

CPP 1: Focus: Molecularly Functionalized Low-Dimensional Systems I - organized by Antonio Setaro, Carola Meyer, Aravind Vijayaraghvan and Matteo Mannini

Low dimensional nanostructures like nanotubes, wires and 2D molecular layers allow for the investigation of physics in reduced dimensions. These low dimensional systems can act as template for the alignment of molecules, which can assume the role of additional building blocks. The resulting functionalized nanostructures can have tailored chemical, optical, magnetic, or electronic properties. Controlled functionalization therefore promotes new device applications such as the detection of spin states in magnetic molecules by electronic transport or the monitoring of molecular switching events using local optical probes. This interdisciplinary focus session aims to gather experts from different fields to promote synergy effects between synthesis, microscopy, spectroscopy, electronics and engineering. The low dimensional materials that are the basis for further functionalization include - carbon and inorganic nanotubes - semiconducting and metallic nanowires - graphene nanoribbons - 2D nanostructures and can be functionalized with molecules or nanoparticles with peculiar magnetic, optical or electronic properties promoting new physical properties and/or offers new opportunities for devices.

Time: Monday 9:30–13:00

Location: C 130

Topical Talk CPP 1.1 Mon 9:30 C 130

Diameter-dependent optical absorption and energy transfer from encapsulated dye molecules to single wall carbon nanotubes — ●SOFIE CAMBRÉ¹, STEIN VAN BEZOUW¹, JOCHEN CAMPO¹, JOERI DEFILLET¹, WIM WENSELEERS¹, DYLAN H. ARIAS², RACHELLE IHLY², ANDREW J. FERGUSON², JUSTIN C. JOHNSON², and JEFFREY L. BLACKBURN² — ¹Physics Department, University of Antwerp, Antwerp, Belgium — ²Chemistry & Nanoscience Center, National Renewable Energy Laboratory, Golden Colorado, USA

The hollow core and well-defined diameters of single-walled carbon nanotubes (SWCNTs) allow for creation of unique one-dimensional hybrid structures by encapsulation of various molecules.[1] Here, we show that the optical properties of dye molecules encapsulated in SWCNTs can be strongly modulated by the SWCNT diameter, indicating very specific diameter-dependent stacking and interactions of the molecules. The filling is thoroughly characterized by optical absorption, resonant Raman, and two-dimensional infrared photoluminescence excitation (PLE) spectroscopy. Energy transfer probed by PLE spectroscopy shows the absorption spectrum of the dyes to be strongly diameter-dependent. The design of these functional hybrid systems, with tuneable dye absorption demonstrates potential for implementation in dedicated photo-conversion devices.

[1] S. Cambré, J. Campo et al., *Nature Nanotechnol.* 10, 248 (2015).

CPP 1.2 Mon 10:00 C 130

Encapsulation of molecules into carbon and boron nitride nanotubes - a comparison — ●KATALIN KAMARÁS¹, ÁRON PEKKER¹, DÁNIEL DATZ¹, HAJNALKA M. TÓHÁTI¹, KATE E. WALKER², GRAHAM A. RANCE², and ANDREI N. KHLOBYSTOV² — ¹Wigner Research Centre for Physics, Budapest, Hungary — ²University of Nottingham, Nottingham, United Kingdom

Encapsulation of small molecules into carbon nanotubes enables the study of special one-dimensional structures as well as chemical reactions in the cavities. We compare encapsulated structures using two kinds of nanotubes: carbon, with an extended π -electron system, and boron nitride, an analogue of carbon nanotubes with a predominantly ionic bonding. The different electronic structures give rise to different behavior in many aspects. Van der Waals interaction between the tube wall and the encapsulated molecule is much weaker in boron nitride, therefore the filling is easily reversible by solvent extraction. Boron nitride being transparent in most of the infrared and visible region, reactions within the tube can be followed by spectroscopy. On the other hand, the strong phonon-polariton mode and the local infrared-active defect modes can be detected by near-field spectroscopy, making it possible to map the defect structure with spatial resolution of the order of a few tens of nanometers. By thermal reactions, different kinds of double-walled nanotubes are produced, including "shielded nanocables" of carbon nanotubes inside boron nitride nanotubes.

