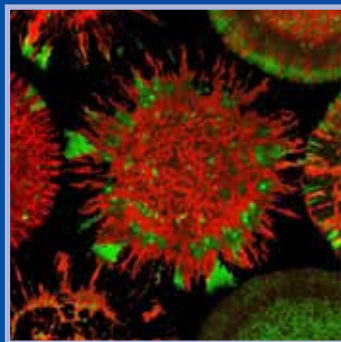
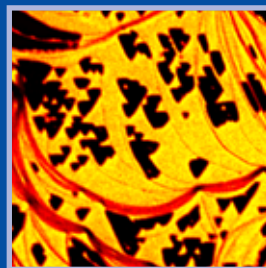
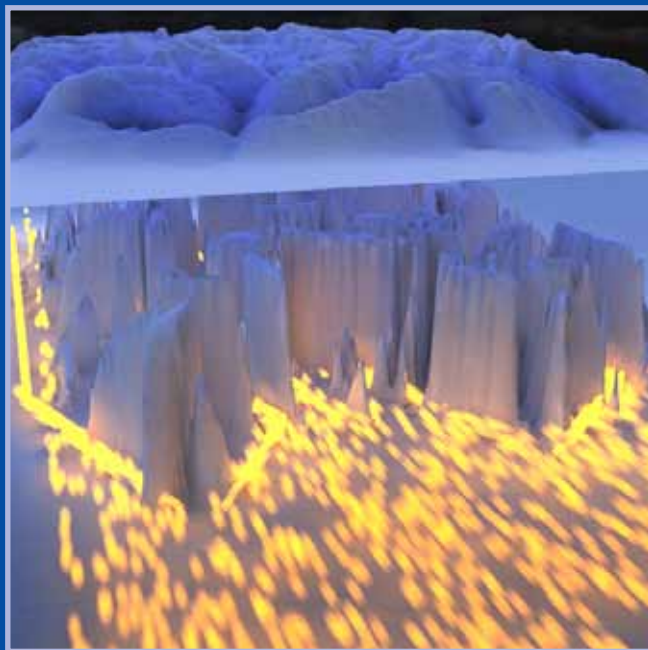


# CENTER FOR NANOSCIENCE

## ANNUAL REPORT 2014



CeNS

Center for NanoScience | LMU

**CON-  
TENTS**

**4**

New Members

**5**

Members' News

**6**

Awards

**7**

Spin-off News

**8**

Events  
& Activities

**13**

Selected Research  
Projects

**51**

Selected  
Publications

**61**

Master's  
and PhD Theses

**66**

Funding

**67**

Imprint

## WELCOME



Writing the preface of the annual report of CeNS is always a pleasure. Right now, CeNS is in its 17<sup>th</sup> year and the wealth of new phenomena and innovations in the field of nanoscience is far from abating, as a look at this report

shows. CeNS is definitely maintaining its youthful spirit!

"CeNS is a grassroots movement." This is what Hermann Gaub likes to say whenever someone asks him what CeNS is. It is hard to think of a more accurate description. CeNS, which is a very small organization in terms of budget and administrative staff, might seem to look a bit out of step at a time when research is increasingly bundled in huge, well-funded structures with a fixed research agenda. Far from it: one of the defining features of CeNS is that – apart from our common interest in things nano – there is no agenda; CeNS people are free to come up with whatever they think might be an interesting project, an interesting cooperation, an interesting new way of teaching nanoscience. CeNS attempts to support as many of these ideas as possible, as flexibly as possible, with a limited budget, but with unlimited confidence in its members: it provides support for ideas which are not yet at a stage to receive large-scale grants but which are well on the way. The enormous number of awards, large grants, spin-offs, and international cooperations based on the initial momentum provided by CeNS more than justifies the CeNS approach. Let me just mention some of the prizes the spin-offs have won: NanoTemper received the Deutscher Gründerpreis, arguably the most prestigious award for new companies – next to the German Future Award of the German President, for which Nanion Technologies were nominated. For more, turn to the following pages.

A particular highlight of 2014 was due to the US National Science Foundation and its program on the Physics of Living Systems (PoLS). Last year's annual meeting of the network took place in Munich and attracted more than 200 participants from all over the globe; CeNS (and the collaborative research center SFB 1032 "Nanoagents") acted as hosts, a tribute to the standing Munich nanoscience has acquired worldwide.

As every year, a further highlight was provided by our annual conference in San Servolo, Venice, where we

"walked and talked at the nanoscale", focusing on the workings of nanoscale communication and transport phenomena. For the first time, we housed both PhD students and more advanced researchers and speakers on the island San Servolo itself, to make exchanges between our students, CeNS members and outside speakers more intensive and fruitful.

Another experiment is a new format for the CeNS publication awards: every year selecting the winners is one of the most pleasant and difficult duties of the CeNS board, because of the quality of the submitted papers. Sometimes, structure helps decision-making, and so we now award prizes in three categories, namely for the best interdisciplinary publication, for scientific breakthroughs, and for the best publications by CeNS junior scientists.

Last year has also seen some major changes in the board of CeNS, which had previously been expanded from three to five members to reflect the enormous diversity of scientific activities. Joachim Rädler and Thomas Bein retired from the board; our new board members are Dieter Braun from the Faculty of Physics and Achim Hartschuh from the Department of Chemistry. We welcome our new board members and thank our "board alumni" for all their dedication and work; we call them alumni as we hope and expect that their expertise will stay with us. Our innovation of having three student representatives elected by the PhD students has added new perspectives and will be continued by the new student representatives.

As every year, on behalf of all CeNS members, the most sincere thanks of the board go to the people without whom all this would not have been possible: Susanne Hennig, our managing director, Marilena Pinto, our program manager, and Claudia Leonhardt, our team assistant – their energy and commitment is just amazing!

I do hope that you will enjoy reading the annual report of CeNS for 2014 as much as we enjoyed all the activities it unites – doing research, teaching, innovating, and exchanging ideas in the fascinating world of the small: there is plenty of room at the bottom. Have fun!

**Prof. Ulrich Schollwöck**

Spokesman of the Scientific Board of CeNS

## NEW MEMBERS

### DR. PHILIPP PAULITSCHKE

LMU Munich



Dr. Philipp Paulitschke studied physics at the LMU Munich. In 2006 he worked on his diploma thesis at the chair of Prof. Jörg Kotthaus. During this period he developed a new method of fabricating inverted conical GaAs-Nanowires. In his

PhD studies he investigated the mechanical properties of these nanowires in different environments. After finishing his PhD in 2011, Dr. Paulitschke adapted his know-how in solid state physics to biological systems like human cancer cells and bacteria. During this time he filed three patent applications and received a €1.2 million BMBF-grant to continue his work in developing high-throughput screening techniques. Since 2014 Dr. Paulitschke has led a research group at the chair of Prof. Joachim Rädler.

### DR. RALF JUNGSMANN

MPI of Biochemistry and LMU Munich



Dr. Ralf Jungmann studied physics at Saarland University and graduated in 2006 having worked on his diploma thesis in the group of Prof. Paul Hansma (UCSB). He continued his research in the group of Prof. Fritz Simmel and

earned a doctorate from TU Munich in 2010. After his postdoctoral training at the Wyss Institute for Biologically Inspired Engineering at Harvard University in the groups of Prof. Peng Yin and Prof.

William Shih from 2011 to 2014, Dr. Jungmann started an independent Emmy Noether research group at the MPI of Biochemistry and LMU Munich in December 2014.

Dr. Jungmann's research focuses on the development of novel imaging tools for biological and biomedical applications. His group combines tools from structural and dynamic DNA nanotechnology with single-molecule fluorescence methods, especially targeted towards the development and application of super-resolution microscopy techniques.

### DR. MICHAEL A. NASH

LMU Munich



Dr. Michael A. Nash earned a B.S. in Cybernetics with a specialization in biomedical systems, graduating with highest honors from the UCLA in 2006. He went on to earn a Ph.D. in Bioengineering and Nanotechnology from the University of

Washington – Seattle in 2010. After receiving postdoctoral training at the Chair for Applied Biophysics at LMU from 2011 to 2013, Dr. Nash began an independent research group in May 2013. Dr. Nash has received national and international fellowship awards from the U.S. Department of Homeland Security, the U.S. National Science Foundation, the Alexander von Humboldt Foundation, and from the Branco Weiss Society in Science foundation based at the Swiss Federal Institute of Technology (ETH Zurich). His research group is based in the broad area of biological nanomaterials, and is currently focused on elucidating sequence-structure-function relationships within cellulosomes, the multi-component protein networks used by anaerobic bacteria for biomass energy conversion.

## CALLS & APPOINTMENTS



**Prof. Hubert Krenner** (University of Augsburg) was appointed professor of experimental physics (W2) at the University of Augsburg.



**Prof. Ernst Wagner** (LMU) accepted an offer as guest professor at Sichuan University (Chengdu, China) from 2014 to 2017.

## ERC GRANTS

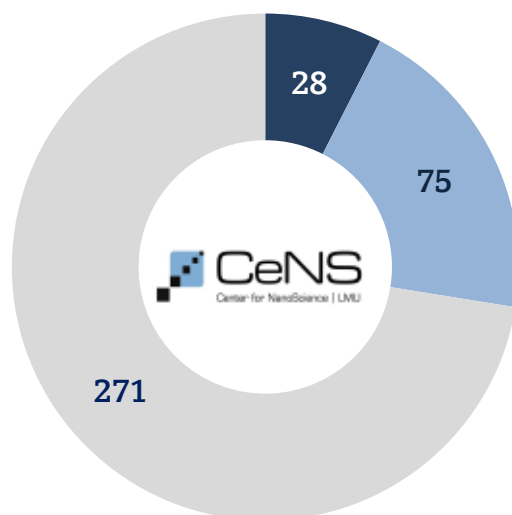


**Prof. Bettina Lotsch** (LMU and MPI for Solid State Research) received an ERC Starting Grant for her project COFLeaf - Fuel from sunlight: Covalent organic frameworks as integrated platforms for photocatalytic water splitting and CO<sub>2</sub> reduction.



**Prof. Thorben Cordes** (University of Groningen) was awarded an ERC starting grant for investigations of mechanisms of membrane transport (SM-IMPORT). In the next five years Cordes' group will use novel single-molecule approaches to understand the molecular mechanisms of ABC transporters

## CENS MEMBERSHIP NUMBERS



- Ordinary CeNS members
- Extraordinary CeNS members
- CeNS Associates (Master & PhD students, postdocs)

## AWARDS



**Prof. Andreas Bausch** (TUM) received the Academy Prize of the Berlin-Brandenburgische Akademie der Wissenschaften.



**Prof. Dieter Braun** (LMU) received the "Simons Collaboration on the Origins of Life" Award.



**Prof. Hendrik Dietz** (TUM) was awarded the Gottfried Wilhelm Leibniz Award of the DFG.



**Dr. Carsten Grashoff** (MPI of Biochemistry) won the Leopoldina Early Career Award 2014.



**Prof. Peter Hänggi** (University of Augsburg) became Elected Member of the European Academy of Science. He also received the "Distinguished scientist" award and medal of the Ben-Gurion University of the Negev, Israel.



**Prof. Ernst Wagner** (LMU) won the PHOENIX Pharmaceuticals Science Award 2014 (together with D. Edinger, R. Kläger, M. Noga, S.V. Wegner, J.P. Spatz, G. Winter, and A. Besheer).

## CENS PUBLICATION AWARDS

Each year, CeNS awards prizes for excellent publications by CeNS members which have been published during the past 12 months. This year, the candidates submitted numerous articles which appeared in high-impact journals between October 2013 and October 2014.

On Friday, November 28, the winners of the 2014 CeNS Publication Awards were announced to the CeNS members during a celebratory event. The awards were presented in the new categories "Best Interdisciplinary Publication", "Scientific Breakthrough", and "Best Junior Scientist Publication". Altogether 10 publications were distinguished (see page 52 ff for the winning publications).

■ [www.cens.de/research/cens-publication-award](http://www.cens.de/research/cens-publication-award)



Dr. Ulrich Lächelt (AG Wagner, 1st from left) and Prof. Don Lamb (2nd from left), here with CeNS spokesman Prof. Ulrich Schollwöck, received one of the publication awards in the category "Best Interdisciplinary Publication".



## **IBIDI**

The German "Stifterverband" awarded ibidi GmbH with their seal of quality for the company's ongoing and focused commitment to research and development. ibidi, the leading expert in functional cell-based assays, participates in a vast number of research projects and works with academic institutes to provide innovative solutions for customers.

