PhD STUDIES COURSE UNIT DESCRIPTION

Name of subject	Field of science, code	Faculty / Center	Department
Organometallic Chemistry	Chemistry N 003	Faculty of Geosciences and Chemistry/institute of Chemistry	Department of Organic Chemistry
Student's workload	**Credits**	**Student's workload**	**Credits**
Lectures	3	Consultations	1
Independent study	4	Seminars	1

Course annotation

Classification, nomenclature of organometallic compounds. Origin of bond "carbon-metal". π-complexes, stability of organometallic complexes. Ligands. Organomagnessium compounds, their structure, methods of synthesis, properties. Synthesis of polyfunctionalized Grignard reagents and application in organic synthesis. Organolithium compounds, their stucture, methods of synthesis and chemical properties, influence of aggregation, structure peculiarities and ligands on the reactivity of organolithium compounds. Ortho- and transmetallation reactions. Organotin compounds. Trialkyltin halogenides, stannanes: synthesis, properties, applications in organic synthesis. Radical halogen hydrogenolysis and alkylation of activated double bond by alkyl halogenides in the presence stannanes (formation of C-C bond). Organocopper compounds, their structure, synthesis and reactivity. Regio and stereoselectivity of reactions. Application of mixed organocuprates in synthesis of organic compounds. Organoboron compounds Boranes, their structure. Alkyl boranes (ThBH2, 9-BBN, Sia2BH and others), chiral boranes (Lgf_2BH, $IpcBH_2$, Ipc_2BH and others), organoboronic acids and esters. Regio- and stereoselectivity of hydroboration reaction and other chemical properties of organoboranes (protonolysis, halogenolysis, carbonylation cyanidation reactions, etc.), application in the synthesis of various classes of organic compounds. Organosilicon compounds. Comparison of carbon and silicon. Organic silanols and silicones. Silenes and polysilenes. Vinyl, aryl, alyl, acyl silanes: synthesis and reactions with electrophilic reagents. Brook rearrangement. Enolic silylethers, silylacetals: synthesis and properties. □-Hydroxysilanes. Peterson reaction. Transition metal catalysis reactions. C-C, C-O, C-N bonds formation reactions, their application for the synthesis of aryl and heteroaryl organic compounds. Palladium(0) catalyzed reactions. Steps of catalysis cycle, stereochemistry. Heck reaction, its regio- and stereochemistry. Cross-coupling reactions (Suzuki, Stille, Sonogashira, Negishi, Kumada reactions. Organonickel compounds. Structure. Formation. Ni catalysed cross-coupling reactions, C-C bond formation by Ni-catalyzed photoredox reactions. Advantages and disadvantages of organonickel compounds in organic synthesis.

Reading list

Scientific articles in international science journals such as J. Organomet. Chem.; Organometallics, Advanced Synthesis and Catalysis, JACS, J. Org. Chem, ACIE, Org. Letters, J. Materials chemistry C, Chem. Materials, etc.
Sigitas Tumkevičius. Chemistry of Organometallics (in Lithuanian). – Vilnius: UAB TEV, 2012, 202 p.
Gary O. Spessard, Gary L. Miessler. Organometallic Chemistry. 2nd Ed. Oxford University Press, 2009, 752p.
Modern Organonickel Chemistry. Ed. Y. Tamaru. WILEY-VCH, 2005, 327 p.
P. R. Jenkins. Organometallic Reagents in Synthesis. - New York: Oxford University Press, 2001.
Metal-Catalyzed Cross-Coupling Reactions, Second, Completely Revised and Enlarged Edition, 2004 Eds: Armin de Meiejere, Francois Diederich.
J. Tsuji. Palladium Reagents and Catalysts. Innovations in Organic Synthesis.-J.Wiley and Sons, 1999, 560 p.

The names of consulting teachers	Science degree	Main scientific works published in a scientific field in last 5 year period
Jelena Dodonova-Vaitkūnienė (main) Sigitas Tumkevičius	Dr. Habil. Dr.	1. Polita, Artūras; Žvirblis, Rokas; Dodonova-Vaitkūnienė, Jelena; Shivabalan, Arun Prabha; Maleckaitė, Karolina; Valinčius, Gintaras. Bimodal effects on lipid droplets induced in cancer and non-cancer cells by chemotherapy drugs as revealed with a green-emitting BODIPY fluorescent probe // Journal of materials chemistry B. Cambridge : Royal Society of Chemistry. ISSN 2050-750X.

