / min, temperature 25°C, UV detection at 254 nm

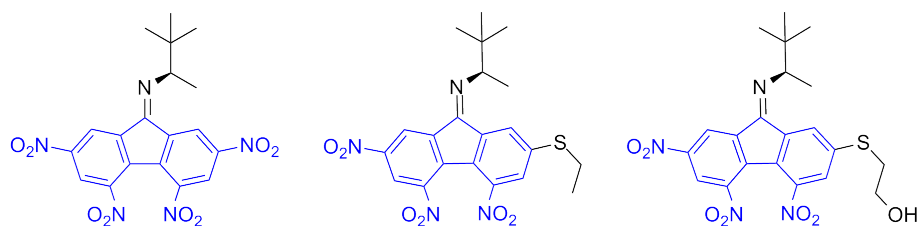
Chiral separation of helicenes

(J. Storch, storchj@icpf.cas.cz; joint project with Lach-ner, s.r.o.; supported by TACR, project No. TA04010082)

The main objective of the project is the development of cheap and effective technology for chiral separation of unsubstituted and substituted helicenes in sufficient quantity enabling further applied research. The sub-objective of the project is to bring new charge-transfer (CT) agents capable of enantiodiscrimination of helicenes. Only optically pure helicenes have the potential to be applied in diverse areas of use such are molecular functional layer (OFET, OLED), liquid crystal display (LCD) and special semiconducting polymers. [Ref. 8]

Within this year we were focused on the synthesis of the electronically deficient cinchonidine and fluorenone CT-agents and complexation studies with various helicenes. Results obtained will be further used for improvement of structures in order to improve enantiodiscrimination abilities and increase stability constant.



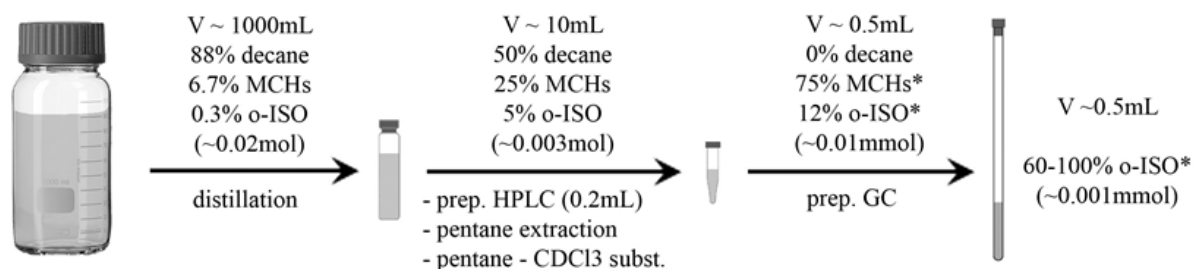


Cinchonidine and fluorenone CT-agents

The rearrangement of 1-methylcyclohex-1-ene during hydrodesulfurization of FCC gasoline over supported Co(Ni)Mo/Al₂O₃ sulfide catalysts: the isolation and identification of branched cyclic C7 olefins

(J. Sýkora, sykora@icpf.cas.cz; project supported by GACR, project No. P106/11/0902)

In the study of simultaneous hydrodesulfurization of 1-benzothiophene and the olefin hydrogenation of 1-methylcyclohex-1-ene we encountered a rearrangement of 1-MCH during the first step of catalytic hydrogenation, which yielded various branched cyclic olefins; mainly ethylcyclopentene and dimethylcyclopentene isomers. The volatile isomerization products were isolated directly from diluted reaction mixture via combination of chromatographic techniques including preparative gas chromatography, and were undoubtedly assigned by NMR spectroscopy. The precise identification of the isomerization products was required for subsequent detail kinetic study. [Ref. 20]



*estimated from ¹H NMR data

Overview of the isolation procedure

BIO-OPT-XUV Research team advancement at the FBME CTU

(G. Kuncová, kuncova@icpf.cas.cz; supported by MEYS, ESF, project No. CZ.1.07/2.3.00/20.0092)

The project is focused on strengthen education and build up a team at the FBME (Faculty of Biomedical Engineering) CTU. In the academic year 2014/2015, experiments of two Mc. projects of the students of FBME CTU were realized in the laboratory of Immobilized Biocatalyst and Optical Sensors. The topics of these projects were enzymatic optical sensor and optical fiber biosensor of glucose.