The Stifterverband is a business community initiative that advocates the long-term improvement of the German education and research landscape. In order to achieve this goal, the Stifterverband provides funding for universities and research institutes, supports talents, analyses the higher education system, and devises recommendations for policy and business.

■ [www.ibidi.de](http://www.ibidi.de)



## **NANION TECHNOLOGIES**

The management team at Nanion Technologies was one of three nominees for the Deutscher Zukunftspreis, the German president's award for technology and innovation. The team was nominated for Nanion's latest automated screening platform, the SyncroPatch 384/768PE, which enables completely new strategies in drug discovery and scientific research.

The Deutscher Zukunftspreis (German Future Award), with which the German Federal President rewards cutting-edge technological innovations which also have a high potential for commercial success and societal benefit, is the country's most prestigious award for technology and innovation.

■ [www.nanion.de](http://www.nanion.de)



## **NANOTEMPER TECHNOLOGIES**

NanoTemper Technologies was awarded the "Deutscher Gründerpreis 2014", an award for German companies with an extraordinary growth rate and the potential to become a market leader.

The "Deutscher Gründerpreis" is the most important award for outstanding entrepreneurs in Germany. Since 2002, this annual award has honored innovative and successful companies, thus encouraging the formation of new companies.

In addition, NanoTemper Technologies was awarded the "BioProcess Award 2014" in the category Best Technology Application - Analytical, an award for outstanding technology applications dedicated to the development of biopharmaceuticals and therapeutics.

■ [www.nanotemper-technologies.com](http://www.nanotemper-technologies.com)



## **A PERFECT TEAM - ATTOCUBE AND NEASPEC**

In February 2014, attocube acquired a majority share in Neaspec GmbH. Neaspec - a spin-off from the MPI for Biochemistry – specializes in developing scanning near-field optical microscopes (SNOM). These microscopes break the resolution limit of existing conventional optical microscopes and therefore open up completely new applications for nanoanalytical characterization. attocube – the market leader in the cryogenic microscopy market – will profit from the cooperation by expanding its portfolio with further elaborate measurement techniques in nanotechnology.

■ [www.attocube.com](http://www.attocube.com)

■ [www.neaspec.com](http://www.neaspec.com)



### CENS WORKSHOP VENICE 2014

**“Walk and Talk at the Nanoscale”** – this was the motto of the 2014 CeNS workshop in Venice. For the 10<sup>th</sup> time, CeNS researchers and invited speakers gathered on the charming island of San Servolo for a varied nanoscience program. The program committee had drawn up an impressive schedule with renowned speakers from all over the world: Alberto Amo, Phaedon Avouris, Charles Baroud, Dimitri Basov, Kobi Benenson, Nynke Dekker, Maria Garcia-Parajo, Alex Hamilton, Stephen Hart, Thomas Ihn, Liedewij Laan, Delia Milliron, Moein Moghimi, Lukas Novotny, Hermann Sellier, Manuel Théry, and Sven Vogel. In addition, six researchers (Ralf Jungmann, Khaled Karrai, Heinrich Leonhardt, Stefan Ludwig, Christian Plank, and Philip Tinnefeld) and four junior scientists from CeNS presented their research. The talks covered a wide range of topics from nanomedicine, single-molecule studies, and synthetic biology to plasmonics and quantum phenomena. Moreover, CeNS graduate students presented and held a lively discussion of their latest results during the two poster sessions.

■ [www.cens.de/calendar/past-workshops-events/venice-2015](http://www.cens.de/calendar/past-workshops-events/venice-2015)

### FOCUS WORKSHOPS

#### International “Physics of Living Systems” Meeting Munich (iPoLS)

The Physics of Living Systems (PoLS) Student Research Network is a trans-institutional community-based network of graduate students and educators. The program targets synergy of theoretical and experimental research exploring the most fundamental physical processes that living systems utilize to perform their functions in dynamic and diverse environments.

The second international PoLS meeting, which took place in Munich from July 21 to 24, 2014, was attended by over 200 participants from 14 institutions. It was organized by Prof. Don Lamb and Prof. Dieter Braun (both LMU) in cooperation with Prof. Zan Luthey-Schulten (University of Illinois), assisted and financially supported by the management teams of CeNS and the SFB1032.

Over 70 diverse talks by faculty and graduate students gave a remarkable insight into the world of physics of living systems. In addition, all participants got the chance to present and discuss their work during the poster sessions. The different



Participants of the CeNS Workshop Venice 2014.





Lively poster session at the iPoLS meeting.

universities also presented posters on the training of the next generation of biophysics students and their approach to teaching biophysics.

As part of the meeting, Prof. Klaus Schulten (University of Illinois) gave a lecture on "Physics and Life – the magnetic sense of migrating birds", which was open to the Munich public at the Deutsches Museum, while the international participants enjoyed a guided tour through the Center for New Technologies ZNT at the Deutsches Museum.

■ [www.cens.de/international/joint-workshops/pols-2014/](http://www.cens.de/international/joint-workshops/pols-2014/)



iPoLS group picture at LMU main building.

#### 4<sup>th</sup> European Workshop on Advanced Fluorescence Imaging and Dynamics

In December 2014, Prof. Don Lamb organized a workshop for about 50 participants on advanced concepts in fluorescence imaging techniques and instrumentation. The workshop was supported by CeNS, the Institute of Physical Chemistry at LMU Munich, and the Nanosystems Initiative Munich

(NIM) in collaboration with the Laboratory of Fluorescence Dynamics (University of California, Irvine). The program consisted of advanced theoretical lectures by nine international speakers, computer based training on data analysis and simulations, and hands-on laboratory training using the fluorescence microscopy instrumentation of the LMU. Topics included Advanced Fluorescence Correlation Spectroscopy (FCS), Imaging Correlation Spectroscopy (ICS), Number and Brightness Analysis (N&B), the Phasor Approach to FRET, the Photon Counting Histogram (PCH), Burst Analysis, and Single Particle Tracking (SPT) in three dimensions.

■ [www.cup.uni-muenchen.de/pc/lamb/workshop](http://www.cup.uni-muenchen.de/pc/lamb/workshop)



Participants of the Advanced Microscopy Workshop.

#### Advanced Workshop on Landau-Zener Interferometry and Quantum Control in Condensed Matter

The ICTP - Eurasian Centre for Advanced Research (ICTP-ECAR), CeNS (represented in the organizing committee by Dr. Stefan Ludwig), and the Nanosystems Initiative Munich organized the Advanced Workshop on Landau-Zener Interferometry and Quantum Control in Condensed Matter at the ICTP-ECAR Centre, IZTECH, Izmir (Turkey), from September 29 to October 3, 2014. The workshop addressed recent developments on Landau-Zener dynamics and related quantum control in complex systems, including (but not limited to) many body effects in ultracold gases, dissipative Landau-Zener transitions, Landau-Zener interferometry in superconducting qubits, double and triple quantum dots, spin & charge qubits, N-V centers and nano-mechanical systems. About 80 participants gathered in order to exchange ideas and shape new links beyond the traditional community boundaries.

■ <http://ictp-ecar.org/events/workshop>

## CENS MEETS INDUSTRY

Career opportunities after the PhD are as diverse as the scientific focus of the CeNS groups. For the 14<sup>th</sup> time, CeNS junior scientists had the opportunity to learn about possible career paths at the event “CeNS meets Industry” in July 2014. Five speakers presented their companies and career paths, ranging from the pharmaceutical industry (Dr. Fabian Heinemann, Roche Diagnostics) to R&D at the scan solutions manufacturer ScanLab (Dr. Christoph Wienken) and at Applied Materials, the global leader in precision materials engineering solutions for the semiconductor, flat panel display, and solar photovoltaic (PV) industries (Dr. Kulpreet Virdi). In addition, Dr. Stefan Duhr, CEO of Nano-Temper Technologies, gave valuable insights into the development of this very successful CeNS spin-off. Last but not least, Dr. Stefan Völk (DLR Oberpfaffenhofen) explained how nanophysics and space exploration mesh together. The traditional



CeNS summer party that followed was a perfect opportunity for all CeNS members and guests to chat, network, and relax, accompanied by the CeNS band “UnCeNSiert” and child care for the youngest guests.

■ [www.cens.de/calendar/past-workshops-events/cens-meets-industry-2014](http://www.cens.de/calendar/past-workshops-events/cens-meets-industry-2014)

## JUNIOR NANOTECH NETWORK



The fifth Junior Nanotech Network was organized jointly with the Center for Nanoscience and Nanotechnology at Tel Aviv University. After the visit of the Israeli PhD students to Munich in 2013, eight PhD students from CeNS travelled to Tel Aviv for the second part of the exchange from January 27 to February 16, 2014. After a happy reunion with the Israeli students, the participants started their lab rotations to perform hands-on experiments, taught by their peer students. The lab work was complemented by a nano-biophysics workshop and a Raman spectroscopy workshop with two rotating groups. Another highlight was the winter school on topics in nanoscience and nanotechnology at Kibbutz Hagoshrim.

Besides the interesting scientific program, the visit to Israel was filled with several leisure time activities that brought the participants closer to Israeli culture and history. During a guided tour of Tel Aviv, the PhD students heard about the short, but interesting history of the city. An even closer connection to the history, the different religions and cultures, and also conflicts could be felt during a tour of Jerusalem. In addition, the participants got a glimpse of the different landscapes and Israel's nature at the winter school in Hagoshrim and during a visit to Masada and the Dead Sea.

■ [www.cens.de/international/exchange-programs/jnn](http://www.cens.de/international/exchange-programs/jnn)





## PATENTS: HOW TO PROTECT YOUR IDEAS

On December 18 and 19, 2014, CeNS organized a workshop for 25 postdocs and PhD students on intellectual property and patent protection. Patent attorney Dr. Stefan Huebner started with a presentation on how to protect nanotechnology inventions successfully, introducing the most fundamental aspects of IP law. Ms. Sonja Hüttich (LMU Patents Service) continued with a talk about IP services at LMU Munich, including examples of successful CeNS spin-offs. The third talk by Dr. Richard Michalitsch (EPO) addressed the patenting procedure at the European Patent Office. The afternoon ended with a discussion of career opportunities in the IP sector.

On the second day, the participants put themselves into the roles of patent attorneys and judges. They worked in groups on a patent infringement case and finally presented their arguments in a mock trial. The lively discussions during the case study made the participants aware of the pitfalls of a patent claim, and helped them to realize how difficult it might be to protect a claim properly.

■ [www.cens.de/calendar/past-workshops-events/patents-how-to-protect-your-ideas](http://www.cens.de/calendar/past-workshops-events/patents-how-to-protect-your-ideas)

## CENS STUDENT REPRESENTATIVES

After the successful introduction of the CeNS student representatives 2013, three successors were elected from seven candidates in March 2014. 51% of all CeNS associates took part in the online election. Klara Malinowska, Jochen Müller, and Sonja Westermayer (all from the Faculty of Physics) continued established events like the seminar "Science in a Nutshell" but also started new initiatives, e.g., a welcome event for new CeNS associates, a Christmas event at Science Rocks! with diverse 5-minute talks, and a workshop on IT security. In addition, the CeNS associates invited a speaker to the CeNS colloquium for the first time and gave creative input for the ceremony for the CeNS publication awards. The commitment of the student representatives and of all CeNS associates clearly demonstrates that the spirit of CeNS is maintained by the CeNS junior scientists.

■ [www.cens.de/graduate-students/student-representatives](http://www.cens.de/graduate-students/student-representatives)

## KEY QUALIFICATION WORKSHOPS

Effective writing skills are essential for the success of all PhD students. CeNS junior scientists expanded their knowledge and worked on their own texts during the two-day workshop "**Optimizing writing strategies for getting published in English**" in March 2014. At the initiative of the CeNS student representatives, a workshop on "**Supervising and leading in science**" was organized in August 2014, which turned out to be popular not only with PhD students but also with postdocs. In addition, several CeNS junior scientists attended the **seminars organized by the LMU Entrepreneurship Center**.

■ [www.cens.de/calendar/past-workshops-events](http://www.cens.de/calendar/past-workshops-events)



Discussion round at the IP workshop.



CeNS student representatives 2014: Klara Malinowska, Jochen Müller and Sonja Westermayer.



