



UNIVERSITATEA DIN
BUCUREȘTI
VIRTUTE ET SAPIENTIA



Universitatea Babeș-Bolyai
Cluj-Napoca

FUNCTIONALIZED HIERARCHICAL STRUCTURES ON GRAPHENE EXHIBITING MAGNETIC, ADSORPTION AND CATALYTIC PROPERTIES

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UNITATEA EXECUTIVA
PENTRU FINANTAREA
INVATAMANTULUI
SUPERIOR, A CERCETARII
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Partners and Management

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Project Budget

| No. | BUDGET CHAPTER (EXPENSES) | 2018 (lei) | 2019 (lei) | 2020 (lei) | 2021 (lei) | 2022 (lei) | TOTAL (lei) |
|-----|---------------------------|----------------|------------------|------------------|------------------|----------------|------------------|
| 1 | SALARIES | 307.500 | 670.000 | 985.000 | 1.235.000 | 387.500 | 3.585.000 |
| 2 | INVENTORY | 343.240 | 2.340.000 | 277.500 | 268.000 | 136.760 | 3.365.500 |
| 3 | MOBILITY | 45.000 | 99.000 | 99.000 | 40.000 | 30.000 | 313.000 |
| 4 | OVERHEAD | 148.935 | 251.000 | 324.750 | 373.250 | 138.565 | 1.236.500 |
| | TOTAL BUDGET | 844.675 | 3.360.000 | 1.686.250 | 1.916.250 | 692.825 | 8.500.000 |

Abstract

The present research proposal aims to develop a series of directions which are less or non-explored to date in the chemistry of graphene. Its objectives rely on the experience of the four participants in organic synthesis, organometallic chemistry, molecular magnetism and catalysis. The project will stimulate not only the enhancement of the value of previously synthesized compounds by the partners, but also the development of an original chemistry. The hierarchical organization of organometallic – classical transition metal complexes on graphene surface is a step forward in materials science. The design of 3-D frameworks incorporating graphene is original and opens interesting perspectives for applications. The grafting of magnetic and luminescent complexes on graphene could bring an important added value in molecular magnetism. The catalytic processes to be investigated are carefully selected, in order to address important problems in organic synthesis, environmental protection and energy. The project will focus on the following major objectives: (i) design of networks by covalent connections between the decorated graphene sheets; (ii) design of graphene-based hybrid materials with appropriate organometallic/metalloid units as ligands for transition metals; (iii) single molecule magnets and luminescent molecules grafted on graphene; (iv) functionalization of graphene with macrocycles, cryptands and rotaxanes for organocatalytic reactions; (v) development of multifunctional catalysts for controlled cascade reactions; (v) applications in catalysis (the valorization of the CO₂ emissions; the hydrogenation of nitro-alkenes and mixtures of acetylene-ethylene; C-C and C-N coupling reactions) and gas sorption. A special attention in these studies will be addressed to the investigation of the catalytic mechanisms.

Objectives

The main objectives of the present project are:

O1. Assembling hierarchically organized architectures incorporating graphenes.

O2. Exploring graphene-grafted SMMs and luminescent molecules.

O3. Gas storage and gases separation with rational designed hierarchical architectures.

O4. Investigation of the newly designed hierarchical (supra)molecular architectures grafted onto graphenes in catalysis.

Dissemination of Results - 2018

Conferences

1. *Sinteza și caracterizarea de noi compuși organometalici ai stibiului(III) și bismutului(III) de tipul $[2-(GF^*)C_6H_4]_nMX_{3-n}$ ($M = Sb, Bi; n = 1-3; GF^* = -CH=O, -CH=NCH_2C_6H_4N-2', -CH=NCH_2C_6H_4N-4'$), F.-A. Adăscăliței, C. Silvestru, la Conferința Școlilor Doctorale din Consorțiul Universitaria, Căciulata, Octombrie 31 - Noiembrie 3, **2018** (oral presentation).*

2. *New hypercoordinated diorganotin(IV) with dithiocarbamate or tetraorganodichalcogenimidodiphosphinato ligands, E. Denes, N. Chiorean, A. Silvestru, A XXXVII-a Conferință Națională de Chimie, Căciulata, Octombrie 2-5, **2018** (poster).*

Dissemination of Results - 2018

Conferences

3. *Synthetic "host molecules", mechanically interlocked and self assembled architectures: from design to applications*, Ion Grosu, A XXXVII-a Conferință Națională de Chimie, Căciulata, Octombrie 2-5, **2018** (plenary lecture).