Printed Optical Chemical Sensors (POS)

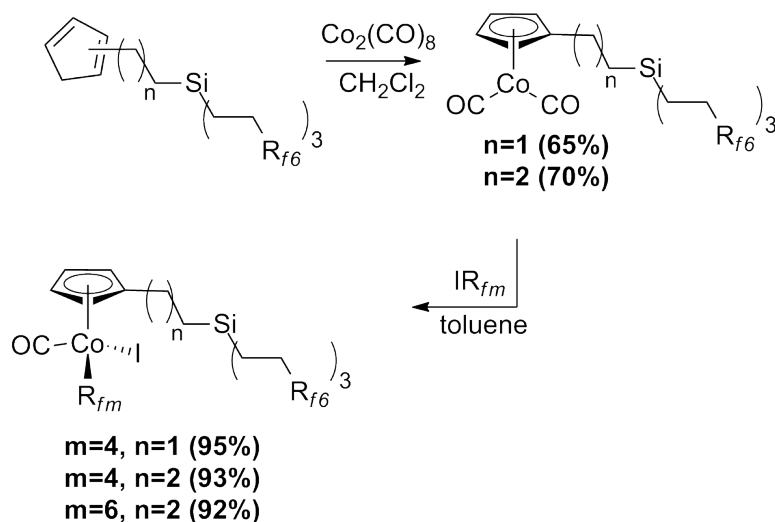
(G. Kuncová, kuncova@icpf.cas.cz; joint project with Invos, s.r.o.; supported by TACR, project No. TA03010544)

Experimental work was focused on the development of optical detector of oxygen. On demand of industrial partner such oxygen detector have to be visible (oxygen is indicated by change of color) printable and cheap. We prepared a series of sensor compositions.

Highly fluoruous cyclopentadienes for applications in catalysis

(J. Čermák, cermak@icpf.cas.cz; supported by GACR, project No. P106/12/1372)

Two new fluoruous tags based on omega-[tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-silyl]alkyl substituents (alkyl = ethyl, propyl) synthesized previously were used to prepare cyclopentadienes (the mixtures of 1- and 2-substituted isomers) which bore the tags. Cyclopentadienylcobalt(I) dicarbonyl complexes were subsequently obtained from the reactions of the cyclopentadienes with dicobalt octacarbonyl. Oxidative additions of 1-iodoperfluoroalkanes on the cobalt(I) complexes provided cobalt(III) complexes with one of their four ponytails bonded directly to the metal and with a stereocenter at the metal. [Ref. 16]

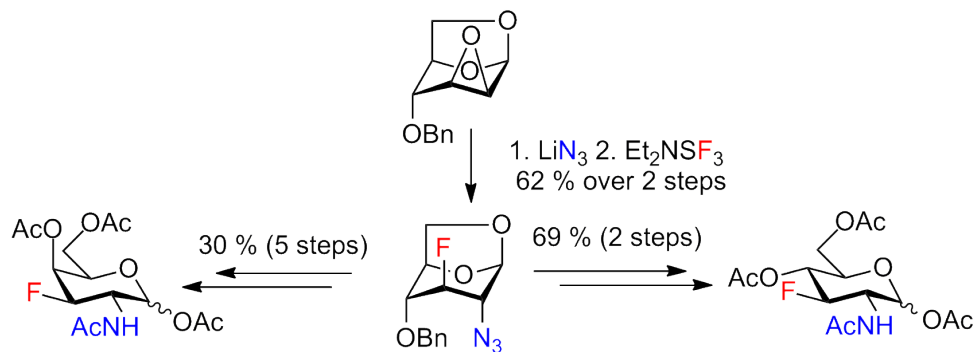


Synthesis of cobalt(I) dicarbonyl complexes and oxidative addition of iodo(perfluoro)alkanes

A convenient route to peracetylated 3-deoxy-3-fluoro analogs of D-glucosamine and D-galactosamine from a Černý epoxide

(J. Karban, karban@icpf.cas.cz; supported by ICPF)

1,6:2,3-dianhydro-4-O-benzyl- β -D-mannopyranose has been conveniently transformed into peracetylated 3-deoxy-3-fluoro analogues of D-glucosamine and D-galactosamine in four or six steps, respectively, in an overall yield of 43 % or 19 %, respectively. In addition, our approach furnished selectively protected fluorohydrins which are useful synthetic intermediates with potential for a regioselective functionalization or glycosylation at C4. Investigation towards this application and an extension of our methodology to other fluorinated hexosamines is currently underway in our laboratory. [Ref. 9]