## CENS TRAVEL AWARDS

In 2014, fourteen CeNS PhD students successfully applied for a CeNS Travel Award. They presented their results at international conferences and workshops like the EMRS Spring Meeting, the ACS Autumn National Meeting, or the Biophysical Society Annual Meeting. Examples of three awardees illustrate their contributions:



**Philipp Nickels** (Prof. Tim Liedl's group) presented unpublished results about "Force Balances Made from DNA" at the **20<sup>th</sup> International Conference on DNA Computing and Molecular Programming in Kyoto, Japan**, in September 2014.

Together with the group of Prof. Tinnefeld (TU Braunschweig), he constructed a molecular force clamp using the DNA origami technique. The entropic spring behavior of single-stranded DNA is used in this device to apply various constant forces on a DNA duplex. This molecular tool is currently being used to analyze the force-dependent binding and bending behavior of the transcription factor TBP (TATA binding protein) to duplex DNA in single-molecule experiments.



**Alexandra Schmidt** (Prof. Bein's group) presented her results on a highly biocompatible and light-responsive nanocarrier system based on mesoporous silica nanoparticles (MSNs) for advanced drug delivery applications in an oral contribution at

the **E-MRS Spring Meeting 2014** in Lille. These porous silica nanoparticles were modified with an on-board red-light sensitive photosensitizer, which allows endosomal escape after cell uptake, and a highly biocompatible supported lipid bilayer (SLB), which acted as a capping system to prevent premature cargo release. Two different targeting ligands were successfully incorporated into the SLB to achieve specific cellular uptake. In collaboration with the group of Prof. Bräuchle, the performance of these nanocarriers was investigated on different cancer cell lines by fluorescent live-cell imaging. Alexandra received the E-MRS Graduate Student

Award for her contribution on multifunctional mesoporous silica nanoparticles as advanced drug delivery vehicles.



At the **Gordon Research Seminar "Single Molecule Approaches to Biology"**, **Lena Voith von Voithenberg** (Prof. Lamb's group) presented a poster on "Conformational dynamics during spliceosome assembly investigated by sin-

gle-pair FRET". Conformational changes of a spliceosomal subunit were observed upon RNA binding and dynamic motions could be characterized using single-pair Förster resonance energy transfer. At the Gordon Research Conference, single-molecule FRET extended to three colors was explained and results obtained from measurements with triple-labeled molecular chaperones were described (poster title "Conformational dynamics of molecular chaperones investigated by single molecule multicolor Förster resonance energy transfer"). These results provide information on the coordination of motion between different protein domains.

■ [www.cens.de/research/cens-travel-award](http://www.cens.de/research/cens-travel-award)

## CENS CALL FOR APPLICATIONS

Since 2009, CeNS has been successfully coordinating an annual international call for applications for open PhD positions. Last year, PhD positions from 12 groups were offered. In addition, for the first time four postdoc positions were advertised. 156 applicants from 28 countries applied via the CeNS online application tool, and 24 of them were selected for a Skype interview. Thirteen candidates from nine countries were finally invited to attend the CeNS selection workshop. They met their prospective PIs, the selection committee (Prof. Lamb, Prof. Liedl and Prof. Veigel) as well as the CeNS management and the student representatives. Furthermore, they were able to gain first impressions of Munich during a guided city tour and dinner in a typical Bavarian restaurant.

■ [www.cens.de/careers/international-call-for-phd-students-and-postdocs](http://www.cens.de/careers/international-call-for-phd-students-and-postdocs)

# SELECTED RESEARCH PROJECTS





## SELECTED RESEARCH PROJECTS

- 1 **E. Frey, M. Opitz** Chemical warfare and survival strategies in bacterial range expansions
- 2 **S. Wuttke** Functionalization of metal-organic frameworks
- 3 **F. Keilmann** Ultrafast infrared dynamics on a nanometer scale
- 4 **O. Lieleg, M. Opitz** Erosion stability of *Bacillus subtilis* biofilms
- 5 **E. Weig, J.P. Kotthaus** Energy losses of nanomechanical resonators induced by atomic force microscopy-controlled mechanical impedance mismatching
- 6 **M. Lackinger, W.M. Heckl** Bottom-up fabrication of covalent organic nanostructures by on-surface polymerization
- 7 **M. Opitz, O. Lieleg** Carbohydrate-coating reduces adhesion of biofilm forming *Bacillus subtilis* to gold surfaces
- 8 **R. Metzler** Sensing viruses by mechanical tension of DNA
- 9 **R. Metzler** Tracer particle motion in flexible gel networks
- 10 **E. Wagner, D.C. Lamb** Targeted pDNA and siRNA carriers based on sequence-defined oligomers
- 11 **P. Schwill** Reconstitution of protein gradient oscillations in artificial membrane compartments
- 12 **C. Bräuchle, T. Carell** siRNA nanostructures for cellular uptake
- 13 **P. Müller-Buschbaum, L. Schmidt-Mende** Inner film morphology and molecular orientation in thin films for organic photovoltaics investigated with *in-situ* and *ex-situ* advanced scattering
- 14 **A. Holleitner** Ultrafast electronic read-out of diamond NV centers coupled to graphene
- 15 **T. Bein, J. Feldmann** Oriented thin films of a benzodithiophene covalent organic framework
- 16 **B. Nickel, F. Keilmann** Sub-micron phase coexistence in small-molecule organic thin films revealed by infrared nano-imaging
- 17 **A. Högele** Optical thermometry of a quantum dot in the millikelvin range
- 18 **D. Braun, M.A. Nash** Thermophoresis of thermoresponsive polymer phase transition
- 19 **U. Gerland** Replication-guided nucleosome packing and nucleosome breathing expedite the formation of dense arrays
- 20 **A. Hartschuh, A. Högele** Antenna-enhanced optoelectronic probing of carbon nanotubes
- 21 **S. Ludwig, S. Manus, P. Hänggi** Characterization of qubit dephasing by Landau-Zener-Stückelberg-Majorana interferometry
- 22 **D. Braun** Measurement of thermophoresis in living cells and water-in-oil bubbles
- 23 **J. Lipfert** Double-stranded RNA under force and torque
- 24 **C. Bräuchle, T. Bein** Insights into nanoscale electrophoresis of single dye molecules in highly oriented mesoporous silica channels
- 25 **C. Bräuchle, M. Schneider, A. Wixforth** Methods for precise quantification of nanoparticle uptake into cells
- 26 **B. Lotsch** Crystalline carbon nitride nanosheets for improved visible-light hydrogen evolution
- 27 **D. Fattakhova-Rohlfing, T. Bein** Ultrasmall dispersible crystalline nickel oxide nanoparticles as high performance catalysts for electrochemical water splitting
- 28 **M.A. Nash, H.E. Gaub** Polymerization-based amplification for detection and imaging of biomass enzyme activity
- 29 **C. Ochsenfeld, T. Carell** Ribose-protonated DNA base-excision repair: a combined theoretical and experimental study
- 30 **H.E. Gaub, M.A. Nash, P. Tinnefeld** A small, versatile and mechanically probed lab on a chip
- 31 **J. Wintterlin** Low energy electron microscopy of the desorption of molecules from solid surfaces
- 32 **A. Wixforth, H. Krenner** Surface acoustic waves as a powerful tool for semiconductor nanophotonics

- 33 **T. Bein, D. Fattakhova-Rohlfing** Tailoring the morphology of mesoporous titania thin films through biotemplating with nanocrystalline cellulose
- 34 **T. Liedl, T. Lohmüller** Plasmonic DNA-origami nanoantennas for surface-enhanced raman spectroscopy
- 35 **C. Bräuchle, E. Wagner** Drug delivery with pDNA polyplexes
- 36 **T. Bein, A. Hartschuh, D. Trauner** Extraction of photogenerated electrons and holes from a covalent organic framework integrated heterojunction
- 37 **J.O. Rädler, B. Nickel** Cellular self-organization on micro-structured surfaces for high-throughput screening
- 38 **T. Bein** Solution deposition-conversion for planar heterojunction mixed halide perovskite solar cells
- 39 **D. Lamb, P. Tinnefeld** Dynamics of transcription factors
- 40 **A. Wixforth** Bioactivity and cellular uptake of distinct nanoparticles in human endothelial cells
- 41 **D. Braun** Understanding size-shielding transition and seebeck effect in thermophoresis
- 42 **C. Bräuchle, D. Lamb**: Highlight Article for the Chemistry Nobel Prize 2014 on super high resolution microscopy

## 1

## CHEMICAL WARFARE AND SURVIVAL STRATEGIES IN BACTERIAL RANGE EXPANSIONS

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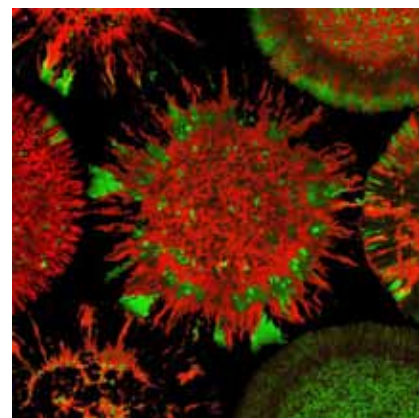
**Dr. Madeleine Opitz (LMU München, Faculty of Physics)**

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It is a long-standing question how biodiversity evolves and is maintained when species compete for new territory. Both limited control over experimental parameters and the overwhelming complexity of theoretical models have hindered progress in understanding of what determines the success of species during dispersal. In a joint experimental and theoretical work, the researchers investigated how the interplay between two archetypes of competition, resource competition and interference competition, governs biodiversity when three strains of *Escherichia coli* expand in

range. The strains interacted via toxins, with one strain producing the toxin colicin, and the others being either sensitive or resistant to it. By means of genetic engineering, the researchers gained control over the growth rates of the three strains. This control enabled them to study distinct ecological scenarios in which the interaction hierarchy between strains was either cyclic or hierarchical. Using independent experimental data on the growth of individual strains, the researchers were able to calibrate a computational model of the dispersal process. The model provided a quantitative and

comprehensive understanding of the interplay between resource and interference competition. It



Expanding colonies of colicin resistant, producing, and sensitive *Escherichia coli*.

was successfully applied to predict parameters for which a coexistence of all three strains could be observed in experiments.

■ **M.F. Weber, G. Poxleitner, E. Hebisch, E. Frey, M. Opitz:** *Chemical warfare and survival strategies in bacterial range expansions*; J. R. Soc. Interface, 10.1098/rsif.2014.0172 (2014)\*

## 2

### FUNCTIONALIZATION OF METAL-ORGANIC FRAMEWORKS

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Metal-organic frameworks (MOFs) are a new class of materials synthesized in a building-block fashion from metal-ion vertices, interconnected with organic linker molecules in a self-assembly process, to create highly tailorable crystalline materials with pores of nanometer dimensions. The success of MOFs in different field of applications (e.g., gas storage/separation, catalysis, sensing, drug delivery) depends on the availability of efficient methods for pore surface functionalization. One major focus of our group in

2014 was the development of novel functionalization concepts for MOFs and at the same time the evaluating of these concepts. The central idea is to find efficient methods for pore surface functionalization of MOFs.

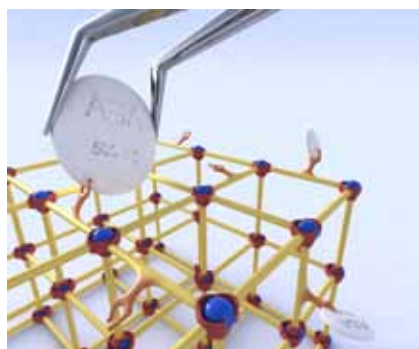
In this context the use of unsaturated metal sites in MOFs as a modification point for pore surface functionalization was studied. This strategy is based on Lewis acid-base interactions, where the coordinatively unsaturated metal sites (CUS) of the MOF are the Lewis acid sites, and the organic molecules (functionality), containing heteroatoms with lone electron pairs, serve as Lewis bases.<sup>[1]</sup> In the subsequent study a solvent-free and time efficient postsynthetic modification of MOFs had successfully been developed, until now the quickest functionalization method so far.<sup>[2]</sup> Last but not least, different peptide coupling reagents were used for the covalent attachment of drugs and biomolecules inside the pores of MOFs.<sup>[3]</sup> Peptide coupling reagents have the advantage to work under mild condi-

tions; under room temperature and in water. After finding the best peptide coupling reagent, its performance was evaluated for coupling molecules from life science and pharmacy, e.g. the analgesic acetylsalicylic acid (also known as the registered trade name Aspirin – see Figure).

