UNIVERSITATEA DIN BUCUREȘTI

VIRTUTE ET SAPIENTIA

Universitatea Babes-Bolyai
Cluj-Napoca

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

Financial support: UEFISCDI

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INOVARE SI CREATIVITATE
UNITATEA EXECUTIVA PENTRU FINANTAREA INVATAMANTULUI SUPERIOR, A CERCETARII DEZVOLTARII SI INOVARII

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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.

MAIN ACHIEVEMENTS

1. Elaboration of a general strategy for grafting heterometallic 3d-4f magnetic and luminescent complexes on graphene by employing pyrene functionalized carboxylates. Moreover, we successfully extended this strategy towards systems containing -SH groups in order to be attached on gold surface.

2. The one-pot preparation of powerful multifunctional heterogenous catalysts as hybrid Me1@Me2@PAF materials. These materials are highly efficient catalysts for many cross-coupling (Suzuki-Miyaura, Sonogashira, Stille) or CuAAC reactions. The metals trapped as nanoparticles in the PAF are exclusively issued from the catalysts employed for the synthesis of the PAFs (by Sonogashira crosscoupling reaction) and no additional metals were required. The hybrid Me1@Me2@PAF catalysts revealed a high recyclability and for many reactions an outstanding catalytical activity in water.

3. Particle size-controlled Co-Fe alloy nanoparticles wrapped on N-doped graphitic for CO_2 hydrogenation and reverse water gas shift.

MAIN ACHIEVEMENTS

4. Engineering active sites on reduced graphene oxide by (i) doping microporous graphitic carbons and (ii) hydrogen plasma irradiation, mimicking bifunctional metal/supported catalysts in hydrogenation reactions.

5. Magnetic Fe@Y composites as efficient recoverable catalysts for the valorization of the recalcitrant marine sulfated polysaccharides.

6. The design, synthesis and characterization in solution and solid state of several new precursors – organic, phosphorus-organic or organometallic species – able to be grafted on graphene oxide surface through covalent bonds or to decorate the graphene surface by π-π stacking. These precursors contain different donor atoms able to chelate or to act as pincer ligands for different monometallic as well as homo or hetero polymetallic fragments with appropriate properties either before or after the functionalization of the graphene / GO material.

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]$_n$$MX_{3-n}$ (M = Sb, Bi; n = 1-3; GF* = −CH=O, −CH=N$CH_2C_6H_4$N-2', −CH=N$CH_2C_6H_4$N-4')*, F.-A. Adăscăliței, C. Silvestru, la *Conferința Școlilor Doctorale din Consorțiul Universitaria*, Căciulata, Octombrie 31 - Noiembrie 3, **2018** (oral presentation).

2. *New hypercoordinateddiorganotin(IV) with dithiocarbamato or tetraorganodichalcogenimidodiphosphinatoligands,* 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 Crişan, 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. Raţ, V. Dorcet, T. Roisnel, C. Silvestru and Y Sarazin, *Chem. Eur. J.* (2019) *published on-line*. DOI: 10.1002/chem.201904713

2. *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

3. *N-Doped Defective Graphene from Biomass as Catalyst for CO_2 Hydrogenation to Methane,* B. Jurca, C. Bucur, A. Primo, P. Concepción, V.I. Parvulescu, H. García, *ChemCatChem* 11 (2019) 985-990.

4. *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.

Dissemination of Results - 2019

Articles

5. *CO_2 Methanation Catalized by Oriented MoS_2 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.

6. *Batch versus flow stereoselective hydrogenation of a-acetamido-cinnamic acid catalyzed by an Au(I) complex,* A. Negoi, B. Cojocaru, V.I. Parvulescu, N. Imlyhen, M. Gouygou, *Mol. Catal.* 474 (2019), Article number 110420

7. *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

Conferences

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

2. *Novel [$Zn^{II}Ln^{III}$] luminiscent 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. *Combinații 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 [$Zn^{II}Ln^{III}$] luminiscent 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. *Combinații 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 Consorțiul 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 arhitectures supported by catemers of 2,7-dipyridylfluorene with ortho-, meta- or para- diiodotetrafluorobenzene isomers,* Lidia Pop, Ioana G. Grosu, Maria Miclăuş, 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, nternational Conference „Students for Students” Cluj-Napoca, 3-7 aprilie 2019, (prezentare orala)

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 Studențești, București, 24-25 mai 2019, (prezentare orala)

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, Conferinţa Naţională a Şcolilor Doctorale din Consorţiul UNIVERSITARIA, Ediţia a II-a Timişoara, 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.

Dissemination of Results - 2020

Articles

1. *Heterometallic metallacyclophanes constructed from side-off bicompartmental ligands,* M. Andruh, M. Mocanu, A.A. Patrascu, S. Ionescu, *J. Coord. Chem.,* 2020, acceptat, DOI: 10.1080/00958972.2020.1798940

2. *Luminescent [$Zn^{II}Ln^{III}$] complexes anchored on graphene. Synthesis and crystal structures of [$Zn^{II}Eu^{III}$] and [$Zn^{II}Tb^{III}$] complexes decorated with pyrene groups*, A.A. Apostol, I. Mihalache, T. Mocanu, O. Tutunaru, C. Pachiu, R. Gavrila, C. Maxim, M. Andruh, *Appl. Organomet. Chem*., acceptat, DOI: 10.1002/AOC.6126

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. Miclăuş, N.D. Hădade, A. Terec, A. Bende, M. Bărboiu; I. Grosu, *Cryst. Growth Des.* 2020, 20, 5, 3429–3441

Dissemination of Results - 2020

Articles

4. *Click synthesis and complexation properties of a new unsymmetrical macrocycle bearing 1,4-dioxabenzene and triazole units,* C.C. Anghel, T.A. Cucuiet, E. Bogdan, A. Crișan, M. Matache, L. Pop, A. Terec, N.D. Hădade, *Rev. Roum. Chim.*, 2020, 65(6), 567-572.

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.*, 2020, 65(7-8), 699-705.

6. *Molecular structures of (2-bromophenyl)diphenylstibane and {2'-bromo-[1,1'-biphenyl)-2-yl}diphenylstibane*, M. Olaru, K. T. Kegyes, C. I. Raţ, *Rev. Roum. Chim.,* 2020, 65(7-8), 719-724

Dissemination of Results - 2020

Articles

7. *Halogen-Bonded Organic Frameworks (XBOF) of perfluoroiodo- and perfluorodiiodobenzene with 2,2',7,7'-tetrapyridyl-9,9'-spirobifluorene,* L. Pop, I.G. Grosu, M. Miclăuş, N.D. Hădade, A. Pop, A. Bende, A. Terec, M. Barboiu, I. Grosu, *Cryst. Growth Des*., **2020***,* acceptat.

8. *Synthesis of esters of diaminotruxillic bis-amino acids by Pd-mediated photocycloaddition of analogs of the Kaede protein chromophore*, E.P. Urriolabeitia, P. Sánchez, A. Pop, C. Silvestru, E. Laga, A.I. Jiménez, C. Cativiela, *Beilstein J. Org. Chem.*, **2020**, *16*, 1111-1123.

9. *Hypercoordinated triorganotellurium(IV) derivatives of chalcogen-centred organophosphorus ligands*, E. Denes, A. Beleagă, A. Silvestru, *Inorg. Chim. Acta*, **2020**, *511*, 119841.

Dissemination of Results - 2020

Articles

10. *New hypercoordinated triaryltelluronium derivatives of organophosphorus ligands. Synthesis and structural characterization*, E. Denes, M. Vlassa, C. Silvestru, A. Silvestru, *Rev. Roum. Chim.*, **2020**, *submitted*.

11. *[2,6-Bis(dimethylaminomethyl)phenyl]mercury(II) acetate, [2,6-$(Me_2NCH_2)_2C_6H_3$]Hg(OAc) - a useful N,C,N pincer-containing intermediate for selective palladation of 1,3-$(Me_2NCH_2)_2C_6H_4$*, L. Kiss, S. Sergiu, M. Vlassa, A. Silvestru, C.I. Raț, C. Silvestru, *Rev. Roum. Chim.*, **2020**, *submitted*.

12. *Group 11 metal complexes of the pyrazole-derived diorganoselenide $(pzCH_2CH_2)_2Se$. Synthesis, solid state structure and solution behavior*, R. Popa, V. Lippolis, A. Silvestru, *Inorg. Chim. Acta*, **2020**, *submitted*.

Dissemination of Results - 2020

Articles

13. *Reactivity of a carbonyl moiety in organotin(IV) compounds. Novel Pd(II) and Cu(II) complexes supported by organotin(IV) ligands*, A.-A. Someșan, C. Silvestru, R.A. Varga, *Dalton Trans.*, **2020**, *submitted*.

14. *Synthesis and characterization of palladium decorated on the ternary nanocomposite of graphene oxide, $MnFe_2O_4$ nanoparticles and PAMAM dendrons as heterogeneous catalyst for reduction of nitroaromatic compounds*, K. Karami, A. Ramezanpour, M. Kharaziha, C. Silvestru, **2020**, *submitted*.

15. *Hypercoordinated diorganoantimony(III) compounds of types $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbL$ and $[PhCH_2N(CH_2C_6H_4)_2]SbL$ (L = Cl, ONO_2, OSO_2CF_3). Synthesis, structure and catalytic behavior in the Henry reaction,* R. Şuteu, C.I. Raţ, C. Silvestru, A. Simion, N. Candu, V.I. Pârvulescu, A. Silvestru, *Appl. Organometal. Chem.* 34 (2020) e5393

Dissemination of Results - 2020

Articles

16. *Magnetic Fe@Y composites as efficient recoverable catalysts for the valorization of the recalcitrant marine sulfated polysaccharide ulvan*, J. Prech, E. Ioannou, V. Roussis, V. Kuncser, I. Podolean, S. Coman, V. Valtchev, V.I. Parvulescu, *ACS Sustain. Chem. Eng.* 8 (2020) 319-328.

17. *∞3[Cu_2(mand)$_2$(hmt)]–MOF: A synergetic effect between Cu(II) and hexamethylenetetramine in the Henry reaction,* H. Szalad, N. Candu, B. Cojocaru, T. Pasatoiu, M. Andruh, V.I. Parvulescu, *Chemistry 2* (2020) 50-62.

18. *Multifunctional nanocomposites with non-precious metals and magnetic core for 5-HMF oxidation to FDCA,* A. Tirsoaga, M. El Fergani, N. Nuns, P. Simon, P. Granger, V.I. Parvulescu, S.M. Coman, *Appl. Catal. B, Environ.* 278 (2020) Article number 119309.

Dissemination of Results - 2020

Articles

19. *Nanometer-thick films of antimony oxide nanoparticles grafted on defective graphenes as heterogeneous base catalysts for coupling reactions,* A. Simion, N. Candu, B. Cojocaru, S. Coman, C. Bucur, A. Forneli, A. Primo, I.C. Man, V.I Parvulescu, H. Garcia,, *J. Catal.* 390 (2020) 135-149.

20. P. Granger, V.I. Parvulescu, Application of Ionic Liquids for Sustainable Catalysis, in *Heterogeneous Catalysis for Energy Applications***,** T.R Reina, J. A Odriozola (Eds.), The Royal Society of Chemistry, 2020, chapter 10, 304-360.

21. *Solvent-free ketalization of polyols over germanosilicate zeolites: the role of the nature and strength of acid sites,* I. Podolean, J. Zhang, M. Shamzhy, V.I. Pârvulescu, J. Čejka, *Catal. Sci. Technol.*, 2020, 10, 8254-8264.

Dissemination of Results - 2020

Conferences

1. A. Primo, J. He, B. Jurca, B. Cojocaru, C. Bucur, H. Garcia, V.I. Parvulescu, Efficient hydrogenation of CO_2 to methane over oriented MoS_2 nanoplatelets supported on few layers graphene, 11th International Conference on Environmental Catalysis, 6th-9th September 2020, Manchester, UK (oral presentation).

Dissemination of Results - 2021

Articles

1. *Valmet chiral Schiff-base ligands and their copper(II) complexes as organo, homogeneous and heterogeneous catalysts for Henry, cyanosilylation and aldol coupling reactions.* Z. Arora, D.-I. Eftemie, A. Spinciu, C. Maxim, A. Hanganu, M. Tudorache, B. Cojocaru, O.D. Pavel, P. Granger, M. Andruh, V. I. Parvulescu, *ChemCatChem*, **2021**, *13*, 4634.

2. *Luminescence thermometry based on one-dimensional benzoato-bridged coordination polymers containing lanthanide ions*. A. Topor, D. Avram, R. Dascalu, C. Maxim, C. Tiseanu, M. Andruh, *Dalton Trans*., **2021**, *50*, 9881.

3. *Cu(II) and Ag(I) complexes of the pyrazole-derived diorganoselenide $(pzCH_2CH_2)_2Se$. Synthesis, solid state structure and solution behavior*, R.A. Popa, V. Lippolis and A. Silvestru, *Inorg. Chim. Acta*, **2021**, *520*, 120272.

Dissemination of Results - 2021

Articles

4. Ioan Stroia, Ionut Teodor Moraru, Maria Miclăuş, Ion Grosu, Claudia Lar, Ioana Georgeta Grosu, Anamaria Terec, **Solid-State and Theoretical Investigations of Some Banister-Type Macrocycles with 2,2'-Aldoxime-1,1'-Biphenyl Units,** Frontiers in Chemistry, **2021**, *96*, Article number 750418.

