Research and Collaboration Workshop

Interaction of Inorganic Clusters, Cages, and Containers with Light

Château Liblice 16-18th|11|2021

16 th of November	17th of November	18th of November
	7:00 - 9:00 Breakfast	7:00 - 10:00 Breakfast and departure
	9:00 - 10:15 o Jaroslav Zelenka o Jan Hynek o Alexis Verger	
	10:15- 10:45 Coffee break	
	 10:45 - 12:00 Stéphane Cordier Fabien Grasset Maria Amela-Cortes 	
	12:00 - 14:30 Lunch buffet	
	 14:30 – 16:15 Daniel Roca Sanjuán (online) Luis Cerdán (online) Antonio Francés-Monerris Michael Londesborough / Jonathan Bould 	
16:00 - 17:00 Coffee break	16:15 - 16:45 Coffee break	
17:00 - 18:00 Introduction talk	 16:45 - 18:00 Martin Lamač Karel Škoch Miroslav Krůs 	
18:00 – 20:00 Buffet dinner	10.00 01.00	
20:00-23:00 Poster session and wine tasting (marble room)	18:00 - 24:00 Dinner and networking	

Metabolic aspects of PDT, X-PDT and antibacterial PDT

Jaroslav Zelenka



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Photodynamic therapy (PDT) is a therapeutic approach based on the light-induced, photosensitizer-mediated, transition of molecular oxygen into highly-reactive singlet state. The resulting oxidative stress damages living tissues of interest. In its classical form, PDT is a well-established method for the therapy of cancer, especially skin tumors. Recent development introduced highly promising alternative applications such as deeply penetrating near infrared PDT and X-ray-induced PDT (X-PDT), or antibacterial PDT, which could be employed also for the eradication of antibiotic-resistant microbial biofilms. Here we present data from the experiments with octahedral molybdenum clusters, very efficient blue-light photosensitizers, which could be employed also for X-PDT and antibacterial PDT. We have found that efficiency of PDT is modulated by metabolism and microenvironment of cancer and biofilm cells. Hypoxia, lack of carbohydrates, acidosis, accumulation of metabolic waste products, and oxidative stress are common in tumor microenvironment and bacterial biofilms. Interestingly, such harsh conditions showed a clear synergy with PDT on cell death. Taken together, an attempt to approximate the natural metabolic states of both bacterial biofilms as well as cancer cells may dramatically enhance the development of novel photosensitizers and modes of PDT.

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Koncošová M, Vrzáčková N, Křížová I, Tomášová P, Rimpelová S, Dvořák A, Vítek L, Rumlová M, Ruml T, Zelenka J. Inhibition of Mitochondrial Metabolism Leads to Selective Eradication of Cells Adapted to Acidic Microenvironment. Int J Mol Sci. 2021;22:10790. doi: 10.3390/ijms221910790.
 Zelenka J, Koncošová M, Ruml T. Targeting of stress response pathways in the prevention and treatment of cancer. Biotechnol Adv. 2018;36:583-602. doi: 10.1016/j.biotechadv.2018.01.007.

Preparation and singlet oxygen generation of microporous solids based on oxoporphyrinogen (OxP) building blocks

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Oxoporphyrinogens (**OxPs**) are organic dyes derived from the oxidation of the antioxidantsubstituted porphyrin tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin. The oxidation leads to the rearrangement of the conjugated π -system and red shift of the absorption spectrum compared to the parent porphyrin. The nonplanar geometry of the **OxP** molecule contains 4 nitrogen atoms where additional alkyl substituents can be attached. Recently, we have proved that tetraalkylated OxPs are efficient generators of singlet oxygen (quantum yields up to $\Phi = 0.37$), ¹O₂, which is an oxidizing agent highly useful for photodynamic therapy or organic oxidative transformations.