4. *New pyridine/hydroquinone based [2]rotaxanes: synthesis of the building blocks* Teodor-Aurelian Cucuiet, Cătălin Anghel, Niculina D. Hădade, Ion Grosu, A XXXVII-a Conferință Națională de Chimie, Căciulata, Octombrie 2-5, **2018** (poster).

5. *Conformational versatility of a new macrocycle based on 1,3-dioxane units*, Alexandra Bogdan, Andreea Pentronela Crișan, Ionuț-Tudor Moraru, Ion Grosu, A XXXVII-a Conferință Națională de Chimie, Căciulata, Octombrie 2-5, **2018** (poster).

Dissemination of Results - 2019

Articles

1. *Lead(II) siloxides*, A.-A. Someșan, E. Le Coz, C. I. Raț, V. Dorcet, T. Roisnel, C. Silvestru and Y Sarazin, *Chem. Eur. J.*, **2019**, *published online*. DOI: [10.1002/chem.201904713](https://doi.org/10.1002/chem.201904713)

2. *Molecular structures of (2-bromophenyl)diphenylstibane and {2'-bromo-[1,1'-biphenyl]-2-yl}diphenylstibane*, M. Olaru, K. T. Kegyes and C. I. Raț, **2019**, *submitted*.

3. *Halogen bonds (N---I) at work: supramolecular catemeric architectures of 2,7-dipyridylfluorene with ortho, meta- or para-diiodotetrafluorobenzene isomers*, I.G. Grosu, L. Pop, M. Miclăuș, N.D .Hădade, A. Terec, A. Bende, M. Bărboiu; I. Grosu, *Cryst. Growth Des.*, *submitted* (revisions are requested)

Dissemination of Results - 2019

Articles

4. *Click synthesis and complexation properties of a new unsymmetrical macrocycle bearing 1,4-dioxabenzene and triazole units*, C.C. Anghel, Teodor A. Cucuiet, E. Bogdan, A. Crișan, M. Matache L. Pop, A. Terec, N.D. Hădade, *Rev. Roum. Chim.*, 2019, accepted

5. *Selective Hydration of Electron-Rich Aryl-Alkynes by a Schrock-type Molybdenum Alkylidene Catalyst*, A. Crișan, A. Pop, E. Bogdan, M. Matache, L. Pop, A. Terec, I. Grosu, N.D.Hădade, *Rev. Roum. Chim.*, 2019, accepted

6. *Spirobifluorene-based porous organic polymers as efficient porous support for Pd and Pt for the selective hydrogenations*, M. Trandafir, L. Pop, N.D. Hădade, I. Hristea, C.M. Teodorescu, F. Krumeich, J.A. van Bokhoven, I. Grosu, V.I. Parvulescu, *ChemCatChem* 11 (2019) 538-549

Dissemination of Results - 2019

Articles

7. *N-Doped Defective Graphene from Biomass as Catalyst for CO₂ Hydrogenation to Methane*, B. Jurca, C. Bucur, A. Primo, P. Concepción, V.I. Parvulescu, H. García, ChemCatChem 11 (2019) 985-990.

8. *Nitrogen-doped graphene as metal free basic catalyst for coupling reactions*, N. Candu, I. Man, A. Simion, B. Cojocaru, S. Coman, C. Bucur, A. Primo, H. Garcia, V.I Parvulescu, J. Catal. 376 (2019) 238-247.

9. *Advances in porous and nanoscale catalysts for viable biomass conversion*, P. Sudarsanam, E. Peeters, E.V. Makshina, V.I. Parvulescu, B.F. Sels, Chem. Soc. Rev. 48 (2019) 2366-2421.

Dissemination of Results - 2019

Articles

10. *CO₂ Methanation Catalized by Oriented MoS₂ Nanoplatelets Supported on few Layers Graphene*, A. Primo, J. He, B. Jurca, B. Cojocaru, C. Bucur, V.I. Parvulescu, H. Garcia, *Appl. Catal. B: Environ.* 245 (2019) 351-359.