5. *Reactivity of a carbonyl moiety in organotin(IV) compounds. novel Pd(II) and Cu(II) complexes supported by organotin(IV) ligands*, A.-A. Someșan, C. Silvestru and R. A. Varga, *New J. Chem.*, **2021**, *45*, 3817-3827.

6. *Synthesis and characterization of the ternary graphene oxide, MnFe2O4 nanoparticles, and Polyamidoamine dendrons nanocomposite decorated with palladium as a heterogeneous catalyst for nitroaromatics reduction*, A. Ramezanpour, K. Karami, M. Kharaziha, C. Silvestru and P. Bayat, *Appl. Organomet. Chem.*, **2021**, e6329. DOI: 10.1002/aoc.6329

Dissemination of Results - 2021

Articles

7. *Halogen-Bonded Organic Frameworks (XBOF) of perfluoroiodo- and perfluorodiiodobenzene with 2,2',7,7'-tetrapyridyl-9,9'-spirobifluorene,* L. Pop, I.G. Grosu, M. Miclăuş, N.D. Hădade, A. Pop, A. Bende, A. Terec, M. Barboiu, I. Grosu, *Cryst. Growth Des*., **2021**, *21(2)*,1045-1054.

8. *Recent progress and prospects in catalytic water treatment*, Vasile I. Parvulescu, Florence Epron, Hermenegildo Garcia, Pascal Granger, *Chem. Rev., DOI: 10.1021/acs.chemrev.1c00527.*

9. *Co−Fe Nanoparticles Wrapped on N Doped Graphitic Carbons as Highly Selective CO_2 Methanation Catalysts,* Bogdan Jurca, Lu Peng, Ana Primo, Alvaro Gordillo, Vasile I. Parvulescu, and Hermenegildo García: *ACS Appl. Mater. Interfaces* **2021**, 13, 36976−36981.

Dissemination of Results - 2021

Articles

10. *Co-Fe Clusters Supported on N-Doped Graphitic Carbon as Highly Selective Catalysts for Reverse Water Gas Shift Reaction*, Peng, L., Jurca, B., Primo, A., Parvulescu, V.I., García, H., *ACS Sustainable Chemistry and Engineering*, 2021, 9(28), 9264–9272.

11. *Engineering hydrogenation active sites on graphene oxide and N-doped graphene by plasma treatment*, Magureanu, M., Mandache, N.B., Rizescu, C., Parvulescu, V.I., Garcia, H., *Applied Catalysis B: Environmental*, 2021, 287, 119962.

12. *Improvement of catalytic activity of graphene oxide by plasma treatment*, Magureanu, M., Mandache, N.B., Gherendi, F., Garcia, H., Parvulescu, V.I., *Catalysis Today*, 2021, 366, 2–9.

Dissemination of Results - 2021

Conferences

1. Marius Andruh: **Noncovalent interactions – useful tools in crystal engineering**. *Invited lecture,* Online-ICNI: the Online Symposium of the International Conference on Noncovalent Interactions, Strasbourg, 5th July 2021

2. Marius Andruh: **Noncovalent interactions – useful tools in crystal engineering**. *Invited lecture,* Zilele Academice Clujene, 21-22 octombrie 2021.

3. Diana-Ioana Eftemie, Adela Spinciu, Cătălin Maxim, Zinnia Arora, Ana-Maria Hanganu, Mădălina Tudorache, Bogdan Cojocaru, Octavian D. Pavel, Pascal Granger, Marius Andruh, Vasile I. Pârvulescu, **Chiral-Copper(II) Complexes Anchored On Carboxylated Graphene Oxide For Catalytic Applications,** Workshop Contemporary Solutions for Advances Materials with High Impact on Society - CoSolMat, 11th -15th October 2021, Bucharest Romania

Dissemination of Results - 2021

Conferences

4. Adrian Apostol, Teodora Mocanu, Cătălin Maxim, Oana Tutunaru, Cristina Pachiu, Marius Andruh, **Co-crystallization on graphene support,** Sesiunea de Comunicări Științifice Studențești, ed. a 16-a, 28-29 mai 2021, București

5. Ion Grosu, **Cyclophanes, Cryptands and Supramolecular Polymers with Pyridine, Phenothiazine and Triazine Units,** XXIX European Colloquium on Heterocyclic Chemistry, 26-28 April 2021 – virtual (postponed from August 2020, Rouen) – Keynote Lecture

6. E. Denes and C. Silvestru, *Novel di- and triorganolead(IV) complexes containing tetraphenyldichalcogenoimidodiphosphinato ligands*, *The 3rd Young Researchers' International Conference on Chemistry and Chemical Engineering (YRICCCE III)*, Cluj-Napoca, România, 4-5 iunie 2021 (prezentare orală).

Dissemination of Results - 2021

Conferences

7. A. Silvestru, *Organometallic compounds of heavy pnicogens. Synthesis, structure and catalytical applications*, *Zilele Academice Clujene*, Cluj-Napoca, Romania, 21-22 octombrie 2021 (conferință plenară).

8. E. Kapronczai (Denes), C. Silvestru, *Novel diorganotin(IV) and diorganolead(IV) complexes containing tetraphenyldichalcogenoimidodiphosphinato ligands*, *Zilele Academice Clujene*, Cluj-Napoca, Romania, 21-22 octombrie 2021 (prezentare orală)

9. O.D. Pavel, R. Zavoianu, R. Birjega, V.I. Pârvulescu, *Tailoring lamellar materials: a crucial key to enhance the catalytic efficiency for the synthesis of fine chemicals*, 7th UK Catalysis Conference, 6-8 January 2021, London, United Kingdom (conferință plenară).

10. V.I. Pârvulescu, Up-grading biomass processses in the presence of Nb-based catalysts, 2021 International Symposiumon Zeolites and Related Porous Materials, 28-29 September 2021, Qingdao, China (conf. plenară).

Dissemination of Results - 2021

Conferences

11. V.I. Pârvulescu, Catalysts in the circular economy concept, Contemporary Solutions for Advanced Materials with High Impact on Society Workshop (CoSolMat) 2021 (Norway-Island-Romania), 11-15 October 2021, Bucharest, Romania (conferință plenară).

12. V.I. Pârvulescu, Co−Fe Supported on N Doped Graphitic Carbon as Highly Selective Catalysts for Reverse Water Gas Shift and Sabatier Reactions, Indo-French Symposium "Functionalized Materials for Sustainable Catalytic and Related Applications, 26-28 October, Strasburg, France (conferință plenară).

13. Z. Arora, D. Eftemie, A. Spinciu, C. Maxim, M. Andruh, V.I. Parvulescu, Symbiotic organo- and metal catalytic enanioselective synthesis of β-nitroalcohols by enantiopure Cu (II) complex anchored on Graphene oxide, in Cutting-Edge Homogeneous Catalysis (CEHC-1), 4-6 th May 2021, Toulouse, France, p.42 (prezentare orala).

Dissemination of Results - 2021

Conferences

14. V.I. Pârvulescu, Catalysis (Catalysts) in the circular economy concept, Zilele Academice Clujene 2021, October 21-22, Cluj-Napoca, Romania (conferință plenară).

15. M. El Fergani, N. Candu, P. Granger, V.I. Parvulescu, S.M. Coman, Catalytic properties of (MOx@Nb and Nb)-zeolites based catalyst in the oxidation of glucose and HMF, Workshop on “Water in Zeolites“, Liblice, Republica Cehă, September 19-22, 2021 (prezentare orală).

16. M. El Fergani, N. Candu, M. Tudorache, P. Granger, V.I. Parvulescu, S.M. Coman, Nb@graphite-like carbon catalysts synthesis: a new way of humins valorization, 5th EuChemS Conference on Green and Sustainable Chemistry (5th EuGSC), 26th – 29th September 2021(prezentare orală).

17. M. El Fergani, N. Candu, P. Granger, V.I. Parvulescu, S.M. Coman, Non-precious metal-based magnetic catalysts for the production of diacids, 5th EuGSC European Conference on Green and Sustainable Chemistry, Thessaloniki, September 19-22, 2021(prezentare orală).

Dissemination of Results - 2022

Articles

1. *C,O-chelated organotin(IV) derivatives as potential anticancer agents: synthesis, characterization and cytotoxic activity*, A.-A. Someșan, S.-M. Vieriu, A. Crăciun, C. Silvestru, P. Chiroi, A. Nutu, A. Jurj, R. Lajos, I. Berindan-Neagoe, R.A. Varga, *Appl. Organomet. Chem.*, **2022**, 36, e6540. DOI: 10.1002/aoc.6540

2. Novel Macrocycles Embedding p,p'-Terphenyl Units: Synthesis, Characterization, Single Crystal Xray Molecular Structures and Theoretical Investigations, I. Stroia, A. Pop, M. I. Nan, E. Bogdan, A. Terec, N. D. Hădade, I. Grosu, Rev. Roum. Chim. **2022.** (accepted)

3. Silver(I) complexes with a luminescent tripodal Schiff base ligand derived from fluorene-2-carboxaldehyde, Ana Diana Popa, Augustin M. Madalan, Polyhedron **2022**, 220 115849. DOI: 10.1016/j.poly.2022.115849

Dissemination of Results - 2022

Articles

4. Novel Macrocycles Embedding p,p'-Terphenyl Units: Synthesis, Characterization, Single Crystal Xray Molecular Structures and Theoretical Investigations I. Stroia, A. Pop, M. I. Nan, E. Bogdan, A. Terec, N. D. Hădade, I. Grosu, Rev. Roum. Chim. **2022**, DOI: / ISSN:0035-3930 (accepted)

5. Supramolecular architectures in novel diphenyl(aryl)tin(IV) chlorides, Caterina Afloarei, Ioana Barbul, Adrian-Alexandru Someșan, Cristian Silvestru, Richard A. Varga, Polyhedron **2022,** 222, 115894 , DOI: 10.1016/j.poly.2022.115894

6. Macrocyclic Compounds Formed in the Reaction of 3,7-Bis(ortho-, meta- or para-formylphenyl) phenothiazines with meta-Bis(aminomethyl)benzene: Experimental and Theoretical Investigations, I. Stroia, M. I. Nan, E. Bogdan, A.Terec, N. D. Hădade, I. Grosu, **2022**, Doi: ISSN:0035-3930/Rev. Roum. Chim. (accepted)

Dissemination of Results - 2022

Articles

7. Doped Microporous Graphitic Carbons as MetalFree Catalysts for the Selective Hydrogenation of Alkynes to Alkenes, Ana Primo, Alejandra Rendón-Patiño, Cristina Bucur, Alina Jurca, Bogdan Cojocaru, Vasile I.Parvulescu, Hermenegildo Garcia, Journal of Catalysis, **2022**, *405*, 355-362. DOI: 10.1016/j.jcat.2021.11.034

8. Catalytic transformation of the marine polysaccharide ulvan into rare sugars, tartaric and succinic acids, Iunia Podolean, Simona M. Coman, Cristina Bucur, Cristian Teodorescu, Stefanos Kikionis, Efstathia Ioannou, Vassilios Roussis, Ana Primo, Hermenegildo Garcia, Vasile I. Parvulescu, Catal. Today **2022**, *383*, 345–357. DOI: 10.1016/j.cattod.2020.06.086

9. Recent Progress and Prospects in Catalytic Water Treatment, V. I. Parvulescu, F. Epron, H. Garcia, P. Granger, Chem. Rev. **2022**, DOI: 10.1021/acs.chemrev.1c00527

Dissemination of Results - 2022

Articles

10. *A New Nitronyl-nitroxide Ligand for Designing Binuclear LnIII Complexes: Syntheses, Crystal Structures, Magnetic and EPR Studies*, Mihai Răducă, Daniel O. T. A. Martins, Cristian A. Spinu, Mihaela Hillebrand, Floriana Tuna, Gabriela Ionita, Augustin M. Mădălan, Constance Lecourt, Jean-Pascal Sutter, Marius Andruh, Eur. J. Inorg. Chem. **2022**, e2022001. DOI: 10.1002/ejic.202200128

11. *Sonogashira Synthesis of New Porous Aromatic FrameworkEntrapped Palladium Nanoparticles as Heterogeneous Catalysts for Suzuki−Miyaura Cross-Coupling,* Lidia Cata, Natalia Terenti, Cristina Cociug, Niculina Daniela Hadade, Ion Grosu, Cristina Bucur, Bogdan Cojocaru, Vasile I. Parvulescu, Michal Mazur, Jirĭ Čejka, ACS Appl. Mater. Interfaces **2022**, 14, 10428−10437, DOI: 10.1021/acsami.1c24429

Dissemination of Results - 2022

Articles

12. Synthesis and structural characterization of organoantimony(III) carboxylates/ 2022/ ISSN: 0277- 5387/ Polyhedron/ A. A. Tomuta, R. G. Dornea, C. I. Rat, H. J. Breunig/ in preparation.

13. Neutral and ionic complexes containing an [2-{O(CH2CH2)2NCH2}C6H4]Pd(II) fragment: synthesis, characterization and catalytic activity for Suzuki cross-coupling reaction/ 2022/ ISSN: 0268-2605/ Appl. Organomet. Chem./ R. Fontana, K. Levente, C. Silvestru/ in preparation.