■ [1] **S. Wuttke, C. Dietel, F. M. Hinterholzinger, H. Hintz, H. Langhals, T. Bein:** *Turn-on fluorescence triggered by selective internal dye replacement in MOFs*, Chem. Commun. 50, 3599 (2014)

[2] **H. Hintz and S. Wuttke:** *Solvent-Free and Time Efficient Postsynthetic Modification of Amino-Tagged Metal-Organic Frameworks with Carboxylic Acid Derivatives*; Chem. Mater. 26, 6722 (2014)

[3] **H. Hintz and S. Wuttke:** *Postsynthetic modification of an amino-tagged MOF using peptide coupling reagents: a comparative study*; Chem. Commun. 50, 11472 (2014)



Covalent attachment of acetylsalicylic acid on a metal-organic framework by using a peptide coupling reagent. Image: C. Hohmann/NIM

## ULTRAFAST INFRARED DYNAMICS ON A NANOMETER SCALE

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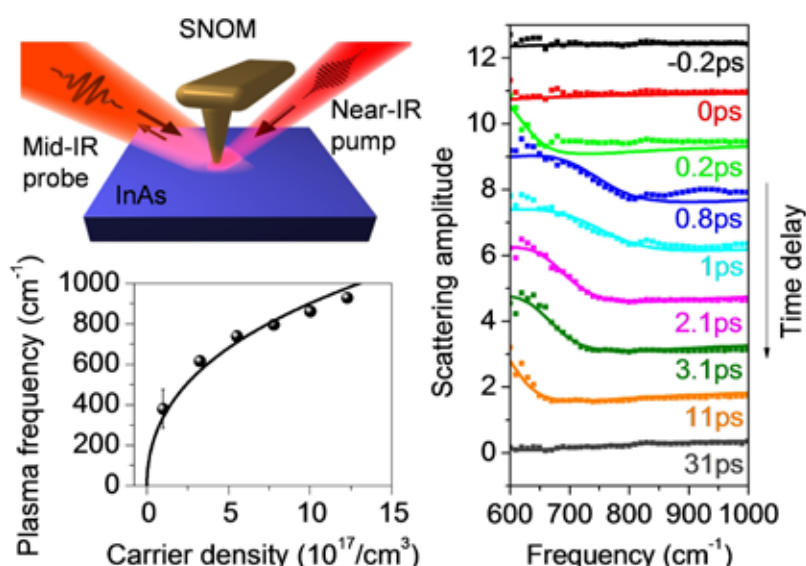
Conductivity can be measured by contactless microwave or infrared reflection, hence, the near-field microscope (SNOM, developed by CeNS-spin-off Neaspec GmbH) can map conductivity at nanoscale spatial resolution of typically 20 nm. This powerful tool was now extended to capture conductivity changes in ultrashort time. For this, local infrared spectra are collected at varying time delay after periodically photo-exciting a reversible sample state. In the example of Fig. 1 ultrashort (100 fs) near-infrared pulses generate mobile charge carriers in InAs whose spectral signature is interrogated by ultrashort (100 fs)

mid-infrared supercontinuum pulses. At delay up to 1 ps the spectra show a build-up of spectral intensity in the mid infrared, signalling a phase of inter-valley transfer. After this the spectra exhibit a well-defined plasma edge - allowing to extract also the carrier mobility - which recedes to lower frequency as the carrier density reduces by recombination.

A future SNOM operation with even lower-frequency (THz) continua would allow to follow this recombination, as well as the initial excitation, to much smaller carrier densities. Such a sensitivity will also be adequate to locally map the relatively low

conductivity of conducting polymers and organic conductors, and thus pinpoint, for example, inhomogeneities and barriers that impede transport. It might furthermore enable the still untouched application area of ultrafast infrared near-field probing of vibrational resonances, for example, of molecular machines such as a single photosynthetic reaction center! In a second study single-layer graphene was pumped by ultrashort near-infrared pulses. Owing to its Dirac band structure no carriers are generated but the existing carriers are accelerated to high energies. The initial nonequilibrium phase could not be resolved, but the regime of "hot electrons" could be followed as it cools on 200 fs and 2 ps time scales, respectively, due to optic-phonon and acoustic-phonon interaction. Mapping an inhomogeneous area of few-layer graphene allowed to demonstrate nanoscale resolution and to identify abrupt lateral changes in the dynamics.

■ M. Wagner, Z. Fei, A.S. McLeod, A.S. Rodin, W. Bao, E.G. Iwinski, Z. Zhao, M. Goldflam, M. Liu, G. Dominguez, M. Thiemens, M.M. Fogler, A.H. Castro Neto, C. N. Lau, S. Amarie, F. Keilmann, and D.N. Basov: *Ultrafast and nanoscale plasmonic phenomena in exfoliated graphene*



**Fig. 1:** Pump-probe mid-infrared spectroscopy at 200 fs temporal resolution is demonstrated at 20 nm spatial resolution, far below the diffraction limit, by operating a near-field microscope (SNOM) with 100-fs mid-infrared supercontinuum pulses. Local InAs spectra reveal rich carrier dynamics after passage of near-infrared pump pulses.

revealed by infrared pump-probe nanoscopy; *NanoLetters* 14, 894 (2014)

M. Wagner, A.S. McLeod, S.J. Maddox, Z. Fei, M. Liu, R.D. Averitt, M.M. Fogler, S.R. Bank, F. Keilmann, and D.N. Basov: *Ultrafast dynamics of*

*surface plasmons in InAs by time-resolved infrared nanospectroscopy*; *NanoLetters* 14, 4529 (2014)

## 4

### EROSION STABILITY OF BACILLUS SUBTILIS BIOFILMS

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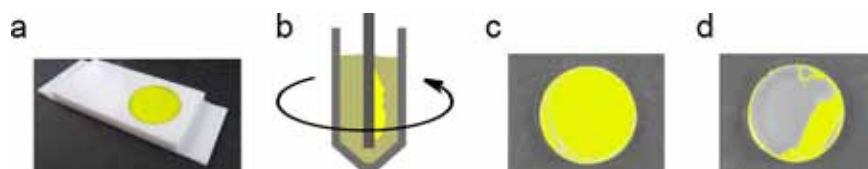
Dr. Madeleine Opitz (LMU München, Faculty of Physics)

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Bacteria can grow in adverse and challenging environments, e.g. in the presence of toxic substances such as disinfectants or metal ions. Yet, to do so, they need to rely on the protective abilities of self-produced biopolymers into which the bacteria embed themselves. Such a community of embedded bacteria is referred to as a bacterial biofilm. Many problems caused by bacterial biofilms can be traced back to their high resilience towards chemical perturbations and their extraordinary sturdiness towards mechanical forces. However, the molecular mechanisms that link the mechanical properties of a biofilm

with the ability of bacteria to survive in different chemical environments remain enigmatic. In this project, the erosion stability of *B. subtilis* is quantified. *B. subtilis* is a soil-dwelling gram-positive bacterium, but it has recently also been found in the human gut. *B. subtilis* strains are used for biotechnology applications and have emerged as model organisms for biofilm formation. The strain used in this study was isolated from an oil field and can form biofilms on solid surfaces. The erosion stability of *Bacillus subtilis* (*B. subtilis*) biofilms depends on the chemical environment. These biofilms can utilize the absorp-

tion of certain metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  into the biofilm matrix to avoid erosion by shear forces. This mechanical protection is often accompanied by an increase in the shear stiffness of the biofilm that is induced by the absorbed metal ions. Interestingly, many of these metal ions are toxic for planktonic *B. subtilis* bacteria. However, their toxic activity is suppressed when the ions are absorbed into the biofilm matrix. Our experiments clearly demonstrate that the biofilm matrix has to fulfill a dual function, i.e. regulating both the mechanical properties of the biofilm and providing a selective barrier towards toxic chemicals.



The erosion stability of *B. subtilis* biofilms (yellow layer in the shown pictures) towards shear forces in aqueous environments is increased by selected metal ions. Biofilms are grown on agar patches (a), exposed to shear forces (b) and the degree of erosion is quantified. Metal ions greatly reduce biofilm erosion (c) compared to an erosion experiment in pure water (d).

■ S. Grumbein, M. Opitz, O. Lieleg: *Selected metal ions protect Bacillus subtilis biofilms from erosion*; *Metallomics*, RSC, 6(8), 1441-1450 (2014)



## ENERGY LOSSES OF NANOMECHANICAL RESONATORS INDUCED BY ATOMIC FORCE MICROSCOPY-CONTROLLED MECHANICAL IMPEDANCE MISMATCHING

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Prof. em. J.P. Kotthaus (LMU München, Faculty of Physics) ■ [www.nano.physik.uni-muenchen.de](http://www.nano.physik.uni-muenchen.de)

Since the invention of the scanning tunneling microscope, a variety of scanning probe techniques have proven themselves as viable and highly susceptible sensors for a wide range of applications. One of these newly established methods, so-called mechanical impedance mismatch imaging, enables to gain insight into the mechanical damping of freely suspended nanomechanical resonators. In particular it allows to explore and manipulate the impact of clamping losses, a widely discussed damping mechanism in

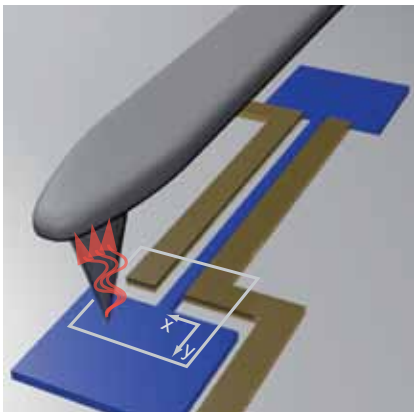
nanoelectromechanical systems which frequently limits the performance of devices.

To this end, the tip of an atomic force microscope acts as a local perturbation, pushing down on a specific point in the clamping region of a nanoelectromechanical resonator with a force of a few nanonewtons. This little disturbance has a vast impact on the resonator vibrations, increasing the dissipation of its flexural modes by at least one order of magnitude, depending on its exact position. This is a consequence of a transfer of vibrational energy into the cantilever, which is theoretically described by a reduced mechanical impedance mismatch between the resonator and its environment. A theoretical model for this mismatch, in conjunction with finite element simulations of the evanescent strain field of the mechanical modes in the clamping region, allows to quantitatively analyze

data on position and force dependence of the tip-induced damping.

For the case of a strongly stressed silicon nitride nanostring resonator it can be deduced that a sufficiently large impedance mismatch prevents the influence of clamping loss and thus enables the large observed quality factors of several 100,000 under vacuum and at room temperature. Even more, the observed tip-induced control of clamping loss offers the prospect of engineering the energy exchange in future nanomechanical resonator networks.

■ **J. Rieger, A. Isacsson, M.J. Seitner, J. P. Kotthaus, E.M. Weig:** *Energy losses of nanomechanical resonators induced by atomic force microscopy-controlled mechanical impedance mismatching*; Nature Communications 5, 3345 (2014)



Schematic of the nanomechanical system and the AFM tip as a controlled local perturbation of the resonator's acoustic environment (not to scale). The tip-induced flow of energy from the nanomechanical resonator (blue) into the cantilever (grey) is represented by corrugated red arrows.

## BOTTOM-UP FABRICATION OF COVALENT ORGANIC NANOSTRUCTURES BY ON-SURFACE POLYMERIZATION

PD Dr. Markus Lackinger, Prof. Wolfgang M. Heckl (TU München, Department of Physics and TUM School of Education, and Deutsches Museum) ■ [www.2d-materials.com](http://www.2d-materials.com)

Low-dimensional covalent organic nanostructures are promising novel materials for future nanotechnology applications in e.g. sensors, molecular electronics, and gas separation. The bottom-up fabrication by polymerization of appropriate monomers on solid surfaces features many advantages and has already yielded encouraging results. In particular, on-surface Ullmann coupling was proven suitable for interconnecting monomers into networks: brominated or iodinated precursor molecules are deposited onto catalytically active metal surfaces. The weakly bonded halogen substituents are split off, whereby reactive sites are created for C-C coupling. Even though Ullmann coupling works reliably and provides access to great structural and chemical versatility, the resulting covalent

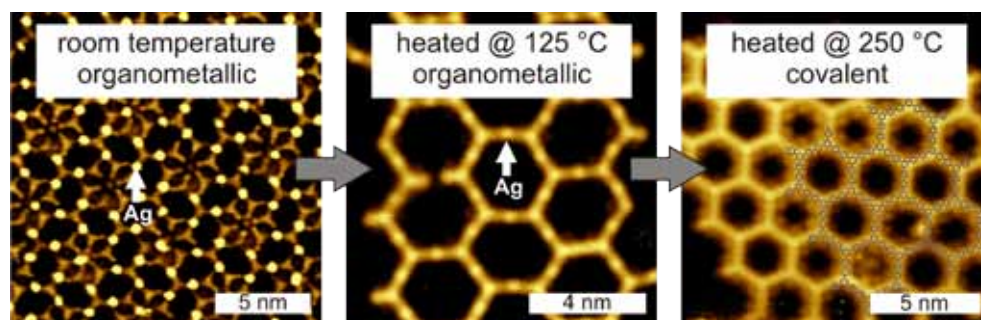
nanostructures still suffer from relatively high defect densities. One objective of this project is a profound understanding of Ullmann coupling. To this end the influence of reaction parameters as surface temperature and deposition rate as well as the role of the specific surface are studied. On Au(111) statistical analysis of STM data revealed that the amount of specific defects increases with temperature, suggesting thermal activation. Accordingly, the development of synthetic protocols for a polymerization at lower temperature is a viable strategy to improve the network quality.

