



Le carbone dans tous ses états

Symposium on "Carbon-based Nanomaterials :
from Chemistry to Applications"

Institut de Physique et de Chimie des Matériaux de Strasbourg IPCMS
Campus de Cronenbourg

13 octobre 2009



PROGRAM

8H45-9H00 Welcome by Marc Drillon and introduction by D. Felder-Flesch and A. Bianco

Chairman: Alberto BIANCO

9H00-9H50 "Fullerenes and nanotubes see the light (!)"

Dirk M. Guldi

Department of Chemistry and Pharmacy and Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany"

9H50-10H40 "Fullerenes for photovoltaics"

Nazario Martin

Departamento de Química Orgánica, Facultad de Química, Universidad Complutense; IMDEA-Nanociencia, Cantoblanco. Madrid, Spain

10H40-11H10 Coffee and poster session

11H10-11H55 "Functionalization of Carbon Nanotubes for Materials and Nanomedical Applications : Synthesis and Challenges"

Maurizio Prato

Dipartimento di Scienze Farmaceutiche, University of Trieste, Italy

11H55-13H30 Brunch and poster session

Chairman: Jean-Louis GALLANI

13H30-14H20 "Nanoscale diamond: production, properties, functionalisation and applications"

Anke Krueger

Institut für Organische Chemie, Universität Würzburg, Am Hubland Würzburg, Germany

14H20-15H10 "The world of endohedral fullerenes"

Lothar Dunsch

Leibniz-Institut für Festkörper- und Werkstofforschung, Abt. Elektrochemie und leitfähige Polymere, Dresden, Germany

15H10-15H40 Coffee and poster session

Chairman: Jean-François NIERENGARTEN

15H40-16H30 "Processable nanocarbons: Solutions of carbon nanotubes and graphene"

Alain Pénicaud

Centre de Recherche Paul Pascal – CNRS Université Bordeaux-I Av. Schweitzer, 33600 Pessac, France

- 16H30-17H10 "Novel synthetic routes for donor-type graphite intercalation compounds"
Claire Hérold
Laboratoire de Chimie du solide minéral LCSM –UMR 7555, Université Henri Poincaré, Faculté des Sciences, Vandoeuvre, France
- 17H10-18H00 "Soft-Materialization of Fullerene Assemblies and Beyond"
Takashi Nakanishi
¹Organic Nanomaterials Center, National Institute for Materials Science (NIMS), Japan
²MPI-NIMS International Joint Laboratory, Max Planck Institute of Colloids and Interfaces, Germany
³PRESTO, Japan Science and Technology Agency (JST), Japan

Conclusions and remarks

ABSTRACTS

FULLERENES AND NANOTUBES SEE THE LIGHT (!)

Dirk M. Guldi

*Department of Chemistry and Pharmacy and Interdisciplinary Center for Molecular Materials (ICMM),
Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, Erlangen, Germany*

Multifunctional carbon nanostructures are currently under active investigation for producing innovative materials, composites, and optoelectronic devices, whose unique properties originate at the molecular level. Among the wide variety of carbon allotropes recently discovered, C_{60} , single wall carbon nanotubes (SWNT) and single wall carbon nanohorns (SWNH) are of particular interest. C_{60} is entirely made of pentagons and hexagons resulting in 0.78 nm sized truncated icosahedral carbon spheres. In contrast, the structure of SWNT has a cylindrical shape, which can be conceptually generated by wrapping a one-atom-thick layer of a graphene sheet into a seamless cylinder. The diameter of most SWNT is around 1 nm – similar to that of C_{60} – with a tubular length that can reach many thousands of times their diameter. Importantly, based on different arrangements, SWNT possess different electrical properties, which are the result of the electrons moving differently in the tube depending on the SWNT arrangement. SWNH, on the other hand, are typically constituted by tubes of about 2-5 nm of diameter and 30 to 50 nm long, which associate with each other to give rise to round-shaped aggregates of 100 nm of diameter. Their large surface areas and inner nanospaces are of great importance, since they ensure a great affinity, for example, with organic electron donors.

The accomplishment of multiple-performance objectives in a single system necessitates combining these carbon allotropes with other classes of materials. Our past work has mapped out compounds that proved particularly useful: active organic materials such as porphyrins / phthalocyanines and oligomers / polymers. We have demonstrated that linking these molecular building blocks creates enormous synergisms in going much beyond just harnessing the features of the individual subunits or constituents. Eventually it enables the control over molecular arrangement – well-defined ensembles and superstructures with widely differing property values – and results in the development of the necessary tools for fine-tuning properties on the molecular, nanoscale level.