CPP 1.3 Mon 10:15 C 130

Carbon nanotubes as templates for 1D nanostructures via a one-reactant-one-pot method — ●THOMAS CHAMBERLAIN — University of Leeds, Leeds, UK

Harnessing functional properties which emerge at the nanoscale is the key to developing superior materials for catalytic, electronic and

biomedical applications. The internal cavity of single-walled carbon nanotubes provides an effective template for control of the exact positions and orientations of molecules and atoms and has been successfully applied to the construction of nanoscale architectures from a variety of metals, organic molecules, and inorganic compounds [1-3]. Low-dimensional inorganic materials, including transition metal chalcogenides, are of particular interest as their semiconducting properties can be precisely tuned by shaping their structures into nanoribbons. While the host-nanotube can control the dimensions of the inorganic structure, the stoichiometry is much more difficult to control.

An all-in-one molecular precursor that contains all necessary elements in correct proportion for the desired product, encapsulated in SWNTs and subsequently converted into the nanomaterial offers a highly effective solution to this challenge. This new strategy for nanoribbon synthesis and characterisation at the nanoscale can enable the formation of previously inaccessible quasi one-dimensional nanomaterials suitable for a variety of technological applications.

References: 1), T. Chamberlain et al., *ACS Nano*, 11(3), 2509-2520 (2017), 2), A. Botos et al., *J. Am. Chem. Soc.*, 138(26), 8175-8183 (2016), 3), C. Stoppiello et al. *Nanoscale*, 9, 14385-14394, (2017).

CPP 1.4 Mon 10:30 C 130

Peapods with endofullerene single-molecule magnets — ●RASMUS WESTERSTRÖM¹, FABIAN FRITZ^{2,3}, CHRISTIN SCHLEIER⁴, STANISLAV M AVDOSHENKO⁴, ALEXEY A POPOV⁴, and CAROLA MEYER^{2,3} — ¹Synchrotron Radiation Research, Lund University, 22100 Lund, Sweden — ²Department of Physics, University Osnabrück, 49076 Osnabrück, Germany — ³Peter Grünberg Institute (PGI-6), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany — ⁴Leibniz Institute for Solid State and Materials Research (IFW), 01069 Dresden, Germany

Rare-earth-based endofullerene nanomagnets belong to the group of single-molecule magnets (SMMs), a class of molecules that exhibits an intrinsic magnetic bistability at low temperatures. Here we present a structural, chemical, and magnetic characterization of one-dimensional chains of endofullerene nanomagnets encapsulated in carbon nanotubes (CNTs), so-called peapods. It is demonstrated that unique peapod bundles can be located and studied by scanning transmission X-ray microscopy (STXM) and high-resolution transmission electron microscopy (HRTEM). By correlating HRTEM and STXM images, we show that structures down to 30 nm are resolved with chemical contrast and record nanoscale X-ray absorption spectra from endohedral lanthanide ions embedded in individual CNT bundles. Magnetic characterization of samples consisting of bundles of CNTs filled with Dy₂ScN@C₈₀ SMMs was performed using X-ray magnetic circular dichroism (XMCD), and the magnetic properties of these one-dimensional arrays will be discussed.

CPP 1.5 Mon 10:45 C 130

[Selective covalent functionalization of carbon nanotubes activated by light — ●GEORGY GORDEEV¹, THOMAS ROSENKRANZ², STEPHANIE REICH¹, and RALPH KRUPKE^{2,3} — ¹Department of Physics, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — ²Institute of Materials Science, Technische Universität Darmstadt, Darmstadt, Germany — ³Institute of Nanotechnology, Karlsruhe Institute of Technology, Karlsruhe, Germany

The diazonium reaction on nanotubes has recently attracted attention due to the ability of forming bright, fluorescent quantum defect states. The resonant light has been reported to accelerate and tune the reaction velocity. The latter is proportional to the energetic difference between transition energy and incident light. In our study, we demonstrate how a single chirality can be preferably functionalized by tuning optical excitation. We have performed the functionalization on a mixed chirality sample, resonantly exciting (9,7) tube. We monitored the reaction in situ via Raman spectroscopy. A dramatic difference between dark and illuminated areas in the functionalization degree was observed. The material outside the active spot did not demonstrate any changes from the pristine sample. The successful functionalization of the illuminated material was confirmed by resonant Raman scattering. The shift of transition energies and the number of sp³ defects was significantly higher in the resonantly excited nanotubes. The optically induced selectivity of the diazonium reaction paves a way of tuning and improving photonic devices based on nanotubes and can allow a large-scale single chirality enrichment of nanotubes.