Interestingly, changing the surface to Ag(111) completely changes the reaction pathway. Instead of directly forming new covalent bonds, organometallic reaction intermediates occur where the monomers are inter-

connected via C-Ag-C bonds. These metastable organometallic interlinks can be converted into covalent bonds by mild annealing. Below the conversion temperature, however, the organometallic bonds become reversible. Accordingly, as illustrated in the figure, equilibration of organometallic networks can be used to fabricate covalent networks with improved structural quality.

■ J. Eichhorn, D. Niekarz, O. Ochs, D. Samanta, M. Schmitt, P. Szabelski, M. Lackinger: *On-surface Ullmann coupling: The influence of kinetic reaction parameters on the morphology and quality of covalent networks*; ACS Nano 8, 7880-7889 (2014)

J. Eichhorn, T. Strunskus, A. Rastgoo-Lahrood, D. Samanta, M. Schmitt, M. Lackinger: *On-Surface Ullmann Polymerization via Intermediate Organometallic Networks on Ag(111)*; Chem. Commun. 50, 7680-7682 (2014)



STM images of Ullmann coupling on Ag(111) via organometallic intermediates. Left: disordered organometallic network obtained directly after room temperature deposition. Center: equilibrated hexagonal porous organometallic network obtained after mild annealing. Right: covalent network obtained by thermally activated conversion of an equilibrated organometallic network, whereby the ordered arrangement is preserved.

## CARBOHYDRATE-COATING REDUCES ADHESION OF BIOFILM FORMING BACILLUS SUBTILIS TO GOLD SURFACES

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Bacteria embed themselves with secreted biopolymers forming a community that is referred to as a biofilm. Growth of these bacterial biofilms in pipes, or on medical implants/catheters causes severe problems in healthcare and industry. The prevention of bacterial adhesion - the first step in colonization and biofilm formation - is therefore very important. The researchers present a new approach that allows the analysis of bacterial adhesion with high sensitivity in real-time, while testing several different surfaces in parallel.

Using the cantilever-array technique, they demonstrate that coating of gold surfaces with different carbohydrates can result in a significant reduction of bacterial adhesion of the biofilm forming bacterium *Bacillus subtilis* NCIB 3610 to gold surfaces. Investigation of the underlying molecular interactions suggests that adhesion to gold surfaces is mediated by thiol-groups present in proteins of the bacterial cell membrane or biofilm matrix proteins expressed by this strain. Furthermore, their data indicate that

adhesion of *B. subtilis* NCIB 3610 to carbohydrate-coated gold surfaces is facilitated by interactions between carbohydrates installed on the cantilever gold surface and an exopolysaccharide expressed by this strain.

■ S. Kesel, A. Mader, P.H. Seeberger, O. Lieleg and M. Opitz: *Carbohydrate-coating reduces adhesion of biofilm forming Bacillus subtilis to gold surfaces*; Appl. Environ. Microbiol. 80(19):5911. DOI:10.1128/AEM.01600-14 (2014)

## SENSING VIRUSES BY MECHANICAL TENSION OF DNA

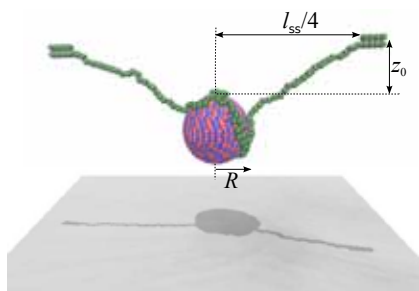
Prof. Ralf Metzler (University of Potsdam, Institute for Physics and Astronomy)

■ [www.agnld.uni-potsdam.de](http://www.agnld.uni-potsdam.de)

The rapid worldwide spread of severe viral infections, often involving novel mutations of viruses, poses major challenges to our health care systems. This means that tools that can efficiently and specifically diagnose viruses are much needed. To be relevant for a broad application in local health care centers, such

tools should be relatively cheap and easy to use. We demonstrate from analytical calculations and extensive simulations that the macroscopic detection of viruses based on the induction of a mechanical stress in a bundle of pre-stretched DNA molecules upon binding of viruses to the DNA is possible and offers a

good potential for diagnostic devices. We show that the affinity of the DNA to the charged virus surface induces a local melting of the double-helix into two single-stranded DNA. This process effects a mechanical stress along the DNA chains leading to an overall contraction of the DNA. Our results suggest



Schematic of single-stranded DNA-virus binding. The virus surface consists of attractive and neutral patches.

that when such DNA bundles are incorporated in a supporting matrix such as a responsive hydrogel, the presence of viruses may indeed lead to a significant, macroscopic mechanical deformation of the matrix. We discuss the biophysical basis for this effect and characterise the physical properties of the associated DNA melting transition. In particular, we reveal several

scaling relations between the relevant physical parameters of the system. We promote this DNA-based assay as a possible tool for efficient and specific virus screening.

■ **J. Shin, A.G. Cherstvy, and R. Metzler:** *Sensing viruses by mechanical tension of DNA in responsive hydrogels*; Phys. Rev. X 4, 021002 (2014)

## 9

### TRACER PARTICLE MOTION IN FLEXIBLE GEL NETWORKS

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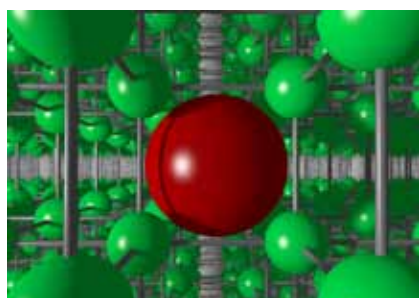
Mesh-like, structured environments are a defining property in various systems: biological cells are equipped with a characteristic mechanical network consisting of actin and other bio-filaments through which submicron particles diffuse or are actively transported. Inside eukaryotic nuclei, biomolecules diffuse through the complex chromatin network. Particles in a biofilm move through a flexible, porous

bacterial matrix, and in cellular tissues the intercellular space is filled with a mesh-like extracellular matrix. In novel clinical diagnosis tools pathogens diffuse in a hydrogel.

How do particles diffuse through a flexible, fluctuating mesh such as a hydrogel? When the particles are much smaller or larger than the typical mesh size, not surprisingly they diffuse normally or are fully immobilised. We here consider the physically interesting case when the size of the particle is comparable to the typical mesh size (Figure). From extensive Brownian dynamics simulations we elucidate the micro- and mesoscopic principles behind the complex tracer dynamics. The

time averaged mean squared displacement (TAMSD) and the van Hove cross-correlation function (TAHCF) demonstrate the occurrence of significant anomalous tracer diffusion and highly cooperative mesh fluctuations, allowing relatively large particles to move in the gel albeit at massively reduced diffusivity. We obtain this anomalous diffusion behaviour and the crossover to the terminal normal diffusion for different gel stiffness and three different tracer sizes.

■ **A. Godec, M. Bauer, and R. Metzler:** *Collective dynamics effect transient subdiffusion of inert tracers in gel networks*; New J. Phys. 16, 092002 (2014)



Schematic of the tracer particle (red) in a network of gel beads (green) connected by Morse springs (gray sticks).

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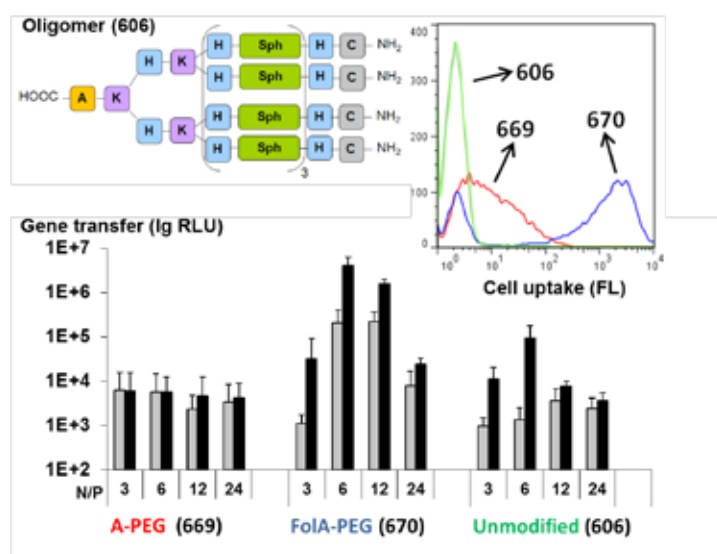
nucleic acid carriers was selected from a library of more than 800 sequence-defined cationic oligomers which had been generated by solid-phase synthesis. These carriers contain artificial oligoamino acids such as Stp or Sph for nucleic acid binding, protection and medi-

ing intracellular release from endosomes. To convert such promising carriers into receptor-targeted and surface shielded agents, native chemical ligation (NCL, Figure 1) was applied for site selective coupling of polyethylene glycol (PEG) containing terminal folic acid as targeting ligand (or terminal alanine as targeting negative control ligand). In most cases, the folic acid-PEG-ligated oligomers displayed a strongly improved cellular binding, uptake and gene transfer into receptor-positive KB cells as compared to the alanine-PEG controls (Figure 2). Fluorescence correlation spectroscopy (FCS) after 1 min up to 90 min incubation demonstrated stability of polyplexes in 90% serum. The screen revealed different requirements for DNA and siRNA polyplexes, identifying different topologies most beneficial for DNA or siRNA delivery.

■ C.Y. Zhang, P. Kos, K. Müller, W. Schrimpf, C. Troiber, U. Lächelt, C. Scholz, D.C. Lamb, E. Wagner: *Native Chemical Ligation for Conversion of Sequence-defined Oligomers into Targeted pDNA and siRNA Carriers*; J. Control. Release 180, 42 (2014)\*



**Figure 1:** Native chemical ligation (NCL) for conversion of cationic oligomers into receptor-targeted, PEG shielded nucleic acid carriers.



**Figure 2:** Example of a histidinylated four-arm oligomer 606 (unmodified, upper left), demonstrating superior cellular uptake (upper right) and luciferase DNA gene transfer (lower panel) with NCL-based incorporation of folate-PEG (670) over an alanine control A-PEG (669) or no modification (606).



## RECONSTITUTION OF PROTEIN GRADIENT OSCILLATIONS IN ARTIFICIAL MEMBRANE COMPARTMENTS

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Self-organization of proteins into large-scale structures is of pivotal importance for the organization of cells. The Min protein system of the bacterium *Escherichia coli* is a prime example of how pattern formation occurs via reaction-diffusion. We have previously demonstrated how Min protein patterns on flat supported membranes are influenced by membrane shape. Lately, we additionally probed the influence of membrane surface topology as a regulatory element. Using microstructured membrane-clad soft polymer substrates, Min protein patterns can be aligned. We demonstrate

that Min pattern alignment starts early during pattern formation and show that macroscopic millimeter-sized areas of protein patterns of well-defined orientation can be generated. Confining the Min self-organizing system in membrane containers with constant volume, the patterns are turned into regular oscillations and stable gradients, which help to position downstream processes, such as the assembly of the bacterial division machinery.

