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Professor Yulia Budnikova

A Tribute

This special issue of Arkivoc is dedicated to Professor Yulia H. Budnikova in recognition of her 35 years of experience in science and to acknowledge her contribution to organic electrochemistry

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Yulia Hermanovna Budnikova was born on 10th October, 1965 in Kazan to scientists-chemists Herman K. Budnikov and Tat'yana V. Troepolskaya. In 1987 she graduated from Kazan State University with a Diploma in Chemistry. She began her 35-year research career at the A.E. Arbuzov IOPC. She joined the group of Yu. M. Kargin studying electrochemically induced processes in the formation of organophosphorus compounds and obtained her PhD in this field in 1990. Over the years of work in the Institute, she has gone from Junior Researcher to the Principal Investigator, and in 2008 she became the Head of Laboratory of Electrochemical Synthesis. Her dedication, great capacity for work and ability to find the right solution allowed her to obtain her Doctor of Science (DSc) degree in 1999 on the topic of "Mechanisms of homogeneous electrochemical reactions in the breaking and formation of phosphorus and carbon bonds".

To date, YHB has published more than 200 scientific articles in Russian and international journals devoted to the electrosynthesis, catalysis and reactivity of organoelement compounds. She has published several reviews on important areas of chemistry, authored one book and four chapters in monographs. Among her scientific publications there is research performed in cooperation with well-known specialists from leading institutions in Russia, France, Italy, Germany, Kazakhstan, and Moldova. She is currently collaborating in various fields of chemistry with scientists from the USA, Germany, and China.

The scientific projects of Professor Budnikova have been supported by Russian and international grants (Russian Science Foundation, RFBR, INTAS), including a joint RFBR-NSF grant (USA), a grant from the President of the Russian Federation, the Ministry of Education and Science of Russian federation, and the Programs of the OKHNM RAS.

Professor Budnikova is a Laureate of the LA Chugaev Prize 2018 - for outstanding work in the of chemistry of complex compounds, namely, "Coordination compounds in the electrochemical synthesis of effective catalysts and electrocatalysts of practically significant reactions" and is an Honored Scientist of the Republic of Tatarstan. In her leisure time, YHB enjoys collecting art and winemaking.

Research Interests

In her very first publication in 1990 Professor Budnikova studied the electrochemical synthesis of phosphorus derivatives from elemental phosphorus, and since that time she has been interested in the redox reactivity of organoelemental compounds and their practical applications in organic synthesis. Her research interests over the years have been broadly based, but include three main areas: (i) electrochemically induced transformations of organophosphorus compounds, (ii) redox properties and reactivity of organometallics and heterocycles and(iii) functionalization of C-H bonds under electrocatalytic conditions.

The strategy proposed by Professor Budnikova for the electrochemical synthesis of transition metal complexes — effective catalysts or electrocatalysts, as well as key intermediates of significant reactions (oligomerization/functionalization of olefins, synthesis of organophosphorus and other organoelemental compounds with carbon-element bonds) is, a symbiosis of organic electrosynthesis, catalysis, materials science, bio- and environmental chemistry. Most of her publications belong to the first quarterly high-ranking journals.

Professor Budnikova and co-workers utilized electrochemical methods for preparation of various tertiary phosphines on the basis of cross-coupling reactions of diphenylchloro- and phenyldichlorophosphines with aryl halides or C-halogen derivatives of sulfur- or nitrogen-containing heterocycles.[1] The method was shown to be efficient for both aromatic halides with acceptor and donor substituents in the ring and also heteroaromatic species (pyridine, thiophene, pyrimidine and pyrazole halides) giving yields of 45 to 70 %.