14. Organolead(IV) and inorganic lead(II) compounds containing tetraphenylimidodichalcogenodiphosphinato ligands / 2022/ ISSN: 1477-9234/ Dalton Trans./ E. Denes, C. Silvestru/ in preparation.

PROJECT PN-III-P4-ID-PCCF-2016-0088

FINAL REPPORT

Functionalized hierarchical structures on graphene exhibiting magnetic, adsorption and catalytic properties

1. Summary of the context and overall objectives of the project
The objectives of the project for the 2018-2022 period focused on:

A. Assembling hierarchically organized architectures incorporating graphenes. Design, synthesis, and characterization of new functionalized graphenes along with *(i)* hierarchically organized 3D architectures via connection of various self-assembling and/or reactive groups to single layer graphenes, *(ii)* chemical connection of macrocycles, cryptands, and rotaxanes to appropriate functionalized graphene sheets, and *(iii)* decoration of graphene surface with element-organic and/or main group organometallic functionalities and heterometallic 3d-4f complexes will be employed. As a consequence of the feedback resulted from the next three main objectives, the structural details of the new architectures will be improved.

B. Exploring graphene-grafted SMMs and luminescent molecules. Synthesis and characterization of specific heterometallic 3d-4f complexes followed by systematic spin dynamics and luminescent properties investigation of the heterometallic 3d-4f complexes grafted onto graphene will be conducted. Optimization of the obtained systems based on the feedback from the magnetic and luminescent investigations will be performed.

C. Gas storage and gases separation with rational designed hierarchical architectures. The ability of the new synthesized hierarchical architectures to act as adsorbents for gaseous pollutants and odorant molecules, for hydrogen and methane storage, carbon dioxide capture, etc. will be tested. Besides adsorption, the modified graphenes will be also used for the separation of gases, such as: hydrogen and deuterium, hydrogen from oxygen and nitrogen.

D. Investigation of the newly designed hierarchical architectures grafted onto graphenes in catalysis. In the catalysis part, the project challenges the application of the new obtained materials in very tempting processes like: *(i)* valorization of the CO_2 emissions, *(ii)* hydrogenation of nitroalkenes and mixtures of alkynes-alkenes,*(iii)* C-C and C-N coupling reactions, and *(iv)* organocatalytic reactions.

2. Work performed from the beginning of the project to the end of the period covered by the report and main results achieved so far

Synthesis of graphenes and their functionalization

Several graphene-type materials have been synthesized: *(i)* single layer reduced-graphene (Gr), *(ii)* graphene oxide (GO), *(iii)* reduced graphene oxide (rGO), *(iv)* nitrogen-doped graphene[(N)G] (Activity 1.3), and *(v)* graphene functionalized with CH=O, COOH and NH_2 groups (G-CH=O, GO-CH_2-COOH, G-NH_2 and G-CH_2-NH_2 (prepared in collaboration with *The National Institute for Research and Development of Isotopic and Molecular Technologies – INCDTIM, Cluj-Napoca*) (Activities 1.1.3 / 2.1.3 / 3.1.3). Functionalization and then hierarchical structures were produced by treating GO-COOH and (N)Gr-COOH with hexamethylene diamine. The produced structures were characterized by XRD,

spectroscopy (ATR, DRUV-Vis, Raman, XPS), texture (Activities 2.1.4 and 2.2.2). A similar methodology has been applied for the characterization of the graphenes functionalized with macrocycles, criptands, and rotaxanes (Activity 2.3.2) and after their decoration with element-organic functionalities or metalo-organic compounds (Activity 2.4.2). The material resulted by grafting the phosphor(V)-organic derivative $(S=PPh_2)_2N(CH_2)_3NH_2$ on GO was also investigated (Activity 3.1.3).

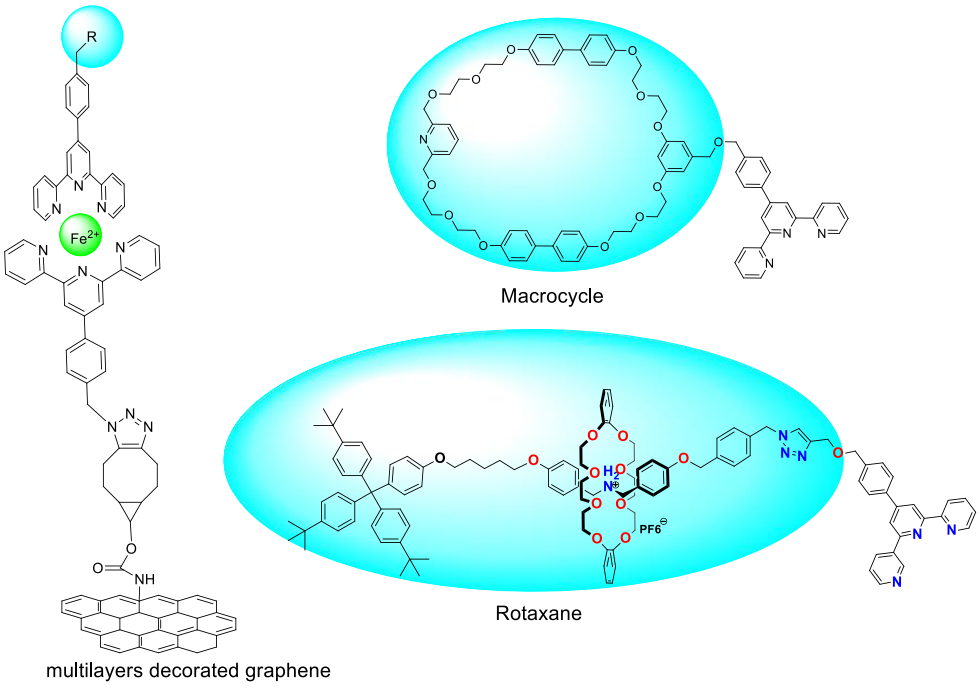
Various other precursors were prepared starting from 3-aminopropyltriethoxysilane (3-APTES) or organophosphorus(V) derivatives, *e.g.* $(E=PPh_2)_2N(CH_2)_3Si(OEt)_3$ or $(E=PPh_2)_2N(CH_2)_3NH_2$ (E = O, S, Se), as well as $(Ph_2P)_2N(CH_2)_3Si(OEt)_3$ and $(O=PPh_2)NH(CH_2)_3Si(OEt)_3$ (Activities 1.2.3 / 2.4.1 / 3.4.1). Phosphorus-free precursors, *e.g.* $O=C(Me)CH=C(Me)NH(CH_2)_3Si(OEt)_3$ and $[(3,5\text{-dmpz})CH_2CH_2]_2N(CH_2)_4$(anthracen-9-yl) (dmpz = 3,5-dimethylpyrazol-1-yl), were also synthesized (Activity 5.1.2).

Organometallic precursors functionalized to be anchored on appropriate GO or graphene-functionalized materials, *e.g.* $R_2M[C_6H_4(CH=O)\text{-}4]$ [M = Sb, Bi; R = $2\text{-}(Me_2NCH_2)C_6H_4$], $(2\text{-}Ph_2PC_6H_4)_2Sb(C_6H_4CN\text{-}4)$ or $(2\text{-}Ph_2PC_6H_4)_2Sb(C_6H_4NH_2\text{-}4)$, were prepared and characterized (Activities 1.2.3 / 2.4.1 / 3.4.1). Related new $(2\text{-}Me_2NC_6H_4)_2SbCl$ and $(2\text{-}Me_2NC_6H_4)_2SnMeCl$, useful precursors for the preparation of pincer metalloligands for transition metals, were also obtained. Organometallic species appropriated to be grafted by π-π stacking on graphene, such as $[2\text{-}(Me_2NCH_2)C_6H_4]_2MO(O)C(CH_2)_3$(pyren-1-yl) (M = Sb, Bi), $[2\text{-}\{(CH_2O)_2CH\}C_6H_4]_2Sn(Ph)(CH_2)_4$(anthracen-9-yl), $[2\text{-}(O=CH)C_6H_4]_2Sn(Ph)O(O)C(CH_2)_3$(pyren-1-yl) or $[2\text{-}(3'\text{-}PyCH_2N=CH)C_6H_4]_2Sn(Ph)O(O)C(CH_2)_3$(pyren-1-yl) (Activities 2.4.1 / 3.4.1 / 4.9.3), were also prepared.

Transition metal complexes with specific properties were obtained using such organophosphorus and phosphorus-free organic precursors or organometallics as ligands either before or after they were grafted on graphene materials (Activities 2.5.3 / 4.9.3), *e.g.* 1:1 complexes of $[(3,5\text{-dmpz})CH_2CH_2]_2N(CH_2)_4$(anthracen-9-yl) with CuI, AgOTf, $PdCl_2$·or $Zn(ClO_4)_2$, or ionic complexes of $(Ph_2P)_2N(CH_2)_3Si(OEt)_3$ containing organoPd(II) fragments, $[RPd\{(Ph_2P)_2N(CH_2)_3Si(OEt)_3\}]Cl$ [R = $2\text{-}(Me_2NCH_2)C_6H_4$, $2\text{-}\{O(CH_2CH_2)_2NCH_2\}C_6H_4$]. All new ligands and complexes were spectroscopically investigated in solution (multinuclear NMR, MS) and in solid state (UV-Vis, FTIR, powder and single crystal X ray diffraction when appropriate).

Elaboration and preparation of different anchoring systems for the attachment of functional organic molecules to graphene surface (Activities 1.1, 2.1, 3.1, 4.2 and 5.1)

A first method with general applicability, based on click reaction, was elaborated and successfully used. It is based on graphenes decorated with amino groups (aminographenes are commercially available or we obtained them at higher quality by collaborations). In the first step the amino groups react quantitatively with functionalized cyclooctyne molecules and a graphene covered with cyclooctynes is formed. The molecules of interest are decorated with azide group and by a quantitative click reaction were connected to the graphene units. Another approach was based on the reaction of marginal cyclooctynes (already grafted on the graphene) with 4'-[4-(azidomethyl)phenyl]-2,2':6',2''-terpyridine which led to a terpyridine external layer. In the presence of a metal cation (Fe^{2+}, Zn^{2+}) molecules of interest as macrocycles decorated with a terpyridine pendant arm or rotaxanes exhibiting a terpyridine stopper could be attached to the graphene-cyclooctyne network.



Multilayers graphene materials; details of the terminal groups (macrocycle or rotaxane).

A second procedure was based on the synthesis of tripodal systems. To a central tetraphenylmethane core we attached three branches (oligoethyleneoxyde type, *p*-positions) exhibiting at their ends pyrene units and the fourth phenyl group was decorated with a iodine atom (all substituents are in *para* positions). By Suzuki cross coupling reaction, iodine was replaced with a phenylcarboxylate (it can be replaced with many other groups, as required). The three pyrene units located at the end of pendant arms "glue" to graphene surface the molecule and avoid the collapse of the fourth substituent. To this system we attached a macrocycle which exhibits a -O-CH_2-Py-CH_2-O- moiety and which proved to be a good catalyst for CuAAC reactions.

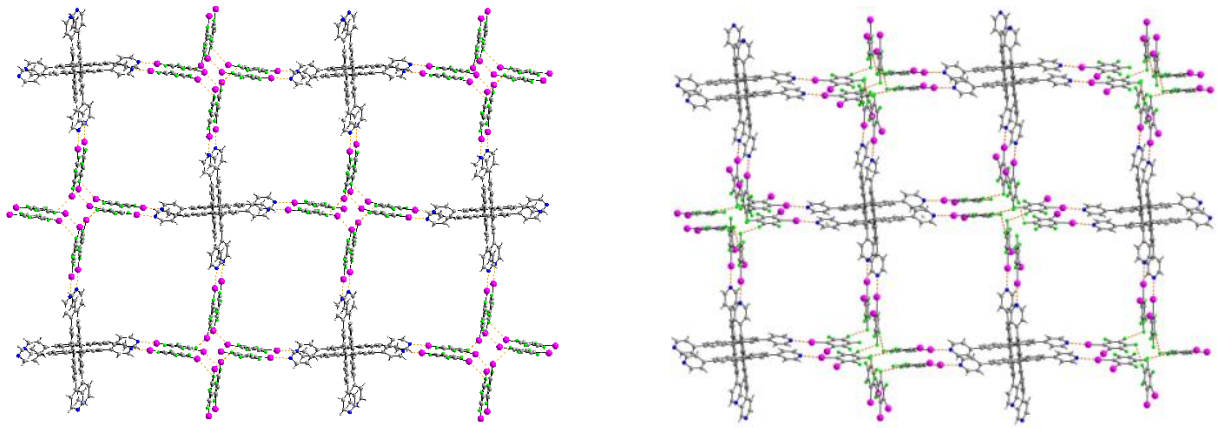
Graphenes decorated with macrocycles, cryptands, rotaxanes and catenanes (Activities 2.3, 2.5, 3.3, 4.1, 4.2, 4.9, 5.1 and 5.4)

