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Fields of research

- Bioremediation of organic pollutants in soil and sewage
- Immobilization of biocatalysts, living cells or enzymes, into organic or organic-inorganic matrices by sol-gel process
- Application of immobilized biocatalysts in optical sensors
- Dehydrocoupling reactions catalyzed by titanium complexes
- Structure of silyl moieties through $J(^{29}\text{Si}-^{13}\text{C})$ couplings as determined by triple $\{^1\text{H}, ^{13}\text{C}\}^{29}\text{Si}$ NMR experiment
- Synthesis of helicene derivatives
- Fluorinated carbosilane metallodendrimers

Applied research

- Enzymatically catalyzed synthesis of alkyd resins
- Development of new analytical methods
- Analytical services to the research departments of ICPF

Research projects

Monitoring and remediation of environmental pollution with advanced organic-inorganic materials – MOREPIM

(G. Kuncová, kuncova@icpf.cas.cz; supported by MEYS, KONTAKT, project No. ME 892)

The research has been focused on inorganic and organic-inorganic matrices, which are employed in design of whole cell optical fiber sensors, and on physiology of microorganisms immobilized inside these matrices. [Refs. 15, 23, 35, 36]

Whole cell optical sensors (WOCOS)

(G. Kuncová, kuncova@icpf.cas.cz; supported by MEYS, KONTAKT, project No. ME 893)

We demonstrated the model laboratory protocol of application of free cells of bioluminescent bioreporter *P. putida* TVA8 as a sensor of organic pollutants, which are dissolved in water. The heights of bioluminescence maxima were proportional to toluene concentration in the range 0–26 mg L⁻¹. Twenty-three organic pollutants (10³ × diluted saturated solutions) and the samples from wastewater treatment plant were tested as bioluminescent inducers. *P. putida* TVA8 do not respond in a linear manner, hence there is no direct correlation with the chemical concentration. However, after range finding, as is the case for chromatographic analysis, the luminescence values can be related to a dose–response curve. [Refs. 8, 9, 12]

BIO-OPT-XUV (BOX) Research Team Advancement at the Faculty of Biomedical Engineering, Czech Technical University in Prague

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

The aim of this project is to strengthen education and research with a focus on the interactions of the optical (OPT) and the extreme ultraviolet (XUV) radiation with biological objects (BIO), and to further build up a research team at the FBME/CTU.

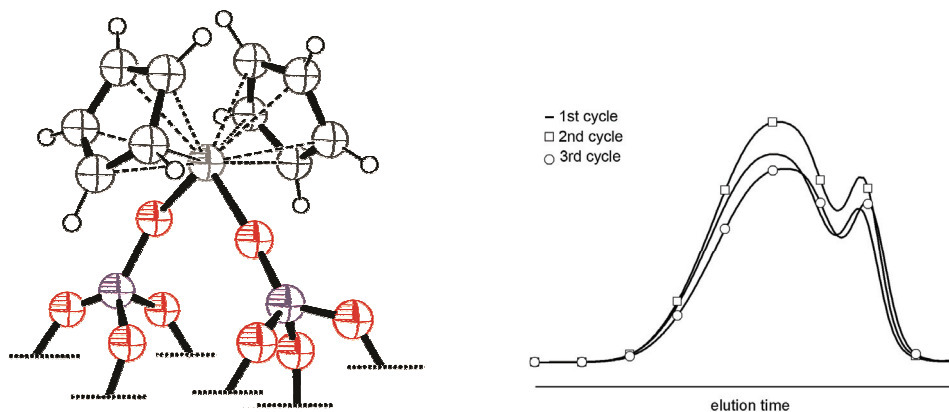
As a result, new innovative young academic workers (PhD and Master candidates in the fields of “Instruments and methods for biomedicine”) will be integrated into the existing team; the post-graduate education in this field will be updated, the existing XUV FBME laboratory’s international collaborative research will be advanced, and its infrastructure will be fortified by the introduction of new topics and methods.