In this presentation, the synthesis and photochemical performances for singlet oxygen generation of a range of oxoporphyrinogen-containing porous coordination polymers (**OxP-PCPs**)¹ and porous organic polymers (**OxP-POPs**) are reported. Oxoporphyrinogens were converted to molecular tectons by the introduction of oligophenylene-carboxylate linkers and incorporated into porous coordination polymers using well-known oxo-Zr(IV)₆ cluster chemistry. Their structures and textural properties were analyzed revealing substantial surface areas up to 650 m² g⁻¹ for the optimum linker length (biphenylyl). The 4-aminobenzyl-substituted OxP was converted into porous organic polymers by reacting with several aromatic tetracarboxydianhydrides (benzene-, naphthalene- and perylene-). The **OxP-POPs** also exhibit permanent porosity with specific surface areas up to 530 m² g⁻¹. After the incorporation of the OxP moiety into microporous solids the high level of ¹O₂ generation activity is maintained, which appears to be superior for singlet oxygen generation to the precursors and to a reported reference material (**PCN-222**). The prepared **OxP-based porous** materials were applied for the <u>selective oxidation</u> of sulfides to sulfoxides. We demonstrate that the excellent singlet oxygen generator oxoporphyrinogen can be successfully incorporated as porous solids and conveniently applied in heterogeneous oxidative transformations.



[1] J. Hynek, D.T. Payne, M.K. Chahal, F. Sciortino, Y. Matsushita, L.K. Shrestha, K. Ariga, J. Labuta, Y. Yamauchi, J.P. Hill, *Mater. Today Chem.* **2021**, *21*, 100534.

Development of molybdenum cluster loaded nanoparticles as stable and efficient tool for photodynamic therapy of ovarian cancer

Alexis Verger



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With a mortality rate of 4.8 for 100,000, ovarian cancer is the 4th leading cause of death by cancer in women. Photodynamic therapy (PDT) is an innovative technique, based on the destruction of malignant cells by reactive oxygen species (ROS) such as singlet oxygen, following excitation of photosensitizers (PS). The development of new PS and their use with polymeric nanoparticles as delivery systems could be an interesting therapeutic perspective. Hexanuclear clusters of molybdenum $(Mo_6(L^i)_8(L^a)_6)^{2-}$ where inner ligands (L^i) are halogen atoms and apical ligands (L^a) are labile inorganic or organic ligands have been widely studied due to their photo-chemical properties. Following photo-activation near 365 nm, clusters show bright photoluminescence with broad emission spectra in the red and near-infrared regions. When the photo-activation occurs in the presence of oxygen, they can act as powerful PS, generating ROS efficiently.

The feasibility of incorporating molybdenum clusters into poly (D, L-lactide-co-glycolide) acid (PLGA) nanoparticles was shown in our team. We present PLGA nanoparticles embedding inorganic molybdenum cluster intended for PDT of cancer. $Cs_2(Mo_6I_8)(OOC_2F_5)_6$ cluster compound (CMIF) loaded nanoparticles (CNPs) were prepared by solvent evaporation method, characterized by DLS, TEM, FT-IR, cluster release and photo-physical studies (absolute quantum yield and emission spectra). A2780 ovarian cell viability was evaluated with MTT assay following treatment with CNPs following photo-activation at 365 nm. Freshly prepared CNPs showed spherical shapes, zeta potential values around -40 mV, polydispersity indexes below 0.16 and sizes between 100 and 150 nm according to the polymer-to-cluster mass ratio (P/C). CMIF encapsulation efficiencies increased from 68 to 97% when P/C was increased from 1 to 5. CNPs colloidal stability was maintened during 90 days. CMIF photophysical properties were preserved following incorporation in PLGA nanoparticles and oxygen singlet emission signal could be detected following CNPs photo-activation at 375 nm. A2780 ovarian cancer cell viabilities (IC50) following treatment with non-activated CNPs (P/C: 1, 2.5 and 5 respectively) were 24.2 +/- 0.4μ M, 19.1 +/- 0.1μ M and 23.2 +/- 0.1μ M, while following photo-activation at 365 nm these values were decreased to $3.7 \pm 0.1 \mu$ M, $1.8 \pm 0.1 \mu$ M and $2.4 \pm 0.1 \mu$ M. This result is mainly due to ROS generation.

This work presents CMIF as a novel PS for PDT and suggests PLGA nanoparticles as an efficient delivery system intended for tumor targeting.