I will highlight the opportunities that rest on fullerenes and single wall carbon nanotubes within the context of charge transfer reactions in novel chemical as well as light driven systems with high tensile strength. A fundamental aspect of our research is to integrate such functions without sacrificing the structural and electronic integrity of the material. In this context, I will survey our concepts to generate functional entities using the bottom up approach, that is, to design, manipulate, characterize, examine, and understand the potential of carbon materials as a novel platform for stable electron donor-acceptor hybrids and conjugates. Important aspects will include the impact, the benefits and some of the promises that evolve from charge transfer reactions involving carbon nanostructures with high tensile strength on i) the stabilization of radical ion pair states, ii) multi electron catalytic reactions, and iii) photoelectrochemical / photovoltaic solar energy conversion.

FULLERENES FOR PHOTOVOLTAICS

Nazario Martín

Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, E-28040 Madrid, Spain IMDEA-Nanociencia. Cantoblanco. Madrid, Spain.

(Tel., +34 91 3944227; nazmar@quim.ucm.es)

Fullerenes are electron accepting carbon allotropes which have received a lot of interest as materials for photovoltaic (PV) applications, by blending with a variety of semiconducting polymeric materials. The former devices were based on the concept of mixing an electron donor polymer (p-type component) and the fullerene derivative as the acceptor (n-type component) in two layer (p/n) photovoltaic cells, in which the electronic interaction was limited to the interface between both materials. A further improvement resulted from the concept of "bulk heterojunction" solar cells, which drastically enhanced the interaction between the two components and, therefore, the efficiency of electron transfer and the photovoltaic device.

In this lecture, the basic concepts of the organic fullerene-based PV devices will be presented, followed by those results from our group directed to the preparation of alternative fullerenes in the search for better materials and efficiencies. The ordering of fullerenes on solid surfaces will be also presented. Finally, the last approaches to new fullerene-based materials as alternatives to the more "classic" systems will be also discussed.

FUNCTIONALIZATION OF CARBON NANOTUBES FOR MATERIALS AND NANOMEDICAL APPLICATIONS : SYNTHESIS AND CHALLENGES

Maurizio Prato

*Dipartimento di Scienze Farmaceutiche, University of Trieste, Piazzale Europa 1, 34127
Trieste, Italy
prato@units.it*

Carbon nanotubes (CNT) have generated great expectations due to their electronic and mechanical properties. However, high molecular weights and strong intertube forces keep CNT together in bundles, making their manipulation, characterization and analytical investigation very difficult. The organic functionalization offers the great advantage of producing soluble and easy-to-handle CNT. As a consequence, the compatibility of CNT with other materials, such as polymers, is expected to improve. In addition, once properly functionalized, CNT become soluble in many solvents, so that their solution properties can be studied. Many functionalized carbon nanotubes may find useful applications in the field of materials science and technology, including photovoltaics. Also in medicinal chemistry carbon nanotubes are set to play an important role. Their use as drug delivery scaffolds and substrates for vaccines has already been demonstrated. CNT functionalized with bioactive moieties are particularly suited for targeted drug delivery. In fact, not only they become less toxic but also exhibit a high propensity to cross cell membranes.

However, the organic modification of CNT is not yet a well established field. The intrinsic low chemical reactivity of CNT, coupled with the difficulty in characterizing and purifying the reaction products, make this discipline difficult and fascinating at the same time. Among the many ways available, several strategies have been devised to solubilize nanotubes. Among these, the most successful are: 1) the covalent functionalization of sp^2 carbons at the sidewalls with organic pendant groups and 2) the non-covalent functionalization through supramolecular interactions (e.g., π - π stacking interactions), which allows the formation of stable suspensions.

Within this contribution, we will review our most recent achievements in the field of synthesis of functionalized carbon nanotubes and their applications in materials science and medicinal chemistry. Not only can CNT function as useful components in polymer composites and photovoltaic devices, but they are excellent carriers for drug delivery and ideal substrates for neuronal growth.

NANOSCALE DIAMOND: PRODUCTION, PROPERTIES, FUNCTIONALISATION AND APPLICATIONS

Anke Krueger

*Institut für Organische Chemie, Universität Würzburg, Am Hubland
D-97074 Würzburg
krueger@chemie.uni-wuerzburg.de*

Nanoscale diamond particles can be either produced by detonation synthesis or by jetmilling micrometric HTHP diamond. These methods lead to different nanoscale diamond materials. Detonation diamond, with a particle size of ~ 5 nm is available in large quantities, possesses highly functionalised surface, and roundish particle shape. Due to interparticle bonds, electrostatic interaction and π - π interaction it exists in the form of strongly bound agglomerates. HTHP derived nanodiamond on the other hand consists of strongly faceted, irregularly shaped particles with a larger size distribution. Its surface is usually less functionalised.