11. *Batch versus flow stereoselective hydrogenation of α -acetamidocinnamic acid catalyzed by an Au(I) complex*, A. Negoii, B. Cojocaru, V.I. Parvulescu, N. Imlyhen, M. Gouygou, *Mol. Catal.* 474 (2019), Article number 110420

Dissemination of Results - 2019

Conferences

1. *Novel [Zn^{II}Ln^{III}] luminescent coordination compounds deposited of graphene*, A.A. Apostol, T. Mocanu, C. Maxim, I. Mihalache, O. Tutunaru, C. Pachiu, M. Andruh, Sesiunea de Comunicări Științifice Studentești, ediția a 15-a, Facultatea de Chimie, Universitatea din București, 24-25 mai 2019. (prezentare orală)

2. *Novel [Zn^{II}Ln^{III}] luminescent coordination compounds deposited of graphene*, A.A. Apostol, T. Mocanu, C. Maxim, I. Mihalache, O. Tutunaru, C. Pachiu, M. Andruh, EuroNanoForum 2019, București, 12-14 iunie 2019. (poster)

3. *Combinatii complexe [Zn^{II}Ln^{III}] luminescente atașate pe suport de grafenă*, A.A. Apostol, T. Mocanu, C. Maxim, I. Mihalache, O. Tutunaru, C. Romanițan, C. Pachiu, M. Andruh, Sesiunea de Comunicări Științifice a Studenților, Masteranzilor și Doctoranzilor "Chimia – Frontieră deschisă spre cunoaștere", Iași, 20-21 iunie 2019. (prezentare orală)

Dissemination of Results - 2019

Conferences

4. *Novel [Zn^{II}Ln^{III}] luminescent coordination compounds deposited of graphene*, A.A. Apostol, T. Mocanu, C. Maxim, I. Mihalache, O. Tutunaru, C. Pachiu, M. Andruh, Romanian International Conference on Chemistry and Chemical Engineerig, ediția a 21-a, Constanța - Mamaia, 4-7 septembrie 2019. (poster)

5. *Combinatii complexe [Zn^{II}Ln^{III}] atașate pe suport de grafenă*, A. Apostol, T. Mocanu, C. Maxim, I. Mihalache, O. Tutunaru, C. Romanițan, C. Pachiu, M. Andruh, Conferința Națională a Doctoranzilor din Consorțiu Universitaria, ediția a 2-a, Timișoara, 11-14 noiembrie 2019. (prezentare orală)

6. *Self Assembled Architectures, Innovative Porous Organic Polymers and "Host Molecules": from Design to Applications*, I. Grosu, “; Zilele Academice Iesene, Iasi, 2-4 octombrie 2019 (Conferinta plenara)

Dissemination of Results - 2019

Conferences

7. *Metal-Free Self Assembled Architectures: from Design to Applications*, I. Grosu, “Marius Andruh, Coordination Chemistry and Friends” Symposium, Bucuresti, 31 oct. – 1 nov. 2019 (prezentare orală)

8. *Active-metal template synthesis of a [2]rotaxane using „click” chemistry*, T.-A. Cucuiet, C.C. Anghel, N.D. Hădade, I. Grosu, 9th International Conference of the Chemical Societies of the South-Eastern European Countries „Chemistry a Nature Challenger”, Târgoviște, 8-11 mai 2019, (poster)

9. *Shape-persistent NDI-based macrocycles with potential application as redox-active materials in organic lithium-ions batteries*, N. D. Hădade, A. Crișan, L. Pop, C. Nicolay, C. Golobciuc, I. Grosu, International Conference "Catalysis and Organic Synthesis" - ICCOS-2019 - Moscow, September 15-20, 2019 (poster)

Dissemination of Results - 2019

Conferences

10. *Supramolecular architectures supported by catemers of 2,7-dipyridylfluorene with ortho-, meta- or para- diiodotetrafluorobenzene isomers*, Lidia Pop, Ioana G. Grosu, Maria Miclăuș, Niculina D. Hădade, Anamaria Terec, Attila Bende, Ion Grosu, 21st European Symposium on Organic Chemistry, July 14th-18th, 2019, Vienna, Austria. (poster)

11. *Towards the synthesis of new [2]rotaxanes using the clipping strategy*, Teodor-Aurelian Cucuiet, Cătălin Anghel, Niculina Hădade, Ion Grosu, International Conference „Students for Students” Cluj-Napoca, 3-7 aprilie 2019, (prezentare orală)

12. *Pyridine-based [2]rotaxanes designed as switchable catalysts in coupling reactions*, Teodor-Aurelian Cucuiet, Cătălin Anghel, Niculina Hădade, Ion Grosu, Sesiunea de Comunicări Științifice Studentești, București, 24-25 mai 2019, (prezentare orală)