Revisting the vibrational and absorption properties of niobium and tantalum clusters for energy saving applications

Stéphane Cordier



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Edge-bridged halide clusters based on the $\{M_6X_{12}\}^{m+}$ core (M = Nb, Ta and X = Cl, Br) have been the topic of many physico-structural investigations both in solution and in the solid-state. The $\{M_6X_{12}\}^{m+}$ cluster core is stabilized by apical ligands of different nature in the solid state and in solution. Recently, we showed the potential of $[Ta_6Br^i_{12}Br^a_6]^{n-}$ and $[Ta_6Br^i_{12}(H_2O)^a_6]^{m+}$ cluster units as ultra-violet (UV) and near-infrared (NIR) filters for energy saving applications.

Despite they are known since a long time, the fundamental correlations between compositions, local symmetry, the electronic structures of $[\{M_6X^{i}_{12}\}L^{a}_{6}]^{m+,0,n-}$ cluster units (L = Br or H₂O, in solution and in the solid-state), redox states, and vibrational and absorption properties are still not well established. Using K₄[$\{M_6X^{i}_{12}\}X^{a}_{6}$] as starting precursor (i: inner, a: apical), we have investigated the behavior of the [$\{M_6X^{i}_{12}\}X^{a}_{6}$]⁴⁻ cluster unit in terms of oxidation properties and chemical modifications both in solution (water and organic solvent) and after recrystallization.

A wide range of experimental techniques in combination with quantum chemical simulations afford new data that allow to reveal the puzzling behavior the cluster units in response to changes in their environment. Apical ligands undergo changes like modifications of interatomic distances to complete substitutions in solution that modify noticeably the cluster physical properties. Changes of oxidation state of the cluster units also occur, which modifies significantly their physical properties, including optical and vibrational properties, which can thus be used as fingerprint. A subtle balance exists between the number of substituted apical ligands and the cluster oxidation state. This study provides new information about the exact nature of the species formed during the transition from solid-state to solutions and vice-versa. From these combined theoretical and experimental investigations, it has been possible to determine the optimum compositions to optimize the the UV and NIR blocking properties of edge-bridged [$\{M_6X^i_{12}\}L^a_6$] cluster units. Moreover, The understanding of the properties of the [$\{M_6X^i_{12}\}L^a_6$] m^{+,0, n-} cluster units thanks to several approaches (MS, Raman and UV-visible spectroscopies, electrochemistry and quantum chemical simulations) were crucial to optimize the shaping of solar control composites.



Functional Nanocomposite Materials Based on Nb₆, Mo₆ and Ta₆ Clusters.

Fabien Grasset



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Nanocomposites based on metal atom clusters for energy, environmental and biotechnology applications



Design of luminescent hybrid polymers based on Mo₆ clusters building blocks

Maria Amela-Cortes



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The combination of transition metal clusters (MC) with polymers polymers allows the design of easy-to-shape-functional materials with enhanced application versatility. $[(M_6L_8^i)L_6^a]^n$ unit (a = apical, i = inner, M = Mo, Re; L = halogen, chalcogen, 1 < n < 8) constitutes the basic building block in the octahedral cluster chemistry and is easily obtained via high temperature solid state synthesis. The delocalization of valence electrons on the whole metallic scaffold of MC leads to unusual electronic, magnetic and optical properties. Concerning the optical properties MC show high emission in the red-NIR area and are able to generate singlet oxygen. To take advantage of their intrinsic properties in applications and prevent self-aggregation, a careful choice of the host matrix and design of metal atom clusters is required. Over the years we have developed various strategies to coordinate metal clusters in obtain highly luminescent homogeneous materials[1] order to and in particular polymernanocomposites, while keeping the integrity of the MC intact. The different strategies will be developed in this presentation along with their optical properties in different polymer matrices, polymethylmethacrylate polyurethane (PUR),[4] (PMMA),[2] (PU),[3] polyurea and polydimethylsiloxane (PDMS)[5] in accordance to targeted applications in lighting, as solar concentrators, sensors and photodynamic therapy. Our recent investigations on the emission properties upon two photon absorption will be also discussed.



[1] Y. Molard, Acc. Chem. Res., 2016, 49, pp.1514-1523.