Macrocycles and cryptands bearing –OCH_2-Py-CH_2O- or bipyridyl units in the cycle [or bridge(s)] and exhibiting anchoring pendant arms (to enable the connection to graphene) were designed, then obtained in order to carry out catalytical processes inside the cavity determined by the macrocycles or the cryptands (in confined spaces). The reactions in confined spaces show lower activation barriers and are more selective (including stereo) and specific. The catalytical processes which are running inside such confined space are *active template* reactions and they are the main procedure for the access to mechanically interlocked supramolecules. A peculiar situation occurred at the macrocyclization of an azidoalkyne by the CuAAC reaction. Surprisingly, an acetylenic coupling reaction took place before macrocyclization and thus the final product was a bismacrocycle which reveals atropoenantiomers. The synthetic targets were successfully fulfilled. The catalytic properties of such macrocycles and cryptands rise by their deposition on graphene. A peculiar attention was dedicated to chiral macrocycles including banister-like compounds (macrocycles embedding biphenyl units connected by bridges with two oxime-ether functionalities) which exhibit axial chirality and "ansa" derivatives with p,p'-terphenyl units which show planar chirality. In both cases (banister and ansa compounds) the chirality is due to the hindrance of the rotation of the aromatic units. Thus, the optical active isomers are in both cases atropoenantiomers. In both cases the enantiomers were separated on chiral columns. The atropoenantiomers of banisters exhibit

moderate racemisation barriers, while the enantiomers of ansa derivatives could not be racemized by heating their solutions at 140°C. The barriers for banisters were determined using dynamic NMR or chiral HPLC methods or the classic racemization by heating the investigated samples. Enantiomers of appropriate ansa derivatives can be incorporated in PAFs using the Sonogashira cross-coupling protocol and to give the access to chiral catalysts for asymmetric cross-coupling reactions

Investigation of the access to 3D structures (Supramolecular Organic Frameworks, SOFs) by Halogen Bonding and Charge Assisted Hydrogen Bonds (CAHB) (Activities 2.2, 3.2, 3.5, 4.2, 5.1 and 5.4)

Smart materials based on the self-assembly of some halogen acceptors (derivatives decorated with Py rings) and halogen donors (iodo- and diiodo-perfluorobenzenes) were obtained by mechanochemical methods and the new solid materials were investigated by UV-Vis, FTIR, powder and single crystal X ray diffraction. The halogen bonds formed with 2,7-dipyridyl-fluorene or 3,6-dipyridylcarbazole determined the association of halogen donors and acceptors in catemers. The 3D arrangement in the crystals was ensure by aromatic-aromatic contacts. In the case of 2,2',7,7'-tetrapyridyl-spiro-9,9'-bifluorene the halogen bonds formed 3D networks with a remarkable porosity. The 3D arrangements (with an unexpected 1/4 ratio among halogen acceptor and halogen donors) are due to the high adaptability of the halogen donors (o-, m-, p-diiodotetrafluorobenzene or iodo-pentafluorobenzene) to form polymers by I---F or F---F contacts and to ensure the arrangement of the I atoms involved in the halogen bonds which mimics the arrangement of the Py units in the halogen acceptor. Supramolecular organic frameworks based on the formation of salt bridge-like contacts among polyamidinium salts and polycarboxylates were also designed and the structures are under evaluation. For CAHB SOFs, 1,3-diamidinium-5-alkyloxybenzene or 1,3,5-triamidiniumbenzene in one side and 5-alkyloxy-1,3-benzene-dicarboxylic acid or 1,3,5-tricarboxyxlic acid on the other side were considered in the aim to have access to 2D SOFs exhibiting hexagonal (honeycomb) channels.



a *b*

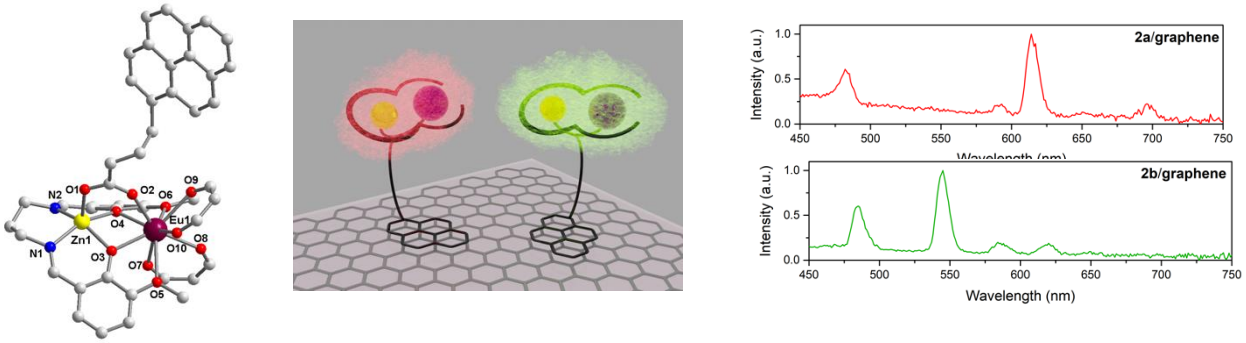
Representations of double 2D units for the supramolecular architectures of 2,2',7,7'-tetrapyridyl-spiro-9,9'-bifluorene with *p*-diiodo-tetrafluorobenzene (a) and *o*-diiodo-tetrafluorobenzene (b) showing the formation of catemers among halogen donor molecules via I---F (a) or F---F (b) contacts.

Luminescent 3d-4f complexes grafted on graphene (Activities 3.5-3.8)

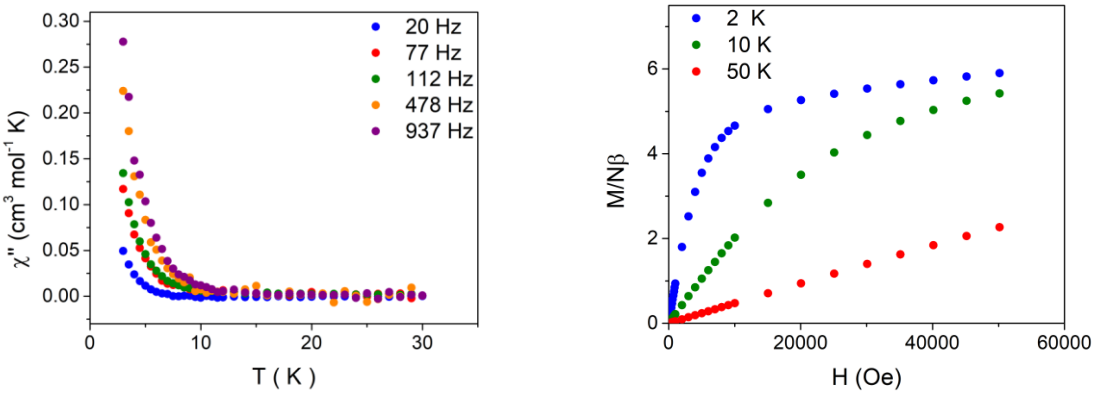
Original heterobinuclear [$Zn^{II}Ln^{III}$] complexes (Ln = Eu, Tb) have been designed in order to be grafted on graphene. The new compounds contain pyrene groups that facilitate the interaction with graphene through π–π stacking interactions. The crystal structures of the two compounds (Eu, Tb) have been solved and proved the presence of the desired pyrene groups, inserted through 1-pyrenebutiric acid.

The hybrid materials show the characteristic luminescence arising from the Ln^{III} ions (Eu^{III}, Tb^{III}). The hybrid materials have been characterized by UV-VIS and Raman spectroscopies, and by SEM, EDAX, and AFM measurements. These measurements indicate a good dispersion and pretty uniform distribution of the complexes on the surface.

The [ZnDy] derivative has been synthesized and crystallographically characterized as well. The presence of the Dy^{III} ion, with a strong uniaxial magnetic anisotropy makes it an excellent candidate for anchoring Single Molecule Magnets (SMMs) on surfaces. DC and AC cryomagnetic investigations reveal that this compound shows slow relaxation of the magnetization (SMM behaviour). The strategy we developed can be easily extended towards other 3d-4f complexes of interest for deposition on graphene. The magnetic investigation of new other [NiDy] derivatives and of the hybrid material indicates that this compounds behaves as a SMM.



Structure of pyrene functionalized luminescent [ZnLn] complexes, their interactions with graphene, and their luminescence on graphene surface (Ln = Eu, Tb).



Magnetic properties (static - *left*, dynamic – *right*) of the [NiDy] system showing its SMM behaviour.

As a consequence of the successful approach described above, we extended our investigation using other compounds that can be grafted onto graphene. These compounds belong to the family of metallacyclophanes and can interact with the graphene through π–π stacking interactions. Two novel metallacyclophanes have been assembled by self-assembly processes involving the trianionic compartmental ligand (L^{3-}), nickel(II) and sodium, respectively potassium ions: $[LNiNa]_2 \cdot C_2H_5OH \cdot H_2O$ and $[LNiK]_2 \cdot C_2H_5OH \cdot H_2O$ (the Schiff-base proligand, H_3L, is obtained by the condensation reaction of *o*-

vanillin and *DL*-2,3-diaminopropionic acid). The sodium derivative has been deposited onto graphene and the hybrid material has been characterized by SEM and EDAX techniques.

The Schiff-base ligands derived from *o*-vanillin, were particularly developed for the design pf 3d-4f complexes. We have shown that *o*-vanillin can easily generate chiral ligands and, consequently, chiral complexes that can be employed in asymmetric catalysis. Two systems have been constructed from a chiral ligand obtained from the condensation reaction between *o*-vanillin and *D*-, respectively *L*-methionine: the enantiomeric sodium complexes, [Na(*L*-valmetH)]·H_2O, [Na(*D*-valmetH)]·H_2O, and the copper(II) complexes, [Cu(*D*-valmet)(H_2O)]·H_2O, [Cu(*L*-valmet)(H_2O)]·H_2O. These systems, grafted on GO, are able to afford active catalysts for three well-documented reactions: *i.e*. the copper-catalyzed asymmetric Henry reaction of benzaldehyde and nitro-methane, carbonyl compounds with trimethylsilyl cyanide and aldol-coupling of benzaldehyde with cyclohexanone (Activity 4.9). This new ligand was also employed to synthesize chiral 3d-4f complexes to be anchored onto GO (Activities 5.3; 5.4.1). The following 3d-4f combinations were investigated: [ZnLn] and [CuLn].

Another system that was developed relies on tripodal ligands featuring fluorene groups suited to stack on graphene surface.

Apart from the objectives indicated in the proposal, we decided to add new others, stimulated by the obtained results. Such an objective concerns the investigation of the co-crystallisation of planar molecules onto the surface of graphene.

Synthesis and application of graphenes in gas-separation processes

Synthesized hierarchical organized graphenes were investigated for the separation of deuterium from different gaseous mixtures (Activity 2.9.1).

Synthesis and characterization of new graphene organized structures

Supported hierarchically organized architectures were evaluated taking as targets: *(i)* the storage capacity of reactive (H_2, CO_2) and inert (CH_4) gases, aromatic odorants (benzene, toluene, styrene and chlorobenzene), aromatic odorants containing nitrogen and functional OH groups (Activity 3.10.1), *(ii)* separation of H_2 from H_2, O_2, and N_2 mixtures focusing applications in energy and selective hydrogenations (Activity 3.11.1). The same structures were investigated for *(iii)* the transformation of CO_2 in added values chemicals (fuels) (Activities 2.10.1 and 3.11.2), and for *(iv)* the hydrogenation of nitro-alkenes and mixtures of alkenes/alkynes (alkenes and functionalized amines). These activities also focused the optimization of the process (Activities 2.11.1 and 3.13.2). Spectroscopic characterization (ATR, Raman) of the interaction of these molecules with the host hierarchically organized architectures has been also carried out (Activity 2.8.1). The chemical functionalized graphenes decorated with macrocycles, criptands and rotaxanes were fully characterized by textural, diffractometric and spectroscopic techniques (Activities 3.1.4, 3.2.2, 3.3.2, and 3.4.2).

The investigation of the new hierarchically organized architectures in more complex catalytic reactions as hydroamination, selective and stereoselective Suzuki-Miyaura, Henry, Buchwald-Hartwig couplings, etc.

More challenging reactions as C-C and C-N couplings, hidroamination and Henry coupling have been also investigated (Activities 2.12.1 and 2.12.4). New MOF structures such as $_{\infty}^{3}[Cu_2(mand)_2(hmt)]$ (H_2mand = mandelic acid; hmt = herxamethylenetetramine) were also investigated in selective hidro-aminations and stereoselective Henry and Buchwald-Hartwig couplings taking individual structures (Activity 3.14.1) and hierarchically organized ones onto graphenes (Activity 3.14.4). Mechanistic investigations taking *in-situ* and operando experiments following spectroscopic (FTIR, ATR, DRUV-Vis,

Raman) and X-ray diffraction measurements evaluated the isomerization of double bonds over Y–carbon and β–carbongraphenic catalysts, and coupling reactions over $_{\infty}^{3}[Cu_2(mand)_2(hmt)]$/graphene catalysts (Activity 3.15.1). A specific design has been mounted in all these investigations (Activity 3.15.4).

Preliminary studies have been carried out on C–C coupling reactions which occur by treatment of organomercury(II) derivatives of the type $(4\text{-}XC_6H_4)_2Hg$ with catalytic amounts of $Pd(OAc)_2$, in CH_2Cl_2, at room temperature, when compounds $4\text{-}XC_6H_4–C_6H_4X\text{-}4'$ [X = CHO, $CH(OCH_2)_2$] were isolated in good yields (60-70%) (Activity 2.12.3).

