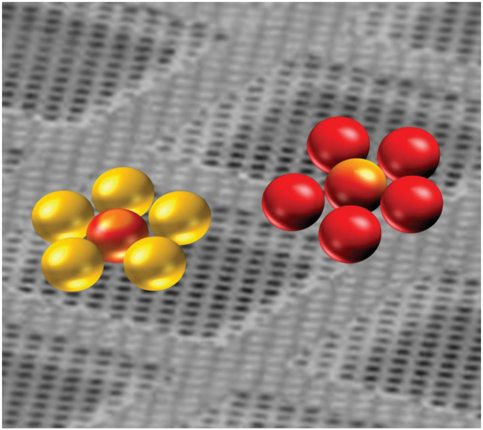
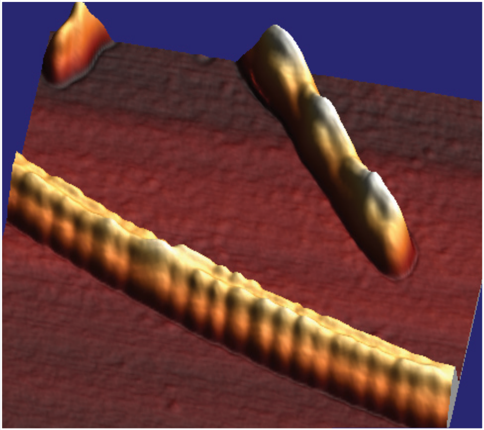
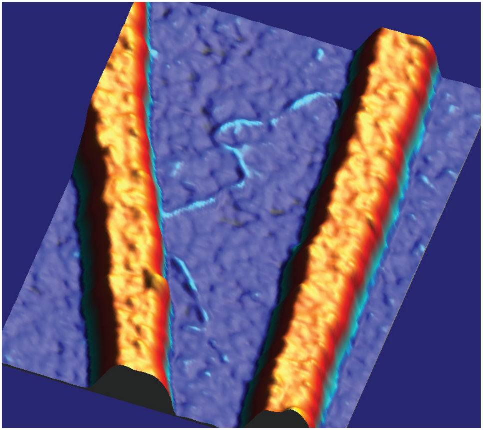
Self Assembly and Molecular Electronics

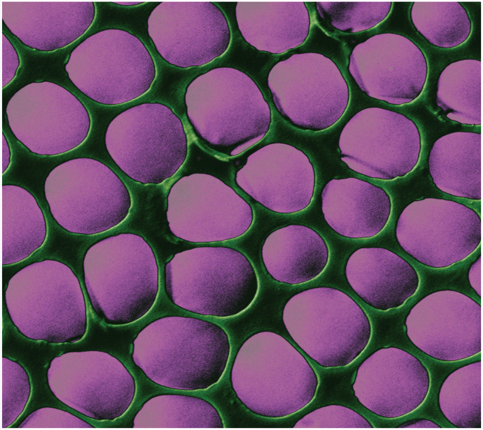
October 11–12, 2012, Aalborg, Denmark

ISBN: 978-87-92329-58-5









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Topics

- DNA-Nanoparticle Conjugates
- Plasmonics and Biosensing
- Molecular Electronics
- Circular Dichroism and Optical Spectroscopy
- Molecular Modeling
- Supramolecular chemistry

Programme

Thursday, October 11, 2012

08:30–09:25 Registration

09:25–09:30 Welcome Address

09:30–10:15
Discrete Conjugates of Nanoparticles with G4-DNA and PNA-DNA Hybrids for Plasmonic and Nanoelectronic Applications
Alexander Kotlyar, Gennady Eidelshtein, Irit Lubitz, Marcello Anzola, Clelia Giannini
Department of Biochemistry and Molecular Biology, George S. Wise Faculty of Life Sciences and The Center of Nanoscience and Nanotechnology, Tel Aviv University, Ramat Aviv 69978, Israel
Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133 Milano Italy

10:15–10:45
Self Assembled Peptide Nanotubes as a Low Cost Nanofabrication Tool
Karsten B. Andersen, Kasper Bayer Frøhling, Dorota Kwasny, Jaime Castillo-León and Winnie Edith Svendsen
DTU Nanotech — Technical University of Denmark
Karsten.andersen@nanotech.dtu.dk

10:45–11:00 Coffee Break

11:00–11:45
pH-Dependent and pH-Independent Self-Assembly of Surfactant-Like Peptides
Leonid Gurevich and Peter Fojan
Department of Physics and Nanotechnology Skjernvej 4A, DK-9220 Aalborg
fp@nano.aau.dk

11:45–12:30

To See or Not to See: Lateral Organization of Membranes and Fluorescence Microscopy

Luis A. Bagatolli

Membrane Biophysics and Biophotonics group/MEMPHYS — Center for Biomembrane Physics, Department of Biochemistry and Molecular Biology, University of Southern Denmark. Campusvej 55, DK-5230, Odense M, Denmark.
e-mail: bagatolli@memphys.sdu.dk. Web: http://memphys.dk/Luis-Bagatolli

12:30–13:30 Lunch (sponsored by Asylum Research) and Poster Session

13:30–14:15

Transport Through Simple Molecules as Benchmarks for Molecular Electronics

Kristian S. Thygesen

Center for Atomicscale Materials Design (CAMD), Department of Physics, Technical University of Denmark, DK2800 Lyngby, Denmark

14:15–15:00

The Interaction of DNA Bases with Gold Substrates

Rosa Di Felice

Center S3, CNR Institute of Nanoscience, 41125 Modena, Italy, rosa.difelice@unimore.it, www.nano.cnr.it

15:00–15:15 Coffee Break

15:15–16:00

Modelling Charge and Spin Transport in DNA Molecules

Rafael Gutierrez

Institute for Materials Science, Dresden University of Technology, Dresden, Germany

16:00–16:30

Quantum Interference in Molecular Junctions

Troels Markussen

Center for Atomicscale Materials Design (CAMD), Department of Physics, Technical University of Denmark, DK2800 Lyngby, Denmark

16:30–16:45 Coffee Break

16:45–17:30

Transport Properties of Graphene Antidot Lattices

Thomas Garm Pedersen

Dept. of Physics and Nanotechnology, Aalborg University, DK-9220 Aalborg Øst, Denmark

17:30–18:00
Zooming in an Excitonic Solar Cell: An ab initio Investigation of the Optically Active Site
Arrigo Calzolari
CNR-NANO Istituto Nanoscienze, Centro S3, Modena Italy

18:00–18:30
Probing Materials Properties at Nanoscale by Novel Methods of Atomic Force Microscopy
S. Magonov, J. Alexander, S. Belikov, C. Wall, S. Lemeshko, and David Trimbach
NT-MDT Europe, High Tech Campus 83, 5656 AG Eindhoven, The Netherlands

19:00–21:00 Gala Dinner at Sohngaardsholm Castle restaurant

Friday, October 12, 2012

09:00–09:45
Charge Transport in Functional Networks of Gold Nanoparticles and Organic Molecules
S. J. van der Molen, E. J. Devid, J.-F. Dayen, M. Kamalakar, D. Golubev, C. M. Guédon, V. Faramarzi, B. Doudin
Kamerlingh Onnes Laboratory, Leiden University, LEIDEN, The Netherlands
Institut de Physique et Chimie des Matériaux de Strasbourg, University of Strasbourg, STRASBOURG, France
Institute of Nanotechnology, Karlsruhe Institute of Technology, KARLSRUHE, Germany

09:45–10:30
Bio-Templated Systems for Nanoelectronics
Danny Porath
Institute of Chemistry, The Hebrew University of Jerusalem, Israel and Center for Nanoscience and Nanotechnology of the Hebrew University porath@chem.ch.huji.ac.il

10:30–11:00 Coffee Break

11:00–11:45
Site-Selective Control of DNA Assembly and Interactions
Shalom J. Wind
Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY, USA

11:45–12:30
Characterization of Conductance Mechanisms of DNA Structures
Jussi Toppari, V. Linko, S.-T. Paasonen, J. Leppiniemi, V. P. Hytönen
Nanoscience Center, Department of Physics, P.O. Box 35, FIN-40014 University of Jyväskylä, Finland
Institute of Biomedical Technology, University of Tampere and Tampere University Hospital, FIN-3314 Tampere, Finland

12:30–13:30 Lunch and Poster Session

13:30–14:15

Electron Transfer Reactions in Redox-Labeled DNA Tethered to Electrodes

Elena E. Ferapontova

Interdisciplinary Nanoscience Center (iNANO) and Center for DNA Nanotechnology (CDNA), Aarhus University, Gustav Wieds Vej 1590-14, DK-8000 Aarhus C, Denmark, elena.ferapontova@inano.au.dk

14:15–15:00

DNA Photophysics: Electronic Coupling Between Multiple Chromophores

Steen Brøndsted Nielsen

Department of Physics and Astronomy, Aarhus University, Denmark

15:00–15:15 Coffee Break

15:15–16:00

Electrostatic Force Microscopy and Conductivity Measurements on DNA and DNA-Peptide Conjugates