Dehydrocoupling reactions catalyzed by titanium complexes

(J. Sýkora, sykora@icpf.cas.cz; joint project with JH IPC, and ICT, supported by GACR, grant No. 203/09/1574)

A series of zirconocene-siliceous catalysts were prepared and their catalytic performance and reusability was tested. [Refs. 4]

Products of dehydrocoupling polymerization reactions were monitored by advanced NMR techniques. The ¹J and ²J ²⁹Si INADEQUATE experiments were used to reveal the connectivities within oligosilane chains. The presence of the branched oligophenylsilanes was confirmed. Furthermore, the formation of silyl-substituted cyclic oligomers and the presence of branched oligophenylsilanes in the catalytic systems studied by other authors were discussed. [Refs. 24-27]



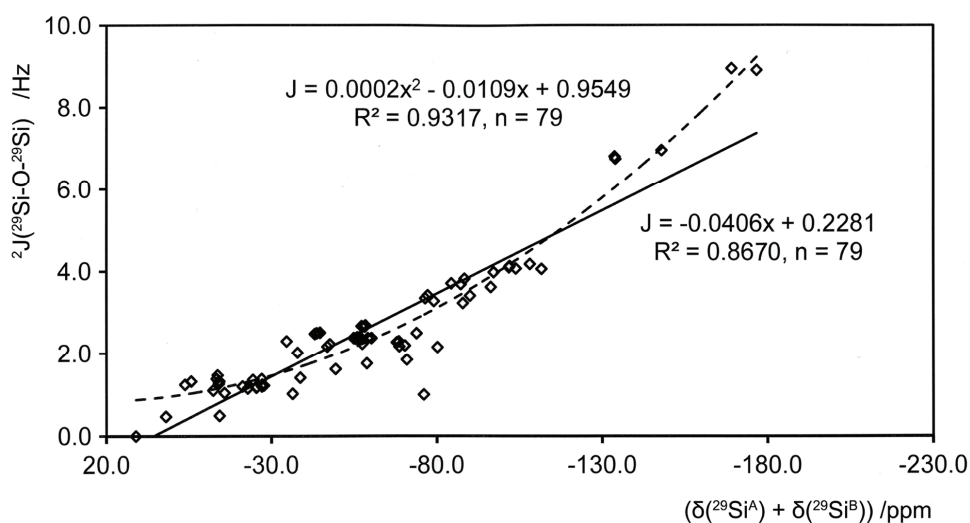
Analysis of Phenylsilane Polymers by Advanced ^{29}Si NMR

Structure of silyl moieties through $J(^{29}\text{Si}-^{13}\text{C})$ couplings as determined by triple $\{^1\text{H}, ^{13}\text{C}\}^{29}\text{Si}$ NMR experiment

(J. Schraml, schraml@icpf.cas.cz; supported by GA ASCR, grant No. IAA400720706)

Within the project new methods for measurement of spin-spin couplings of ^{29}Si and ^{13}C nuclei in solutions were developed. The two most significant results include "Geminal $^2J(^{29}\text{Si}-\text{O}-^{29}\text{Si})$ couplings in oligosiloxanes and their relation to direct $^1J(^{29}\text{Si}-^{13}\text{C})$ couplings" [Ref. 10] and "2D correlation spectra edited by the sign of relative coupling constant" [Ref. 1]. In the first of these two papers the values and signs of geminal spin-spin coupling constants $^{29}\text{Si}-\text{O}-^{29}\text{Si}$ of industrially important siloxanes were published for the first time. Using 75 constants determined in 55 compounds under identical conditions it was shown that these constants are positive and correlate with one-bond $^1J(^{29}\text{Si}-^{13}\text{C})$ couplings, with ^{29}Si chemical shifts and number of oxygenous substituents on the two silicon atoms involved.

In the second paper two new (CSEc and CSEh) pulse sequences were proposed. They allow editing of heteronuclear correlation spectra according to the signs of the selected heteronuclear coupling constants. The information about magnitude of the couplings is preserved. The methods achieve the sensitivity of E.COSY-type experiment. [Ref. 16, 17, 30-32].