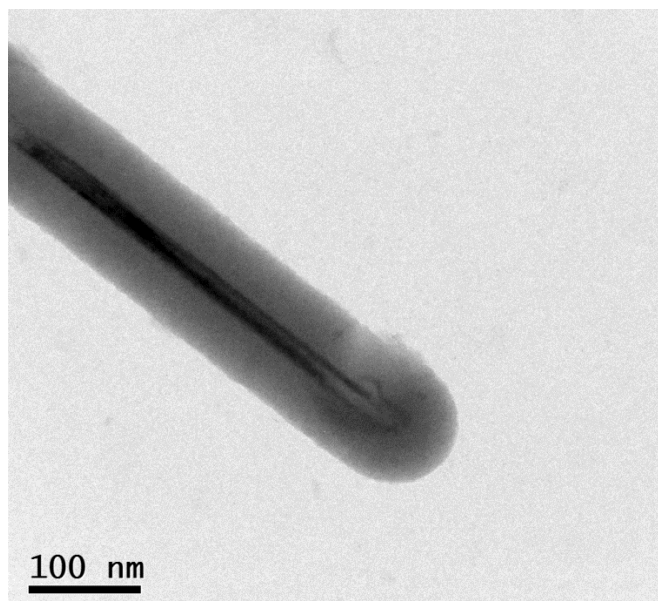


Peracetylated 3-deoxy-3-fluoro analogs of d-glucosamine and d-galactosamine

Silicon Nanowires Grown on Metal Substrates via Self-Catalyst Mechanism

(V. Dřínek, drinek@icpf.cas.cz; supported by GACR, project No. 13-25747S)

Low Pressure Chemical Vapor Deposition (LPCVD) was applied to grow Silicon Nanowires (SiNWs) without any heteroatom catalyst or special pretreatment of substrates used. Silane (SiH_4) as a precursor was pyrolyzed at 500 °C in an oven at molybdenum or iron substrates. NWs were several microns long, about 100 nm thick and possessed core-jacket structure. The thin core is composed of crystalline silicon oriented in $\langle 110 \rangle$ direction whereas the jacket is amorphous silicon. Unlike other approaches this one makes possible to avoid contamination caused by metal heteroatom seeds and/or applying special procedures for substrate pretreatment initializing/supporting NW growth. [Ref. 5]



A silicon nanowire with distinguished crystalline core and amorphous jacket

Novel sensors based on laser ablated graphene

(R. Fajgar, fajgar@icpf.cas.cz; supported by NATO, project No. 984399)

Graphene layers deposited by excimer laser ablation technique on a glass substrate were covered with silver and silver/gold alloy nanoparticles. The ability for Surface-Enhanced Raman Scattering (SERS) was demonstrated. In vacuum, metal nanoparticles with diameter between 10 and 25 nm reaching the polymer/graphene substrates induce graphitization of the graphene sheets as revealed by Raman spectroscopy. Ablation conditions were optimized to preserve graphene layers as a substrate for metal nanoparticles deposition in helium and argon atmosphere. The nanocomposites were characterized by means of spectroscopy, microscopy and diffraction techniques. The SERS substrate performance was tested using model compounds. Highly enhanced signal was observed and sensoric properties of the novel substrates were demonstrated. The substrates were optimized for detection of compounds, interesting from technological and medical aspects (e.g. methylviolet B, arsenazo, beryllon). [Ref. 15]

Sensoric properties of reduced graphene oxide/polymer composite towards pressure changes were demonstrated. The -OH functionalities on the rGO platelets and in the polymer chains were used as reactive sites, linked by the presence of NCO terminated polyurethane prepolymer. The film possesses improved mechanical properties and good bulk electrical conductivity, highly dependent on pressure changes. A sensor study was performed using a

developed device allowing to vary the impacting pressure continually. The mechanical pressure was changed and corresponding resistivity was recorded. The resistance was decreasing by 50% in a range from 0 to 0.2 MPa. Especially low pressures have important influence on the resistivity of the samples. We expect that mechanical pressure influences distribution of the graphene nanoplatelets in the composite which results in resistance changes. [Ref. 2]