Zeinab Esmail Nazari, Julio Gomez and Leonid Gurevich

Institute of Physics and Nanotechnology, Aalborg University, 9220 Aalborg, Denmark.
Dept. Fisica de la Materia Condensada, Universidad Autonoma de Madrid, 28049-Madrid, Spain

16:00–16:45

Electrical Conductivity in MMX Polymers: From Nanoribbons to Macrocrystals

Félix Zamora and Ruben Mas

Departamento de QuímicaInorgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, Ctra. de Colmenar Viejo, Km 15, 28049 Madrid (Spain)

16:45–17:15

Substrate Influence on the Two-dimensional Metallo-supramolecular Self-assembly of TPyB

Mahdi S. Baviloliaei, Dong Lei, Nian Lin, Lars Diekhöner

Department of Physics and Nanotechnology, Aalborg University, Aalborg, Denmark
Department of Physics, Hong Kong University of Science and Technology, Clear water bay, Hong Kong

17:15 Closing Remarks

Poster Presentations

Adsorption of Cytosine on the AU(111) Surface by Density Functional Theory
Marta Rosa, Stefano Corni, Rosa Di Felice
Dept. of Physics, Università di Modena e Reggio Emilia, via G. Campi 213/a, 41125 Modena
Centro S3, CNR Istituto di Nanoscienze, via G. Campi 213/a, 41125 Modena

Electronic Conductance of Functionalized Benzene-Diamine Molecules with the GW Approximation
Chengjun Jin and Kristian Sommer Thygesen
Center for Atomicscale Materials Design (CAMD), Department of Physics,
Technical University of Denmark, DK2800 Lyngby, Denmark

The Many Faces of Diphenylalanine
Mohtadin Hashemi, Leonid Gurevich and Peter Fojan
Institute of Physics and Nanotechnology, Aalborg University, 9220 Aalborg, Denmark

The Nature of the Interaction between Natural and Size-Expanded Guanine with Gold Clusters: A DFT Study
Wenming Sun and Rosa Di Felice
CNR Institute of Nanoscience, S3 Center, Via Campi 213/A, 41125 Modena, Italy

Molecular Combing of DNA and DNA-Peptide Conjugates
Zeinab Esmail Nazari and Leonid Gurevich
Institute of Physics and Nanotechnology, Aalborg University, 9220 Aalborg, Denmark

Development of a Protease Assay Based on Silver Nanoprisms
Ane Kold di Gennaro, Esben Skovsen, Leonid Gurevich, Michael Toft Overgaard, and Peter Fojan
Department of physics and Nanotechnology, Aalborg University, Skjernvej 4A, 9220 Aalborg
Department of Biotechnology, Aalborg University, Sohngaardsholmsvej 47, 9000 Aalborg

Peptide Loaded Nanofibres as a Potential Antimicrobial Surface Coating of Inanimate Surfaces
T. H. B. Eriksen, E. B. Møller, and P. Fojan
The Danish Building Research Institute, Aalborg University, Dr. Neergaards Vej 15, DK-2970, Hørsholm, Denmark, email: the@sbi.aau.dk
Department of Physics and Nanotechnology, Aalborg University, Skjernvej 4A, DK-9220, Aalborg East, Denmark

On the Role of a Single Solvent Molecule on the Absorption by Nitrophenolate Ions in Vacuo
Jørgen Houmøller and Steen Brøndsted Nielsen
Department of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark

Abstracts

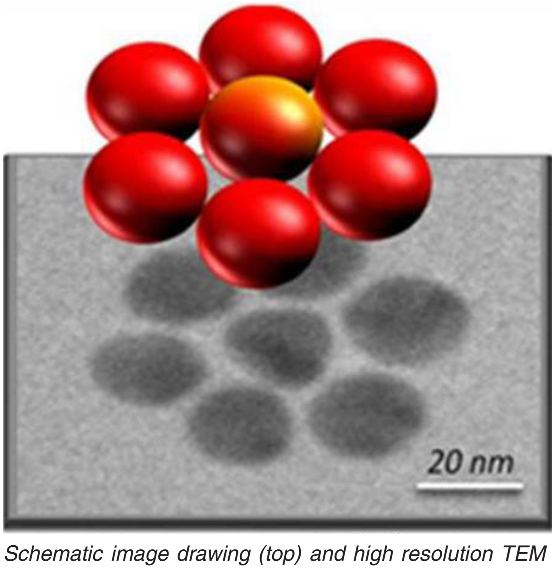
October 11, 2012

09:30–10:15

DISCRETE CONJUGATES OF NANOPARTICLES WITH G4-DNA AND PNA-DNA HYBRIDS FOR PLASMONIC AND NANOELECTRONIC APPLICATIONS

Alexander Kotlyar†, Gennady Eidelshtein†, Irit Lubitz†, Marcello Anzola‡, Clelia Giannini‡
† *Department of Biochemistry and Molecular Biology, George S. Wise Faculty of Life Sciences and The Center of Nanoscience and Nanotechnology, Tel Aviv University, Ramat Aviv 69978, Israel,*
‡ *Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133 Milano Italy*

Conjugates between metal (silver and gold) nanoparticles (NP) and parallel stranded G-quadruplexes (G4-DNA) or double stranded PNA-DNA hybrids have been synthesized. A mixture of DNA-NP conjugates containing discrete number of nanoparticles was prepared by incubation of the DNA (DNA-PNA) functionalized with phosphorothioate residues on both sides of the molecule with equimolar concentrations of NPs. Conjugates containing two particles were efficiently separated from single particles, and nanoparticle trimers and chains of nanoparticles by gel electrophoresis. The molecular morphology of purified NP-G4-DNA [1] and NP-PNA-DNA dimers was confirmed by TEM. The spectroscopic analysis showed the presence of plasmon-mediated interparticle interactions in the above dimers.



Schematic image drawing (top) and high resolution TEM image (bottom) of a NP-flower composed of 15 nm Au-NPs connected by 20 tetrad G4-DNA molecules.

We have also reported the synthesis of stable phosphorothioate oligonu-cleotides-coated gold nanoparticles (Au-NPs) that can be bound to metal surfaces and bare NPs, “sticky particles”. The sticky particles were formed during 2–3 hours incubation of 15 nm citrate-protected NPs with great (more than 100-fold) excess of 20 tetrad G4-DNA molecules functionalized with 5 phosphorothioate residues on either sides. The nanoparticles do not aggregate for months and can tolerate salt concentration as high as 200 mM [2]. The phosphorothioate residues located on their surface of sticky particles can anchor them to non-coated NPs. Incubation of 20-fold excess sticky particles with of non-coated Au-NPs yields flower-shaped structures [2] comprising a central non-coated particle and five-six sticky ones at the periphery (see Fig.).

The absorption band of the structures is shifted towards long wavelengths compared to the band of individual particles indicating for plasmon coupling between closely-spaced interacting particles in the “flower”.

References

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10:15–10:45

SELF ASSEMBLED PEPTIDE NANOTUBES AS A LOW COST NANOFABRICATION TOOL

Karsten B. Andersen, Kasper Bayer Frøhling, Dorota Kwasny, Jaime Castillo-León and Winnie Edith Svendsen
DTU Nanotech — Technical University of Denmark
Karsten.andersen@nanotech.dtu.dk

Self assembled peptide nanotubes from the dipeptide diphenylalanine provide a mean of achieving nanostructured materials at a low cost [1,2]. Recently it has been shown that the formed structures dissolve easily when submerged in most liquids including water, ethanol and phosphate buffers [3] limiting its use in applications like drug-delivery systems or directly in sensing devices. Despite this, we have demonstrated that the nanotubes can withstand prolonged bombardment by ions in a reactive ion etch procedure [4]. In this work we present how these unique properties of the self assembled peptide nanotubes from this dipeptide make them applicable as a fabrication tool in clean room processing enabling a cheap and fast fabrication procedure where organic solvents can be avoided. Namely we have demonstrated how the peptide nanotubes can be used as a masking material in a dry etching procedure for the low cost fabrication of silicon nanowires and furthermore as lift off masks for the creation of nanoslits in gold films. Additionally we have demonstrated that the peptide nanotubes can be aligned on wafer scale using a spincasting approach [5].

Since the structures dissolve in water the removal of the etch mask and the lift off process for gold patterning can be conducted in water so that no organic solvents are required making it possible to work with more fragile materials as well. Finally the detection of single stranded DNA molecules using the silicon nanowires fabricated in the fast and low cost manner described above will be demonstrated.

