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Biofunctionalization of carbon nanostructures

-PhD thesis summary-

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CONTENTS (of the entire thesis)

Keywords: *fullerenes, carbon nanotubes, functionalization, dendrimer*

GENERAL INTRODUCTION

Hydrogen, helium and oxygen are the first three most spread elements in the Universe by mass. The list continues with carbon as the fourth most abundant element being present in every known life form becoming the chemical base for life.

In the periodic table of the elements carbon is positioned in the group 14, has 6 as atomic number and is annotated with symbol C. Being a non-metallic and tetravalent element can form four covalent bonds. Carbon-carbon bonds are extremely stable and strong as well which confers the possibility of formation of an almost infinite number of organic, inorganic, organometallic compounds. In natural state the carbon atom has three isotopes: two stable (^{12}C, ^{13}C) and one radioactive (^{14}C). The most known allotropes of carbon are graphite and diamond.

Due to their unique physical, chemical, electrical, mechanical properties, carbon nanostructures have applications in various fields of nanotechnology such as biotechnology, biochemistry, medicine, electrochemistry, electronics, optics.

My research for present thesis was based mostly on carbon nanotubes and fullerenes physical and chemical functionalization but also deals with dendrimer synthesis. I encountered with this materials first during my dissertation for master degree and discovering how amazing this tiny structures can be. I've chosen to continue my work to discover a smart part of their nano world.

The aims of this thesis are:

- ✓ functionalization of carbon nanotubes by:
  - endohedral route
  - exohedral route

- ✓ catalytic chemically modification of C_{60} fullerenes with alanine using microwave assisted media

- ✓ synthesis and characterization of a new highly water-soluble dendrimer.

CONTENT OF THE THESIS

The thesis is structured in 5 main chapters. In the first chapter literature data is reviewed regarding recent findings in fullerene, carbon nanotube and dendrimer chemistry. The selected literature data deals with the used synthesis methods, functionalization routes, properties and important applications.

Starting with chapter 2 the original contribution of present thesis is presented. The chapters (sections among chapter) are structured in 4 main parts: introduction, materials and methods, results and discussion, conclusions. Finally the last part of the thesis consists of general conclusions, references and contains the publication list.

In chapter 2 is described the endohedral functionalization of different types of carbon nanotubes using an environmental friendly filling procedure namely supercritical carbon dioxide media. In the introduction section is presented the used installation and the principles of this procedure. Three different materials were involved in the synthesis of hybrids: coronene, α-sexithiophene and a fullerene-europium (III) based complex. Coronene and α-sexithiophene have been previously reported to be encapsulated in single-walled carbon nanotubes via sublimation involving high temperatures, therefore the formation of undesired compound like coronene-dimer namely dicoronylene can't be avoided. The Eu (III)-fullerene based complex has been reported for the first time to be encapsulated into single-, double- and multi-walled carbon nanotubes.

In case of endohedral functionalization of P2 single-walled carbon nanotubes with coronene using supercritical CO_2 we have demonstrated, that coronene can form well-ordered stacks inside single-walled carbon nanotubes performing the filling procedure at low temperature and using an environmental friendly method. Also in this way the formation of the undesired dicoronylene was avoided. We could demonstrate that the green fluorescence attributed previously to encapsulated coronene is instead caused by dicoronylene adsorbed on the surface of the nanotubes. The hybrid material was therefore characterized using UV-Vis, ATR-IR and Raman spectroscopy. HR-TEM investigations and also photoluminescence measurements were performed. Finally the encapsulation was proved by the formation of double-walled carbon nanotubes via annealing the coronene-nanotube hybrids.

In the second section of this chapter the encapsulation of α-sexithiophene into P2 single-walled carbon nanotubes is described. After the sc.CO_2 filling procedure was applied, the obtained hybrid material was characterized using spectroscopic and analytical methods. By annealing the hybrid can be converted into graphene nanoribbons.

In the last section of chapter 2 the encapsulation rate of a metallic complex based fullerene derivative was studied. We have demonstrated that the fullerene driven encapsulation allowed to increase the filling ratio within thinner nanotubes and also allowed to control the organization of luminescent molecules within the tubular framework. Characterization of hybrid materials involved UV-Vis, ATR-IR and PL spectroscopy, further XPS and microscopic investigations.

Chapter 3 is divided into two sections. First deals with the exohedral covalent functionalization of multi-walled carbon nanotubes using diamine derivatives namely 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 1,7-diaminoheptane and 1,8-diaminooctane using coupling agents is described. First the pristine nanotubes were oxidized and the coupling of diamines was realized through peptide bond formation. The obtained materials characterization involved elemental analysis, TEM, SEM, EDX determinations and also ATR-IR analysis.