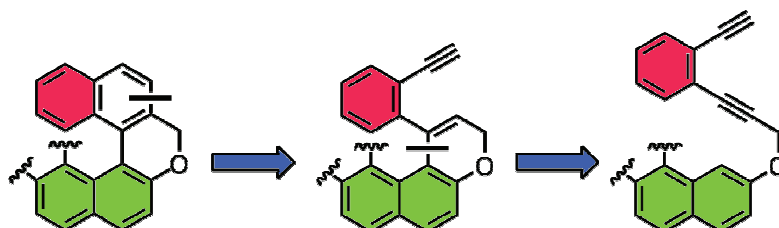


Dependence of $^2J(^{29}\text{Si}-\text{O}-^{29}\text{Si})$ coupling between silicon nuclei Si^{A} and Si^{B} on the sum of their chemical shifts

Synthesis of helicenes *via* cycloisomerization of biphenylnaphthalene and 1,8-diarylnaphthalene derivatives

(J. Čermák, J. Storch, cermak@icpf.cas.cz, storchj@icpf.cas.cz; supported by GACR, grant No. 207/10/1124)

Cycloisomerization of enynes catalyzed by complexes of transition metals represents simple, safe, and convenient to perform even on a larger scale, and therefore meet many of the stringent criteria imposed upon contemporary organic synthesis. In pursuit of our previous investigations in this field, we have described an alternative approach to helicene-like molecules based on a PtCl_x catalyzed tandem cycloisomerization reaction. Its retrosynthetic approach is depicted below. [Refs. 37, 38]

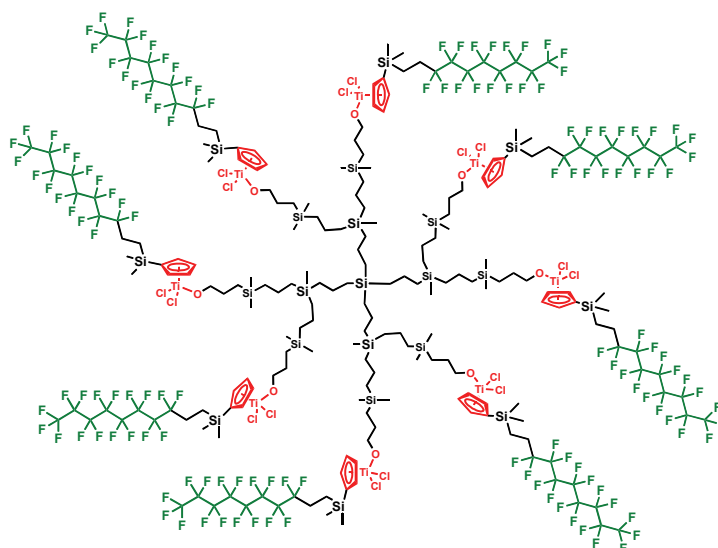


Retrosynthesis of tandem cycloisomerization leading to helicene-like molecules

The structure and synthetic applications of transition metal complexes

(J. Čermák, cermak@icpf.cas.cz; supported by MYES, project No. LC06070)

Dehydration of (perfluoroalkyl)tetramethylcyclopentenols which are the precursors to (perfluoroalkyl)tetramethylcyclopentadienes was studied in detail including kinetic analysis. The principal reaction products are *endo-endo* and *endo,exo* isomers of the cyclopentadienes and some of them are formed by consecutive isomerization from other isomers. Dendritic polyols of the second and third generation were prepared by hydroboration/oxidation, of allyl-terminated carbosilane dendrimers and used as supports for immobilization of cyclopentadienyltrichlorotitanium(IV) complexes through alcoholysis. Reaction of dendrimers with CpTiCl_3 gave metallodendrimers with eight or sixteen OTiCpCl_2 units, whereas the reaction with CpSiFTiCl_3 ($\text{CpSiF} = \text{C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17}$) provided peripherally fluorinated metallodendrimers. [Refs. 2, 18, 19, 21, 34]



Fluorinated metallodendrimer

Enzymatically catalyzed synthesis of alkyd resins (ENZALKYD)