The above results prompted us to deposit $_{\infty}^{3}[Cu_2(mand)_2(hmt)]$ as a MOF, onto graphene/SiO_2 (Activity 3.2). The hybrid material has been characterized by PXRD and shows the characteristic diffraction peaks of the 3D coordination polymer (by comparison with the simulated diffractogram, using the single crystal measurements). It is worth mentioning that $_{\infty}^{3}[Cu_2(mand)_2(hmt)]$, synthesized in our laboratories is readily obtained from very cheap starting materials (this is a crucial condition for the practical applications of MOFs). Another MOF, with smaller pores have been synthesized and crystallographically characterized, using a chloro derivative of mandelic acid. The deposition of this new MOF on graphene is under investigation.

Studies were performed on the catalytic capacity of a new magnetic composite obtained by immobilizing palladium nanoparticles on a multicomponent system ($MnFe_2O_4$, rGO and dendron PAMAM) compared to the reduction of nitroaromatic compounds. Very good results were obtained in reducing 4-nitrophenol with sodium borohydride at room temperature (Activities 3.14.3 / 4.9.3 / 5.4.3).

Various neutral and ionic organoPd(II) fragments [R = $2\text{-}(Me_2NCH_2)C_6H_4$, $2\text{-}\{O(CH_2CH_2)_2NCH_2\}C_6H_4$] were prepared and structurally characterized. They were found to exhibit good catalytic activity for Suzuki cross-coupling reaction using $PhB(OH)_2$, in methanol, at room temperature. Related $[RPd\{(Ph_2P)_2N(CH_2)_3Si(OEt)_3\}]Cl$ and GO-anchored species are under investigation for catalytic activity (Activity 4.9.3 / 5.4.3).

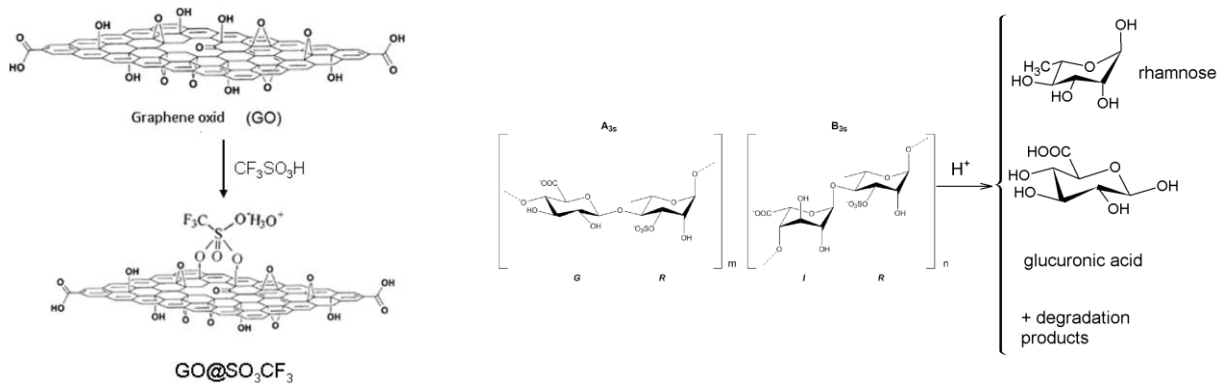
The evaluation of the catalytic performances of the new graphene-derived architectures produced by the project partners has been carried out in a series of reactions. The objective of these investigations was to prove the capability of these new materials to serve as catalysts for different applications of interest such as the fine chemical syntheses and technologic processes of a large interest. For the fine syntheses the research focused:

(*i*) nanometric films catalysts composed of h/boronitride deposited on graphene; these catalysts exhibited high catalytic activity for the synthesis of benzoxazoles via the condensation of *o*-aminophenol with aldehydes. The addition of a base such as K_2CO_3 facilitated the intramolecular cyclo-addition of the phenolic oxygen to imine. The synthesis of the powder h-BN boronitride has been performed as a solid-solid reaction in a ball mill. This material afforded a high activity and selectivity for β-nitroalkene in both the Henry and Knoevenagel condensations (Activities 4.9).

(*ii*) incarcerated Pd nanoparticles in porous aromatic (PAFs) or covalent organic (COFs) frameworks via a Sonogashira protocol in the presence of the homogeneous Pd catalysts. These catalysts demonstrate a high capability to promote heterogeneous catalytic reactions such as the Suzuki-Miyaura coupling. Noteworthy, the turnover frequency of these catalysts was very well preserved over a high number of recyclings without any leaching of the noble metal. This approach opens a new perspective for the valorization of the noble metals utilized in the syntheses of the structured polymers as an effect of the incarceration of the metal in the organic material. The calculated TOF in this reaction was about ~ 12-13, namely with an order of magnitude higher than the homogeneous $[Pd\{P(Ph)_3\}_4]$ catalyst (Activities 4.10).

(*iii*) Generation of solid acid catalysts by modifying graphene oxide with triflates. In accordance with this strategy, graphene oxide was modified with triphlic acid by a treatment under ultrasonication of graphene in the presence of nitric acid, followed by washing and treatment with concentrated triflic acid under strong shaking at 80 ^{o}C for 3-10h. This material showed catalytic activity in the transformation of

marine polysaccharides (ulvan) into platform molecules. The presence of sulphate groups in these structures prevents the use of catalysts containing metal components.



(a) (b)

Synthesis of graphene oxide modified with triflate (a) and capitalization of marine polysaccharides (b)

Depending on the operating conditions, the graphene oxide catalyst modified with triflic acid has proven to be effective in producing compounds such as rhamnose, tartaric acid or succinic. The selectivity of the reaction is also controlled by factors such as temperature (it also influences the speed of the self-hydrolysis reaction), by the reaction atmosphere (the molecular oxygen pressure controls the selectivity to succinic acid), or the concentration of triflate grouping (degradation to glucuronic acid). Also important, the recycling of the catalyst does not proceed with changes in conversion or the selectivity of the reaction.

Investigation of the behavior of the graphene hierarchical organized architectures comprised of metal- and organo-metallic structures for C-C and C-N couplings, chemo- and stereoselective hydroamination, and Henry condensation (Activity 5.4.)

Investigation of the catalytic behavior of the synthesized coordination compounds

Chemo- and stereoselective hydroamination has been carried out in the reaction of imidazole and 1-hexyne and phenyl-hexyne as alkynes was carried out in an autoclave at temperatures in the range 150-300 ^{o}C in the presence of microporous N- and P-doped graphenes. The selectivity to anti-Markovnikov product, a versatile metal-free protocol, was total while the stereoselectivity varied as a function of alkyne and reaction conditions. For 1-alkyne the E/Z ratio varied between 53 and 98 while for phenyl-hexyne between 5 and 52%. Then, powder h-BN boronitride afforded a high activity and selectivity for β-nitroalkene in both the Henry and Knoevenagel condensations.

Oriented metal nanoplatelets such as (Au or Pd) on graphene promoted coupling reactions (as Suzuki-Miyaura) with a high efficiency. The selectivity in these reactions was controlled by the exposed facet.

Investigation of the reactions' mechanisms

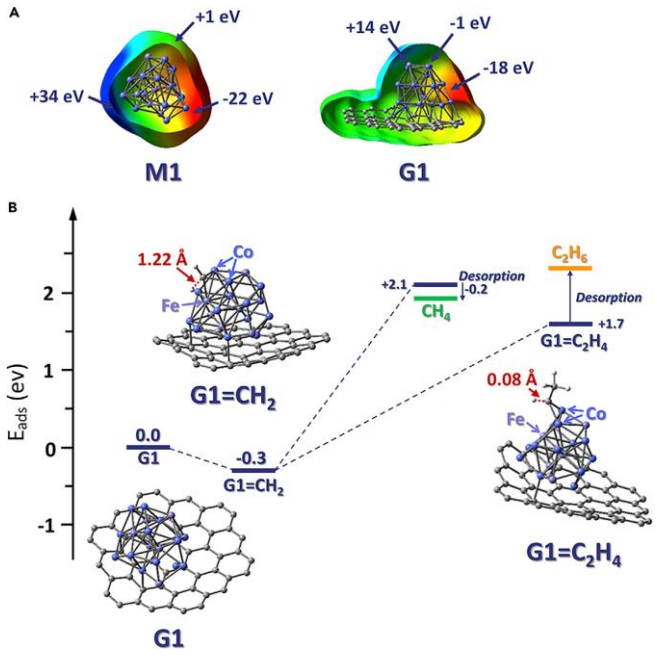
Investigation of the reactions' mechanisms through IR, Raman and UV-Vis spectroscopy and X-Ray diffraction (Activities 5.5).

The project investigated several strategies for the synthesis of new materials and, correlated to this, their catalytic activity and, for the cases they presented this, also the reaction mechanism. This

objective is better exemplified for the catalysts deposited on various graphenes starting from different precursors. These catalysts were investigated in the CO_2 hydrogenation under pressure following five strategies: (*1*) Co−Fe nano-alloys (NP) were incarcerated in graphenes through the pyrolysis of chitosan impregnated with different loadings of Co and Fe where the catalysts showed a high activity for the Sabatier CO_2 to CH_4 reaction with an increase of the activity at temperatures in the range 300−500 °C; (*2*) catalysts were synthesized via the co-precipitation of an acidified (HOAc) solution of chitosan followed by drying and a gradual exchange of water with ethanol, and a supercritical extraction by CO_2 which showed similar performances with those achieved from the strategy (*1*); (*3*) synthesis of the catalysts through the impregnation of chitosan with an alcoholic solution of iron and cobalt acetates in the presence of NaOH, supercritical CO_2 drying and pyrolysis in Argon at 900 o C for 2 h that demonstrated a structural sensitive behaviour; (*4*) Free metal carbocatalysts which graphitic microporous matrices doped with nitrogen or phosphorus. These exhibited a bifunctional character, namely, metallic and basic catalyst associated to non-participating electrons of nitrogen or phosphorus. The calculation of the TOF values confirmed the stability of these materials in the investigated reaction conditions and a superior compared to that that of 2D graphene analogues; (*5*) Generation of solid acid catalysts by modifying graphene oxide with triflates, showing catalytic activity in the transformation of marine polysaccharides (ulvan) into platform molecules. The reaction mechanisms and the stability of these has been checked through in situ and operando IR, Raman and UV-Vis spectroscopy and X-Ray diffraction.

Theoretical calculations

In order to clarify the origin of the high selectivity to C2+ and the role of graphene as a support of bimetallic NPs in CO_2 activation, DFT calculations were performed using a pbe-D3/def2-SVP algorithm. For this purpose, 20 atoms with a $Co_{14}Fe_6$ composition similar to that of catalyst 3 were considered models. The initial random geometry was optimized both in the absence and in the interaction with a graphene sheet. The experimental data collected in this study confirmed the significant role of graphene on the activity of bimetallic catalysts. Based on this finding, the differences in CO_2 adsorption on Co-Fe alloys deposited on graphene were analyzed. The information resulting from the surface analysis of the molecular electrostatic potential (MEP) on the unsupported Co-Fe clusters (Model M1) and the supported ones (Model G1) revealed two regions, one highly positively charged [+34 eV (M1)] the other negative [-22 eV (M1)] that become greatly attenuated [+14 and -18 eV (G1)] when Co-Fe NP interacts with graphene.



precursors of methane and ethane in functional pbe-D3 and def2-SVP basic set. Enabling C-H bindings is highlighted by red dotted lines.

Under these conditions, it is easy to predict that the positive regions (blue color) should be repellent for the adsorption of CO_2 [$^{\delta+}$(C) = 0.30], while strong adsorption should be carried out in the negative regions (red color), even if they do not support the subsequent desorption process. Therefore, the catalytic process is considered to occur in the border between the above-mentioned negative and positive regions. Another important conclusion of these calculations results from the analysis of the electrostatic potential map that compares the levels M1 and G1 in the range of +1 to -1 eV calculated for the Co-Fe atoms of the unsupported Co-Fe model. This comparison supports the influence of graphene interaction that changes the electronic density of the Co-Fe cluster and, therefore, the adsorption of CO_2 on it. Based on these preliminary considerations, information was obtained about the dissociation of CO_2 by the interaction of these model clusters with GAS CO_2. CO_2 adsorption was estimated to be possible on both models (E_{ads}, CO_2 = -1.7 and -2.1 eV for M1 and G1, respectively), being more favored on the cluster deposited on graphene. According to the literature, dissociation can take place on a metal carbide (-CH_2-) and the hydrogenation of CO_2 is assumed on the metal surface. The carbide species in the case of graphene clusters (G1 = CH_2) are stabilized (3.8 eV compared to M1 = CH_2) acting as precursors for methane (1.9 eV is theoretically necessary for this reaction) or C2+ compounds, depending on the reaction G1 is CH_2 in interaction with H_2 or with an adsorbed C1 intermediate.

In conclusion, the calculations performed suggest (*i*) greater stability of metal carbenes when Co-Fe clusters are supported on graphene, and (*ii*) a modified electronic distribution is the key factor that favors chain growth on Co-FeNPs@(N)G catalysts compared to unsupported clusters.