[2] a) M. Amela-Cortes, et al., J. Mater. Chem. C., 2014, 2, 1545. b) M. Amela-Cortes, et al., Dalton trans, 2016, 45, 237. c) S. Khlifi, et al., ACS Appl. Mater. Interfaces, 2020, 12 (12), 14400-14407

- [3] M.Amela-Cortes et al., Chem. Commun., 2015, 51, 8177.
- [4] E. Ferreira Molina et al., Chem. Eur. J., 2019, 25, 15248-15251.
- [5] S. Khlifi, et al., Inor. Chem., 2021, 60, 5446-5451.

Excited state absorption in luminescent boranes: Implications for their laser performance and photochemistry

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In a world of increasing specialization, researchers are becoming super experts in a narrow subfield at the expense of sacrificing a global (less specialized) knowledge of the parent field. The lightmatter interaction discipline is not an exception. For example, how can you know if the brand-new compound you have just extracted from the flask is a laser material? If you know virtually nothing about lasers and think that you should consult a laser materials expert, you are probably right. *But, Luis, is there an "easy" way to carry out a first screening and avoid everyone losing precious time*? It is indeed (partly).

In the previous edition of this symposium, I provided a "recipe" or "check list" with the main photophysical signatures to check whether a new compound could potentially become a laser material, and succinctly showed when this recipe failed. In this edition of the symposium, I will start by refreshing in a "turbo-lesson" which are the relevant photophysical signatures to achieve lasing, to later move on to focus on a photophysical effect that can degrade the laser emission and eventually kill it off altogether: Excited State Absorption (ESA). In particular, I will show that the presence of ESA results not only in the loss of laser efficiency, but also in the activation of chemically reactive relaxation pathways and the formation of photochemically produced novel molecular species. I will exemplarize the goodness of the proposed recipe and the influence of ESA with the first laser borane (anti- $B_{18}H_{22}$) [1,2]. The ultimate goal of this talk is that the workshop's attendees learn that when dealing with laser materials and strong light excitation, there is more than meets the eye.



[1] Cerdán et al., "A borane laser," Nat. Commun. 6, 5958 (2015)

[2] Cerdán et al., "Unveiling the role of upper excited electronic states in the photochemistry and laser performance of anti- $B_{18}H_{22}$," J. Mater. Chem. C, 2020, 8, 12806-12818

Accurate prediction of electronic spectra by using multiconfigurational quantum chemistry: From the gas to the condensed phase

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Multiconfigurational quantum chemistry is a tool of computational chemistry that can be applied for achieving an accurate treatment of excited electronic states. By using it in an isolated molecule, a reasonably good description of the physicochemical effects of light-matter interaction is obtained simulating the gas phase conditions. However, in materials and biological systems, chromophores are confined to distinct types of chemical and physical environments, for instance, water solution, inside a pore, at the interlayer space of layered materials, etc. Spectroscopic properties derived from the interaction between the chromophores and light might be significantly affected by the environment giving rise to changes with respect to the behavior of the isolated system. To improve the description beyond the isolated molecule approximation the environment must be considered.

In this work, we will present a computational protocol for determining the absorption cross sections in the gas phase and molar extinction coefficients in condensed phases. It is based on the use of (i) an accurate methodology for describing correctly both the ground and the distinct types of excited electronic states and (ii) an approach for sampling the conformational space of the chromophore (gas phase) or the chromophore-environment complex (condensed phase). Regarding the first point, the complete-active-space second-order perturbation theory (CASPT2) method with the OpenMOLCAS software is a practical option, especially competitive (as compared to others) for electronic transitions to high-energy excited states with important contributions of multiply-excited configuration state functions. For the conformational sampling, three strategies shall be compared. In the gas phase, we will use molecular (classical) dynamics (MD), ab initio molecular dynamics (AIMD) (quantum electrons and classical nuclei) and Wigner sampling (quantum electrons and nuclei). In the condensed phase, these strategies will be combined with a classical treatment of the environment giving rise to MD, hybrid quantum mechanics / molecular mechanics molecular dynamics (QM/MM MD) and Wigner sampling of the chromophore coupled to MD treatment of the environment (Wigner + MD), respectively.



Photo-Switching the Surfactant Character of a Metallacarborane Cluster

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Molecular photo-switches are defined as molecules capable to change their structure upon light irradiation, altering their chemical or photochemical properties. Traditional photo-switches rely on cis/trans photoisomerisations taking place in organic molecules, such as the famous case of retinal, responsible of animal vision. This phenomenon is however not limited only to organic molecules, and, in the last years, several inorganic systems, including borane¹ and carborane systems,² have been identified as photo switches with potential applications in technology and medicine.