Professor Budnikova's research had a significant impact in the field of white phosphorus chemistry. White phosphorus P_4 is a key material for chlorine-free technologies in the synthesis of various organophosphorus compounds. It was found, P_4 could be efficiently converted to phosphines and phosphine

oxides electrocatalytically using transition metal complexes as catalysts under mild conditions.[2] The procedure was also applied to fluoroalkyl phosphines and phosphine oxides syntheses from–white phosphorus and organofluorine halides under the influence of electrochemically generated complexes of nickel or organofluorine nickel σ-complexes.[3]

Professor Budnikova and co-workers developed a ligand -directed phosphonation of C–H aromatic bonds based on C-H activation on palladium catalyts leading to arylphosphonates. In order to empower the ligand -directed phosphonation of C–H aromatic bonds, a series of diphosphonate-bridged dipalladacycles $[(phpy)Pd((EtO)_2P(O))]_2$, $[(bhq)Pd((EtO)_2P(O))]_2$, $[(phpz)Pd(((EtO)_2P(O))]_2$ (phpy = 2-phenylpyridine, bhq = benzo[*h*]quinoline, phpz = 1-phenylpyrazole) was prepared and fully characterized using cyclic voltammetry techniques[4] to elucidate their redox properties, stability in higher oxidation states and the influence of aromatic ligands on the potentials of Pd(III)/Pd(II) and Pd(IV)/Pd(III) transfers. The geometry of the bridged dinuclear Pd complexes was shown to depend on the nature of the bridging ligands and which affects their redox reactivity.

Another single-stage method of direct electrochemical phosphorylation of aromatic C–H bonds resulting in dialkyl aryl phosphonates (aryl = benzene, coumarins) was reported by Professor Budnikova exploiting a novel bimetallic catalyst system Mn^{II}bpy/Ni^{II}bpy. The process occurred under mild conditions with a 1 : 1 reagent ratio giving products in 70 % yields.[5]

Professor Budnikova has developed promising catalysts for hydrogen power engineering based on original redox-active organometallic coordination polymers (MOF) constructed on the basis of phosphine (ferrocenyl-, arylphosphine, etc.) and metallo (Ni, Co, Zn, etc.) - bipyridine blocks.[6-8]

New synthetic analogs of natural hydrogenases based on nickel complexes with cyclic P, N-ligands or pectins as efficient catalysts for the electrochemical generation of hydrogen and its oxidation in fuel cells have been developed by Budnikova's group.[9,10]

A selective oxidative electrochemical functionalization of the C (sp2) -H bond (amination, phosphonation, fluoroalkylation), catalyzed by metal complexes in higher oxidation states, in solution or using catalysts immobilized on silicate nanoparticles, has been realized.[11-16]

A new electrochemical method for the study of insoluble compounds, complexes with charge transfer, nonlinear optical materials, chromophores has been developed.[17-20] New electrochemical approaches to the design and prediction of the efficiency of NLO chromophores have been proposed, based on the electrochemical characteristics of both fragments of complex chromophore molecules and conjugated donor-acceptor systems with intramolecular electron transfer.

Selected Publications

1. "Electron transfer in organonickel complexes of α-diimines: Versatile redox catalysts for C–C or C–P coupling reactions – A review", Klein, A.; Budnikova, Yu. H.; Sinyashin, O. G. *J. Organomet. Chem.* **2007**, *692*, 3156-3166. https://doi.org/10.1016/j.jorganchem.2007.01.021
2. **"**Organic chemistry of elemental phosphorus**"** Milyukov V. A.; Budnikova, Yu H.; Sinyashin O. G**.** *Russian Chem. Rev.* **2005**, *74*, 781 **–** 805**.** https://doi.org/10.1070/RC2005v074n09ABEH001182
3. "Novel electrochemical pathway to fluoroalkyl phosphines and phosphine oxides" D. Y. Mikhaylov, T. V.; Gryaznova, Y. B.; Dudkina, F. M.; Polyancev, Sh. K.; Latypov, O. G.; Sinyashin, Y. H.; Budnikova, *J. Fluorine Chem.* **2013**, *153*, 178-182.