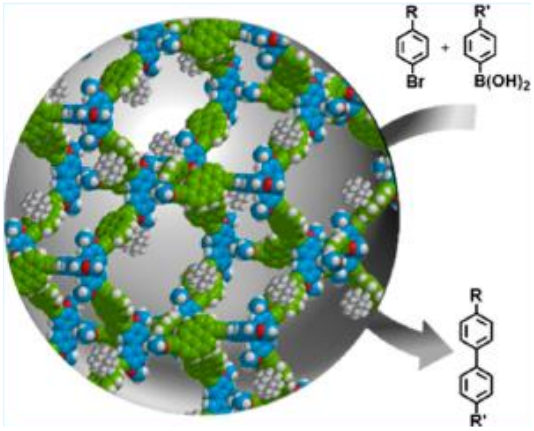
Rotaxanes with role of multifunctional and/or switchable catalysts (Activities 2.3, 2.12, 3.5, 4.2, 4.9 and 5.1)

Rotaxanes with multiple and different stations can be employed as switchable or multifunctional catalysts. One or more of the stations must be catalytic sites. The macrocycle (which is part of the rotaxane) is moved using different stimuli (*p*H, optical, electrochemical) from one station to the other. The catalytic activity of the station bearing the macrocycle is cancelled. Thus, by the controlled slicing of the macrocycle along the axle one catalytic site can be "on" (the macrocycle is at another station) or "off" (the macrocycle covers the station) and we can control (on-off) the behaviour of the catalyst. If by the different positions of the macrocycle different catalytic sites are activated cascade catalytic processes can be carried out. Till now we elaborated the simpler model, which is a rotaxane with two stations, one station is able to catalyse cross-coupling reactions (based on phenantroline or pyridine) and the other station (triazolium) shows no catalytic activity (it is an on-off switchable catalyst). The rotaxanes were deposited on a multilayer decorated graphene via a terpyridine stopper.

COFs as efficient catalysts for cross-coupling reactions (Activities 2.12, 3.13, 3.14, 3.15, 4.2, 4.9, 4.10, 5.1, 5.4 and 5.5)

New COFs were obtained by Sonogashira cross coupling reactions starting from 3,3',6,6'-tetraiodo-spiro-9,9'-bifluorene or 1,3,5,7-tetra-p-iodophenyladamantane and 1,6-diethynylpyrene. The reactions were controlled in order to have ethynyl-pyrene end groups. These terminal groups allowed the deposition of the COF particles via COF-pyrene contacts. The COFs have large pore and retain nanoparticles of Pd (resulted by the reduction of Pd^{2+} catalyst used for the Sonogashira reaction by the excess of 1,6-diethynylpyrene) regularly spread in the mass of the COF. These new hybrid materials COF@Pd catalyzed (as they issued from the synthesis) successfully Suzuki-Miyaura cross coupling reactions (yields >90 %) and revealed a high recyclability (no significant modification of the yields after 5 uses) A careful investigation of the COFs revealed the presence of small amounts of copper species (0, +1). Starting from this observation we investigated these COFs as catalysts for Sonogashira, Stille and

CuAAC reactions. The results were excellent in terms of yields, recyclability and reaction conditions. Many of the processes could be carried out in water (despite the quite low solubility of the compounds) and the reactions underwent with a very low ratio catalyst/reagents. Cascade CuAAC-Sonogashira reaction were also successfully performed. The catalytic activity in different reactions and with different substrates was evaluated using NMR investigations.

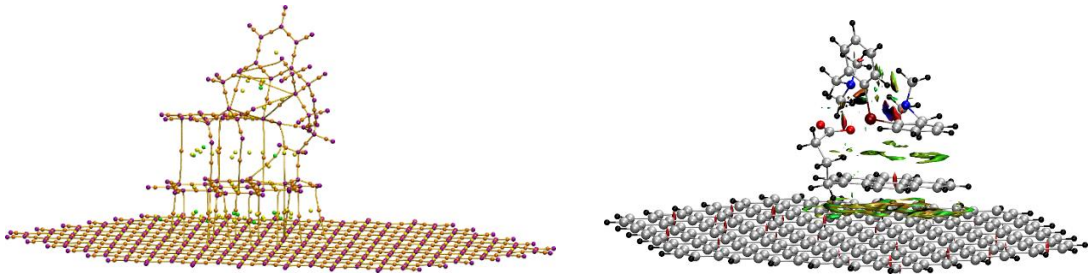


Representation of the hybrid Me@PAF material obtained in the Sonogashira cross-coupling reaction of 3,3',6,6'-tetraiodo-spiro-9,9'-bifluorene with 1,6-diethynylpyrene and of its catalytic role for high yields Suzuki-Miyaura cross-coupling reactions.

Synthesis of new structured-graphene materials were investigated as adsorbents and catalysts in processes of importance, *i.e.* the gas-separation, production of energy and of fine chemicals. The originality of the use of such materials for the production of energy has already been recognized by an international patent. An important progress is that of tailoring the active sites with a control of the selectivity for the hydrogenation of CO_2 to either CO or hydrocarbons with different molecular sizes. Besides the practical importance of these objectives the project achieved results in a better understanding of catalysis on graphene-carbon based materials and identification of the active sites. The association with the plasma treatment allowed tailoring of the graphene active site and also the population of these. The characterization of the produced materials by X-Ray diffraction, spectroscopic, textural and also advanced electron microscopy also allowed a better understanding of the synthesis of such catalysts and their catalytic behaviour.

Theoretical studies by DFT methods of the interactions and mechanisms in which graphene-element-organic compounds architectures are involved (Activities 4.15.3 / 4.10.3 / 5.5.3)

Several metal compounds appropriated to be grafted by π-π stacking on graphene, *e.g.* the organometallic species $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbO(O)C(CH_2)_3$(pyren-1-yl), $R_2Sn(Ph)O(O)C(CH_2)_3$(pyren-1-yl) [R = 2-(O=CH)C_6H_4, 2-(3'-PyCH_2N=CH)C_6H_4], some complexes of [(3,5-dmpz)$CH_2CH_2]_2N(CH_2)_4$(anthracen-9-yl), etc., were selected for a theoretical study of the interactions of graphene-organometallic / inorganic compound architectures. Using specific programs, possible conformers were first assessed, and the conformer with the lowest energy was selected for DFT studies. Thus, for $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbO(O)C(CH_2)_3$(pyren-1-yl), in addition of intramolecular coordination of nitrogen atoms to antimony atom, both Menshutkin-type interactions between the metal and the pyrenyl group, respectively π···π interactions between a phenyl group and the pyrenyl moiety were found. The structure of the organoantimony species / graphene adduct has been optimized; the chosen conformer binds non-covalently *via* the pyrene-1-yl group to the graphene layer. These interactions are confirmed by AIM analysis and the NCI analysis.



RDG (reduced density gradient) surface for the organoantimony species / graphene adduct. Non-covalent interactions are represented with *green*, strong interactions with *blue*, and strong rejections with *red*.

3. Progress beyond the state of the art and expected results until the end of the project

The progress beyond the state of the art as an effect of the work produced to date circumscribe to several new research opportunities: *(i)* possibility to tune the textural properties of graphenes making these applicable in separation of gases at normal operational conditions; *(ii)* association of graphene layers controlling adsorption and diffusion of gases with different kinetic diameters; *(iii)* expanding the role of carbon materials (graphenes) as green recoverable-based catalysts for the production of energy (methane) by recycling CO_2 emissions and of hydrocarbons for chemical applications; *(iv)* use of hierarchically organized architectures in more complex organic catalytic reactions; *(v)* investigation for the first time of co-crystallization processes of planar molecules (organic, organometallic) on the graphene surface, by manipulating complementary (donor-acceptor) supramolecular interactions; to the best of our knowledge, such systematic studies have never been performed; *(vi)* design of new original molecular compounds to be deposited on graphene or graphene-oxide in order to obtain novel catalysts as well as luminescent materials.

All these objectives and the complexity of the project stimulated the development of new synthetic pathways in molecular chemistry, with a much more general relevance.

4. Results indicators

Indicators	**Description / Name**	**No.**
Articles published/accepted/under evaluation in ISI indexed journals	*Article title/Year/DOI/ISSN or eSSN/Journal/ Authors/ Status (under evaluation/accepted/published)* 1. Catalytic Properties of 3D Graphene-Like Microporous Carbons Synthesized in a Zeolite Template/2018/DOI: acscatal.7b04086/ ISSN: 2155-5435/ ACS Catal./ P. Sazama, J. Pastvova, C. Rizescu, A. Tirsoaga, V.I. Parvulescu, H. Garcia, L. Kobera, J. Seidel, J. Rathousky, P. Klein, I. Jirka, J. Moravkova, V. Blechta/ published. 2. Engineering active sites on reduced graphene oxide by hydrogen plasma irradiation: Mimicking bifunctional metal/supported catalysts in hydrogenation reactions/ 2018/ DOI: 10.1039/C7GC03397D/ ISSN: 1463-9270/ Green	**50**

	Chem./ A. Primo, A. Franconetti, M. Magureanu, N.B. Mandache, C. Bucur, C. Rizescu, B. Cojocaru, V.I. Parvulescu, H. Garcia/ published. 3. Graphene film-supported oriented 1.1.1 gold(0) versus 2.0.0 copper(I) nanoplatelets as very efficient catalysts for coupling reactions/ 2018/ DOI: 10.1007/s11244-018-1043-x/ ISSN: 1022-5528/Top. Catal./ N. Candu, A. Simion, S.M. Coman, A. Primo, I. Esteve-Adell, V.I. Parvulescu, H. Garcia/ published. 4. From glucose direct to succinic acid: an optimized recyclable bi-functional Ru@MNP-MWCNT catalyst/ 2018/ DOI: 10.1007/s11244-018-1012-4/ ISSN: 1022-5528/Top. Catal/ I. Podolean, B. Cojocaru, H. Garcia, C. Teodorescu, V.I. Parvulescu, S.M. Coman/ published. 5. Bimetallic Oriented ($\overline{Au}/\overline{Cu_2O}$) versus monometallic 1.1.1 $\overline{Au}(0)$ or 2.0.0 $\overline{Cu^2}O$ Graphene Supported Nanoplatelets as Very Efficient Catalysts for Michael and Henry Additions/ 2018/ DOI: 10.1002/ejoc.201801443/ ISSN: 1099-0690/ EurJOC/ A. Simion, N. Candu, S.M. Coman, A. Primo, I. Esteve-Adell, V. Michelet, V.I. Parvulescu, H. Garcia/ published. 6. Spirobifluorene-based porous organic polymers as efficient porous support for Pd and Pt for the selective hydrogenations/ 2019/ DOI: 10.1002/cctc.201801247/ ISSN: 1867-3899/ ChemCatChem/ M. Trandafir, L. Pop, N.D. Hădade, I. Hristea, C.M. Teodorescu, F. Krumeich, J.A. van Bokhoven, I. Grosu, V.I. Parvulescu/ published. 7. N-Doped Defective Graphene from Biomass as Catalyst for CO_2 Hydrogenation to Methane/ 2019/ DOI: 10.1002/cctc.201801984/ ISSN: 1867-3899/ ChemCatChem/ B. Jurca, C. Bucur, A. Primo, P. Concepción, V.I. Parvulescu, H. García/ published. 8. CO_2MethanationCatalized by Oriented MoS_2 Nanoplatelets Supported on few Layers Graphene/ 2019/ DOI: 10.1016/j.apcatb.2018.12.034/ ISSN: 0926-3373/ Appl. Catal. B: Environ. / A. Primo, J. He, B. Jurca, B. Cojocaru, C. Bucur, V.I. Parvulescu, H. Garcia/ published. 9. Batch versus flow stereoselective hydrogenation of α-acetamido-cinnamic acid catalyzed by an Au(I) complex/ 2019/ DOI: 10.1016/j.mcat.2019.110420/ ISSN: 2468-8231/ Mol. Catal./ A. Negoi, B. Cojocaru, V.I. Parvulescu, N. Imlyhen, M. Gouygou/ published. 10. Nitrogen-doped graphene as metal free basic	