The cobaltabis(dicarbollide) anion ([*o*-COSAN]⁻, Figure 1) is a well-known metallacarborane that exists in different dispositions, namely the *cisoid*, *gauche*, and *transoid* rotamers, according to the relative positions of the two $[C_2B_9H_{11}]^{2-}$ units that sandwich the Co^{III} atom.³ In the dark, the most favourable *cisoid* arrangement has amphiphilic properties, allowing the formation of vesicles and micelles. In this talk we will demonstrate that the population of triplet excited states induces a *cisoid* to *transoid* rotation, switching temporarily off the surfactant properties of the molecule.² These properties can be recovered *via* the non-radiative repopulation of the ground state.



Figure 1. Chemical structure of ([*o*-COSAN]⁻ (left) and disposition of the carbon atoms, shown as circles in blue and orange, for the three rotamers (right).

[1] A. Francés-Monerris, J. Holub, D. Roca-Sanjuán, D. Hnyk, K. Lang and J. M. Oliva-Enrich, Photochromic System among Boron Hydrides: The Hawthorne Rearrangement, J. Phys. Chem. Lett., 2019, 10, 6202–6207.

[2] A. M. A. Abdelgawwad, J. A. M. Xavier, D. Roca-Sanjuán, C. Viñas, F. Teixidor and A. Francés-Monerris, Light-Induced On/Off Switching of the Surfactant Character of the o-Cobaltabis(dicarbollide) Anion with No Covalent Bond Alteration, Angew. Chem. Int. Ed., 2020, 60, https://doi.org/10.1002/anie.202111493.

[3] D. C. Malaspina, C. Viñas, F. Teixidor and J. Faraudo, Atomistic Simulations of COSAN: Amphiphiles without a Head-and-Tail Design Display "Head and Tail" Surfactant Behavior, Angew. Chem. Int. Ed., 2020, 59, 3088–3092.

A luminescent love story: The boranes

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What motivates a scientist? Is it the excitement of discovery? Is it the benefits of development and progress? Is it the relationships made, both with colleagues and molecules?

The boranes are a group of inorganic clusters unavailable in nature but made accessible in the laboratory of the skilled borane chemist. Their structures display symmetrical polyhedral beauty, and their properties offer diverse application in many fields. In recent years, we have developed the understanding of the remarkable luminescence from the macropolyhedral borane *anti*-B₁₈H₂₂, demonstrating its utility as a new class of laser material.¹ *anti*-B₁₈H₂₂ is also of particular interest as it fluoresces in the elusive blue region of the spectrum with a quantum yield approaching unity,² it is highly photostable,¹ and it is readily soluble in organic polymer matrices.¹ These are all factors of general practical benefit regarding the fabrication of optical devices. Furthermore, we have demonstrated that the luminescent properties of *anti*-B₁₈H₂₂ may be modified by the introduction of substituents or ligands to the borane cluster that replace the terminal hydrogen atoms with groups such as -SH,³ alkyls,⁴ iodine,⁵ and pyridine⁶ to give molecules capable of, for example, environment-sensitive thermochromic luminescence,⁶ single-molecule multiple emissions,⁴ and the photosensitization of oxygen.⁵

In this contribution, we will present how the use of chemical, physical and computational analyses of our growing portfolio of derivatives of *anti*- $B_{18}H_{22}$ provides us deep insights into the photophysical and photochemical functioning of these compounds.



[1] L. Cerdán et al. Nat. Commun. 2015, 6, 5958.

[2] M. G. S. Londesborough et al. Inorg. Chem. 2012, 51 (3), 1471-1479.

[3] V. Sauri et al. Inorg. Chem. 2013, 52 (16), 9266-9274.

[4] J. Bould *et al. Inorg. Chem.* **2020**, 59 (23), 17058-17070; M. G. S. Londesborough *et al. Inorg. Chem.* **2020**, 59 (5), 2651-2654.

[5] M. G. S. Londesborough et al. Inorg. Chem. 2019, 58 (15), 10248-10259.

[6] M. G. S. Londesborough et al. Adv Opt Mater 2017, 5 (6), 1600694.