(G. Kuncová, kuncova@icpf.cas.cz; joint project with SYNPO, a.s.; supported by MIT, project No. 2A-3TP1/108)

The project is aimed at application of regioselective lipase type enzyme catalysts in the first step of alkyd resin synthesis, so called alcoholysis, which is based on reesterification of vegetable oils with low molecular weight polyols. The used enzymes will be studied in immobilized form on solid organosilicate polymeric carriers. The developed technology of innovated production of alkyd resins will be more environmentally friendly, will lower cost and energy demands, will improve security of work, and help to form new or better quality products, and thus will increase the competitiveness of Czech products on the European market.

Enzymatic glycerolysis of soybean oil catalyzed with the commercial lipase catalyst Novozym 435 has been carried out at 45-52 °C in a stirred tank and fixed-bed reactor, using *tert*-butyl alcohol as a solvent. The effects of reaction conditions on the glycerolysis were evaluated and optimum parameters found for the monoacylglycerol (MAG) production (yield > 85 %). Unlike the batch glycerolysis, in the packed bed reactor, the catalyst retained its activity in long-term operation, regardless of the reaction conditions used. The continuous transesterification of the oil with trimethylolpropane (TMP) afforded a mixture of monoacyl- and diacylglycerols in 90 % yield. The high yield of monoacyl-TMP (71 %) along with 24 % of 1-monoacyl- and 5 % of 2-monoacylglycerol gives evidence of the efficiency of the process. [Ref. 3]

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: ^{29}Si and ^{119}Sn NMR

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

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: ICT, Faculty of Chemical Engineering, postgraduate course “Optical sensors for measurement in chemical and biological reactors”

Publications

Original papers

- [1] Blechta V., Schraml J.: 2D Correlation Spectra Edited by the Sign of Relative Coupling Constant. *Magn. Reson. Chem.* 49(3), 111-116 (2011).
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- [6] Kubec R., Krejčová P., Šimek P., Václavík L., Hajšlová J., Schraml J.: Precursors and Formation of Pyrithione and Other Pyridyl-Containing Sulfur Compounds in Drumstick Onion, *Allium stipitatum*. *J. Agric. Food. Chem.* 59(10), 5763-5770 (2011).
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- [9] Kuncová G., Pazlarová J., Hlavatá A., Ripp S., Sayler G.S.: Bioluminescent Bioreporter *Pseudomonas putida* TVA8 as a Detector of Water Pollution. Operational Conditions and Selectivity of Free Cells Sensor. *Ecol. Indic.* 11(3), 882-887 (2011).
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- [12] Rychtáriková R., Kuncová G.: Metoda vyhodnocování antimikrobiální aktivity počítačovým prahováním barev. (Czech) Assessment of Antimicrobial Activity via Computational Tresholding of Colours. *Chem. Listy* 105(6), 493-498 (2011).
- [13] Schraml J., Kubec R., Kučerová P.: Determination of Substitution Sites in Monosubstituted Five-Membered Aromatic Heterocycles. *Magn. Reson. Chem.* 49(3), 147-150 (2011).
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Review papers

- [15] Kuncová G., Trögl J.: Mikroorganismy imobilizované do anorganických nosičů. (Czech) Living Microorganisms Immobilized in Inorganic Matrices. *Chem. Listy* 105(11), 830-838 (2011).

International conferences

- [16] Blechta V., Schraml J.: Detection of Signed Homonuclear Couplings between Low Abundant Nuclei. 26th NMR Valtice, Book of Abstracts, C-16, Valtice, Czech Republic, 1-4 May 2011.
- [17] Blechta V., Schraml J.: Detection of NMR Spectra Edited by Signs of Coupling Constants. Magnetic Moments in Central Europe, Program and Book of Abstracts, p. 16, Tatranská Lomnica, Slovakia, 16-20 March 2011.