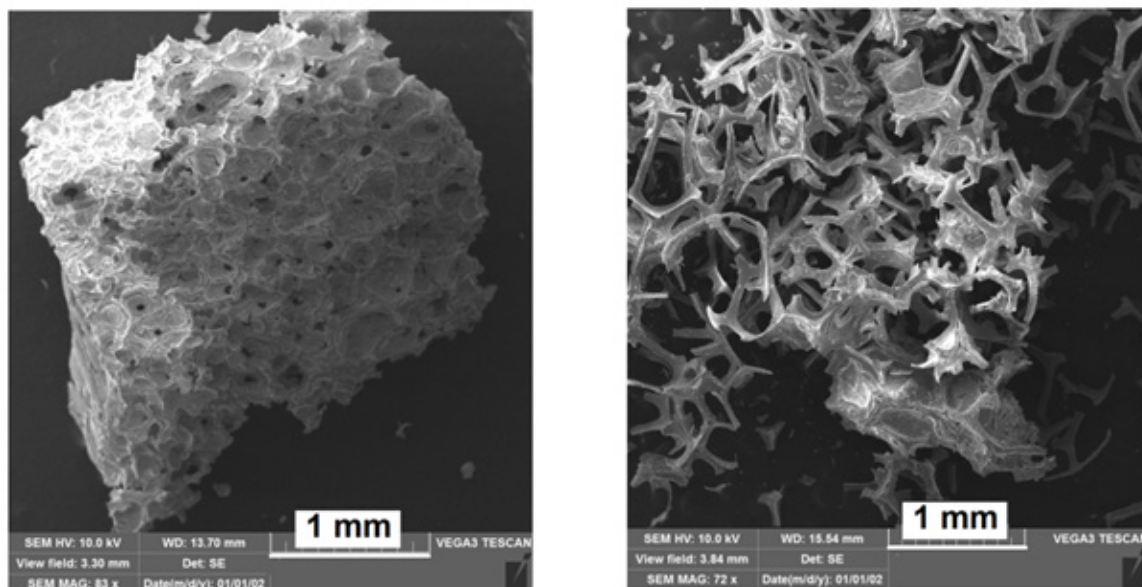
Highly efficient catalyst and process for degradation of resistant antibiotics

(J. Pola, pola@icpf.cas.cz; supported by TACR, project No. TA04020860)

The aim of the project is (a) the development and efficiency verification of a new-type nanocomposite heterogeneous catalysts for technological process of advanced oxidative degradation of refractory antibiotics occurring in waste waters, (b) the development and optimization of a model reactor for this process, (c) the development and optimization of a model technological process in combination with MBBR system for biological waste water post-treatment. The novel catalysts based on grains of ferrous spinels will be laser-immobilized on high surface mesostructured walls of macroporous glass/ceramic carriers and will have high priorities in efficient adsorption of pollutant molecules to high-surface mesoporous glass structure and in pollutants degradation taking place exclusively on the incorporated grains.

The catalytic systems will be prepared by laser ablative deposition from the bulk precursors using different laser irradiation sources, they will be characterized by physical and spectral methods before and after hydroperoxide treatment, and their catalytic efficiency in decomposition of hydroperoxide and degradation of a model refractory pollutant will be evaluated and compared.

Successful solution of partial objectives will significantly improve current complex technology for waste water treatment by additional decontamination stage. The suggested technology will prevent escape of resistant antibiotics and will decrease the content of residual products of waste water biological treatment to surface waters and will thereby eliminate increasing harmful effects of these drugs and other organic compounds in ecosystem.