■ **K. Zieske, P. Schwille:** *Reconstitution of self-organizing protein gradients as spatial*

*cues in cell-free systems;* eLife10.7554/eLife.03949 (2014)

**G. Rivas, S.K. Vogel, P. Schwille:** *Reconstitution of cytoskeletal protein assemblies for large-scale membrane transformation;* Curr Opin Chem Biol 22, 18-26 (2014)

**K. Zieske, J. Schweizer, P. Schwille:** *Surface topology assisted alignment of Min protein waves;* FEBS Lett 588, 2545-2549 (2014)

## siRNA NANOSTRUCTURES FOR CELLULAR UPTAKE

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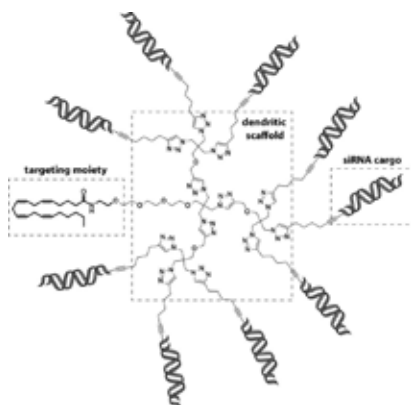
**Prof. Thomas Carell** (LMU Munich, Department of Chemistry)

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The development of dendritic siRNA nanostructures that are able to penetrate even difficult to transfect cells such as neurons with the help of a special receptor ligand, is shown here. The nanoparticles elicit strong siRNA

responses, despite the dendritic structure. A siRNA dendrimer directed against the crucial rabies virus (RABV) nucleoprotein (N protein) and phosphoprotein (P protein) allowed the suppression of the virus titer in

neurons below the detection limit. The cell-penetrating siRNA dendrimers, which were assembled using click chemistry, open up new avenues toward finding novel molecules able to cure this deadly disease.



■ K. Brunner, J. Harder, T. Halbach, J. Willibald, F. Spada, F. Gnerlich, K. Sparrer, A. Beil, L. Möckl, C. Bräuchle, K.-K. Conzelmann, T. Carell:

A dendritic siRNA nanostructure with an anandamide targeting unit to induce cellular uptake.

*Cell-Penetrating and Neurotargeting Dendritic siRNA Nanostructures*; Angew. Chem. Int. Ed. 53(51), 1946 (2015); *Dendritische Nanostrukturen zur rezeptorvermittelten Aufnahme von siRNA in neurale Zellen*; Angew. Chem. 126(51), 1968 (2015)

13

## INNER FILM MORPHOLOGY AND MOLECULAR ORIENTATION IN THIN FILMS FOR ORGANIC PHOTOVOLTAICS INVESTIGATED WITH IN-SITU AND EX-SITU ADVANCED SCATTERING

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Prof. Lukas Schmidt-Mende (University of Konstanz, Physics Department)

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Advanced scattering methods as grazing incident small and wide angle X-ray scattering (GISAXS/GIWAXS) and resonant soft X-ray scattering (RSoXS) with the opportunity to polarize the X-ray beam (P-RSoXS) provide a variety of possibilities to get a unique insight to the inner “life” of thin films. While GIWAXS is sensitive to molecular arrangements in crystalline parts of the material probed, with GISAXS and RSoXS the nanoscale structure of the inner film morphology is probed from nanometers to several hundred nanometers. The investigations are based on conjugated polymer systems for organic photovoltaic (OPV) application. We investigate in-situ printing and GIWAXS measurements of co-solvent modified PEDOT:PSS, a printable

polymer alternative to transparent conductive oxide electrodes (TCOs). Further the anisotropy of modified PEDOT:PSS film is investigated with P-RSoXS, GIWAXS and GISAXS. Last, a highly hexagonal-ordered and nanostructured interface for all-polymer solar cells is examined by RSoXS, giving an example for the strength of resonant scattering for proving the inner film structure of unique systems. In total these techniques pave the way for investigating all relevant length scales in thin films for OPV application.

■ Claudia M. Palumbiny, Christoph Heller, Christoph J. Schaffer, Volker Körstgens, Gonzalo Santoro, Stephan V. Roth, and Peter Müller-Buschbaum: *Molecular Reorientation*

*and Structural Changes in Cosolvent-Treated Highly Conductive PEDOT:PSS Electrodes for Flexible Indium Tin Oxide-Free Organic Electronics*, J. Phys. Chem. C 118(25), 13598 (2014)

Thomas Pfadler, Mihael Coric, Claudia M. Palumbiny, Andreas C. Jakowetz, Karl-Philipp Strunk, James A. Dorman, Philipp Ehrenreich, Cheng Wang, Alexander Hexemer, Rui-Qi Peng, Peter K.H. Ho, Peter Müller-Buschbaum, Jonas Weickert, and Lukas Schmidt-Mende: *Influence of Interfacial Area on Exciton Separation and Polaron Recombination in Nanostructured Bilayer All-Polymer Solar Cells*, ACS Nano 8(12), 12397 (2014)

## ULTRAFAST ELECTRONIC READ-OUT OF DIAMOND NV CENTERS COUPLED TO GRAPHENE

Prof. Alexander Holleitner (TU München, Walter Schottky Institut and Physics Department)

■ [www.nanoptronics.de](http://www.nanoptronics.de)



Artistic sketch of a spin in a nitrogen vacancy center coupled to an electronic read-out circuit. Image: C. Hohmann/NIM.

On the nanometer scale, non-radiative energy transfer processes can have an efficiency close to

unity. We describe how such a transfer can be used to electronically read-out color centers such as nitrogen vacancy centers in diamond. Such centers are considered to play a fundamental role in new quantum information technologies. The read-out is achieved by a graphene layer located only a few nanometers away from the diamond. Via the non-radiative energy transfer, additional charge carriers are generated in the graphene, which are detected as an ultra-fast current signal. The experi-

ment is performed on a picosecond timescale, where the transfer efficiency is highest.

■ **A. Brenneis, L. Gaudreau, M. Seifert, H. Karl, M.S. Brandt, H. Huebl, J.A. Garrido, F.H.L. Koppens, and A.W. Holleitner:** *Ultrafast electronic readout of diamond nitrogen-vacancy centres coupled to graphene;* Nature Nanotechnology, Doi:10.1038/nnano.2014.276 (2014)

## ORIENTED THIN FILMS OF A BENZODITHIOPHENE COVALENT ORGANIC FRAMEWORK

Prof. Thomas Bein (LMU München, Department of Chemistry)

Prof. Jochen Feldmann (LMU München, Physics Department)

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■ [www.phog.physik.lmu.de](http://www.phog.physik.lmu.de)

Alkylammonium metal trihalide perovskite solar cells have recently attracted enormous interest. They can achieve very high power conversion efficiencies, already approaching poly-crystalline Si. Previously, record-breaking flat heterojunction devices have only been shown to operate efficiently when a Cl-I mixed halide perovskite was vacuum-deposited. In

this project, we demonstrate a solution-based approach for a flat heterojunction, i.e. not requiring a titania scaffold, that matches the performance achieved with vacuum deposition (approaching 15% power conversion efficiency). The removal of the titania scaffold is an important advance which reduces series resistance losses. Our results greatly exceed the performance

of previously reported solution-processed, planar heterojunction perovskite solar cells. Specifically, we show that planar  $\text{PbI}_2$  films can be fully converted within 5 minutes to the methylammonium(MA)-based  $\text{MAPbI}_{3-x}\text{Cl}_x$  perovskite structure by immersion in a heated solution mixture of MAI and MAI. We find that the presence of chloride critically impacts the lifetime of

photoexcited species in the active material resulting in greatly enhanced charge collection efficiencies, enabling almost complete sunlight capture and electron-conversion in 400 nm thick films.

■ **Dana D. Medina, Veronika Werner, Florian Auras, Raphael Tautz, Mirjam Dogru, Jörg Schuster, Stephanie Linke, Markus Döblinger, Jochen**

**Feldmann, Paul Knochel, and Thomas Bein:** *Oriented Thin Films of a Benzodithiophene Covalent Organic Framework*; ACS Nano 8, 4042 (2014)

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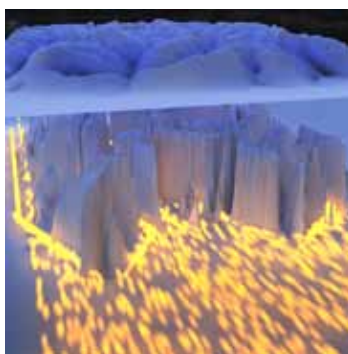
## SUB-MICRON PHASE COEXISTENCE IN SMALL-MOLECULE ORGANIC THIN FILMS REVEALED BY INFRARED NANO-IMAGING

PD Dr. Bert Nickel, Dr. Fritz Keilmann (LMU München, Faculty of Physics)

■ [www.softmatter.physik.uni-muenchen.de](http://www.softmatter.physik.uni-muenchen.de)

In semiconductor-based components, the mobility of the charge-carrying particles – electrons and their positively charged counterparts, known as holes – should be as high as possible. There have been conflicting reports concerning the effect of the granularity and crystallinity of the organic semiconducting thin film on the separation and transport of charge carriers inside. Bert Nickel and his colleagues took a closer look at the molecular structure of a thin film of pentacene, a prototype organic semiconductor. Fritz Keilmann and the scientists at Neaspec GmbH, a spin-off from the Center for NanoScience at LMU, developed a laser-based, high-resolution imaging method. With this technique, they illuminated the extremely fine tip of an atomic force microscope with a focused infra-red laser beam. The tip acts as a nano-antenna and converts the incident radiation into an intense near-field light source with a diameter of about 20 nanometers. This suffices to provide a high-prec-

sion analysis of the structure of the semiconducting film – which reveals the spatial arrangement of its component molecules. Surprisingly, the experiments showed that, while the flat grains of pentacene that make up the thin organic film often appear homogeneous over large regions, these areas are interrupted by inclusions in which the pentacene molecules are ordered in a different pattern or crystalline phase. In these areas, the pentacene molecules are more strongly tilted than those in neighboring regions. It is suspected that these inclusions inhibit charge-carrier transport in the organic layer, rather like rocks in a river perturb the flow of water.



Differences in crystal structure on extremely short scales are not only relevant to the operation of high-conductivity electronic components such as the transistor element investigated in this new study. They also play a crucial role in organic solar cells, which are made up of several such molecular layers. Up until now, it has been very difficult to access these structures experimentally. This new method can make a valuable contribution to our understanding of these layered systems and to organic electronics in general.

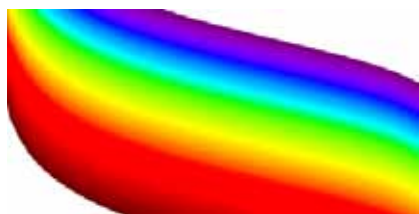
■ **C. Westermeier, A. Cernescu, S. Amarie, C. Liewald, F. Keilmann, B. Nickel:** *Sub-micron phase coexistence in small-molecule organic thin films revealed by infrared nano-imaging*; Nature Communications 5, doi: 10.1038/ncomms5101 (2014)\*

A 3-D depiction of the newly discovered inclusions. The yellow lines represent the scattering of charge carriers at inclusion boundaries. Image: C. Hohmann/NIM.

## OPTICAL THERMOMETRY OF A QUANTUM DOT IN THE MILLIKELVIN RANGE

Prof. Alexander Högele (LMU München, Faculty of Physics)

■ [www.nano.physik.uni-muenchen.de/nanophotonics](http://www.nano.physik.uni-muenchen.de/nanophotonics)



The temperature of electrons in a semiconductor sample placed inside a cryostat can differ from the temperature of the thermal bath, particularly at temperatures below 1 K. The Högele lab has developed an all-optical thermometry technique to measure the temperature of a two-dimensional electron system that is coupled to a nearby quantum dot with spin-selective

optical transitions. The electron spin-state population in a quantum dot is governed by thermalization with the electron reservoir and can be directly probed with resonant laser spectroscopy. In the presence of a finite magnetic field the relative population of the lowest Zeeman-split electron states depends on the temperature. By measuring the strength of the respective optical excitations it is possible to determine the temperature of the quantum dot electrons and therefore also that of the two-dimensional electron system that is coupled to the dot. The group

demonstrated the experimental implementation of the technique in the sub-Kelvin temperature range where it is most sensitive, and where the electron temperature is not necessarily given by the cryostat base temperature.