15 min. break

Topical Talk CPP 1.6 Mon 11:15 C 130
Self-organization and energy transfer in non-covalent porphyrin - carbon nanotube supramolecular hybrids — GÉRAUD DELPORT², JEAN-SÉBASTIEN LAURET², STÉPHANE CAMPIDELLI³, FABIEN VIALLA¹, and ●CHRISTOPHE VOISIN¹ — ¹Laboratoire Pierre Aigrain, Ecole Normale Supérieure, Université Paris Diderot, Paris, France — ²Laboratoire Aimé Cotton, Université Paris Saclay, Orsay, France — ³LICSEN, CEA, Saclay, France

Functionalization of nanostructures with organic dyes brings the power and flexibility of organic chemistry to the nano-world and extends considerably the range of applications of nanomaterials. Nevertheless, covalent grafting of molecules may be detrimental to the intrinsic properties of the nano-object, whereas purely noncovalent approaches often yield assemblies of poor stability. We developed a micelle assisted supramolecular chemistry to create stable noncovalent complexes of porphyrin molecules attached to single-wall carbon nanotubes. We show that the stability of this assembly is partly due to porphyrin-porphyrin intra-layer interactions yielding a self-organized layer of porphyrin molecules with long-range ordering of the porphyrin orientation with respect to the nanotube axis. This arrangement results in original optical properties of the compound with polarization selective energy transfer. We discuss possible applications of this approach to the metrology of carbon nanotubes.

CPP 1.7 Mon 11:45 C 130

Surface magnetism of self-assembled metallofullerenes on metals — DENIS KRYLOV¹, CHIA-HSIANG CHEN¹, FUPIN LIU¹, LUKAS SPREE¹, STANISLAV AVDOSHENKO¹, SEBASTIAN SCHIMMEL¹, RASMUS WESTERSTRÖM², JAN DREISER³, CHRISTIAN HESS¹, and ●ALEXEY POPOV¹ — ¹Leibniz Institute for Solid State and Materials Research, Dresden, Germany — ²Synchrotron Radiation Research Lund University, Sweden — ³Swiss Light Source, Paul Scherrer Institut, Villigen PSI, Switzerland

Molecules with bistable magnetic ground state and slow relaxation of magnetization are known as single molecule magnets (SMMs). Information storage or spintronic applications envisaged for SMMs require contacting the molecules to conducting electrodes. Therefore, magnetic properties of SMMs on such surfaces should be well understood. However, whereas hundreds of transition metal and lanthanide based SMMs have been (and are being) reported, the studies of surface magnetism in monolayers of SMMs are very scarce, and hysteresis of magnetization on conducting substrates has been observed so far only for TbPc₂, Fe₄, and Dy₂ScN@C₈₀.

Endohedral metallofullerenes DyScN@C₈₀ and Dy₂ScN@C₈₀ are robust SMMs combining structural stability with relatively high blocking temperature of magnetization, which allows their sublimation or chemical modification without decomposition of the magnetic core. In this work we use Scanning Tunneling Microscopy and X-ray magnetic circular dichroism to study structural and magnetic properties of sub-monolayers of metallofullerenes assembled on metallic substrates.

CPP 1.8 Mon 12:00 C 130

Spin-resolved photoemission measurements on a Fullerene monolayer adsorbed on Cu(111) — ●HENNING STURMEIT¹, LAURA KUGLER¹, JOHANNES STÖCKL², BENITO ARNOLDI², DAVIDE BOSSINI¹, BENJAMIN STADTMÜLLER², MARTIN AESCHLIMANN², STE-

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Spin-resolved photoemission is a powerful method for the study of metal-organic interfaces. It allows to directly probe the effects of the interaction between the organic adsorbate and the metallic substrate on their electronic structure as well as its influence on the spin properties of the interface. In a recent work [1] it was reported that layered structures of C₆₀ and metallic thin films show emerging ferromagnetic properties even with dia- or paramagnetic metals. Strong indications that the magnetic moment is localized in the metallic layer as well as at the interface were reported, although the physical origin of the ferromagnetic ordering is not yet fully understood. In this framework we performed spin-resolved photoemission measurements on an 4X4 - C₆₀ monolayer adsorbed on a Cu(111) surface. We found spin polarized photoemission features in the valence band of the system, although no clear signature of ferromagnetic ordering is detected.