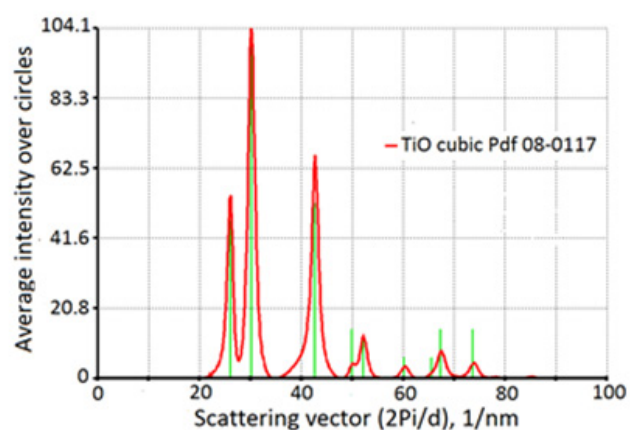
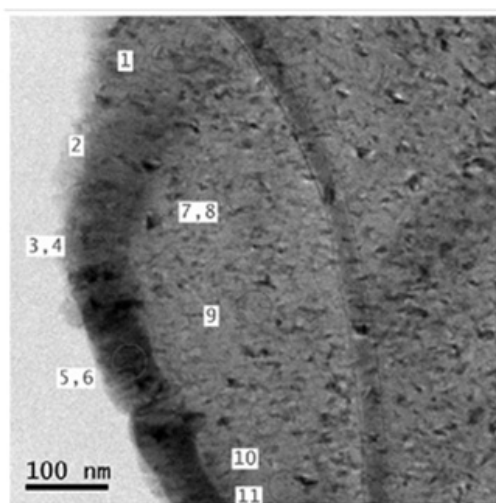


Representative structures of sol-gel-prepared samples of porous glass

Porous and macroporous titanium surfaces with embedded submicrometer-sized Si-, SiO_x- and TiO_x- moieties for enhancing bone osseointegration and adhesion to titanium implants

(J. Pola, pola@icpf.cas.cz; supported by TACR, project No. TA04010169)

The main goals of the project are the development and optimization of a new-type of biocompatible surfaces of titanium implants for enhanced osseointegration and adhesion of bone tissue, a know-how for the production of the novel model implants, and finally the fabrication of model samples for commercial sphere. The partial goals are (a) fabrication of macroporous surface layers of bulk titanium by using laser radiation-induced structural modification of titanium, (b) penetration of sol-gel polymerizing titania and silica precursors into these layers to achieve macro-porous bicontinuous titanasilicate structures, (c) laser-induced incorporation of SiO_x and TiO_x nanoparticles and hydrated SiO_x and TiO_x nanoparticles into these structures catalyzing the growth of bone tissue, and (d) incorporation of hydroxyapatite grains into these structures, which will serve as seeds of growing bone tissue.



TEM and EDS of films deposited by ArF laser ablation of titanium monoxide

International co-operations

Centre for Environmental Biotechnology, University of Tennessee, Knoxville, TN, USA:

Improved biomaterials for the encapsulation of living cells

Environmental Sciences Division Oak Ridge National Laboratories, Oak Ridge, TN, USA:

Application of nanomaterials and novel organic-inorganic materials in optical sensors

Graz University of Technology, Graz, Austria: ²⁹Si and ¹¹⁹Sn NMR

Institut de Chimie Moléculaire de Reims, CNRS 7312, France: ESI-MS of titanocene-containing dendrimers

Lehrstuhl für Organische Chemie I, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany: Chemistry of hetero[n]phenacenes

Faculty of Technology and Metallurgy, University of St. Cyril & Methodius, Skopje, Republic of Macedonia: Preparation of SERS active substrates based on graphene

King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia: Preparation of Ag/C nanocomposites by laser-induced carbonization of n-hexane

Southeast University, Department of Physics, Nanjing, China: Preparation of Ag/C nanocomposite by laser-induced carbonization of n-hexane

POLYMAT, Institute for Polymer Materials, San Sebastian, Spain: Laser ablation of graphene-based composites

Visitors

Despina Spaseska, University of St. Cyril & Methodius, Skopje, R. Macedonia

Akihiko Ouchi, National Institute of Advanced Industrial Research and Technology, Tsukuba, Japan

Helena Grennberg, Uppsala University, Sweden

Teaching

J. Čermák: UJEP, Faculty of Science, courses “Organic Chemistry I and II”, “Chemistry of Heterocyclic and Organometallic Compounds”, “Introduction to the Spectral Methods in Organic Chemistry”

G. Kuncová: UCT, Faculty of Chemical Engineering, postgraduate course “Optical Sensors for Measurement in Chemical and Biological Reactors”

Publications

Original papers

- [1] Andresová A., Storch J., Traikia M., Wagner Z., Bendová M., Husson P.: Branched and Cyclic Alkyl Groups in Imidazolium-Based Ionic Liquids: Molecular Organization and Physico-chemical Properties. *Fluid Phase Equilib.* 371, 41-49 (2014).
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