https://doi.org/10.1016/j.jfluchem.2013.04.009

4. "Electrochemical properties of diphosphonate-bridged palladacycles and their reactivity in arene phosphonation" Gryaznova, T.; Dudkina, Y.; Khrizanforov, M.; Sinyashin, O.; Kataeva, O.; Budnikova, Y. *J. Solid State Electrochem.* **2015**, *19*, 2665 – 2672. https://doi.org/10.1007/s10008-015-2875-y
5. "Novel approach to metal-induced oxidative phosphorylation of aromatic compounds" Khrizanforov M.N.; Strekalova S. O.; Kholin K. V.; Khrizanforova V. V.; Kadirov M. K.; Gryaznova T. V.; Budnikova Y. H. *Catalysis Today* **2017**, *279*, 133 – 141. https://doi.org/10.1016/j.cattod.2016.06.001
6. "Synthesis, structure, and electrochemical properties of 4,5-diaryl-1,2,3-triphosphaferrocenes and the first example of multi(phosphaferrocene)" Petrov A. V.; Zagidullin A. A.; Bezkishko I. A.; Khrizanforov M. N.; Kholin K. V.; Gerasimova T. P.; Ivshin K. A.; Shekurov R. P.; Katsyuba S. A.; Kataeva O. E.; Budnikova Yu. H.; Miluykov V. A. *Dalton Trans.* **2020**, *49*, 17252-17262. https://doi.org/10.1039/D0DT03281F
7. "3D Ni and Co Redox-Active Metal-Organic Frameworks Based on Ferrocenyl Diphosphinate and 4,4'-Bipyridine Ligands as Efficient Electrocatalysts for Hydrogen Evolution Reaction" Khrizanforova V.; Shekurov R. P.; Milyukov V. A.; Khrizanforov M.; Bon V.; Kaskel S.; Gubaidullin A. T.; Sinyashin O. G.; Budnikova Y. H. *Dalton Trans.* **2020**, *49*, 2794 – 2802. https://doi.org/10.1039/C9DT04834K
8. "Zn and Co redox active coordination polymers as efficient electrocatalysts" Shekurov R.; Khrizanforova V.; Gilmanova L.; Khrizanforov M.; Miluykov V.; Kataeva O.; Yamaleeva Z.; Burganov T.; Gerasimova T.; Khamatgalimov A.; Katsyuba S.; Kovalenko V.; Krupskaya Y.; Kataev V.; Büchner B.; Bon V.; Senkovska I.; Kaskel S.; Gubaidullin A.; Sinyashin O.; Budnikova Y. *Dalton Transactions* **2019**, *48*, 3601 – 3609. https://doi.org/10.1039/C8DT04618B
9. "A nickel-based pectin coordination polymer as an oxygen reduction reaction catalyst for proton-exchange membrane fuel cells" Kadirov M. K.; Minzanova S.; Nizameev I.; Mironova L. G.; I. Gilmutdinov I., Khrizanforov M.; Kholin K. V.; Khamatgalimov A. R.; Semenov V.; Morozov V.; Kadirov D. M.; Mukhametzyanov A.; Budnikova Y. H.; Sinyashin O. G. *Inorg. Chem. Front.* **2018**, *5*, 780-784. https://doi.org/10.1039/C7QI00770A
10. "In situ electrochemical synthesis of Ni(I) complexes with aminomethylphosphines as intermediates for hydrogen evolution" Khrizanforova V. V.; Morozov V. I.; Strelnik A. G.; Spiridonova Yu. S.; Khrizanforov M.N.; Burganov T.; Katsyuba S. A.; Latypov Sh. K.; Kadirov M. K.; Karasik A. A.; Sinyashin O. G.; Budnikova Y. H. *Electrochimica Act* **2017**, *225*, 467–472. https://doi.org/10.1016/j.electacta.2016.12.081
11. "Electrochemically Driven and Acid-Driven Pyridine-Directed *ortho*-Phosphorylation of C(sp^2)–H Bonds" Gryaznova T. V.; Khrizanforov M. N.; Levitskaya A. I.; Rizvanov I. Kh.; Balakina M. Yu.; Ivshin K. A.; Kataeva O. N.; Budnikova Yu. H *Organometallics* **2020**, *39*, 2446–2454. https://doi.org/10.1021/acs.organomet.0c00247
12. "Copper or Silver-Mediated Oxidative C(sp^2)–H/N–H Cross-Coupling of Phthalimide and Heterocyclic Arenes: Access to N-Arylphthalimides" Gryaznova T. V.; Kholin K. V.; Nikanshina E. O.; Khrizanforova V. V.; Strekalova S. O.; Fayzullin R. R.; Budnikova Y. H. *Organometallics* **2019**, *38*, 3617-3628. https://doi.org/10.1021/acs.organomet.9b00443