[1] F. Al Ma'Mari, T. Moorsom, G. Teobaldi et al., Nature, 524 (7563), 69-73 (2015)

CPP 1.9 Mon 12:15 C 130

Magnetic behavior of Single Molecule Magnets thin films on low dimensional substrates — ●GIULIA SERRANO¹, IRENE CIMATTI¹, BRUNETTO CORTIGIANI¹, EMILIO VELEZ-FORT², LUIGI MALAVOLTI³, DAVIDE BETTO², NICHOLAS B. BROOKES², ABDELKARIM OUERGI⁴, EDWIGE OTERO⁵, MATTEO MANNINI¹, and ROBERTA SESSOLI¹ — ¹Department of Chemistry and INSTM RU, University of Florence, Via della Lastruccia 3, 50019, Sesto Fiorentino (FI), Italy. — ²European Synchrotron Radiation Facility, 71, avenue des Martyrs CS 40220, 38043 Grenoble Cedex 9, France. — ³Max-Planck Department for Structural Dynamics, Luruper Chaussee 149, 22761 Hamburg, Germany. — ⁴Centre de Nanosciences et de Nanotechnologies, Université Paris-Sud, Université Paris-Saclay, C2N Marcoussis, 91460 Marcoussis, France. — ⁵Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin BP48 91192 Gif-sur-Yvette Cedex, France.

Single Molecule Magnets (SMMs) represent suitable building blocks for spintronic applications. Up to now, the intensive research to confine SMMs on solid substrates has shown promising results for Fe₄ complexes SMMs on metal substrates. However, strong molecular interactions with the substrate may have detrimental effects on the SMMs magnetic properties, necessitating further exploration to be fully understood. Here we present the study of single-layers of the archetypal bis(phthalocyaninato) Terbium(III) complex (TbPc₂) SMM on low-dimensional substrates as graphene and TiO₂ nanoislands, demonstrating that the use of graphene results an effective strategy for preserving the magnetic bistability of SMMs.

CPP 1.10 Mon 12:30 C 130

Lanthanide-Functionalised Two Dimensional Transition Metal Dichalcogenides — ●DAVID LEWIS — School of Materials, University of Manchester

Nanostructures provide a unique platform on which to assemble molecular layers.[1] Functionalisation of transition metal dichalcogenides (TMCDs) in particular, provides a facile route by which to produce new advanced composite nanomaterials that have advanced optoelectronic properties.[2]

Assembly of molecular lanthanide (III) complexes onto two-dimensional TMDCs provides an attractive opportunity by which to extend the latter's advanced materials properties. For example, we have recently shown that 2D molybdenum disulfide nanosheets can be functionalised with both Eu³⁺ and Gd³⁺ complexes simultaneously.[3] The resulting nanomaterials display long photoluminescence emission lifetimes of 0.8 ms from the Eu³⁺ emission in the red region of the electromagnetic spectrum (570 to 720 nm), derived from the 5D₀ to 7F_j electronic f-f transitions, whilst having strong paramagnetic response in EPR spectra, and thus could be used as a bimodal optical probe / magnetic resonance imaging contrast agent. The approach could be extended by exploring the whole range of lanthanide elements available for assembly on 2D surfaces. This talk will explore the feasibility of these exciting possibilities.

References [1] (a) Lewis et al, Chem Commun, 2006, 1433, (b) Lewis et al Coord. Chem. Rev. 2014, 273, 213. [2] Knirsch et al ACS Nano 2015, 9, 6018. [3] McAdams et al, Adv Func. Mater. 2017, 1703646.

CPP 1.11 Mon 12:45 C 130

Magnetic subunits within a single molecule-surface hybrid —

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Single molecule-surface hybrid systems are a promising platform for molecular spintronics due to their adjustable magnetic properties [1, 2]. In this contribution we demonstrate the creation of multiple

intramolecular subunits within a single molecule-surface hybrid system employing *ab initio* density functional theory and spin-polarized scanning tunneling microscopy [3].

Upon deposition of a polycyclic aromatic molecule onto a ferromagnetic surface an asymmetric (chiral) adsorption geometry is obtained. This gives rise to the formation of different structural, electronic and magnetic properties of each aromatic ring hybridizing with the surface. Finally, this leads to the creation of magnetic subunits which are distinguished from one another by their exchange coupling strength [3].

[1] N. Atodiresei *et al.*, Phys. Rev. Lett. **105**, 066601 (2010).

[2] R. Friedrich *et al.*, Phys. Rev. B **91**, 115432 (2015).

[3] V. Heß *et al.*, New J. Phys. **19**, 053016 (2017).