		eISSN 2050-7518. 2024, vol. 12, iss. 12, p. 3022-3030. DOI: 10.1039/d3tb02979d. 2. Serevičius, Tomas; Skaisgiris, Rokas; Tumkevičius, Sigitas; Dodonova-Vaitkūnienė, Jelena; Juršėnas, Saulius Antanas. High reverse intersystem crossing rate diminishes the impact of conformational disorder phenomenon in solid-state TADF // Advanced optical materials. Weinheim : John Wiley and Sons Inc. eISSN 2195-1071. 2024, vol. 12, iss. 36, art. no. 2401819, p. [1-6]. DOI: 10.1002/adom.202401819. 3. Polita, Artūras; Stancikaitė, Milda; Žvirblis, Rokas; Maleckaitė, Karolina; Dodonova-Vaitkūnienė, Jelena; Tumkevičius, Sigitas; Shivabalan, Arun Prabha; Valinčius, Gintaras. Designing a green-emitting viscosity-sensitive 4,4-difluoro-4-bora-3a,4a-diaza- s -indacene (BODIPY) probe for plasma membrane viscosity imaging // RSC advances. Cambridge : Royal Society of Chemistry (RSC). ISSN 2046-2069. eISSN 2046-2069. 2023, vol. 13, iss. 28, p. 19257-19264. DOI: 10.1039/D3RA04126C. 4. Žvirblis, Rokas; Maleckaitė, Karolina; Dodonova-Vaitkūnienė, Jelena; Jurgutis, Džiugas; Žilėnaitė, Rugilė; Karabanovas, Vitalijus; Tumkevičius, Sigitas; Vyšniauskas, Aurimas. A red-emitting thiophene-modified BODIPY probe for fluorescence lifetime-based polarity imaging of lipid droplets in living cells // Journal of materials chemistry B. Cambridge : Royal Society of Chemistry. ISSN 2050-750X. eISSN 2050-7518. 2023, vol. 11, iss. 17, p. 3919-3928. DOI: 10.1039/d3tb00305a. 5. Serevičius, Tomas; Skaisgiris, Rokas; Banevičius, Dovydas; Tumkevičius, Sigitas; Dodonova-Vaitkūnienė, Jelena; Juršėnas, Saulius Antanas. Modulation of nonradiative emission decay rate by spacer unit in donor-acceptor TADF compounds // Dyes and pigments. London : Elsevier. ISSN 0143-7208. eISSN 1873-3743. 2023, vol. 220, art. no. 111711, p. [1-6]. DOI: 10.1016/j.dyepig.2023.111711. 6. Tomas Serevičius, Rokas Skaisgiris, Sigitas Tumkevičius, Jelena Dodonova-Vaitkūnienė, Saulius Juršėnas. Understanding the temporal dynamics of thermally activated delayed fluorescence in solid hosts // Journal of materials chemistry C. Cambridge : Royal Society of Chemistry (RSC). 2023, vol. 11, iss. 36, p. 12147-12155. DOI: 10.1039/D3TC02347H. 7. Polita, Artūras; Stancikaitė, Milda; Žvirblis, Rokas; Maleckaitė, Karolina; Dodonova-Vaitkūnienė, Jelena; Tumkevičius, Sigitas; Shivabalan, Arun Prabha; Valinčius, Gintaras. Designing a green-emitting viscosity-sensitive 4,4-difluoro-4-bora-3a,4a-diaza- s -indacene (BODIPY) probe for plasma membrane viscosity imaging // RSC advances. Cambridge : Royal Society of Chemistry (RSC). ISSN 2046-2069. eISSN 2046-2069. 2023, vol. 13, iss. 28, p. 19257-19264. DOI: 10.1039/D3RA04126C. 8. Maleckaitė, Karolina; Narkevičius, Domantas; Žilėnaitė, Rugilė; Dodonova-Vaitkūnienė, Jelena; Toliautas, Stepas; Tumkevičius, Sigitas; Vyšniauskas, Aurimas. Give or take: effects of electron-accepting/-withdrawing groups in red-