In the second section is presented the physical absorption of lipase B from *Candida antarctica* on the surface of single-walled carbon nanotubes. The immobilized enzyme was characterized using elemental analysis, transmission electron microscopy and via Bradford assay its protein content was determined. It was also investigated its enzymatic activity in two acylation reaction.

It was found, that the enzyme in its immobilized form on nanotubes presented no catalytic activity in the enzymatic synthesis of enantiomerically pure (*R*)- and (*S*)- ethyl 3-hydroxy-3-(2-aryl-thiazol-4-yl) propanoates, but it showed high activity and selectivity for the acylation of *rac*-1-phenyl ethanol. Also it was suitable for acylation of phenyl ethanol. Further investigations are included on the list of future plans regarding use and catalytic activity of the immobilized enzyme on nanotube support.

Chapter 4 presents the findings related to alanine-functionalized [60] fullerene. The used covalent functionalization novel method involves metallic catalyst presence namely bis(ciclopentadienyl)hafnium(IV) dichloride and microwave assisted media. The obtained adducts were characterized using analytical tools and spectroscopic determinations were also performed. XPS calculations showed that the adduct containing the free amino group in the sidewall chain is formed in higher rate than the cyclized one.

Chapter 5 is dedicated to synthesis and characterization of a novel highly-water soluble dendrimer. The dendrimer core is 1,3,5-tris(bromomethyl)benzene and is derivatized with diethanolamine molecules. The constructed zero generation of the dendrimer containing six free end-hydroxyl groups was characterized using NMR spectroscopy and mass spectrometry. The findings were in good agreement with the structure of the synthesized compound. Its ammonium salt also underwent NMR characterization. It was observed an unexpected splitting of the aromatic protons signal which leaded to the conclusion that two isomers were formed.

It was also proved that $-CH_2$ protons of the diethanolamine chains are diastereotopic. The synthesis of the first generation is in progress and future plans include derivatization of dendrimer with alanine-fullerene molecules.

GENERAL CONCLUSIONS

The aims of this thesis presented in the general introduction part were achieved.

The endohedral functionalization of different types of carbon nanotubes using an environmental friendly filling method namely supercritical carbon dioxide mediated encapsulation was realized for coronene, α-sexithiophene and N-5-(3-ethylimidazolium)-pentyl-[Eu(III)tetrakis(2-naphtoyltrifluoro-acetonato)] aza-[60] fullerene.

In case of COR@SWCNT:

- the absence of the high intensity Raman modes of dicoronylene from the product spectra indicates that the undesired dicoronylene formation was avoided due to the applied filling method
- it was found that the minimal temperature at which coronene molecules trapped inside the P2-SWCNTs cavities transform into an inner tube is 1250 °C giving rise to double-walled carbon nanotubes
- filling carbon nanotubes with coronene at low temperature (50 °C) under supercritical conditions yielded well-ordered stacks of coronene, as HRTEM images revealed, this giving corroboration to the hypothesis that dicoronylene is formed at filling procedures performed at high temperatures.

In case of 6T@SWCNT:

- 6T@SWCNT can be obtained not only by sublimation at high temperature, but at low temperature as well
- Raman spectra confirmed the encapsulation due to the shifted RBM mode of filled nanotube sample
- 6T molecules present luminescent properties once encapsulated.

In case of 1·[EuL_4]@CNTs:

- this method allowed to increase the filling ratio within thinner carbon nanotubes (SW, DW) and also to control the organization of the chromophores within the tubular framework
- the luminescent complex kept his photophysical property even encapsulated into nanotubes which could make these nano-carrier hybrids suitable for biosensing.

The exohedral functionalization of carbon nanotubes was also performed by covalently attaching diamines and by physical immobilization of lipase B from *Candida antarctica*.

In case of covalent functionalization five different diamines were attached to multi-walled carbon nanotubes via peptide bonding. It was found that:

- the optimal temperature interval is between 40 and 50 °C
- 1,6-diamino hexane functionalization took place with a small yield confirmed by elemental analysis and ATR-IR spectroscopy as well
- shorter alkyl chain containing diamine-nanotube derivatives show different spectral behaviour than longer ones.

The 1,4-diamine modified nanotubes underwent cytotoxicity testing and the results returned that below 25 μg/mL diamine-modified nanotubes are nontoxic for the A549 cell line.

Immobilization of CaL-B on the surface of single-walled carbon nanotubes was confirmed by elemental analysis and TEM imaging. The protein content of the CaL-B-SWCNT adduct was determined using the Bradford protein assay.

Functionalization of fullerene C_{60} with alanine in microwave assisted media via catalysis was also realized confirmed by XPS measurements. Toxicology test revealed that the concentration of fullerene and fullerene derivative below which cellular apoptosis is not present is 0.2 mg/mL.