Dissemination of Results - 2019

Conferences

13. *Sinteza unui nou [2]rotaxan printr-o reacție active metal template CuAAC*, Cătălin Anghel, Teodor A. Cucuiet, Niculina Hadade și Ion Grosu, Conferința Națională a Școlilor Doctorale din Consorțiul UNIVERSITARIA, Ediția a II-a Timișoara, 11– 14 noiembrie 2019

14. *Towards the synthesis of new NDI-based shape persistent macrocycles* Cyril Nicolay, Cătălin Anghel, Ion Grosu, Niculina D. Hădade, International Conference „Students for Students” Cluj-Napoca, 3-7 aprilie 2019, poster

15. *Heterocyclic diorganopnicogen compounds. Synthesis, structure and catalysis*, Anca Silvestru, Răzvan Șuteu, Ana Maria Toma, la 9th International Conference of the Chemical Societies of the South-East European Countries, Târgoviște, România, 8-11 Mai, **2019** (prezentare orală).

Dissemination of Results - 2019

Conferences

16. *Novel ambiphilic proligands containing antimony*, Corina Stoian, Ciprian I. Rat, Cristian Silvestru, la 9th International Conference of the Chemical Societies of the South-East European Countries, Târgoviște, România, 8-11 Mai, **2019** (poster).

17. *Novel homo-and heteroleptic Pb(II) species*, Adrian-Alexandru Someșan, Cristian Silvestru, Yann Sarazin, la 27th GECOM CONCOORD, Roz Armor, Erquy, France, 19-24 Mai, **2019** (poster).

18. *Tetrakis(4-carboxyphenyl)stannane - a versatile building block for heterometallic coordination polymers*, Alexandru Sava, Teodora Mocanu, Cristian Silvestru, Marius Andruh, Sergiu Shova, la 27th GECOM CONCOORD, Roz Armor, Erquy, France, 19-24 Mai, **2019** (poster).

Dissemination of Results - 2019

Conferences

19. *Main Group heavy metal compounds containing tetraphenylimidodiselenodiphosphinato ligands*, Cristian Silvestru, 14th International Conference on the Chemistry of Selenium and Tellurium, Santa Margherita di Pula (CA), Italia, 3-7 Iunie, **2019** (prezentare orală).

20. *New hypercoordinated triorganotellurium compounds with organophosphorus ligands*, Eleonora Denes, Anca Silvestru, la 14th International Conference on the Chemistry of Selenium and Tellurium, Santa Margherita di Pula (CA), Italia, 3-7 Iunie, **2019** (poster).

21. Graphenes: A great challenge as support and catalysts for organic reactions, environment remediation and energy production, V.I. Pârvulescu, 5th Indo-French Symposium on Functionalized Materials for Sustainable Catalytic and Related Applications, MATSUCAT-2019, 26 February – 1 March, 2019, Pune, India. (Conferinta plenara)

Dissemination of Results - 2019

Conferences

22. *Graphene film-supported oriented antimonium nanoplatelets as very efficient catalysts for Michael and Henry additions*, CHAOSV.I. Pârvulescu, (C-H Activation in Organic Synthesis) 6th Workshop, 3-5 April, 2019, Ayia Napa, Cyprus

23. *Engineering active sites by hydrogen plasma irradiation: Mimicking bifunctional metal/supported catalysts in hydrogenation reactions*, A. Primo, A. Franconetti, H. Garcia, M. Magureanu, N. Mandache, C. Bucur, C. Rizescu, B. Cojocaru, V.I. Parvulescu, 14th EUROPACAT, Germany, August 18-23, 2019.

24. *The direct catalytic synthesis of dicarboxylic acids from glucose*, N. Candu, M. El Fergani, A. Tirsoaga, V. I. Parvulescu, S. M. Coman, 8th Asia Pacific Congress in Catalysis (APCAT8), 4–7th August 2019, Bangkok, Thailand

Dissemination of Results - 2019

Conferences

25. *Transition-metal binuclear complexes as new graphene-supported heterogeneous catalysts*, I. Podolean, V.I. Parvulescu, M. Andruh, 8th Asia Pacific Congress in Catalysis (APCAT8), 4–7th August 2019, Bangkok, Thailand.

26. *Marine ulvan polysaccharide as a valuable pool of rare sugars*, I. Podolean, B. Cojocaru, S. Coman, E. Ioannou, S. Kikionis, V. Roussis, A. Primo, H. Garcia, V. I. Parvulescu, 5th International Congress on Catalysis in Biorefineries – CATBIOR 2019, 23-27 September 2019, Turku, Finland