We have developed several methods for the mechanical and/or chemical deagglomeration of nanodiamond leading to stable colloidal solutions of the material. This enables the application of wet-chemical methods for the surface functionalisation of these nanoparticles. Besides the silanisation using different trialkoxysilanes it is now possible to establish stable C-C bonds using arylation by diazonium salts or cycloaddition reaction on fullerene-like surface structures.

Functionalised diamond nanoparticles are highly valuable for a variety of applications. This includes the use as a non-bleaching, non-blinking fluorescence label. This application makes use of the luminescence of N-V centres (nitrogen-vacancy defects) in the diamond lattice. The same defects in the negatively charged state can be used for a variety of spin-related applications such as magnetometry. Other applications of nanoscale diamond include targeted drug delivery, immobilisation of enzymes and catalysts, polymer composites as well as electronic applications.

[1] G. Balasubramanian, I. Y. Chan, R. Kolesov, M. Al-Hmoud, J. Tisler, C. Shin, C. Kim, A. Wojcik, P. R. Hemmer, A. Krueger, T. Hanke, A. Leitenstorfer, R. Bratschitsch, F. Jelezko, J. Wrachtrup, *Nature* **2008**, *455*, 648-652. [2] F. Neugart, A. Zappe, F. Jelezko, C. Tietz, J. P. Boudou, A. Krueger, J. Wrachtrup, *Nano Lett.* **2007**, *7*, 3588-3591. [3] for a short review see: A. Krueger, *Adv. Mater.* **2008**, *20*, 2445-2449.

THE WORLD OF ENDOHEDRAL FULLERENES

Lothar Dunsch

*Leibniz-Institut für Festkörper- und Werkstoffforschung ,
Abt. Elektrochemie und leitfähige Polymere
Helmholtzstrasse 20, D-01069 Dresden, Germany*

A general review on the recent development in endohedral fullerenes is given. The endohedral fullerenes are a type of carbon nanostructures which offer a large variety of stable fullerene cages as well as of the included atoms, ions or clusters. The species incorporated can stabilize fullerene cages which are not to be isolated in the empty form like C_{72} or C_{74} or are completely unstable as the non-IPR structures C_{66} and C_{68} . Furthermore for higher cages several new isomers are isolable in the endohedral form and for cages like C_{98} or C_{100} the endohedral fullerene is the only way to get these cages available. On the other hand fullerene cages can provide an ideal environment with their internal space, which enables the stabilization of highly reactive atoms and clusters.

Starting with simple atomic inclusions like nitrogen in fullerenes the presentation of endohedral fullerenes is at first focused on the metallofullerenes. They are extended to new clusterfullerenes like $Sc_2C_2@C_{84}$ and $Sc_3N@C_{80}$. The latter type of fullerenes is now available to a very large extent of structures. A new fullerene synthesis is used to get endohedral fullerenes as the main product of the fullerene synthesis. Upon studying the influence preparation a large variety of endohedral structures like $Dy_3N@C_{80}$, $Ho_3N@C_{80}$, $Tm_3N@C_{80}$, $Y_3N@C_{80}$, $Tb_3N@C_{80}$, $Sc_3N@C_{80}$ and mixed nitride cluster fullerenes were isolated.

The influence of the incorporated structure as well as that of the cage isomerism on the electronic properties of the endohedral fullerenes is followed with special emphasis on spectroscopic properties (ESR, UV-Vis-NIR, Raman and IR spectroscopy) as well as the electrochemical behaviour (cyclic voltammetry) of these endohedral structures. The special situation of the nitridecluster fullerenes is demonstrated for magnetic structures. Raman spectroscopic data gave especially strong support in the description of the endohedral fullerene structure.

In the general outlook the role of new routes for endohedral fullerenes is pointed out to open all potentialities of the endohedral fullerene for different fields of applications.