The synthesis and characterization of a novel highly-water soluble zero generation dendrimer was successfully achieved. The six end-hydroxyl groups containing compound was characterized using NMR spectroscopy and mass spectrometry analysis which confirmed the structure. The ^{1}H-NMR spectra of the ammonium salt of the target compound revealed an unexpected splitting of the signals which leaded to the conclusion that two conformations were formed.

The original contributions were presented at 5 international conferences and included in 6 scientific publications.

Also 2 more articles are in progress regarding the findings in fullerene functionalization and dendrimer synthesis.

LIST OF PUBLICATIONS related to the thesis

Articles

Melinda-Emese Füstös, Mircea-Vasile Diudea, Gabriel Katona, Functionalization of multi-walled carbon nanotubes with diamino-alkyl moieties, *Studia Universitatis Babes-Bolyai Seria Chemia*, **2011**, EMT-special issue, accepted

(I.F. = 0.129)

B. Botka, M. E. Füstös, G. Klupp, D. Kocsis, E. Székely, M. Utczás, B. Simándi, Á. Botos, R. Hackl, K. Kamarás, Low-temperature encapsulation of coronene in carbon nanotubes, *Physica Status Solidi B,* **2012**, 249(12), 2432-2435

(I.F. = 1.489)

Bea Botka, Melinda E. Füstös, Hajnalka M. Tóháti, Katalin Németh, Gyöngyi Klupp, Zsolt Szekrényes, Dorina Kocsis, Margita Utczás, Edit Székely, Tamás Váczi, György Tarczay, Rudi Hackl, Thomas W. Chamberlain, Andrei N. Khlobystov, Katalin Kamarás, Interactions and Chemical Transformations of Coronene Inside and Outside Carbon Nanotubes, *Small*, **2013**, DOI: 10.1002/smll.201302613

(I.F. = 7.823)

Laura Maggini, Melinda-Emese Füstös, Thomas W. Chamberlain, Cristina Cebrián, Mirco Natali, Marek Pietraszkiewicz, Oksana Pietraszkiewicz, Edit Székely, Katalin Kamarás, Luisa De Cola, Andrei N. Khlobystov, Davide Bonifazi, Fullerene-driven encapsulation of a luminescent Eu(III) complex in carbon nanotubes, *Nanoscale*, **2013**, DOI: 10.1039/C3NR05876J

(I.F.= 6.233)

M. A. Naghi, A. Varga, M. E. Füstös, G. Katona, V. Zaharia, Heterocycles 35: CaL-B mediated synthesis of optically pure (*R*)- and (*S*)- ethyl 3-hydroxy-3-(2-aryl-thiazol-4-yl)propanoates, *Tetrahedron Asymmetry*, **2013**, submitted

(I.F.= 2.115)

Posters presented at international conferences

Füstös Melinda-Emese, Katona Gabriel, Diudea Mircea-Vasile, Functionalization of multi-walled carbon nanotubes with diamino-alkyl moieties, *XVIIth International Conference on Chemistry*, **Cluj-Napoca**, Romania, November 3-6, **2011**

Füstös Melinda-Emese, Tóháti Hajnalka-Mária, Laura Maggini, Davide Bonifazi, Kamarás Katalin, Székely Edit, Simándi Béla, Utczás Margita, Egyfalú szén nanocsövek töltése fullerénszármazékkal szuperkritikus CO_2-ban (Filling of single-walled carbon nanotubes with fullerene-derivative using supercritical CO_2), *Szuperkritikus Oldószerek Analitikai és Műveleti Alkalmazása- Nemzetközi Konferencia- (International conference on Supercritical Fluid Extraction)*, **Budapest**, Hungary, May 24, **2012**

Melinda-Emese Füstös, Hajnalka-Mária Tóháti, Edit Székely, Béla Simándi, Norbert Alekszi, Katalin Kamarás, Encapsulation of α-sexithiophene in single-walled carbon nanotubes using supercritical CO_2, *Xth International Krutyń Summer School-„Frontiers in Science & Technology of Carbon Nano-Materials"*, **Krutyń**, Poland, June 19-25, **2012**

This poster received the „Best poster" award.

Short talks at international conferences

Füstös Melinda-Emese, Dima Norbert, Katona Gabriel, C_{60}-fullerének funkcionalizálása (Functionalization of C_{60} fullerenes), *XVIIIth International Conference on Chemistry*, **Băile Felix**, Romania, November 22-25, **2012**

Dima Norbert-Artur, Füstös Melinda-Emese, Katona Gabriel, Triszmetilén benzol centrumú dendrimer előállítása és jellemzése (Synthesis and characterization of trismethylene benzene core dendrimer), *XIXth International Conference on Chemistry*, **Baia Mare**, Romania, November 21-24, **2013**