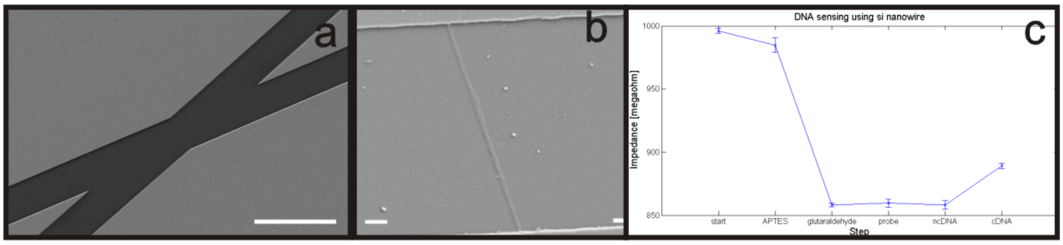

Illustration of different structures formed using the peptide nanotube as masking material in a lift off process (a) for the fabrication of nanoslits in gold surfaces and in a dry etching procedure (b) for the realization of a silicon nanowire [5]. In c) detection of single stranded DNA with the fabricated silicon nanowire is shown. Scalebars in SEM images corresponds to 2 μm.

References

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3. Andersen et al., Nanoscale, (2011), 3, 994–998
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11:00–11:45

pH-DEPENDENT AND pH-INDEPENDENT SELF-ASSEMBLY OF SURFACTANT-LIKE PEPTIDES

Leonid Gurevich and Peter Fojan
Department of Physics and Nanotechnology Skjernvej 4A, DK-9220 Aalborg
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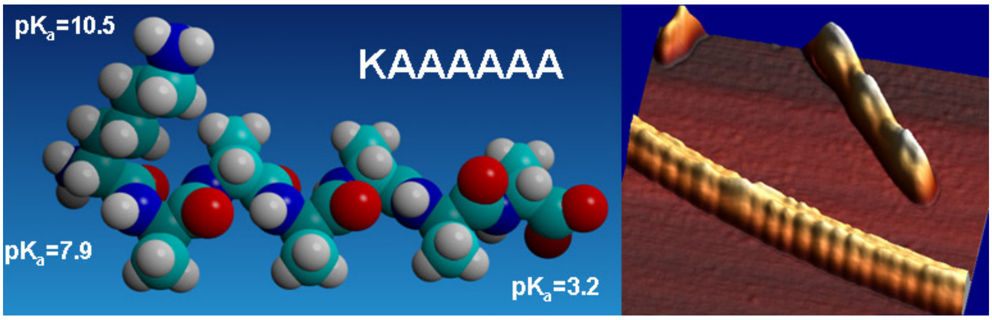
Self-assembly of amphiphilic peptides designed during the last years by several research groups leads to a large variety of 3D-structures that already found applications in stabilization of large protein complexes, cell culturing systems etc. In this report, we present synthesis and characterization of a novel family of amphiphilic peptides KA_5, KA_6 and KA_6W that exhibits clear charge separation controllable by pH of the environment. As the pH changes from acidic to basic, the charge on the ends of the peptide molecule varies eventually leading to reorganization of KA_6 micelles and even micellar inversion. On contrary, the bulky geometry of the tryptophan residue in KA_6W limits the variation of the surfactant parameter and hence largely prevents assembly into spherical or cylindrical micelles while favouring flatter geometries. On the other hand, wedge-like shape of a shorter KA_5 peptide also becomes suboptimal for micelle formation and leads to ribbon-like structures.

The studied short peptide families demonstrate formation of ordered aggregates with well-defined secondary structure from short unstructured peptides and provide a simple system where factors responsible for self-assembly can be singled out and studied one by one. The ability to control the shape and structure of peptide aggregates can provide basis for novel designer pH sensitive materials including drug delivery and controlled release systems.



Left panel: Space filling model of KA_6 peptides. pKa values for charged groups were calculated using APBS (Adaptive Poisson-Boltzmann solver).
Right panel: AFM image of KA_6 micelles observed at pH=7.

11:45–12:30

TO SEE OR NOT TO SEE: LATERAL ORGANIZATION OF MEMBRANES AND FLUORESCENCE MICROSCOPY

Luis A. Bagatolli
Membrane Biophysics and Biophotonics group/MEMPHYS — Center for Biomembrane Physics, Department of Biochemistry and Molecular Biology, University of Southern Denmark. Campusvej 55, DK-5230, Odense M, Denmark.
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Lipids have been traditionally considered to play a fairly nonspecific role in biological systems, being rather dull with respect to those described for proteins and genes. As pointed out by Mouritsen in his book "Life as a Matter of Fat" (1) this likely arose from the powerful concept of molecular *structure* that has influence scientists' way of thinking throughout the 20th century. The central dogma is that *molecular structure controls function*. Lipids apparently do not possess functionally related molecular structures as important molecules like proteins, DNA and RNA. However, lipids are capable to self-assemble in aqueous media and create non-covalent linked supramolecular structures with very biologically relevant physical properties. These very fascinating structures show high compositional complexity and versatile functional capabilities, largely overlooked in the most popular model for biological membranes, i.e. the fluid mosaic model (2, 3).

The idea that lipid-lipid interactions may form stable lipid domains in biological membranes was proposed almost four decades ago (4). However, this "non-random lateral organization of membranes" has not been acknowledged, particularly from the biology field, until the (still) controversial "raft" hypothesis was postulated (5). In the last 40 years, there has been extensive research to elucidate coexistence of lipid domains in membranous systems (mainly liposomes but also cell membranes) using an array of experimental techniques. Generally, most of these experimental techniques produce mean parameters on the basis of data collected from bulk solution of many liposomes (or cells) and lack spatially resolved information about membrane lateral organization at the level of single membranes, a quality that can be provided by fluorescence microscopy related techniques (6). This spatially resolved information allowed for example comparison of the lateral structure of artificial lipid mixtures with particular biological membranes (6–9). In this talk examples of comparative studies among the lateral structure of artificial lipid mixtures, natural lipid mixtures (both with and without membrane proteins) and finally membranes containing full composition under controlled environmental conditions will be presented.

References

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13:30–14:15

TRANSPORT THROUGH SIMPLE MOLECULES AS BENCHMARKS FOR MOLECULAR ELECTRONICS

Kristian S. Thygesen

Center for Atomicscale Materials Design (CAMD), Department of Physics, Technical University of Denmark, DK2800 Lyngby, Denmark

Accurate theoretical modeling of the electronic conductance of a molecule connected to source and drain electrodes has been a long-standing challenge since the first measurements of electron transport in single-molecule junctions in the mid 90s. First-principles calculations based on density functional theory (DFT) have been very popular, however, calculated conductance values systematically overestimate experiments by up to two orders of magnitude. Here we show that the so-called GW method, which is based on many-body perturbation theory, predicts quantitatively accurate conductance values for a number of simple molecular junctions thus bridging the gap between theory and experiments. The important role of the energy level alignment at the metal-molecule interface is discussed, and the use of transition voltage spectroscopy (TVS) and thermoelectric measurements for determining the position of the HOMO and LUMO levels in the junction is assessed on basis of first-principles calculations.

14:15–15:00

THE INTERACTION OF DNA BASES WITH GOLD SUBSTRATES

Rosa Di Felice*
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41125 Modena, Italy
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The interaction of molecules with inorganic substrates is a crucial issue for applications in molecular electronics. It influences important factors such as the immobilization efficiency and the charge injection through the interface. Moreover, mechanical aspects connected to the unfolding of biological molecules are important.

I will present recent efforts in my group to tackle these problems, based on density functional theory calculations and molecular dynamics simulations. I will discuss various physico-chemical and computational matters: (i) the relevance of van-der-Waals interactions to obtain reliable computational results; (ii) the development of a classical force field to simulate the possible unfolding of DNA molecules on a gold surface; (iii) the nature of the molecule/substrate bonds, ranging from chemical bonding to hydrogen bonding; (iv) the role of chemical modifications of DNA bases to improve device performance; (v) the effect of the length of the spacer chain for attachment of functionalized DNA to an electrode.

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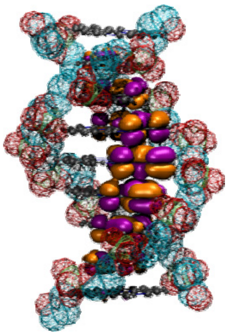
*Coworkers at S3: Marta Rosa, Wengmin Sun, Stefano Corni.

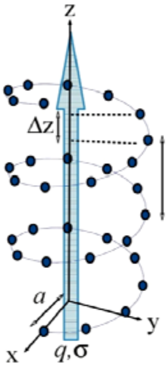
15:15–16:00

MODELLING CHARGE AND SPIN TRANSPORT IN DNA MOLECULES

Rafael Gutierrez
Institute for Materials Science,
Dresden University of Technology, Dresden
Germany



Disclosing the electrical response properties of DNA-based molecular junctions has been in the focus of experimental and theoretical research over the past two decades. Despite great progress in the field, a unifying treatment of charge transport in such systems has not been fully settled due to the intrinsic complexity of biomolecules and due to the interplay of many factors affecting charge motion. In this talk, we review our work on transport in DNA molecular wires, centered around the development of a hybrid method based on a combination of classical molecular dynamics simulations, quantum-chemical calculations, and model Hamiltonian approaches. The core of the approach consists in a mapping of the biomolecular electronic structure, as obtained from density-functional based calculations of molecular structures along molecular dynamics trajectories, onto a low-dimensional model Hamiltonian [1]. We apply the methodology to study charge transport in presence of mismatches [2], as well as to investigate differences in the electrical response between regular DNA and DNA including oxoguanosine [3].