		fluorescent BODIPY molecular rotors // Molecules. Basel : MDPI AG. eISSN 1420-3049. 2022, vol. 27, iss. 1, art. no. 23, p. 1-14. DOI: 10.3390/molecules27010023. 9. Serevičius, Tomas; Skaisgiris, Rokas; Dodonova-Vaitkūnienė, Jelena; Fiodorova, Irina; Genevičius, Kristijonas; Tumkevičius, Sigitas; Kazlauskas, Karolis; Juršėnas, Saulius Antanas. Temporal dynamics of solid-state thermally activated delayed fluorescence: disorder or ultraslow solvation? // Journal of physical chemistry letters. Washington : American Chemical Society. ISSN 1948-7185. 2022, vol. 13, no. 7, p. 1839-1844. DOI: 10.1021/acs.jpclett.1c03810. 10. Jurgutis, Džiugas; Jarockytė, Greta; Poderys, Vilius; Dodonova-Vaitkūnienė, Jelena; Tumkevičius, Sigitas; Vyšniauskas, Aurimas; Rotomskis, Ričardas; Karabanovas, Vitalijus. Exploring BODIPY-Based sensor for Imaging of intracellular microviscosity in human breast cancer cells // International journal of molecular sciences. Basel : MDPI. ISSN 1422-0067. eISSN 1422-0067. 2022, vol. 23, iss. 10, art. no. 5687, p. 1-17. DOI: 10.3390/ijms23105687. 11. Maleckaitė, Karolina; Dodonova-Vaitkūnienė, Jelena; Žilėnaitė, Rugilė; Tumkevičius, Sigitas; Vyšniauskas, Aurimas. Red fluorescent BODIPY molecular rotor for high microviscosity environments // Methods and applications in fluorescence. Bristol : IOP Publishing. ISSN 2050-6120. eISSN 2050-6120. 2022, vol. 10, iss. 3, art. no. 034008, p. 1-8. DOI: 10.1088/2050-6120/ac7943. 12. Skaisgiris, Rokas; Serevičius, Tomas; Dodonova, Jelena; Banevičius, Dovydas; Kazlauskas, Karolis; Tumkevičius, Sigitas; Juršėnas, Saulius Antanas. Tuning of HOMO-LUMO localization for achieving thermally activated delayed fluorescence // Journal of luminescence. Amsterdam : Elsevier. ISSN 0022-2313. eISSN 1872-7883. 2022, vol. 241, art. no. 118473, p. [1-7]. DOI: 10.1016/j.jlumin.2021.118473. 13. T. Serevicius, R. Skaisgiris, G. Kreiza, **J. Dodonova**, K. Kazlauskas, E. Orentas, **S. Tumkevicius,** S. Jursenas. TADF parameters in solid-state: an easy way to wrong conclusions. *Journal of physical Chemistry A*, **2021**, *125*, 7, 1637-1641; https://dx.doi.org/10.1021/acs.jpca.0c10391 14. T. Serevičius, R. Skaisgiris, I. Fiodorova, G. Kreiza, D. Banevičius, K. Kazlauskas, **S. Tumkevičius,** S. Juršėnas. Single-exponential solid-state delayed fluorescence decay in TADF compounds with minimized conformational disorder. *Journal of Materials Chemistry C,* **2021***, 9,* 836-861. https://doi.org/10.1039/D0TC05503D 15. J. Jovaisaite, D. Cīrule, A. Jeminejs, I. Novosjolova, M. Turks, P. Baronas, R. Komskis, **S. Tumkevicius**, G. Jonusauskas, S. Jursenas. Proof of principle of a purine D–A–D' ligand based ratiometric chemical sensor harnessing complexation induced intermolecular PET. *Physical Chemistry Chemical Physics*, **2020**, *22* (45), 26502-26508; https://dx.doi.org/10.1039/d0cp04091f 16. T. Serevičius, **J. Dodonova,** R. Skaisgiris, D. Banevičius, K. Kazlauskas, S. Juršėnas, **S.**

		Tumkevičius. Optimization of the carbazole–pyrimidine linking pattern for achieving efficient TADF. *Journal of Materials Chemistry C,* **2020***, 8,* 11192—11200; https://dx.doi.org/10.1039/d0tc02194f 17. T. Serevičius, R. Skaisgiris, **J. Dodonova,** L. Jagintavičius, D. Banevičius, K. Kazlauskas, **S. Tumkevičius**, S. Juršėnas. Achieving Submicrosecond TADF Lifetime and Highly Efficient Electroluminescence by Fine Tuning of Phenoxazine-Pyrimidine Structure. *ACS Applied Materials and Interfaces*, **2020**, *12*, 10727−10736. https://dx.doi.org/10.1021/acsami.9b21394 18. T, Serevicius, R. Skaisgiris, I. Fiodorova, V. Steckis, **J. Dodonova**, D. Banevicius, K. Kazlauskas, S. Jursenas, **S, Tumkevicius**. Achieving efficient deep-blue TADF in carbazole-pyrimidine compounds. *Organic Electronics,* **2020**, *82,* art.no. 105723; https://doi.org/10.1016/j.orgel.2020.105723 19. T. Serevičius, R. Skaisgiris, **J. Dodonova**, K. Kazlauskas, S. Juršėnas, **S. Tumkevičius**. Minimization of solid-state conformational disorder in donor–acceptor TADF compounds. *Physical Chemistry Chemical Physics*, **2020**, *22*, 265-272; DOI: 10.1039/C9CP05907E

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