Luminescence, Singlet Oxygen Photosensitization, and Photoredox Catalysis by Group 4 Metallocene Complexes with Chelating Ligands

Martin Lamač



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Novel light-harvesting compounds and materials are in high demand for applications in various fields including synthetic chemistry, catalysis, medicine and visualization technologies.

We have developed cationic group 4 metallocene complexes stabilized by pendant imine, pyridine, or P=E (E = O, S, Se) donor groups as stable crystalline $[B(C_6F_5)_4]^-$ salts either by protonation of the intramolecularly bound ketimide moiety in neutral complexes by PhNMe₂H⁺[B(C₆F₅)₄]⁻ or by chloride ligand abstraction from the complexes by M[B(C₆F₅)₄] (M = Li or K) or by in situ generated Et₃Si⁺[B(C₆F₅)₄]⁻. Another series of complexes was obtained by combining the "Cp*₂M²⁺" fragment with anionic *N*,*O*-chelating ligands. The cationic complexes of Zr and Hf, compared to the corresponding neutral species, exhibited significantly enhanced luminescence predominantly from triplet ligand-to-metal (³LMCT) excited states with lifetimes up to 62 µs and quantum yields up to 90% in the solid state. DFT calculations were performed to explain the structural features and optical and electrochemical properties of the complexes.¹

The complexes are currently under investigation as photosensitizers of singlet oxygen (quantum yields of up to 77 % in solution were observed)² and for applications in photoredox catalysis.



 Dunlop, D.; Večeřa, M.; Gyepes, R.; Kubát, P.; Lang, K.; Horáček, M.; Pinkas, J.; Šimková, L.; Liška, A.; Lamač, M. *Inorg. Chem.* **2021**, *60*, 7315-7328.
 Lamač, M.; Dunlop, D.; Lang, K.; Kubát, P. J. Photochem. Photobiol. A, accepted.

Boranes, Borenium cations, Borataalkenes and Boraalkenes: on the nature of their frustrations and unsaturations

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When searching for new types of reactivity, many synthetic chemists have been recently attracted towards main-group element chemistry. It was found that many reactions previously limited to be mediated by transition metals can be similarly performed using systems relying on elements such as boron or phosphorous and therefore bypass the economical and ecological issues associated with use transition metals as reagents and catalysts.

This lecture will briefly discuss some of the new aspects in main group element chemistry such as so called "Frustrated Lewis Pairs" and reactivity of π -bonding between boron and carbon atoms mainly in respect of searching for new reactivities, which might be possibly elevated for new catalytic transition-metal free transformations. Examples from our recent work will be shown.



[1] G.C. Welsch, R.R.San Juan, J.D. Mausda, D.W. Stephan, Science, 2006, 314, 1124

- [2] K. Škoch, C.G. Daniliuc, G. Kehr, G. Erker, Chem. Commun, 2020, 56, 12178.
- [3] K. Watanabe, A. Ueno, X. Tao, K. Škoch, X. Jie, S. Vagin, B. Rieger, C.G. Daniliuc, M. Letzel,
- G. Kehr, G. Erker, Chem. Sci. 2020, 11, 7349
- [4]K. Škoch, C.G. Daniliuc, G. Kehr, G. Erker, Angew. Chem. Int. Ed. 2021, 60, 6757
- [5] C. Chen, C.G. Daniliuc, G. Kehr, G. Erker, Angew. Chem. Int. Ed. 2021, 133, 20058