In the second part of the talk, a recent problem will be addressed, which has attracted very much attention: the possibility to use DNA as a spin filter. High values of spin polarization in DNA self-assembled monolayers have been recently measured [4], but an explanation of the observed behavior has remained elusive. We have recently suggested, in the frame of a simple model Hamiltonian approach, that highly spin-selective transport of electrons through a helically shaped electrostatic potential is possible, suggesting a close connection between chirality and spin [5].

References

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16:45–17:30

TRANSPORT PROPERTIES OF GRAPHENE ANTIDOT LATTICES

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Graphene is the ultimate two-dimensional material and the properties of this extraordinary material have been explored in great detail. The vanishing band gap, however, severely restricts application in electronic and optoelectronic devices. The formation of graphene antidot lattices (GALs) has been suggested as a way of obtaining a sizeable band gap [1–2]. In this talk, the structural and electronic properties of GALs are described. The transport properties are discussed with an emphasis on geometric and band gap effects. Simple barrier and tunnelling devices are analyzed and compared to models based on the Dirac approximation.

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17:30–18:00

ZOOMING IN AN EXCITONIC SOLAR CELL: AN AB INITIO INVESTIGATION OF THE OPTICALLY ACTIVE SITE

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By means of ab initio DFT calculations, we characterize the optoelectronic and transport properties of the main subsystems that form the active layer of a prototypical excitonic solar cell, based on hybrid molecular-dye/ZnO interfaces. Firstly, we characterize the optoelectronic properties of a natural sensitizer, i.e. cyanin dye [1,3] and we analyze the effects of the hydration and thermal dynamics on the optical properties of cyanin in aqueous solution. Furthermore, we report on the functionalization of the non-polar ZnO(10-10) surface upon the adsorption of the chromophore linker [3] and we demonstrate the effects of the interface formation on the optoelectronic properties of the system. Finally we compare our results with recent experimental findings.

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18:00–18:30

PROBING MATERIALS PROPERTIES AT NANOSCALE BY NOVEL METHODS OF ATOMIC FORCE MICROSCOPY

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Atomic force microscopy (AFM) (1), in which a micro-fabricated probe with a nanometer-size apex is employed for force interactions with a sample surface, has been evolved from a high-resolution profiling technique to a comprehensive characterization method commonly applied to studies structures and properties at small scales. The basic function of AFM is the real-space visualization of surface morphologies and compositional mapping of heterogeneous materials. High-sensitivity of the method to local mechanical, adhesive and electromagnetic properties is "under the hood" of the compositional imaging of polymer materials. Stiff lamellar structures embedded into an amorphous polymer are best resolved in AFM images obtained at elevated tip-sample mechanical interactions. Conductivity of carbon black particles forming a percolated network in filled elastomers helps the visualization of these particles in the multi-component materials. Advancing materials technology to a large degree relies on compounding of components in the micron and nanometer scales, whereas the small-scale functional structures and devices are in focus of many industries. These developments require the appropriated characterization methods and this elevates the importance of AFM due to its capability of probing the local materials properties. The advances and challenges of quantitative measurements of mechanical and electric/dielectric properties of polymers and related materials with AFM is the subject of this contribution.

The experimental results presented in the paper were obtained with scanning probe microscopes NTEGRA Prima and Solver NEXT made by NT-MDT. These microscopes are equipped with an electronic controller that allows simultaneous multi-frequency measurements with four lock-in amplifiers. The AFM measurements were performed with commercial Si and Si/Pt probes and in a number of different modes: contact mode, amplitude modulation, nanoindentation, single-pass Kevin force microscopy (KFM), etc. The microscope software in addition to traditional instrument control and image processing function has the analysis segments for quantitative mechanical and dielectric studies.

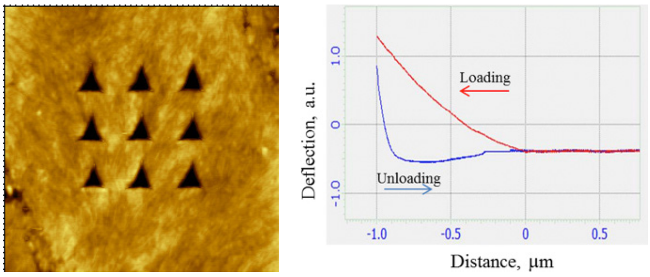

Figure 1. Left — Height image of LLDPE surface with the indents. The image size is $2\,\mu\mathrm{m} \times 2\,\mu\mathrm{m}$. Right — the typical loading/unloading DvZ curve.

The basic information about tip-sample mechanical interactions is obtained from the dependence of the probe deflection on the tip-sample distance (DvZ) measured at a particular surface location. By pressing the tip into a sample material and retracting it one can evaluate the sample properties (e.g., elastic modulus, work of adhesion). The unique force sensitivity of AFM and a small size of the probe allow such experiments with nanoscale spatial resolution. At present, a harvesting of DvZ curves can be performed in various modes and at different rates (from sub-Hz to hundreds of kHz) but an extraction of the quantitative nanomechanical data demands as series of experimental and theoretical efforts. Among those are: a characterization of the AFM probe (stiffness, optical sensitivity, tip shape and apex size), a choice of an indentation routine (imaging/indenting) and a proper deformation model. This approach will be demonstrated on several polymers (2) including a sample of low-density polyethylene. The height image of the indents left on this material and the loading/unloading DvZ curves are shown in Fig. 1.

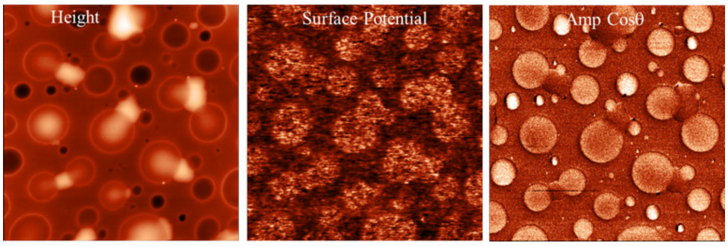

Figure 2. Height (left), surface potential (middle) and amplitude of dielectric response (right) images of the annealed thin film of PS/PVAC blend. The image size is $7\,\mu\mathrm{m} \times 7\,\mu\mathrm{m}$. The electric/dielectric measurements were performed at 3 kHz.

The AFM-based electric techniques involve either a detection of tip-sample electrostatic forces (KFM, capacitance gradients: dC/dZ and dC/dV) or on the use of additional sensor (current, capacitance, microwave analyzer). Fig. 1 shows images obtained in a single-pass mode, which became available with an addition of multiple lock-in amplifiers to the AFM instruments (4). Such multi-frequency studies enhance the AFM capabilities of compositional analysis of heterogeneous materials and polymers utilized for photovoltaics. The practical realization of these capabilities will mean a transfer of dielectric spectroscopy to the submicron range that might provide a pool of new data related to molecular mobility of polymers and other compounds in confined nanometer-scale geometries.

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October 12, 2012

09:00–09:45

CHARGE TRANSPORT IN FUNCTIONAL NETWORKS OF GOLD NANOPARTICLES AND ORGANIC MOLECULES

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Molecular charge transport forms a fascinating part of nanoscience that takes direct advantage of the impressive library of (functional) organic molecules synthesized by organic chemists. Of special interest are molecular switches, in which the electronic communication can be controlled by an external stimulus such as light [1].

To study and manipulate the conductance properties of organic molecules, we choose a robust sample platform. We utilize two-dimensional nanoparticle arrays, in which organic molecules act as molecular bridges between neighboring nanoparticles. The role of the nanoparticles is to define a highly ordered, two-dimensional template. The molecules in turn, form conductive bridges between the particles. Hence, the conductance properties of such a network are a spatial average of the properties of single nanoparticle-molecule-nanoparticle junctions. Moreover, the molecules offer their specific functional properties, such as switchability, to these structures.

In the first part of the talk, I will review our work on photo-switchable diarylethene molecules. These light-sensitive molecules can be toggled between a conjugated on-state and a cross-conjugated off-state. However, it is not trivial if this functionality will survive, once the molecules are coupled to gold. We show that by optimizing the electronic coupling, switchability can be recovered. In this way, we have been able to reversibly switch the

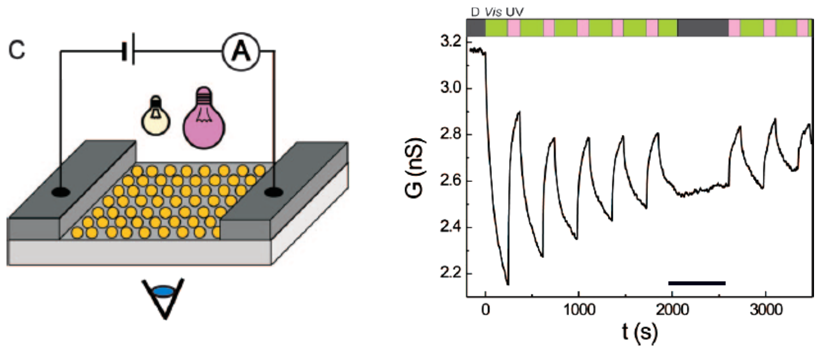

Figure 1. Left: Device concept: a 2D network of gold nanoparticles bridged by molecules is investigated. Right: Example of light-controlled conductance switching of diarylethene molecules in a nanoparticle network [2]

conductance of molecule-nanoparticle networks at room temperature, be it with a low on-off ratio [2].