■ **F. Seilmeier, M. Hauck, E. Schubert, G. J. Schinner, S. E. Beavan, A. Högele:** *Optical thermometry of an electron reservoir coupled to a single quantum dot in the millikelvin range*; Phys. Rev. Applied 2, 024002 (2014)

## THERMOPHORESIS OF THERMORESPONSIVE POLYMER PHASE TRANSITION

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Dr. Michael A. Nash (LMU München, Faculty of Physics) ■ [www.biophysik.physik.lmu.de](http://www.biophysik.physik.lmu.de)

Environmentally responsive polymers are becoming increasingly important in the biomaterials field for use as diagnostic reagents, drug carriers, and tissue engineering scaffolds. Their characterization typically requires large milliliter volumes. In a collaboration between the

Braun Lab and the group of Michael Nash, a method based on thermophoresis could be established. Using the movement of molecules in a temperature gradient, they could measure for the first time directly the lower critical solution temperature with thermophoresis in micro-

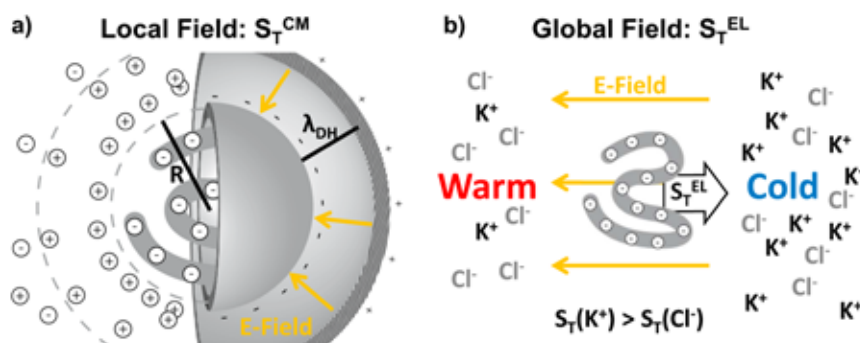
liter volumes. This determines the temperature at which a thermal responsive polymer undergoes a phase transition.

■ **M. Wolff, D. Braun and M.A. Nash:** *Detection of Thermoresponsive Polymer Phase Transition in Dilute Low-Volume Format*



The nanoenvironment around particles determine thermophoresis, i.e. the speed of molecules to move along a temperature gradient. Two effects could be quantified in experiment and fully

modelled: (a) The geometry of ionic shielding leads to different thermophoresis if the ionic shielding is smaller or larger than the molecule (b) The thermophoresis of ions build up an electrical field in the solution and therefore leads to a movement of the charged molecules.



## REPLICATION-GUIDED NUCLEOSOME PACKING AND NUCLEOSOME BREATHING EXPEDITE THE FORMATION OF DENSE ARRAYS

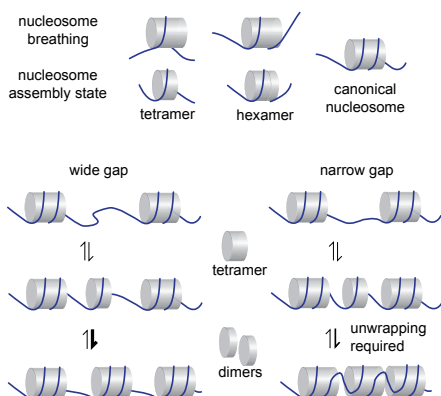
Prof. Ulrich Gerland (TU München, Physics Department) ■ [www.qbio.ph.tum.de](http://www.qbio.ph.tum.de)

It can be frustrating looking for a parking space at the road-side when there are many gaps between parked cars that are too narrow to fit in; one must simply wait until the owner of one of the parked cars decides to leave. It turns out that this common experience bears an analogy to the arrangement of nucleosomes along DNA -a very long substrate on which histone proteins bind (usually without specific

"spaces"), and must form densely packed arrays covering nearly 90% of the genome in yeasts. Before this is possible, random positioning of nucleosomes leads to a kind of 'jamming' similar to the inefficiency of parking-space usage by cars that are irregularly spaced. How these nucleosomes are arranged into regular spacing quickly remains poorly understood. The shifting action of remodeling enzymes has been proposed as a mechanism to resolve sub-optimal arrangements, while we propose another explanation based on biophysical mechanisms. First, we consider whether the progression of the replication fork during replication of the genome could eliminate nucleosome jamming, much like a slow-moving street cleaner revealing parking spaces that are rapidly

filled behind it. Second, we show that transient unwrapping of nucleosomes actually makes them much more like 'bumper cars' that can be "crammed" in-between one-another. This interaction dramatically speeds up the process by which long arrays of regularly spaced nucleosomes are formed. Since real cars do not exhibit this kind of elasticity, however, this mechanism will unfortunately provide no aid in the search for a parking space.

■ **B. Osberg, J. Nuebler, P. Korber, and U. Gerland:** *Replication-guided nucleosome packing and nucleosome breathing expedite the formation of dense arrays*; Nucleic Acids Research 42, doi: 10.1093/nar/gku1190 (2014)



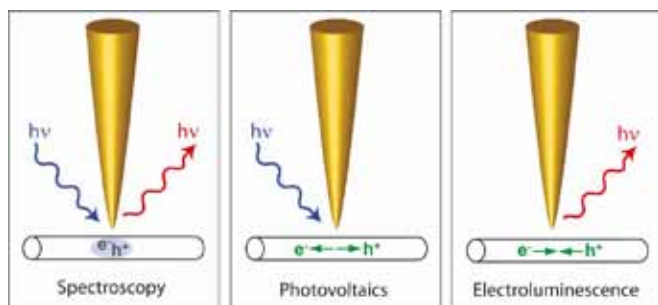
## ANTENNA-ENHANCED OPTOELECTRONIC PROBING OF CARBON NANOTUBES

Prof. Achim Hartschuh (LMU München, Chemistry Department)

■ [www.cup.uni-muenchen.de/pc/hartschuh](http://www.cup.uni-muenchen.de/pc/hartschuh)

Prof. Alexander Högele (LMU München, Faculty of Physics)

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**Figure 1:** Applications of antenna enhancement: a) Optical spectroscopy, b) Photovoltaics and c) Electroluminescence.

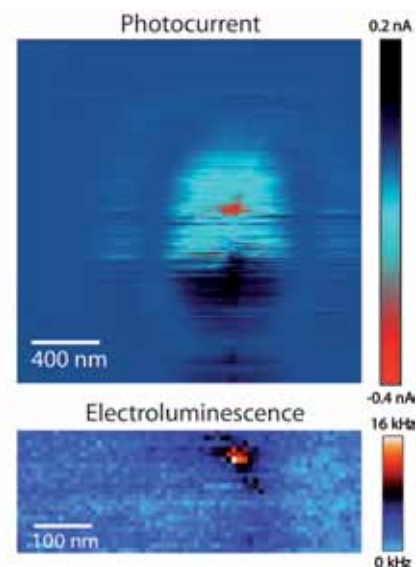
During the last two decades rapid progress in the research field of new nanomaterials and technologies to complement conventional silicon systems has been made. A variety of electronic and optoelectronic devices that involve different nanostructures have been realized, such as field-effect transistors, photovoltaic and light-emitting devices often based on carbon as active component. Due to the size-mismatch between the wavelength of visible light and the dimensions of these devices the full potential of the nanomaterial could not be exploited in optoelectronic applications so far. For the same reason the details of the electrical-to-optical and optical-to-electrical transduction mechanisms remain hidden in conventional optical microscopy. In the radio frequency range this size-mismatch is compensated by macroscopic antenna struc-

tures since more than a century. Optical antennas are metallic nanostructures capable of

converting free-propagating visible radiation into localized energy and vice versa. The Hartschuh and Högele group reported on the first antenna-enhanced optoelectronic microscopy studies on nanoscale devices. By coupling the emission and excitation to a scanning optical antenna, they were able to locally enhance the electroluminescence and photocurrent along a carbon nanotube device. They showed that the emission source of the electroluminescence can be point-like with a spatial extension below 20 nm. Topographic and antenna-enhanced photocurrent measurements further revealed that the emission takes place at the location of highest local electric field indicating that the mechanism behind the emission is the radiative decay of excitons created via impact excitation. While they demonstrated anten-

na-enhanced optoelectronic probing for carbon nanotubes they expect it to be applicable to a broad range of other materials such as inorganic nanowires and 2D materials as well.

■ **N. Mauser, N. Hartmann, M. S. Hofmann, J. Janik, A. Högele, A. Hartschuh:** *Antenna-enhanced optoelectronic probing of carbon nanotubes*, Nano Lett. 14, 3773-3778 (2014)\*



**Figure 2:** Antenna-enhanced photocurrent (top) and electroluminescence (bottom) measured for the same carbon nanotube device.

## CHARACTERIZATION OF QUBIT DEPHASING BY LANDAU-ZENER-STÜCKELBERG-MAJORANA INTERFEROMETRY

PD Dr. Stefan Ludwig and Stephan Manus (LMU München, Faculty of Physics)

■ [www.nano.physik.uni-muenchen.de/quantumtransport](http://www.nano.physik.uni-muenchen.de/quantumtransport)

Prof. Peter Hänggi (University of Augsburg, Institute for Physics)

■ [www.physik.uni-augsburg.de/theo1/hanggi](http://www.physik.uni-augsburg.de/theo1/hanggi)

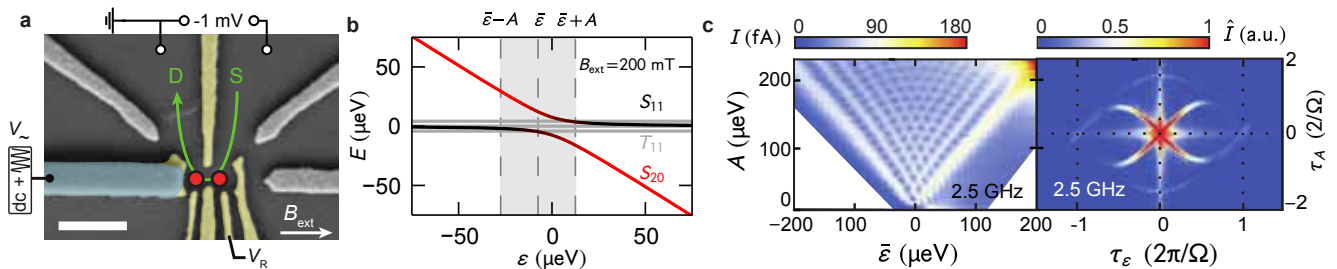
Quantum mechanical two-level systems (qubits) are at the very heart of quantum information processing or can be used as ultra-sensitive detectors. An interesting implementation of qubits are quantum dots embedded in a solid. The coherence time, during which a qubit preserves its known quantum state, is then limited by environmental fluctuations in the crystal matrix.

In the present work, we have defined a charge qubit in a double quantum dot based on single electron tunneling between the two dots. We have performed Landau-Zener-Stückelberg-Majorana interference experiments by periodically driving the eigenstates of this double-well potential across their avoided crossing. It gives

rise to a coherent superposition state of the electron tunneling dynamics resulting in an interference pattern of the occupation of the two dots by our electron. The broadening of this interference pattern, encoded in the current through the double quantum dot, contains crucial information about the fluctuating environment (sensor application) and the coherence time of the qubit (quantum information). We analyze the interference pattern in its 2D Fourier space where, intriguingly, the complex real space patterns are transformed to a beautiful shape dominated by two decaying sinus curves. We achieved an outstanding agreement between the theoretical model and measured data, allowing a deeper understanding of the electron-phonon interac-

tion in semiconductor based nanostructures, a major decoherence source for semiconductor based qubits.

With our method we have established a very general way, based on simple steady state experiments, to determine properties of qubits and their interacting environments. It is applicable to arbitrary qubit systems. In our specific implementation, namely a double quantum dot charge qubit, we found a coherence time 20 times longer than previously estimated. Together with their high clock speed in the GHz range it makes charge qubits a most potential candidate for quantum information applications.



(a) Scanning electron micrograph of the double quantum dot device (scale bar 500 nm). The yellow gold gates are used to electrostatically define the quantum dots (red dots) in a two-dimensional electron system beneath the surface. An external source-drain (S,D) voltage causes a tunneling current through the system. (b) Eigen-energies as function of detuning  $\varepsilon$  between the two dot-energies (for two electrons). The two states drawn in red and black are the qubit states and form an avoided crossing. We apply the modulation  $\varepsilon(t)=\bar{\varepsilon}A\sin(\omega t)$ . (c) Interference pattern measured at  $T=20 \text{ mK}$  in the tunneling current (left) and its 2D Fourier transform (right).