Boranes and proton-boron fusion

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Nuclear fusion represents a holy grail of the nuclear energy. It is commonly considered as a clean source because, in principle, it does not produce any radioactive waste. However, the conventional deuterium-tritium (DT) fusion produces high energy neutrons which can activate reactor vessel and its near vicinity; both in magnetic and inertial confinement fusion. So, the potential large scale radioactive waste has to handle at the life-cycle of the fusion power plant. Thus, the aneutronic reaction of protonboron (pB) accompanied by the release of three alpha particles carrying the energy of 8.7 MeV currently represents a holy grail of the nuclear fusion as it produces no neutrons. This means that such a reaction can be considered as really clean energy source. Furthermore, the entire technology can be more simple and energy production efficiency can be higher in comparison with DT fusion. This can happen due to limited in-material range of alpha particles; thus the stage in which the conversion of fusion released energy to water heating occurs can be avoided. Nonetheless, in comparison with DT fusion, the pB fusion requires extreme conditions for realization (more than 10 times higher temperatures and pressures) because, at typical DT temperatures 5-20 keV, the cross section for pB reaction is extremely small. The experiments performed up to now used as targets boron-doped polyethylene, silicon or quartz; these targets exhibited the alpha yield as high as 1010 particles per laser shot. Nonetheless, as a natural fusion fuel or targets, various boranes can be considered as they are composed only of boron and hydrogen. On the other hand, their interaction with high-power laser and their properties under extreme conditions (high temperature and pressure) is almost unknown. Our aim is mainly to trigger a discussion on the possibilities to use boranes as the fuel of future pB fusion devices. The fundamental principles and trends in inertial confinement fusion will also be introduced and discussed in order to identify potential of boranes as the nuclear fusion fuel for the generation of the clean energy.

BORANES & PROTON-BORON FUSION

1 TRENDS IN INERTIAL CONFINEMENT FUSION 1.1 FOAM LAYERED OR MICRO-/NANO-STRUCTURED TARGETS 1.2 SHOCK IGNITION

- **2** PROTON BORON FUSION
- 3 INTERACTION OF HIGH-POWER LASER WITH BORANES 3.1 SHOCK WAVE PROPAGATION
 - 3.2 EQUATION OF STATE @ HIGH PRESSURES AND TEMPERATURES
 - 3.3 PARTICLE STOPPING POWER

Theoretical Study of the Cobaltabis(dicarbollide) Anion Absorption Properties and of Some Iodinated Derivatives

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Cobaltabis(dicarbollide) anion is a well-known metallacarborane with multiple applications in many fields including catalysis, redox chemistry, (bio) sensor, medicine, metal-organic frameworks, conducting polymers, and surfactants ^[1,2]. In the last years, a remarkable number of studies devoted efforts to describe its physical and chemical properties, highlighting its thermal and chemical stability given by its strong aromatic character ^[3]. This work aims to study the electronic absorption spectrum of each derivative to rationalize the effect of iodine atoms in specific positions (see Figure 1). A combination of density functional theory (DFT), time-dependent (TD)-DFT and multiconfiguration complete-active-space second order perturbation theory (CASPT2) determinations has been carried out. Results describe the most intense ligand-to-metal charge transfer (LMCT) absorptions and rationalize the red shift observed upon increasing the number of iodine atoms in the derivative series. The band peaking at large wavelengths is identified as a triplet absorption. On the other hand, the possible influence of the metal in the absorption spectroscopy has been studied by replacing the Co³⁺ center by a Fe³⁺ atom.



Figure 1. Structure of the COSAN derivatives. A) Transoid-COSAN, B) 8.8′-diiodide-COSAN, C) 8′,9′,12′,8,9,12-hexaiodide-COSAN, D) 8′,9′,10′,12′,8,9,10,12-octaiodide-COSAN, E) Transoid FESAN.

[1] Guerrero, I., Celemín, Z., Viñas, C., Romero, I., & Teixidor, F. (2020). Metallacarboranes as Photoredox Catalysts in Water. *Chemistry - A European Journal*, *26*(22), 5027–5036.

[2] Abdelgawwad, A. M. A., Xavier, J. A. M., Roca-Sanjuán, D., Viñas, C., Teixidor, F., & Francés-Monerris, A. (2021). Light-Induced On/Off Switching of the Surfactant Character of the o-Cobaltabis(dicarbollide) Anion with No Covalent Bond Alteration. *Angewandte Chemie International Edition*, 60,

[3] Hawthorne, M. F., Young, D. C., Andrews, T. D., Howe, D. V., Pilling, R. L., Pitts, A. D., Reintjes, M., Warren, L. F., & Wegner, P. A. (1968). π-Dicarbollyl Derivatives of the Transition Metals. Metallocene Analogs. *Journal of the American Chemical Society*, *90*(4), 879–896.