Interestingly, if we study charge transport at lower temperatures, the nanoparticles become Coulomb-blockaded. Hence, a much richer set of transport mechanisms is expected. Specifically, at low biases one enters a subregime of inelastic multiple co-tunnelling, where the I(V)-curves exhibit power law behaviour. Remarkably, in this regime the resistance ratio between networks with different molecules is strongly enhanced. This opens the road to artificial amplification of the on-off ratio of switchable devices based on molecule-nanoparticle networks [3].

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09:45–10:30

BIO-TEMPLATED SYSTEMS FOR NANOELECTRONICS

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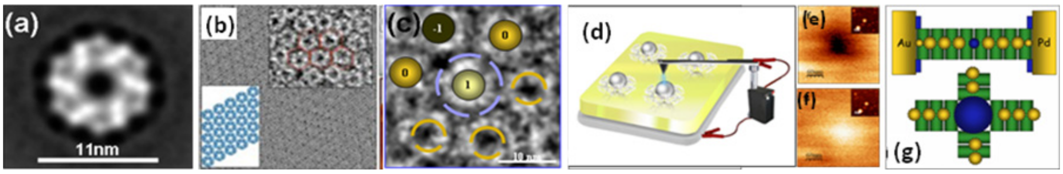

SP1 protein as a basis for nanoelectronic applications: (a) TEM of a single SP1 protein. (b) a large packed ordered array of SP1 molecules. Lower inset: a scheme of the array, upper inset: enlargement of part of the array, where the hexagonal packing is marked. (c) Overlaid scheme of the suggested memory array. (d) Scheme of the suggested omplementation, where the writing is by charging individual particles with AFM and reading by EFM. (e-f) Two charged states of the hybrid and topography (inset). (g) Scheme of chain structures.

In our research we use bio-templated systems to realize one-dimensional conducting nanowires and nanodevices for scientific investigation of electrical charge transport in these systems, for nanoelectronics and for nanotechnology applications. One example is dsDNA and its synthetic derivatives. Within this frame we measured electrical charge transport in dsDNA and G4-DNA, measured their energy level spectra, showed polarizability of G4-DNA and more. I will briefly review this activity. Another example for bio-templated systems is the SP1 protein hybridized with various nanoparticles to form memory units and protein-particles conducting chains. We demonstrate the construction of various building blocks, acquiring specific attachment to gold or Si surfaces, array formation and finally charging and logic operations in hybrid SP1-nanoparticle systems. I will review this activity in more details. The research is conducted by my group in close collaboration with several groups from complementary fields.

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11:00–11:45

SITE-SELECTIVE CONTROL OF DNA ASSEMBLY AND INTERACTIONS

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A central theme in Nanoscience and Nanotechnology is the ability to control, manipulate and study individual molecules and molecular nanostructures. A variety of tools have been developed for this purpose, and over the past two decades single-molecule techniques have become a mainstay in investigations of biophysical and biomolecular systems, resulting in an explosion of new information regarding structure, function and the nature of intermolecular interactions that is simply impossible to access with ensemble averaged measurements. At the same time, tools and techniques originally developed for semiconductor manufacturing have begun to find use in patterning biomolecules on surfaces. Based on this theme, we are developing an approach toward the controlled and ordered arrangement of DNA molecules and nanostructures on lithographically patterned, chemically (or biochemically) functionalized surfaces. In this approach, a “breadboard” consisting of metallic nanodots is patterned by nanoimprint lithography and self-aligned pattern transfer. These nanodots serve as anchors for the chemical or biochemical assembly of DNA and 1D DNA motifs by selective functionalization with single stranded DNA (ssDNA) or other chemical moieties hybridization or through a covalent bond.

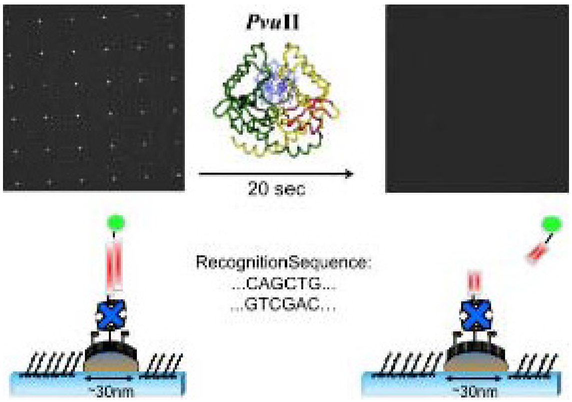

Figure 1. Scheme and epifluorescence microscopy images of enzymatic recognition and cleavage of the nanodot-bound DNA.

Using this platform, we have been able to observe in-situ hundreds of DNA interactions, including DNA hybridization and sequence-dependent DNA-protein interactions (Fig. 1), in real time and in a massively parallel fashion. The precision of the platform and the high selectivity of the binding enables single-molecule resolution. We have also used this platform to study the bivalent attachment of functional nanostructures (Fig. 2). A 1D rigid DNA motif was used as a model for studying directed assembly at the molecular-scale to lithographically patterned nanodot anchors. By matching the inter-nanodot spacing to the length of the DNA nanostructure, we are able to achieve nearly 100% placement yield. By varying the length of single-stranded DNA linkers bound covalently to the nanodots, we are able to study the binding selectivity as a function of the strength of the binding interactions. We analyze the binding in terms of a thermodynamic model which provides insight into the bivalent nature of the binding, a scheme that has general applicability for the controlled assembly of a broad range of functional nanostructures.

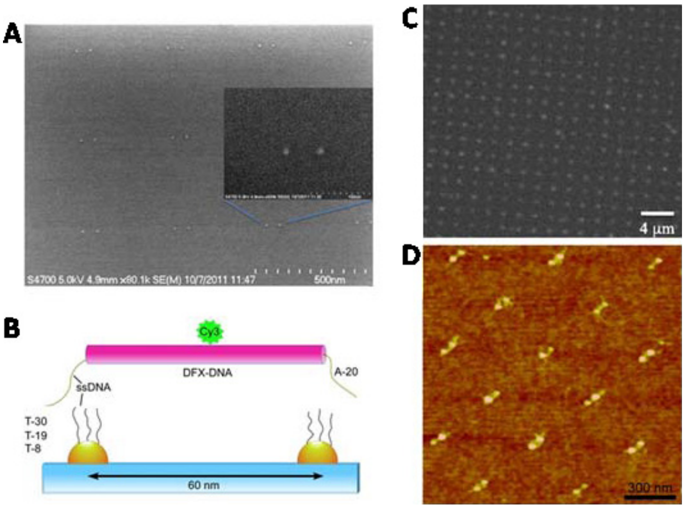

Figure 2. (a) SEM image of an array of ∼5 nm nanodots made of AuPd on a silicon substrate. The separation between two dots in a dimer is 6 nm. Dimers are 400 nm apart. (b) Schematic drawing of the DFX nanostructure attachement to AuPd dot-pairs 6 nm apart. (c) Epifluorescence microscopy image of the dot-pairs array (on glass) bridged by DFX nanostructures. (d) AFM image of dot-pairs connected by DFX nanostructures.

11:45–12:30

CHARACTERIZATION OF CONDUCTANCE MECHANISMS OF DNA STRUCTURES

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The most crucial issues in the realization of functional and multicomponent molecular scale nanodevices are to find a reliable and robust conductor to base the functionalities on, and to obtain a suitable scaffold for the needed nanoscale assembly. For the moment, DNA has been proven to be a very flexible and promising molecule for the latter, mostly due to its striking self-assembly properties. In this respect, the electrical properties of DNA-scaffolds are of a wide interest. On the other hand, also the utilization of the DNA itself as a nanoscale conductor is still under great investigation, mainly inspired by many predictions of its useful conductivity. This increases the interest on DNA electrical properties even more.