	catalyst for coupling reactions/ 2019 / DOI: 10.1016/j.jcat.2019.07.011/ ISSN: 0021-9517/ J. Catal./ N. Candu, I. Man, A. Simion, B. Cojocaru, S. Coman, C. Bucur, A. Primo, H. Garcia, V.I Parvulescu/ published 11. Advances in porous and nanoscale catalysts for viable biomass conversion/ 2019/ DOI: 10.1039/C8CS00452H/ ISSN: 1460-4744/ Chem. Soc. Rev./ P. Sudarsanam, E. Peeters, E.V. Makshina, V.I. Parvulescu, B.F. Sels/ published. 12. Magnetic Fe@Y composites as efficient recoverable catalysts for the valorization of the recalcitrant marine sulfated polysaccharide ulvan/ 2020/ DOI: 10.1021/acssuschemeng.9b05406/ ISSN: 2168-0485/ ACS Sustain. Chem. Eng./ J. Prech, E. Ioannou, V. Roussis, V. Kuncser, I. Podolean, S. Coman, V. Valtchev, V.I. Parvulescu/ published. $13^{\infty}{}_{3}[Cu_2(mand)_2(hmt)]$–MOF: A synergetic effect between Cu(II) and hexamethylenetetramine in the Henry reaction/ 2020/ DOI: 10.3390/chemistry2010006/ ISSN: 2624-8549/ Chemistry/ H. Szalad, N. Candu, B. Cojocaru, T. Pasatoiu, M. Andruh, V.I. Parvulescu/ published. 14. Multifunctional nanocomposites with non-precious metals and magnetic core for 5-HMF oxidation to FDCA/ 2020 / DOI: 10.1016/j.apcatb.2020.119309/ ISSN: 0926-3373/ Appl. Catal. B, Environ./ A. Tirsoaga, M. El Fergani, N. Nuns, P. Simon, P. Granger, V.I. Parvulescu, S.M. Coman/ published. 15. Nanometer-thick films of antimony oxide nanoparticles grafted on defective graphenes as heterogeneous base catalysts for coupling reactions/ 2020/ DOI: 10.1016/j.jcat.2020.07.033/ ISSN: 0021-9517/ J. Catal. / A. Simion, N. Candu, B. Cojocaru, S. Coman, C. Bucur, A. Forneli, A. Primo, I.C. Man, V.I Parvulescu, H. Garcia/ published. 16. Solvent-free ketalization of polyols over germanosilicate zeolites: the role of the nature and strength of acid sites/ 2020/ DOI: 10.1039/D0CY01662D/ ISSN: 2044-4761/ Catal. Sci. & Technol./ I. Podolean, J. Zhang, M. Shamzhy, V.I. Pârvulescu, J. Čejka/ published 17. Lead(II) siloxides/ 2019/ DOI: 10.1002/chem.201904713/ ISSN: 0947-6539/ Chem. Eur. J./ A.-A. Someșan, E. Le Coz, C. I. Raț, V. Dorcet, T. Roisnel, C. Silvestru, Y Sarazin/ published. 18. Molecular structures of (2-bromophenyl)-	

	diphenylstibane and {2'-bromo-[1,1'-biphenyl)-2-yl}diphenyl-stibane/ 2020/ DOI: 10.33224/rrch.2020.65.7-8.10/ ISSN: 0035-3930/ Rev. Roum. Chim./ M. Olaru, K. T. Kegyes, C. I. Raţ/ published. 19. Synthesis of esters of diaminotruxillic bis-amino acids by Pd-mediated photocycloaddition of analogs of the Kaede protein chromophore/ 2020/ DOI: 10.3762/bjoc.16.98/ ISSN: 1860-5397/ Beilstein J. Org. Chem./ E. P. Urriolabeitia, P. Sánchez, A. Pop, C. Silvestru, E. Laga, A. I. Jiménez, C. Cativiela/ published. 20. Hypercoordinated triorganotellurium(IV) derivatives of chalcogen-centred organophosphorus ligands/ 2020/ DOI: 10.1016/j.ica.2020.119841/ ISSN: 0020-1693/ Inorg. Chim. Acta/ E. Denes, A. Beleagă, A. Silvestru/ published. 21. New hypercoordinated triaryltelluronium derivatives of organophosphorus ligands. Synthesis and structural characterization/ 2021/ DOI: 10.33224/rrch.2021.66.1.03/ ISSN: 0035-3930/ Rev. Roum. Chim./E. Denes, M. Vlassa, C. Silvestru, A. Silvestru/ published. 22. {2,6-Bis[(dimethylamino)methyl]phenyl}mercury(II) acetate, $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Hg(OAc)$ – a useful intermediate for selective palladation of 1,3-$(Me_2NCH_2)_2C_6H_4$/ 2021/ DOI: 10.33224/rrch.2021.66.2.07/ ISSN: 0035-3930/ Rev. Roum. Chim./L. Kiss, S. Sergiu, M. Vlassa, A. Silvestru, C. I. Raț, C. Silvestru/ published. 23. Cu(II) and Ag(I) complexes of the pyrazole-derived diorganoselenide $(pzCH_2CH_2)_2Se$. Synthesis, solid state structure and solution behavior/ 2021/ DOI: 10.1016/j.ica.2021.120272/ ISSN: 0020-1693/ Inorg. Chim. Acta/ R. Popa, V. Lippolis, A. Silvestru/ published. 24. Reactivity of a carbonyl moiety in organotin(IV) compounds: novel Pd(II) and Cu(II) complexes supported by organotin(IV) ligands/ 2021/ DOI: 10.1039/D0NJ06016J/ ISSN: 1144-0546/ New J. Chem./ A.-A. Someșan, C. Silvestru, R. A. Varga/ published. 25. Synthesis and characterization of ternary graphene oxide, $MnFe_2O_4$ nanoparticles, and Polyamidoamine dendrons nanocomposite decorated with palladium as heterogeneous catalyst for nitroaromatics reduction/ 2021/ DOI: 10.1002/aoc.6329/ ISSN: 0268-2605/	

	Appl. Organomet. Chem./ A. Ramezanpour, K. Karami, M. Kharaziha, C. Silvestru, P. Bayat/ published. 26. Halogen Bonds (N---I) at Work: Supramolecular Catemeric Architectures of 2,7-Dipyridylfluorene with *ortho*-, *meta*-, or *para*-Diiodotetrafluoro benzene Isomers/ 2020/ DOI: 10.1021/acs.cgd.0c00205/ ISSN: 1528-7483/ Cryst. Growth & Des./ I.G.Grosu, L. Pop, M. Miclăuş, N.D. Hădade, A. Terec, A. Bende, C. Socaci, M. Bărboiu, I. Grosu/ published. 27. Halogen-Bonded Organic Frameworks of Perfluoroiodo- and Perfluorodiiodobenzene with 2,2′,7,7′-Tetrapyridyl-9,9′-spirobifluorene/ DOI: 10.1021/acs.cgd.0c01383/ ISSN: 1528-7483/ Cryst. Growth & Des./ L. Pop, I.G. Grosu, M. Miclăuş, N. Hădade, A. Pop, A. Bende, A. Terec, M. Barboiu, I.Grosu/ published. 28. Selective hydration of electron-rich aryl-alkynes by a Schrock-type molybdenum alkylidene catalyst/2020/ DOI: 10.33224/rrch.2020.65.7-8.07/ ISSN: 0035-3930/ Rev. Roum. Chim./ A.P.Crişan, A. Pop, E. Bogdan, M. Matache, L. Pop, A. Terec, I. Grosu, N.D. Hădade/ published. 29. Click synthesis and complexation properties of a new unsymmetrical macrocycle bearing 1,4-dioxabenzene and triazole units/2020/ DOI: 10.33224/rrch.2020.65.6.06/ ISSN: 0035-3930/ Rev. Roum. Chim./T.A. Cucuiet, C.C. Anghel, E. Bogdan, A. Crişan, M. Matache, L. Pop, A. Terec. N.D. Hădade/ published. 30. Heterometallic metallacyclophanes constructed from side-off bicompartmental ligands/ 2020/ DOI: 10.1080/00958972.2020.1798940/ ISSN: 0095-8972/ J. Coord. Chem./ M. Mocanu, A.A. Patrascu, S. Ionescu, M. Andruh/ published. 31. Luminescent [$Zn^{II}Ln^{III}$] complexes anchored on graphene. Synthesis and crystal structures of [$Zn^{II}Eu^{III}$] and [$Zn^{II}Tb^{III}$] complexes decorated with pyrene groups/ 2020/ DOI: 10.1002/aoc.6126/ ISSN: 0268-2605/ Appl. Organomet. Chem./ A. A. Apostol, I. Mihalache, T. Mocanu, O. Tutunaru, C. Pachiu, R. Gavrila, C. Maxim, M. Andruh/ published. 32. Sonogashira Synthesis of New Porous Aromatic Framework-Entrapped Palladium Nanoparticles as Heterogeneous Catalysts for Suzuki−Miyaura Cross-Coupling/2022/https://doi.org/10.1021/acsami.1c24429/ISSN:1944-8244/ ACS Appl. Mater. Interfaces/ L.	

	Cata, N. Terenti, C. Cociug, N. D. Hadade, I. Grosu, C. Bucur, B. Cojocaru, V. I. Parvulescu, M. Mazur, J. Cejka/ published 33. Macrocyclic Compounds Formed in the Reaction of 3,7-Bis(*ortho*-, *meta*- or *para*-formylphenyl) phenothiazines with *meta*-Bis(aminomethyl)benzene: Experimental and Theoretical Investigations /2022/Doi: / ISSN:0035-3930/Rev. Roum. Chim./ I. Stroia, M. I. Nan, E. Bogdan, A.Terec, N. D. Hădade, I. Grosu/accepted 34. Solid-State and Theoretical Investigations of Some Banister-Type Macrocycles with 2,2'-Aldoxime-1,1'-Biphenyl Units / 2021 / DOI 10.3389/fchem.2021.750418/ ISSN: 2296-2646/ Frontiers in Chemistry/ I. Stroia, I.-T. Moraru, M. Miclăuş, I. Grosu, C. Lar, I. G. Grosu, A. Terec/ published 35. Novel Macrocycles Embedding *p,p'*-Terphenyl Units: Synthesis, Characterization, Single Crystal X-ray Molecular Structures and Theoretical Investigations / 2022 / Doi: / ISSN:0035-3930/Rev. Roum. Chim./ I. Stroia, A. Pop, M. I. Nan, E. Bogdan, A. Terec, N. D. Hădade, I. Grosu / accepted 36. *C,O*-Chelated organotin(IV) derivatives as potential anticancer agents: synthesis, characterization and cytotoxic activity/ 2022/ DOI: 10.1002/aoc.6540/ ISSN: 0268-2605/ Appl. Organomet. Chem./ A.-A. Someșan, S.-M. Vieriu, A. Crăciun, C. Silvestru, P. Chiroi, A. Nutu, A. Jurj, R. Lajos, I. Berindan-Neagoe, R. A. Varga/ published. 37. Supramolecular architectures in novel diphenyl(aryl)tin(IV) chlorides/ 2022/ DOI: 10.1016/j.poly.2022.115894/ ISSN: 0277-5387/ Polyhedron/ C. Afloarei, I. Barbul, A.-A. Someșan, C. Silvestru, R. A. Varga/ published. 38. Synthesis and structural characterization of organoantimony(III) carboxylates/ 2022/ ISSN: 0277-5387/ Polyhedron/ A. A. Tomuta, R. G. Dornea, C. I. Rat, H. J. Breunig/ in preparation. 39. Neutral and ionic complexes containing an [2-{$O(CH_2CH_2)_2NCH_2$}C_6H_4]Pd(II) fragment: synthesis, characterization and catalytic activity for Suzuki cross-coupling reaction/ 2022/ ISSN: 0268-2605/ Appl. Organomet. Chem./ R. Fontana, K. Levente, C. Silvestru/ in preparation. 40. Organolead(IV) and inorganic lead(II) compounds containing tetraphenylimidodichalcogenodiphos-	

	phinato ligands / 2022/ ISSN: 1477-9234/ Dalton Trans./ E. Denes, C. Silvestru/ in preparation. 41. Luminescence thermometry based on one-dimensional benzoato-bridged coordination polymers containing lanthanide ions /2021/ DOI: 10.1039/d1dt015504/Dalton Trans./ A. Topor, D. Avram, R. Dascalu, C. Maxim, C. Tiseanu, M. Andruh/published. 42. Valmet chiral Schiff-base ligands and their copper(II) complexes as organo, homogeneous and heterogeneous catalysts for Henry, cyanosilylation and aldol coupling reactions/ DOI: 2021/10.1002/cctc.202101149/ChemCatChem/ Z. Arora, D.-I. Eftemie, A. Spinciu, C. Maxim, A. Hanganu, M. Tudorache, B. Cojocaru, O. D. Pavel, P. Granger, M. Andruh, V. I. Parvulescu/published 43. A new nitronyl-nitroxide ligand for designing binuclear Ln^{III} complexes: syntheses, crystal structures, magnetic and EPR studies /2022/ DOI: 10.1002/ejic.202200128/Eur. J. Inorg. Chem./ M. Răducă, D. O. T. A. Martins, C. A. Spinu, M. Hillebrand, F. Tuna, G. Ionita, A. M. Mădălan, C. Lecourt, J.-P. Sutter, M. Andruh / published. 44. Co-Fe Nanoparticles Wrapped on N-Doped Graphitic Carbons as Highly-Selective CO_2 Methanation Catalysts/DOI: 10.1021/acsami.1c05542/ ACS Appl. Mater. Interfaces/ B. Jurca, L. Peng, A. Primo, A. Gordillo, V.I. Parvulescu, H. Garcia/published. 45. Supported on N-Doped Graphitic Carbon as Highly-Selective Catalysts for Reverse Water Gas Shift/2022/ DOI: 10.1021/acssuschemeng.1c01401/ ACS Sustain. Chem. Eng/ L. Peng, B. Jurca, A. Primo, A. Gordillo, V.I. Parvulescu, H. Garcia/published. 46. Doped Microporous Graphitic Carbons as Metal-Free Catalysts for the Selective Hydrogenation of Alkynes to Alkenes/ 2022/ DOI: 10.1016/j.jcat.2021.11.034/J. Catal. / A. Primo, A. Rendón-Patiño, C. Bucur, A. Jurca, B. Cojocaru, V.I. Parvulescu, H. Garcia/ published. 47. Catalytic transformation of the marine polysaccharide ulvan into rare sugars, tartaric and succinic acids/DOI:	