PROCESSABLE NANOCARBONS: SOLUTIONS OF CARBON NANOTUBES AND GRAPHENE

Alain Pénicaud

Centre de Recherche Paul Pascal – CNRS Université Bordeaux-I Av. Schweitzer, 33600 Pessac, France
penicaud@crpp-bordeaux.cnrs.fr

By reducing carbon nanotubes (CNT) or graphite using alkali metals, the obtained salts are spontaneously soluble in polar organic solvents and form true thermodynamically stable solutions of individualized objects (carbon nanotubes or graphene).[1] We will describe the preparation and characterization of these solutions with more emphasis on the recently obtained graphene solutions.[2] We will also show that these solutions can serve as starting point to controllable functionalisation. We will illustrate that with a series of C_nR functionalized nanotubes (25 < n < 500) where R is a functional group.[3]

[1] Spontaneous Dissolution of a Single Wall Carbon Nanotube Salt, A. Pénicaud, P. Poulin, A. Derré, E. Anglaret, P. Petit, *J. Am. Chem. Soc.*, **2005**, 127,8-9

[2] Solutions of Negatively Charged Graphene Sheets and Ribbons, C. Vallés, C. Drummond, H. Saadaoui, C. A. Furtado, M. He, O. Roubeau, L. Ortolani, M. Monthieux, A. Pénicaud, *J. Am. Chem. Soc.*, **2008**, 130, 15802–15804.

[3] Alkylation of carbon nanotube salts: control over the extent of sidewall functionalization, D. Voiry, O. Roubeau, A. Pénicaud, submitted.

NOVEL SYNTHETIC ROUTES FOR DONOR-TYPE GRAPHITE INTERCALATION COMPOUNDS

Claire Hérold

*Laboratoire de Chimie du solide minéral LCSM –UMR 7555
Université Henri Poincaré, Faculté des Sciences BP 239
54506 Vandoeuvre, France.*

(Tel., +33 3 83684884; e-mail: Claire.Herold@lcsm.uhp-nancy.fr)

Because of the nature of its bonds, graphite appears as an anisotropic material. The presence of the Van der Waals bonds explains its chemical reactivity with various reagents that fill the interlayered galleries, leading to graphite intercalation compounds. The intercalation reaction is always an oxido-reduction reaction with a charge transfer between the graphene planes and the reagent. Strong reducing species such as alkali metals intercalate easily into graphite and appear as efficient intercalation vectors for numerous reagents that are not able to intercalate by themselves. Using molten alkali metal media, several families of binary and ternary graphite intercalation compounds were prepared. Depending on the reagent and the reaction conditions, the intercalated sheets are mono-layered or poly-layered and the crystal structure is commensurate or not with that of graphite. Recently, reactions of lithium-calcium alloys with graphite allowed the synthesis of two superconducting bulk materials CaC_6 and $\text{Li}_3\text{Ca}_2\text{C}_6$ with critical temperatures of 11.5 K and 11.15 K respectively and lithium-europium alloys lead to compounds with anisotropic magnetic properties.

SOFT-MATERIALIZATION OF FULLERENE ASSEMBLIES AND BEYOND

Takashi Nakanishi^{1,2,3}

¹*Organic Nanomaterials Center, National Institute for Materials Science (NIMS),
Japan*

²*MPI-NIMS International Joint Laboratory, Max Planck Institute of Colloids and
Interfaces, Germany*

³*PRESTO, Japan Science and Technology Agency (JST), Japan*

Controlled morphology and dimensionality of carbon-rich nanomaterials has been recently received considerable attention because bulk properties of such carbon materials, e.g. fullerene C₆₀, can be enhanced by fine-tuning of intermolecular interactions. Here, I introduce the unique supramolecular fullerene architectures utilizing the two different intermolecular forces introduced by C₆₀ (π - π) and long aliphatic chains (van der Waals). In this talk, following subjects are lectured. i) Formation of polymorphological architectures of fullerene assemblies with controlled dimensionality.¹⁻³ ii) Highly durable "superhydrophobic surfaces" based on fullerene assemblies.⁴⁻⁵ iii) Long-range ordered "liquid crystals" with comparably high electron carrier mobility.⁶ iv) Room temperature "liquid fullerenes" having redox and carrier transport properties.⁷ v) Sustainable "supramolecular transcription" approach for formation of nano-structured metal surfaces applying fullerene assemblies as its template.⁸ In addition, upcoming new results of fullerene-composite materials will be delivered.

References: [1] *Chem. Commun.* **2005**, 5982. [2] *Small* **2007**, 3, 2019. [3] *J. Am. Chem. Soc.* **2006**, 128, 6328. [4] *Adv. Mater.* **2008**, 20, 443. [5] *Angew. Chem. Int. Ed.* **2009**, 48, 2166. [6] *J. Am. Chem. Soc.* **2008**, 130, 9236. [7] *J. Am. Chem. Soc.* **2006**, 128, 10384. [8] *Chem. Eur. J.* **2009**, 15, 2763.