To be able to measure the electrical properties or otherwise realize the full potential of the bottom-up DNA-nanotechnology, one needs to position these constructs on the chip in a controllable way. We have shown that dielectrophoresis (DEP) can be efficiently utilized to trap DNA molecules and self-assembled structures [1]. Here we have utilised DEP to trap rectangular DNA origami and three-tile-long defined TX-tile constructs between the nanoelectrodes, and characterized the electrical conductivity of them. Both DC and AC characteristics of individual trapped structures, surrounded by atmosphere with different humidity levels, have been fully analyzed by impedance spectroscopy and detailed equivalent circuit modelling, describing the conductivity mechanisms of the structure [2,3]. The results revealed that the nature of the conductivity is a combination of an ionic diffusion and Ohmic conductivity. It also scales with the volume of the structure pointing towards water induced conductivity along the DNA helices, most probably by the layer of polarised water molecules sheathing the DNA. Further measurements on more novel structures, e.g. 3D-origami and hybrid assemblies containing G4-DNA wires, are on the way.

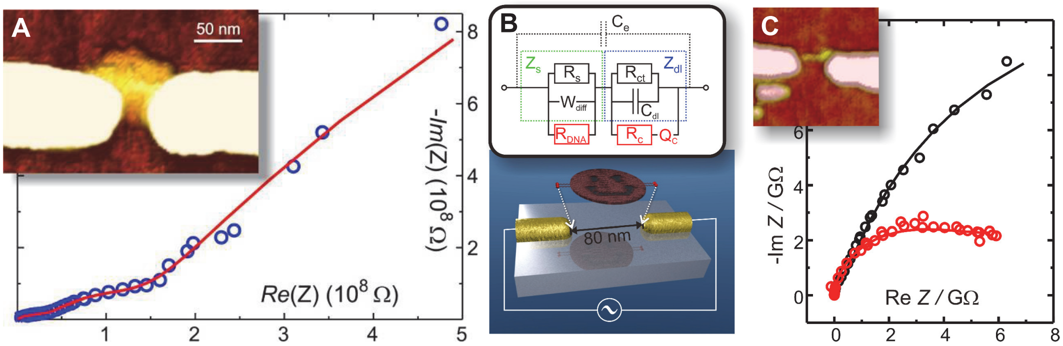

Figure 1. **A** *Inset: AFM Image of a rectangular DNA origami trapped and immobilized between nanoelectrodes. Graph: AC impedance spectroscopy data measured from the structure (circles) and the response of a fitted equivalent circuit (line).* ***B*** *— Upper: Used equivalent circuit model. Lower: Schematic view of trapping of a DNA origami.* ***C*** *— Inset: AFM Image of a TX-tile structure trapped and immobilized between nanoelectrodes. Graph: AC impedance spectroscopy data measured from these structures (circles) and the response of a fitted equivalent circuit (lines).*

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13:30–14:15

ELECTRON TRANSFER REACTIONS IN REDOX-LABELED DNA TETHERED TO ELECTRODES

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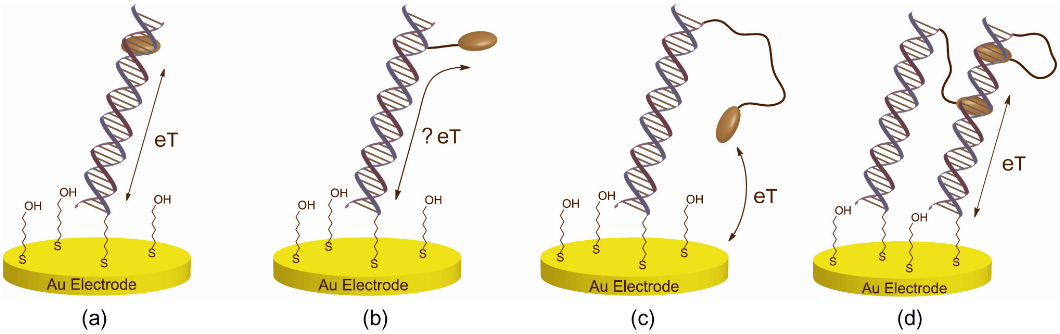
Applications of DNA in DNA-based electronics and electrochemical DNA biosensors strongly depend on electron transfer (ET) properties of individual DNA molecules. In electrochemical studies of ET in surface-tethered redox-labelled DNA, an electrochemical signal stemming from the reaction between redox labels bound to the DNA double strand and the electrode is generally considered as the evidence of the electronic conductivity of DNA [1–4]. While ET mediated by the DNA duplex is unambiguously shown for the case of intercalating redox-active probes [1, 2], data on directional ET between electrodes and DNA-conjugated redox probes show certain extent of inconsistency [3–6].



Here, I will discuss our recent results on electrochemical studies of ET kinetics in DNA duplexes having different type of redox labels, differently conjugated to double stranded DNA [6, 7]. It is shown that in loosely packed DNA monolayers ET between the electrode and the redox label is governed by the motional movements of the probe (and thus DNA) versus the electrode surface, such mechanism being different from the generally considered DNA-mediated ET in dsDNA. I will discuss how interfacial and ET properties of DNA can be modulated for ET not to be observed or be due to the diffusional movements of the redox probe towards the electrode (Figure) [6, 7].

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14.15–15.00

DNA PHOTOPHYSICS: ELECTRONIC COUPLING BETWEEN MULTIPLE CHROMOPHORES

Steen Brøndsted Nielsen
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Excitation of DNA by UV light may lead to mutagenic photoproducts. This vulnerability is compensated for in all living organisms by enzymatic repair of photodamaged DNA. However, since repair is costly, DNA is intrinsically photostable. The nature of excited states of DNA bases is important for this photostability. One protection mechanism is fast nonradiative relaxation to the electronic ground state and another is delocalization of the excitation energy over many bases to prevent subsequent photochemical reactions. In Aarhus we explore the intrinsic photophysics of isolated building blocks of DNA using the electrostatic ion storage ring, ELISA (Fig. 1), in combination with lasers (see Fig. 2). In other experiments, we use the synchrotron radiation facility ASTRID (Fig. 1) for circular dichroism experiments on solvated DNA strands to characterize the electronic transitions, e.g., the number of bases in a strand that electronically couple in the excited state. Recent measurements suggest large electronic communication and a spatial extent of the wavefunction that increases significantly with the excitation energy.

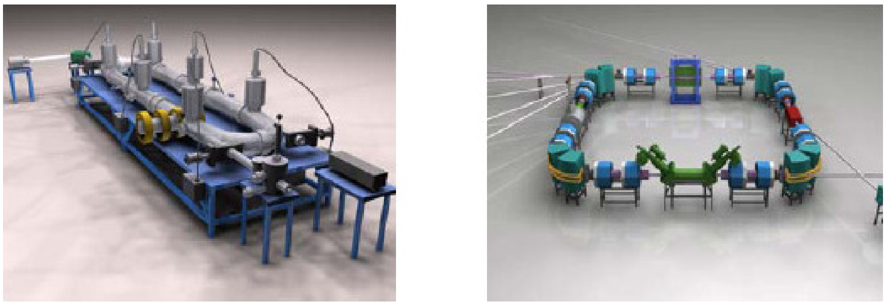

Figure 1. Left: The ELectrostatic Ion Storage ring in Aarhus used for gas-phase spectroscopy experiments on DNA ions. Right: Aarhus STorage RIng in Denmark used for solution-phase spectroscopy experiments on DNA single and double strands.

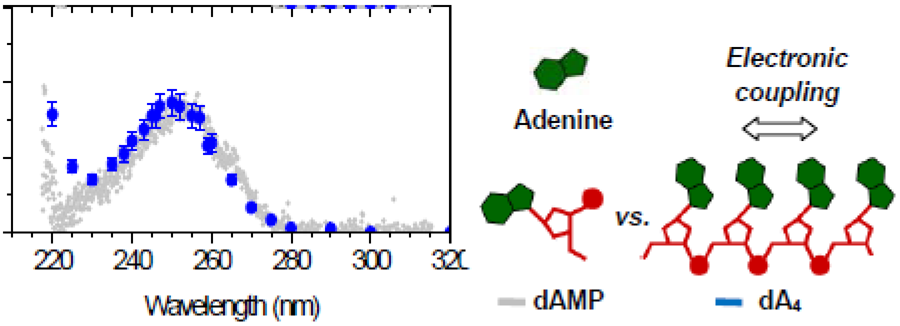

Figure 2. Gas-phase action spectroscopy shows that electronic coupling between adenine bases in short DNA strands leads to a small blueshift of the absorption band in agreement with theoretical predictions.

15:15–16:00

ELECTROSTATIC FORCE MICROSCOPY AND CONDUCTIVITY MEASUREMENTS ON DNA AND DNA-PEPTIDE CONJUGATES

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Phase-shift signal produced by KA_6-coated DNA with the tip bias voltage of -8 V and lift distance of 50 nm.