	10.1016/j.cattod.2020.06.086/2022/ Catal. Today/ I. Podolean, S.M. Coman, C. Bucur, C. Teodorescu, S. Kikionis, E. Ioannou, V. Roussis, A. Primo, H. Garcia, V.I. Parvulescu/published. 48. High C2-C4 Selectivity (over 50 %) in CO_2 Hydrogenation by Particle Size Control of Co-Fe Alloy Nanoparticles Wrapped on N-doped Graphitic Carbon/2022/ DOI: 10.1016/j.isci.2022.104252 /iScience / L. Peng, B. Jurca, A. Primo, A. Gordillo, V.I. Parvulescu, H. Garcia/ published. 49. Recent progress and prospects in catalytic water treatment /2022/ DOI: 10.1021/acs.chemrev.1c00527/ V. I. Parvulescu, F. Epron, H. Garcia, P. Granger/published. 50. Silver complexes with a luminescent tripodal Schif-base ligand derived from fluorene-2-carboxaldehyde /2022/ DOI: 10.1016/j.poly.2022.115849 /Polyhedron/ A. D. Popa, A, M. Madalan/published.	
Articles published/accepted/under evaluation in BDI indexed journals	*Article title/Year/Journal/Authors/Status(under evaluation/ accepted/published)*	**0**
Patent applicationsfilednationallyand internationally	*Patent title/Issuingauthority/Submission date*	**0**
Patentsobtained at national and international level	*Patent title/Issuingauthority/Issuedate* 1. Procedimiento de preparación de un catalizador basado en nanopartículas de hierro, cobalto o sus aleaciones, catalizador preparado y uso/ Oficina Española de Patentes y Marcas/ 28.05.2020 2. Preparation method for preparing a catalyst based on iron nanoparticles, cobalt nanoparticles or alloys thereof, the catalyst thus prepared and use of the catalyst for the selective hydrogenation of carbon dioxide to isobutane/ World Intellectual Property Organization/ 04.06.2020	**2**
Conferences attendance	*Conference name/Type/Title/Year* 1. 1st International Conference on Reaction Kinetics, Mechanisms and Catalysis, RKMC 2018/ Oral/ Modified Graphenes as support and catalysts for organic reactions, a great challenge/ 2018 2. The 8th Tokyo Conference on Advanced Catalytic Science and Technology (TOCAT)/ Oral/ Graphene: an efficient catalyst for coupling reactions/ 2018	**38**

	3. Pre-symposium of ZMPC2018, "International Symposium on Advanced Zeolite Science & Technology"/ Oral/ Catalytic Properties of 3D Graphene-like Microporous Carbons Synthesized in a Zeolite Template/ 2018 4. Twelfth International Symposium on Heterogeneous Catalysis: Catalysis a motor of economy/ Oral/ Graphenes: a great challenge as support and catalysts for organic reactions/ 2018. 5. 5th Indo-French Symposium on Functionalized Materials for Sustainable Catalytic and Related Applications, MATSUCAT-2019/ Plenary/ Graphenes: A great challenge as support and catalysts for organic reactions, environment remediation and energy production/ 2019 6. CHAOS (C-H Activation in Organic Synthesis) 6th Workshop/ Oral/ Graphene film-supported oriented antimoniumnanoplatelets as very efficient catalysts for Michael and Henry additions/ 2019 7. 14th EUROPACAT/ Oral/ Engineering active sites by hydrogen plasma irradiation: Mimicking bifunctional metal/supported catalysts in hydrogenation reactions/ 2019 8. 8th Asia Pacific Congress in Catalysis (APCAT8)/ Oral/ The direct catalytic synthesis of dicarboxylic acids from glucose, 2019 9. 8th Asia Pacific Congress in Catalysis (APCAT8)/ Oral/ Transition-metal binuclear complexes as new graphene-supported heterogeneous catalysts/ 2019 10. 5th International Congress on Catalysis in Biorefineries – CATBIOR 2019/ Oral/ Marine ulvan polysaccharide as a valuable pool of rare sugars/ 2019 11. 11th International Conference on Environmental Catalysis/ Oral/ Efficient hydrogenation of CO_2 to methane over oriented MoS_2 nanoplatelets supported on few layers/ 2020 12. 37th National Conference on Chemistry, Căciulata/ Poster/ New hypercoordinateddiorganotin(IV) with dithiocarbamato or tetraorganodichalcogenimidodiphosphinato ligands/ 2018 13. Conference of Doctoral Schools from the University Consortium, Iași/ Oral/Sinteza și caracterizarea de noi compuși organometalici ai stibiului(III) și bismutului(III) de tipul [2-(GF*)C_6H_4]$_n$MX_{3-n} (M = Sb, Bi; n = 1-3; GF* =	

	−CH=O, −CH=NCH$_2$C$_6$H$_4$N-2′, −CH=NCH$_2$C$_6$H$_4$N-4′)/ 2018 14. 9th International Conference of the Chemical Societies of the South-East European Countries,Târgoviște/ Oral/Heterocyclic diorganopnicogen compounds. Synthesis, structure and catalysis/ 2019. 15. 9th International Conference of the Chemical Societies of the South-East European Countries, Târgoviște/ Poster/Novel ambiphilicproligands containing antimony/ 2019 16. 27th GECOM CONCOORD, Roz Armor, Erquy/ Poster/Novel homo-and heterolepticPb(II) species/ 2019 17. 27th GECOM CONCOORD, Roz Armor, Erquy/ Oral/Tetrakis(4-carboxyphenyl)stannane - a versatile building block for heterometallic coordination polymers/ 2019 18. 14th International Conference on the Chemistry of Selenium and Tellurium/ Santa Margherita di Pula (CA)/ Oral/Main Group heavy metal compounds containing tetraphenylimidodiselenodiphosphinato ligands/ 2019 19. 14th International Conference on the Chemistry of Selenium and Tellurium, Santa Margherita di Pula (CA)/ Poster/New hypercoordinatedtriorgano-tellurium compounds with organophosphorus ligands/ 2019 20. 37th National Conference on Chemistry, Căciulata/ Plenary/Synthetic "host molecules", mechanically interlocked and self assembled architectures: from design to applications/2018 21. 37th National Conference on Chemistry, Căciulata/ Poster/ New pyridine/hydroquinone based [2]rotaxanes: synthesis of the building blocks/ 2018 22. 37th National Conference on Chemistry, Căciulata/ Poster/ Conformational versatility of a new macrocycle based on 1,3-dioxane units/ 2018 23. 9th International Conference of the Chemical Societies of the South-Eastern European Countries, Targoviste/ Poster/ Chemistry a Nature Challenger/ 2019 24. International Conference "Catalysis and Organic Synthesis" ICCOS-2019, Moscow /Poster /Shape-persistent NDI-based macrocycles with potential application as redox-active materials in organic	

	lithium-ions batteries/2019 25. 21st European Symposium on Organic Chemistry, Vienna/ Poster/ Supramolecularhitectures supported by catemers of 2,7-dipyridylfluorene with ortho-, meta- or para-diiodotetrafluorobenzene isomers/ 2019 26. International Conference „Students for Students", Cluj-Napoca/ Oral/Towards the synthesis of new [2]rotaxanes using the clipping strategy/ 2019 27. International Conference „Students for Students" Cluj-Napoca/ Poster/ Towards the synthesis of new NDI-based shape persistent macrocycles / 2019 28. National Conference of Doctoral Schools of UNIVERSITARIA Consortium, Second Edition, Timisoara/ Oral/Synthesis of a new [2]rotaxane by active metal template CuAAC reaction/2019 29. International Conference „Students for Students", Cluj-Napoca/ Oral/ Pyridine-based [2]rotaxanes designed as switchable catalysts in coupling reactions/2019/ 30. EURONANOFORUM 2019, Bucharest/ Poster/ Luminescent complexes grafted on graphene/ 2019. 31. 7th UK Catalysis Conference, 6-8 January 2021, London, United Kingdom / keynote 32. International Symposiumon Zeolites and Related Porous Materials/ Qingdao, China/2021/ keynote 33. Indo-French Symposium "Functionalized Materials for Sustainable Catalytic and Related Applications, , Strassburg, France/ 2021/oral 34. Advanced Materials with High Impact on Society Workshop (CoSolMat) (Norway-Island-Romania/2021 35. 5th EuChemS Conference on Green and Sustainable Chemistry/2021 /oral 36. Cutting-Edge Homogeneous Catalysis (CEHC-1)/Touluse, France /2021/oral 37. European Conference on Molecular Magnetism/Rennes. France/2022 /poster 38. 2nd International Conference on Noncovalent Interactions /keynote/Strasbourg, France /2022.	
Books	*Title/Publishing year/Publishing house/ISBN*	
Book chapters	*Booktitle/chapter title/Publishing year/Publishing house/ISBN* 1. Zeolites and Metal-Organic Frameworks, From Lab	**5**

	to Industry/ Biomass Transformation into Chemicals Using Zeolites and MOFs/ 2018/ Amsterdam University/ ISBN: 9789462985568 2. Photocatalysis, Nanoparticle Design and Characterization for Catalytic Applications in Sustainable Chemistry/ Nanoparticles and Nanocomposites Design/ 2019/ Royal Society of Chemistry/ ISBN: 978-1-78801-490-8 3. Photocatalysis, Nanoparticle Design and Characterization for Catalytic Applications in Sustainable Chemistry/ Plasmonic Photocatalysts for Environmental Applications / 2019/ Royal Society of Chemistry/ ISBN: 978-1-78801-490-8 4. Heterogeneous Catalysis for Energy Applications/ Application of Ionic Liquids for Sustainable Catalysis/ 2020/ The Royal Society of Chemistry/ ISBN: 978-1788017183 5. Advanced Heterogeneous Catalysts Volume 1: Applications at the Nano-Scale/ Advances in heterogeneous catalysis: Concepts of nanocatalysis and single-atom catalysis/ 2020/ ACS SymposiumSeries/ ISBN: 10.1021/bk-2020-1359.ch001	
Other results		

5. Equipment uses

This topic requires a complex investigation and therefore multiple characterization techniques. Accordingly, a large number of techniques (equipments) are currently used. Most of these are already part of the facilities of the teams, *e.g.* single-crystal and powder XRD, spectroscopic techniques [FTIR, DRIF, ATR, DRUV-Vis, Raman (Visible), solution NMR, MS], textural techniques, analytic equipments (gas and liquid chromatographs coupled with MS), while other are available by inter- and national cooperation (XPS, electron microscopy).

We also acknowledge this project for the acquisition of a Raman extension (in the UV region) (326080 RON, acquired 2019.). This equipment is mandatory for the investigation of carbon-based materials, including graphenes. The acquisition of a glove-box (UBB partner 2), an expensive equipment extremely useful for manipulation of air/moisture sensitive compounds, as well as synthesis of organometallic species under inert argon atmosphere, through this project, is highly acknowledged.

At UBB partner 1, the renew of the hoods (three) in organic synthesis laboratory and the opening of a new organic synthesis laboratory at the ICCRR institute (with four new hoods) considerably improved the capacity of synthesis of our group. The new laboratory was equipped with magnetic stirrers with heating systems and temperature control, Dewar reactors, push-syringes and other small but essential equipments. A new diffractometer for single crystal X-Ray diffraction studies was purchased by the UB partners (from three financial sources, including this project).

MAIN ACHIEVEMENTS

1. Elaboration of a general strategy for grafting heterometallic 3d-4f magnetic and luminescent complexes on graphene by employing pyrene functionalized carboxylates. Moreover, we successfully extended this strategy towards systems containing -SH groups in order to be attached on gold surface.

2. The one-pot preparation of powerful multifunctional heterogenous catalysts as hybrid Me1@Me2@PAF materials. These materials are highly efficient catalysts for many cross-coupling (Suzuki-Miyaura, Sonogashira, Stille) or CuAAC reactions. The metals trapped as nanoparticles in the PAF are exclusively issued from the catalysts employed for the synthesis of the PAFs (by Sonogashira cross-coupling reaction) and no additional metals were required to have these catalysts. The hybrid Me1@Me2@PAF catalysts revealed a high recyclability and for many reactions an outstanding catalytical activity in water.

3. Engineering active sites on reduced graphene oxide by (*i*) doping microporous graphitic carbons and (*ii*) hydrogen plasma irradiation, mimicking bifunctional metal/supported catalysts in hydrogenation reactions.

4. Particle size-controlled Co-Fe alloy nanoparticles wrapped on N-doped graphitic for CO_2 hydrogenation and reverse water gas shift.

5. Magnetic Fe@Y composites as efficient recoverable catalysts for the valorization of the recalcitrant marine sulfated polysaccharides.

6. Another important achievement was the design, synthesis and characterization in solution and solid state of several new precursors – organic, phosphorus-organic or organometallic species –able to be grafted on graphene oxide surface through covalent bonds or to decorate the graphene surface by π-π stacking. These precursors contain different donor atoms able to chelate or to act as pincer ligands for different monometallic as well as homo or hetero polymetallic fragments with appropriate properties either before or after the functionalization of the graphene / GO material.

The main objectives of the project have been reached. Moreover, some activities opened new routes towards new projects.

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Project manager,

Marius Andruh