Novel isoreticular Fe³⁺ metal organic frameworks using phosphonate instead of phosphinate binding group

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In recent work [1] we published that replacing carboxylic groups in commonly used linker (terephthalic acid) by phosphinic groups (phenylene-1,4-bis(methyl-phosphinic acid)) can lead to highly stable Fe³⁺ and Al³⁺ MOFs. In case of replacing alkyl group on phosphorus or prolonging of linker, isoreticural structures with similar stability can be made [2]. This time we replaced phoshinate group by phosphonate, which again led to isoreticural structures.



[1] J. Hynek, P. Brázda, J. Rohlíček, M. G. S. Londesborough, J. Demel, Angew. Chem. Int. Ed. 2018, 57, 5016–5019.

[2] D. Bůžek, S. Ondrušová, J. Hynek, P. Kovář, K. Lang, J. Rohlíček, J. Demel, Inorg. Chem. 2020, 59, 5538–5545.

X-ray-induced PDT with Mo clusters

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Photodynamic therapy (PDT) is a method of clinical medicine used for the treatment of various cancer diseases. Principal of this method is an application of photosensitive substance and irradiation with the light of specific wavelength, which can photosensitizer absorb and produce reactive oxygen species (ROS). High concentration of ROS damage the cells and can lead to the cell death. X-ray-induced PDT is more effective than the PDT, because it can penetrate deeper parts of tissues.

Main topic of this work is testing of photosensitive properties of nanoparticles, prepared from molybdenum clusters Na₂[Mo₆I₈(N₃)₆] + Bis-dPEG®11-DBCO(1:4). These nanoparticles were mainly tested on cell culture TRAMP C2 (mouse transgenic prostatic cancer cell line). The nanoparticles were tested for the PDT after irradiation with blue light IC₅₀ was 17.4 µg/mL and dark toxicity of particles was not detected and is higher than > 1.48 mg/mL. From preliminary data was found that after exposure of 1.07 mg/mL nanoparticles we detected significant decrease of proliferation after X-ray irradiation. Viability of the cells and proliferation was measured by resazurin method.

These nanoparticles have a great perspective, mainly due to their water stability, effectivity in both PDT and X-PDT. An in vivo study is also currently underway.



Antimicrobial effects of octahedral molybedum clusters

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As the number of antibiotic-resistant bacterial strains increases each year, the requirement for developing new compounds and methods to combat bacterial growth increases simultaneously. Furthermore, bacterial cells naturally occur in the form of biofilm, which have protective abilities causing it to be more resistant to antimicrobial agents due to extracellular mass and horizontal gene transfer within the biofilm. Bacterial biofilm can have detrimental effects, especially in health care facilities, causing nosocomial infections and further health complications for patients. The aim of this project was to test the effects of two molybdenum-based cluster compounds on bacteria. The cluster complexes were created by copper-free click chemistry between octahedrally coordinated molybdenum core Na₂[Mo₆I₈(N₃)₆] and six BCN-functionalized outer ligands. The resulting compounds were complex 1 - Na₂[Mo₆I₈(N₃-BCN-OH)₆] and complex 2 - Na₂[Mo₆I₈(N₃-BCN-OH)₆]. The mechanism of action was based on the theory of photodynamic therapy, where the clusters acted as photosensitizers activated by a wavelength of 400-450 nm, causing oxidative stress to bacterial cells.

Selected bacterial species represented the most abundant biofilm forming bacteria found in hospitals, two of them were gram negative (*Escherichia coli, Pseudomonas aeruginosa*) and two gram positive (*Staphylococcus aureus, Enterococcus faecalis*). Methods used for assessment of the effects caused by compounds were mainly cultivation and quantification via The Misra and Miles Method or a confocal fluorescent microscopy. The complexes were diluted in dimethyl sulfoxide and tested against planktonic bacterial cells in aqueous bacterial suspension, as a biofilm inhibitor in medium and as a factor causing eradication of fully grown biofilm on a glass surface. Remarkably, toxic effects were shown in all of the executed experiments in 12 and 6 μ M concentration, especially on gram positive bacteria. Complex 2 was shown as more active, yet it provided less consistent results due to precipitation in aqueous solution. Moreover, concentrations used in these experiments were show as non-toxic on tissue cells.

To conclude, these results are promising for further applications, involving active surfaces resistant to bacterial biofilm development, which could be used in hospital and lab settings. Moreover, if possible, in prosthetics, implants or even as a curative.