DNA-based devices are considered to be interesting candidates for nano electronics due to unique properties of DNA such as self-assembly, recognition and self-replication. However, the electrical properties of DNA become a subject of continuous debates in the last decades. In various experimental reports, dsDNA molecules have been reported to behave as an insulator, a semiconductor, or a metal and even exhibited induced superconducting transition at low temperatures. This controversy might be related to drastic changes a DNA molecule experience upon deposition. Once DNA is adsorbed on a solid surface its conformation is changed due to van der Waals, electrostatic and hydrophobic interactions with the substrate. Already at this stage we can expect disturbance of DNA hydration shell as well as inter-strand hydrogen bonding and electrostatic interaction. Subsequent removal of the water molecules and counter ions coordinated with DNA upon drying will further disturb and destabilize the DNA structure. Thus, one can expect that the molecule we deposit and investigate on the solid substrate bears little resemblance to the molecule in its native conformation in biological environment. From this perspective, DNA protected by a coat of short cationic peptides can exhibit better stability and eventually retain its conductive properties.

In this presentation we demonstrate by using Electrostatic Force Microscopy and direct conductivity measurements that coating with certain cationic peptides can indeed improve charge transport properties of DNA. This finding can have important application in DNA molecular electronics and biosensors.

16:00–16:45

ELECTRICAL CONDUCTIVITY IN MMX POLYMERS: FROM NANORIBBONS TO MACROCRYSTALS

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Design and processability of molecules are key issues to produce technologically useful molecular materials. Organic molecules, including oligomers and polymers, have shown excellent processability and properties at the macroscale providing fruitful applications, but their organization as nanomaterials is still very limited. If we focus on components demanding high conductivities, this task becomes even more challenging, since organic molecules usually show limited conductivity values due to localized mechanism of conduction. However, the combination of organic molecules with metal ions seems to open new possibilities towards this end. MMX wires, a particular type of coordination polymers attracted great attention and were extensively studied during the 90's. They were described as one dimensional crystals with a high degree of electrical anisotropy (the conductivity along the wires direction was much higher than along the perpendicular ones). However studies reporting nanostructures of such polymers are still very scarce.

Recently, we reported the first realization of highly conducting nanostructures using a platinum based MMX but at these early stages the conductivity of our ribbons was limited by their structural quality. We have now substantially improved the synthesis of the nanostructures. This remarkable advance allows us accessing the intrinsic properties of this material and making a comprehensive approach to electrical transport at the nano and macro-scales. The primary significance of this work is three-fold. Firstly we are able to determine the *intrinsic* conductivity (the conductivity discounting the influence of defects and contact resistance) of these crystals, resulting in 10^5S/m a value of about two orders of magnitude higher than that of polypyrrole, one of the most known conducting polymers. Second, we corroborate for the first time the already predicted gapless electronic band structure of this compound, which was not possible before due to the defect content in the samples studied, which is a critical knowledge when transferring materials to applications. Third, a comparative study of the properties of the nanoribbons with those of conventional crystal, together with theoretical modeling of the material, allow us elucidating the different electronic transport mechanism at the nano and macroscale; while transport in nanoribbons is limited by the presence of structural defects for macrocrystal the limiting mechanism is interchain hopping. This behavior has been also observed in other conducting polymer, so we expect our results to be expandable to many other polymeric compounds.

The results presented postulate this compound as a good metallic interconnector in nanodevices and allows a comprehensive approach on the different transport mechanisms at the nano- and macroscale to be made.

16:45–17:15

SUBSTRATE INFLUENCE ON THE TWO-DIMENSIONAL METALLO-SUPRAMOLECULAR SELF-ASSEMBLY OF TPyB

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Introduction: Metallo-supramolecular self-assembly gives the opportunity to fabricate a wide range of 2D structures on metal surfaces with applications in catalysis, molecular electronics, magnetism and sensor design [1]. This bottom-up technique can be influenced by coverage, thermodynamic and kinetic effects, electrical simulation, etc to yield different self-assembled structures [1, 2]. The molecule 1,3,5-trispyridylbenzene (TPyB) has earlier been studied in coordination with Cu and Fe atoms on the flat Au(111) and Cu(111) surfaces [3, 4]. Here we present a scanning tunneling microscopy (STM) study of TPyB molecules with coordinating Cu atoms on the modulated surface of Ag/Cu(111) with well-known (9x9) reconstruction due to the lattice mismatch between Ag and Cu. We compare our data with self-assembly on flat Cu(111).

Method: The experiments were done using STM under ultra-high vacuum conditions. TPyB molecules and metal atoms where deposited by thermal evaporators.

Results: TPyB deposition on the Ag/Cu(111) layer results in a well-ordered close-packed molecular structure, similar to what has been seen on Au(111) surface [3]. Upon deposition of Cu atoms onto the surface, the TPyB-Cu coordination transforms the structure into a more open honey-comb network. Whereas the honey-comb structure consists of perfectly symmetric hexagons on the flat surfaces we observe a significant distortion on the Ag/Cu(111) substrate. The periodicity of the reconstruction of the substrate is close to, but not exactly equal, to the periodicity of the TPyB-Cu network. Mostly the structure of molecular networks is governed by molecule-molecule interactions, but apparently the molecule substrate interaction is here strong enough to distort the ordering due to the mismatch between periodicities of the substrate and the molecular network.

Conclusion: In summary we have presented that the substrate topography can have considerable effect on the self-assembly of TPyB-Cu coordination network.

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Poster Presentations

ADSORPTION OF CYTOSINE ON THE AU(111) SURFACE BY DENSITY FUNCTIONAL THEORY

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Introduction and Aims

Understanding the adsorption of DNA bases on inorganic surfaces is a crucial step to grasp the mechanisms of interaction of entire DNA molecules with hard substrates, which is a key issue in different contexts, such as the development of DNA microarray techniques and the implementation of DNA-based molecular electronics. Furthermore, the investigation of the self-assembly of DNA bases on template surfaces is a hot topic in relation to the emergence of life under prebiotic conditions.

We investigate the adsorption of cytosine on Au(111) with the aim of revealing the microscopic nature of the interaction between cytosine and the Au(111) surface, with attention to quantifying the importance of dispersion interactions.

Methods

Our electronic structure calculations are based on periodic-supercell pseudopotential density functional theory (DFT) with the non-local van der Waals (vdW) density functional.

Results

The inclusion of dispersion interactions enhances the value of the adsorption energy and affects the cytosine bonding geometry: with the inclusion of vdW interactions the adsorption energy is four times more negative than without vdW terms, and we also find that a tilted geometry is always favorable relative to a parallel geometry.

The analysis of the electron wave functions gives a remarkable evidence of adsorbate-substrate interaction beyond the pure dispersion regime, with formation of hybrid and bonding orbitals between the adsorbate and the substrate. DFT calculations without vdW exchange-correlation functionals do not show the formation of bonding orbitals.

Conclusions

Our findings point out an interaction that is stronger than pure physisorption, though it does not fall into a chemisorption regime.

Dispersion interactions are crucial for a correct description of the system.

The combined new data for energetics, geometry and electronic structure lead to conclusions in contrast with the common opinion that the surface-molecule interaction is negligible in the process of monolayer formation.

ELECTRONIC CONDUCTANCE OF FUNCTIONALIZED BENZENE-DIAMINE MOLECULES WITH THE GW APPROXIMATION

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We study the effect of side groups (OCH3, CH3, CN, Cl) on the electronic transport properties of 1,4-benzenediamine (BDA) molecular junctions using the non-equilibrium Green function method with different levels of approximations for the exchange-correlation effects, namely DFT-PBE, Hartree-Fock and the many-body GW method. Compared with DFT-PBE and Hartree-Fock, GW provides a better description of the molecular energy levels in the junction and predicts electronic conductance values closer to experiments. Specifically, GW underestimates the experimental conductances by a factor two while DFT-PBE and Hartree-Fock overestimates by a factor three and underestimates by a factor twenty, respectively. Additionally, only GW predicts the sign of the conductance change correctly for all side groups. Our results demonstrate the importance of self-interaction correction on the molecule and the dynamical screening at the metal-molecule interface (image charge effect) and shows that quantitative accuracy in quantum transport calculations is achieved by the self-consistent GW approximation.

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Presentation type: Oral ( ) / Poster (0)

THE MANY FACES OF DIPHENYLALANINE

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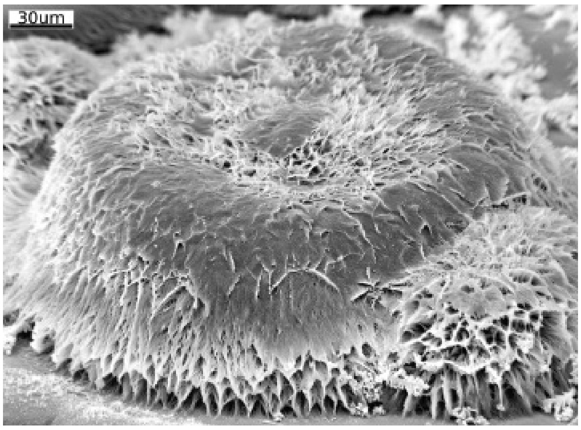

One of the most studied mechanisms of self-assembly of protein subunits is that of amyloidogenesis, the aggregation of soluble and innocuous protein into insoluble protein aggregates known as amyloid fibrils. Research on βamyloids, which are related to Alzheimer's disease, revealed the ability of diphenylalanine (FF) to self-assemble into peptide nanotubes (PNTs).