13. "Nano-architecture of silica nanoparticles as a tool to tune both electrochemical and catalytic behavior of Ni^{II}@SiO_2" Khrizanforov M. N., Fedorenko S. V.; Mustafina A. R., Khrizanforova V. V.; Kholin K. V.; Nizameev I. R.; Gryaznova T. V.; Grinenko V. V.; Budnikova Y. H. *RSC Adv.* **2019**, *9*, 22627–22635. https://doi.org/10.1039/C9RA03421H
14. "Cobalt-Catalyzed Green Cross-Dehydrogenative C(sp^2)-H/P-H Coupling Reactions" Khrizanforov M.; Strekalova S.; Khrizanforova V.; Dobrynin A.; Kholin K.; Gryaznova T.; Grinenko V.; Gubaidullin A.; Kadirov M. K.; Budnikova Y. *Topics in Catalysis* **2018**, *61*, 1949–1956. https://doi.org/10.1007/s11244-018-1014-2
15. "Cyclometalated Nickel Complexes as Key Intermediates in C(sp^2)–H Bond Functionalization: Synthesis, Catalysis, Electrochemical Properties, and DFT Calculations" Dudkina Y. B.; Fayzullin R. R.; Lyssenko K. A.; Gubaidullin A. T.; Kholin K. V.; Levitskaya A. I.; Balakina M. Yu.; Budnikova Y. H. *Organometallics* **2019**, *38*, 1254–1263. https://doi.org/10.1021/acs.organomet.8b00536
16. "Novel approach to metal-induced oxidative phosphorylation of aromatic compounds" Khrizanforov M. N., Strekalova S. O.; Kholin K. V.; Khrizanforova V. V.; Kadirov M. K.; Gryaznova T. V.; Y. H. Budnikova Y. H. *Catalysis Today* **2017**, *279*, 133–141 https://doi.org/10.1016/j.cattod.2016.06.001
17. "Considerations on electrochemical behavior of NLO chromophores: Relation of redox properties and NLO activity" Budnikova Y. H.; Dudkina, Yu. B.; Kalinin A. A.; Balakina, M. Yu. *Electrochimica Acta* **2021**, *368*, 137578. https://doi.org/10.1016/j.electacta.2020.137578
18. "D-π-A chromophores with a quinoxaline core in the π-bridge and bulky aryl groups in the acceptor: Synthesis, properties, and femtosecond nonlinear optical activity of the chromophore/PMMA guest-host materials" Kalinin A. A.; Islamova L. N.; Shmelev A. G.; Fazleeva G. M.; Fominykh O. D.; Dudkina Y. B.; Vakhonina T. A.; Levitskaya A. I.; Sharipova A. V.; Mukhtarov A. S.; Khamatgalimov A. R.; Nizameev I. R.; Budnikova Y. H.; Balakina M. Yu. *Dyes and Pigments* **2021**, 184. https://doi.org/10.1016/j.dyepig.2020.108801
19. "Composing NLO chromophore as a puzzle: electrochemistry-based approach to the design and effectiveness" Budnikova Y. H.; Dudkina Y. B.; Kalinin A. A.; Fazleeva G. M.; Sharipova S. M.; Islamova L.N.; Dobrynin A. B.; Islamov D. R.; Levitskaya A. I.; Balakina M. Yu. *Chem. Phys. Chem.* **2021**, *22*, 1-22. https://doi.org/10.1002/cphc.202100506
20. "D-π-A'-π-A chromophores with quinoxaline core in the π-electron bridge and charged heterocyclic acceptor moiety: Synthesis, DFT calculations, photophysical and electro-chemical properties" Kalinin, A. A., Sharipova, S. M.; Levitskaya, A. I.; Dudkina Y. B.; Burganov T. I.; Fominykh O. D.; Katsyuba S. A.; Budnikova, Y. H.; Balakina, M. Y. *J. Photochem. Photobiol. A* **2021**, *407*, 113042. https://doi.org/10.1016/j.jphotochem.2020.113042