- [18] Čermák Jan, Strašák T.: Carbosilane Dendrimers Decorated with Titanocene Dichloride. 7th International Dendrimer Symposium, Program and Abstracts, p. 63 (B1.5), Gaithersburg, Maryland, USA, 26 June - 1 July 2011.
- [19] Čermák Jan, Strašák T.: Titanocene Dichloride Immobilization on Carbosilane Dendrimers. 19th EuCheMS International Conference on Organometallic Chemistry, Book of Abstracts, P008, Toulouse, France, 3-7 July 2011.
- [20] Kaluža L., Sýkora J., Karban J., Žáček P., Vít Z., Zdražil M.: Hydrodesulfurization of Model Feed Containing Olefins over Al₂O₃, TiO₂, and ZrO₂ Supported Transition Metal Sulfides. 8th European Congress of Chemical Engineering, Programme, P19.01, Berlin, Germany, 25-29 September 2011.
- [21] Krupková A., Čermák Jan: Carbosilane Titanium Metallodendrimers with Polyfluoroalkylated Cyclopentadienyl Ligands. International Symposium on Fluorous Technologies 2011 (ISOFT'11), Programme and Abstracts, P-8, Hong Kong, Hongkong, 30 November - 3 December 2011.
- [22] Křišťál J., Drhová M., Jiříčný V., Kuncová G.: Microreactor Flow System for Enzymatic Reactions. CAMURE-8 & ISMR-7, Book of Abstracts, p. 149, Naantali, Finland, 22-25 May 2011.
- [23] Kuncová G., Šabata S., Kučerová L., Fuzik T., Duchek P.: Lipases in Hierarchically Structured Montmorillonite. XIXth International Conference on Bioencapsulation, Posters, pp. 116-117, Amboise, France, 5-8 October 2011.
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- [25] Pinkas J., Blechta V., Karban J., Sýkora J.: ²⁹Si NMR Phenylsilane Polymer Analysis. 26th NMR Valtice, Book of Abstracts, C-20, Valtice, Czech Republic, 1-4 May 2011.
- [26] Pinkas J., Merna J., Sýkora J.: LC-NMR Analysis of Phenylsilane Polymers. 43rd Symposium on Catalysis, Program and Book of Abstracts, Praha, Czech Republic, 7-8 November 2011.
- [27] Pinkas J., Merna J., Sýkora J.: From Nanocatalysts to Reusable Heterogeneous Catalysts in Phenylsilane Dehydropolymerization. Zing Nanomaterials Conference 2011, Abstracts - Posters, p. 66 (P11), Xcaret, Mexico, 28 November - 02 December 2011.
- [28] Sajfřtová M., Pavela R., Karban J.: Vliv podmínek superkritické extrakce na insekticidní účinky výtažků z routy vonné. (Czech) Effect of Conditions of Supercritical Fluid Extraction on Insecticidal Activity of Isolates from Rue. 58. Konference chemického a procesního inženýrství CHISA 2011, Sborník, p. 166 (V39), Srní, Šumava, Czech Republic, 24-27 October 2011.
- [29] Sajfřtová M., Rochová K., Karban J., Sovová H., Pavela R.: Supercritical Fluid Extraction of Botanical Insecticides from Rue. 11th International Conference on Carbon Dioxide Utilization, Program and Abstracts, p. 207, Dijon, France, 27-30 June 2011.
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- [31] Schraml J., Kurfürst M., Blechta V.: Empirical and Not-so-Empirical Correlations Holding for ²J(²⁹Si-O-²⁹Si) Couplings in Industrially Important Siloxanes. 26th NMR Valtice, Book of Abstracts, C-19, Valtice, Czech Republic, 1-4 May 2011.
- [32] Schraml J., Kurfürst M., Blechta V.: The Relative Signs of Coupling Constants from Inadequate Experiment of Equivalent Nuclei - an Educational Example. Magnetic Moments in Central Europe, Program and Book of Abstracts, p. 20, Tatranská Lomnica, Slovakia, 16-20 March 2011.
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- [38] Bernard M., Sýkora J., Storch J.: Design and Synthesis of Helicene like Molecules. 43rd Symposium on Catalysis, Program Book of Abstracts, P04A, Praha, Czech Republic, 07-08 November 2011.