The PNTs were grown by crystallizing a solution of FF in hexafluoroisopropyl alcohol. The role of charge of the FF subunits was investigated and it was found that positively charged analogues formed vertically aligned tubes, negatively charged analogues formed a minima of tubes, while uncharged analogues formed non-aligned tubes. In anhydrous environment FF formed an amorphous film that, when treated with aniline at temperatures $\geq$100°C, formed peptide nanowires (PNWs). Further treatment of the PNWs with polyaniline yielded core/shell conducting nanowires.

Here we present a study of the self-assembled structures obtained with FF in trifluoroethyl alcohol (TFE). The dependency of the self-assembled structures on time, pH, and the concentration of FF were investigated.

THE NATURE OF THE INTERACTION BETWEEN NATURAL AND SIZE-EXPANDED GUANINE WITH GOLD CLUSTERS: A DFT STUDY

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Abstract

In this paper, we study the interaction of natural and size-expanded guanine molecules with small gold clusters, to shed light on the nature of the N/O-Au bonds and of the unconventional NH... Au hydrogen bonds, as well as on the dependence of these bonds on the charge state of the systems. Based on density functional theory results, it is found that the nature of the N/O-Au bonds between both guanine and its size-expanded form and 3- and 4-atom Au clusters is covalent in the neutral systems. In the -1 charged systems the binding energy decreases by almost 50% with significant change of geometry. Although the NH site in the spacer ring of size-expanded guanine may supply a new acceptor opportunity for forming an additional NH... Au hydrogen bond, this hardly emerges because of the non-planarity and large steric effect. The introduction of a spacer ring in guanine decreases the HOMO-LUMO gap and expands the spatial distribution of electron wave functions, which make size-expanded guanine appealing for charge transfer performance. At the same time it increases the steric hindrance, making the adsorption process more orderly, which is also good in view of molecular electronic devices.

MOLECULAR COMBING OF DNA AND DNA-PEPTIDE CONJUGATES

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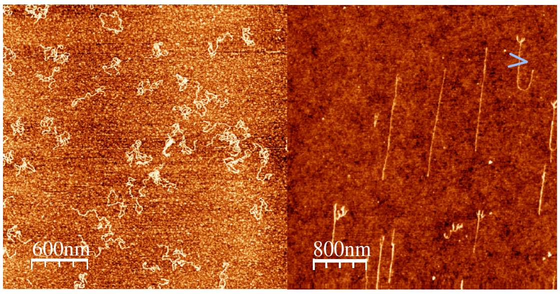
First proposed in 1994, the so-called “Molecular Combing” technique offers a convenient yet effective way to achieve ordered alignments of DNA molecules stretched on a solid surface [1]. Once DNA is stretched with one or both ends attached to the surface, a wide variety of further investigations and manipulations on DNA structure is possible [2]. In this study, we developed a new variation of combing technique -based on a method previously described by Zhang et al. [3]-which resulted in reproducible generation of highly-stretched DNA molecules on silicon dioxide substrate. Not only successful in combing dsDNA with a high quality, the new technique was able to comb a number of DNA-Peptide conjugates which was not possible using other combing methods.

In brief, after functionalization of silicon substrates using gas-phase deposition (N-Octyldimethylchlorosilane, incubation time 2 hours), amount of 30 μl of DNA solution (25 ng/μl) in 20 mM ammonium acetate buffer at $\mathrm{pH} = 5.1$ was deposited as a droplet on highly-hydrophobic silicon substrate. After 6 min incubation at room temperature, the droplet was dragged out of the surface using a pipette tip. In order to comb DNA-Peptide conjugates, an additional step was performed, in which a second droplet containing peptide solution was deposited and combed under the same conditions. Topographic images were obtained using Atomic Force Microscope (AFM) in tapping mode.

Results suggest that using the new combing technique, we could achieve highly-reproducible alignments of DNA stretched on the surface in the desired direction. In addition, the meniscus force applied by this technique was high enough to comb DNA-Peptide conjugates. The technique was also successful in combing DNA and DNA-Peptide conjugates across fabricated Pt/Cr nanoelectrodes. The technique is of great value since it offers a facile and reliable method for combing DNA and DNA derivatives for further applications in nanotechnology.



DNA molecules deposited (left) and combed (right) on silicon surface

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DEVELOPMENT OF A PROTEASE ASSAY BASED ON SILVER NANOPRISMS

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Severe deficiency of the von Willebrand factor (VWF) cleaving protease ADAMTS-13 prevents normal cleavage of large VWF multimers in patients with the disease Thrombotic Thrombocytopenic Purpura (TTP). TTP is a life-threatening disorder and the mortality rates for these patients are still high. Identification of patients with severe ADAMTS-13 deficiency would support the clinician's ability to diagnose and treat the TTP patients correctly. Therefore, a reliable, selective and sensitive protease assay for TTP clinical diagnosis is needed.

We have synthesized a Lanthanide-binding tag peptide containing a trypsin cleavage site (LBTtrp-peptide). This construct mimics the characteristics of the LBT engineered VWF. LBT is a short peptide that binds Tb^{3+} with extremely high affinity. Upon incorporation of Tb^{3+} into LBT it is possible to excite the lanthanide via excitation of the single tryptophan residue located in LBT. Tb^{3+}'s bright luminescence emission is an advantage for background less fluorescence-based biological assays. Additionally, the chemically synthesized LBTtrp contained two cysteine residues in order to couple the peptide onto silver nanoprisms. The silver nanoprisms used for the experiments were 12 nm in height and 70 nm in width.

Here we report the interaction between the tryptophan residue, Tb^{3+} and silver nanoprisms upon coupling and decoupling between LBTtrp and silver nanoprisms in solution. UV-visible spectroscopy, fluorescence spectroscopy and transient absorption spectroscopy confirmed the attachment and cleavage of LBTtrp. When immobilizing LBTtrp onto the silver nanoprisms a 10% decrease in Tb^{3+} luminescence was observed, while a decoupling of the construct by trypsin caused 20% increase in Tb^{3+} luminescence.

Based on the results presented, we demonstrate a proof-of-concept protease assay based on silver nanoprisms without the need for any purification steps. We believe that this type of nanobioassay will allow for a fast and precise detection of ADAMTS-13 activity.

PEPTIDE LOADED NANOFIBRES AS A POTENTIAL ANTIMICROBIAL SURFACE COATING OF INANIMATE SURFACES

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Keywords: Electrospinning; Antimicrobial Peptides; Surface Coating; Drug Delivery.

During the last couple of years there has been an increased awareness of the importance of hygiene in order to reduce the danger level of infections. This is especially a concern when it comes to nosocomial infections caused by multi resistant pathogens. Nosocomial pathogens can persist on inanimate surfaces for weeks and even months [1], which means that inanimate surfaces can act as reservoirs for pathogens if left untreated. Effective reduction of the total amount of pathogens present on the respective surfaces can be difficult to achieve by traditional cleaning [2, 3]. We believe that a combination of traditional cleaning and bioactive surface coatings of inanimate surfaces could be an effective way to reduce the danger level of infections Antimicrobial peptides (AMPs) are prime candidates for being incorporated into such bioactive surface coatings due to their characteristic mode of action both as antimicrobial- and immunological agents.

The focus of the presented work is to explore the possibility of reducing the risk of infections by utilising bioactive nanofibres as an antimicrobial surface coating of inanimate surfaces. To test this hypothesis, polyethylene oxide (PEO) and poly(ε-caprolactone) (PCL) nanofibres loaded with fluorescently labelled AMPs were produced by electrospinning. The tested peptides were dansyl labelled Crabrolin and dansyl labelled Indolicidin. By labelling the AMPs, it was possible to investigate the spatial distribution of the AMPs within the fibres and compare the difference in distribution between an α-helical peptide (Crabrolin) and an unstructured peptide (Indolicidin). Tetracycline was used as a reference compound.

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ON THE ROLE OF A SINGLE SOLVENT MOLECULE ON THE ABSORPTION BY NITROPHENOLATE IONS IN VACUO

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Charge-transfer excitation is highly dependent on the electronic coupling between the donor and acceptor groups. Nitrophenolates are simple model systems for studying the effects of solvent binding on the charge-transfer process. The coupling between the acceptor and donor group is broken for the meta isomer, which make this the perfect system to test the effect of single solvent molecules on a charge-transfer system. Single solvent molecules of water, methanol and acetonitrile where added to the meta isomer. Action spectroscopy was done in the gas-phase at an accelerator mass spectrometer. We identified a Hypsochromic shift for all the solvent complexes. The bare meta ion has an absorption maxima at 532 nm, which blue shifts to 487 nm, 45 nm and 505 nm for the addition of water, methanol and acetonitrile respectively. This experiment shows the effect of solvent molecules on a pure charge transfer excitation, and sets a benchmark for quantum chemical calculations of charge transfer states.

ISBN 978-87-92329-58-5