■ **F. Forster, G. Petersen, S. Manus, P. Hänggi, D. Schuh, Wegscheider, S. Kohler, and S. Ludwig:** *Characterization of Qubit Dephasing by Landau-Zen-*

*er-Stückelberg-Majorana Interferometry*; arXiv:1309.5907, Phys. Rev. Lett. 112, 116803 (2014)

## MEASUREMENT OF THERMOPHORESIS IN LIVING CELLS AND WATER-IN-OIL BUBBLES

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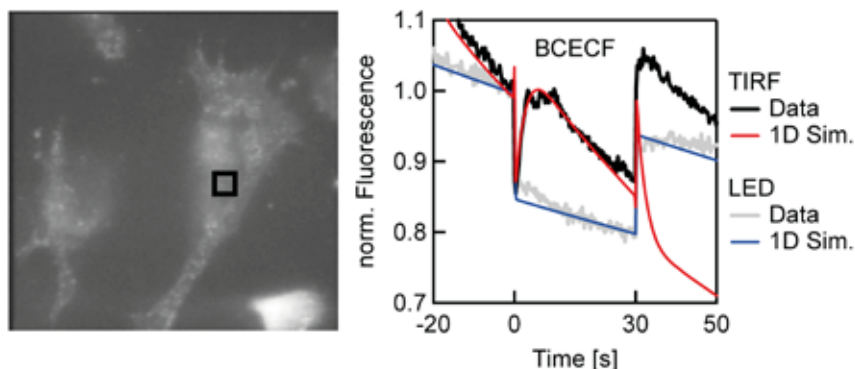
The complexity of biology requires that measurements of biomolecular interactions be performed inside living cells. The Braun lab managed to apply a temperature difference across a living cell and could image thermophoresis of molecules inside the cell. Interestingly, they found a 30-fold reduced diffusion coefficient inside the cell, indicating that molecular movement across the cell cytoplasm is slowed down due to molecular crowding.

Microscale thermophoresis, pioneered by the Braun lab and the CeNS Spinoff Nanotemper, continues to enable novel biomolecule binding affinity measurements. By using acoustic droplet robotics, measurements of bindings could be detected in very small 10 nanoliter water-in-oil droplets, cutting down measurement volumes by a factor of 50. While the approach shows a number of artefacts in practical use, the approach was patented with Nanotemper and

significantly modified approaches might become useful in the long term development of microscale thermophoresis.

■ **M.R. Reichl and D. Braun:** *Thermophoretic Manipulation of Molecules Inside Living Cells*; JACS 136, doi:10.1021/ja506169b (2014)

**M.R. Reichl, M. Herzog, A. Götz and D. Braun:** *Why charged molecules move across a temperature gradient: the role of electric fields*; Physical Review Letters doi:10.1103/PhysRevLett.112.198101 (2014)



Molecule thermophoresis in can be detected inside single living cells. The temperature difference is applied perpendicular to the surface and detected by TIRF microscopy near at the cell's attachment to the cover slip. We find that thermophoretic movement is detected for mobile molecules such as DNA or dye molecules inside the cell.

## DOUBLE-STRANDED RNA UNDER FORCE AND TORQUE

Prof. Jan Lipfert (LMU München, Faculty of Physics) ■ [www.biophysik.physik.uni-muenchen.de](http://www.biophysik.physik.uni-muenchen.de)

Double-stranded DNA (dsDNA) carries our genetic information and has become an icon of molecular biology and bioengineering. While the response of dsDNA to applied forces and torques (i.e. molecules under twist) has been mapped out with increasing precision in a series of landmark experiments, much less is known about the mechanical response of RNA, DNA's molecular cousin. Like DNA,



Artist's impression of a microscopic double-stranded RNA (rendered from a crystal structure) inserted in a macroscopic lathe (as found in the LMU physics machine shop). Image: C. Hohmann/NIM. Reprinted from Chemical Reviews 2015 Feb 11;115(3):1449-74.

RNA can form a right-handed double helix, but its roles in the cell are very different. Whereas DNA is the "storage medium" of the genetic code, RNA is involved in a number of roles in bringing this genetic code to life. We have used magnetic tweezers, where molecules are tethered between a glass surface and a magnetic bead, to probe the response of double-stranded RNA (dsRNA) to applied forces and torques. The key to these measurements was not only a new set of magnetic tweezers instruments that can directly measure torque, but also a novel way to create fully double-stranded RNA constructs suitable for attachment to the surface and the beads. For small forces and torques, dsRNA behaves like an elastic rod, with bending and twist stiffnesses similar to dsDNA. A surprising discovery was made when we investigated another elastic constant known as the twist-stretch coupling: RNA shortens when overwound, while

DNA lengthens, a fact not explained by current models of nucleic acid mechanics. When the forces and torques are increased, dsRNA undergoes structural transitions similar to dsDNA, including the formation of supercoils, melting upon underwinding and the formation of so-called P-RNA upon overwinding. Another big surprise came when we investigated the dynamics of supercoil formation: Under otherwise identical conditions, dsRNA buckles two orders-of-magnitude more slowly than dsDNA. The results provide a base line for the modeling of RNA in more complex biological contexts and pose interesting challenges to current models of nucleic acid mechanics.

■ **J. Lipfert, G.M. Skinner, J.M. Keegstra, T. Hensgens, T. Jager, D. Dulin, M. Köber, Z. Yu, S.P. Donkers, F.C. Chou, R. Das, N.H. Dekker:** *Double-stranded RNA under force and torque: similarities to and striking differences from double-stranded DNA;* PNAS, doi: 10.1073/pnas.1407197111 (2014)



## INSIGHTS INTO NANOSCALE ELECTROPHORESIS OF SINGLE DYE MOLECULES IN HIGHLY ORIENTED MESOPOROUS SILICA CHANNELS

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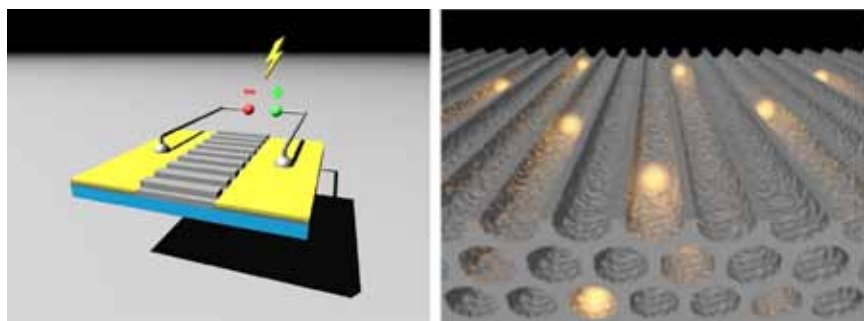
Electrophoresis is an important tool in biochemistry and biology and is commonly used for the separation and analysis of biomolecules. The separation results from the different mobilities of charged molecules depending on their size, charge and conformation as well as their interactions with the host material. However, little is known about the detailed behavior of the guest species inside the host material on a single molecule basis. Typically, electrophoresis is performed at the macroscopic level. With a view on integrating biomolecular separations into micro- and nanofluidic systems and their applications in a massively parallel way, it would, however, be highly desirable to

achieve electrophoretic separation of single molecules at the nanoscale.

In this study, the CeNS groups of Thomas Bein and Christoph Bräuchle show the feasibility of directly observing the controlled movement and separation of differently charged single molecules in highly oriented silica nanochannels under the influence of an electric field. The velocity of the charged molecules increases with increasing electric field strength and can therefore be directly controlled via an external stimulus. Using single molecule fluorescence microscopy, even the movement in single pores inside the mesoporous host can be resolved in space and time and visualized. Based on the single molecule tra-

jectories, the authors propose a model for the internal structure of the host and for the diffusion and interaction of charged and uncharged species in the nanoscale channels. Moreover, unlike in conventional gel electrophoresis, the template-filled nanoscale channels of mesoporous silica provide a mechanically stable, tunable and highly ordered nano-environment for the guest molecules.

■ **M. Davies, B. Rühle, C. Li, K. Müllen, T. Bein, C. Bräuchle:** *Insights into Nanoscale Electrophoresis of Single Dye Molecules in Highly Oriented Mesoporous Silica Channels*; The Journal of Physical Chemistry C 118(41), 24013 (2014)



Schematic representation of the device designed for single-molecule electrophoresis studies, and close-up of the oriented silica nano-channels acting as host.

## METHODS FOR PRECISE QUANTIFICATION OF NANOPARTICLE UPTAKE INTO CELLS

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Prof. Matthias Schneider (Boston University, Department of Mechanical Engineering)

■ [www.bu.edu/me/people/faculty/pz/schneider](http://www.bu.edu/me/people/faculty/pz/schneider)

Prof. Achim Wixforth (University of Augsburg, Institute of Physics)

■ [www.physik.uni-augsburg.de/exp1](http://www.physik.uni-augsburg.de/exp1)

Particle\_in\_Cell-3D is a powerful method to quantify the cellular uptake of nanoparticles. It combines the advantages of confocal fluorescence microscopy with fast and precise semi-automatic image analysis. In this work it is shown how this method was applied to investigate the impact of 310 nm silica nanoparticles on human vascular endothelial cells (HUVEC) in comparison to a cancer cell line derived from the cervix carcinoma (HeLa). The absolute number of intracellular silica nanoparticles within the first 24 h was determined and shown to be cell type-dependent. As a second case study, Particle\_in\_Cell-3D was used to assess the uptake kinetics of 8 nm and 30 nm ceria nanoparticles interacting with human microvascular endothelial cells (HMEC-1). These small nanoparticles formed agglomerates in biological medium, and the particles

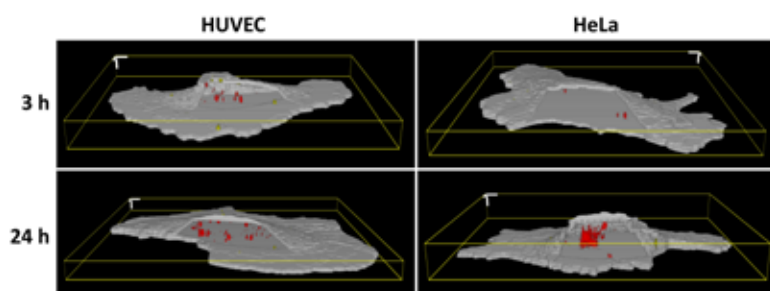
that were in effective contact with cells had a mean diameter of 417 nm and 316 nm, respectively. A significant particle size-dependent effect was observed after 48 h of interaction, and the number of intracellular particles was more than four times larger for the 316 nm agglomerates. Interestingly, the results show that for both particle sizes there is a maximum dose of intracellular nanoparticles at about 24 h. One of the causes for such an interesting and unusual uptake behavior could be cell division.

■ **F.G. Strobl, D. Breyer, P. Link, A.A. Torrano, C. Bräuchle, M.F. Schneider, A. Wixforth:** A surface acoustic wave-driven micropump for particle uptake investigation under physiological flow conditions in very small volumes; *Beilstein Journal of Nanotechnology* 6, 414 (2015)

**F.G. Strobl, F. Seitz, C. Westerhausen, A. Reller, A.A. Torrano, C. Bräuchle, A. Wixforth, M.F. Schneider:** Intake of silica nanoparticles by giant lipid vesicles: influence of particle size and thermodynamic membrane state; *Beilstein Journal of Nanotechnology* 5, 2468 (2014)

**A.A. Torrano, C. Bräuchle:** Precise quantification of silica and ceria nanoparticle uptake revealed by 3D fluorescence microscopy; *Beilstein Journal of Nanotechnology* 5, 1616 (2014)

**C. Strobel, A.A. Torrano, R. Herrmann, M. Malissek, C. Bräuchle, A. Reller, L. Treuel, I. Hilger:** Effects of the physico-chemical properties of titanium dioxide nanoparticles, commonly used as sun protection agents, on microvascular endothelial cells; *J. Nanopart. Res.* 16:2130, 1 (2014)



Representative three-dimensional reconstructions of 310 nm silica nanoparticles taken up by HUVEC or HeLa cells after 3 and 24 h. The membrane region outlining the cells appears in gray. A window was purposefully open in the 3D perspectives so as to allow the visualization of intracellular particles (in red).

## CRYSTALLINE CARBON NITRIDE NANOSHEETS FOR IMPROVED VISIBLE-LIGHT HYDROGEN EVOLUTION

Prof. Bettina V. Lotsch (LMU München, Department of Chemistry and MPI for Solid State Research, Stuttgart)

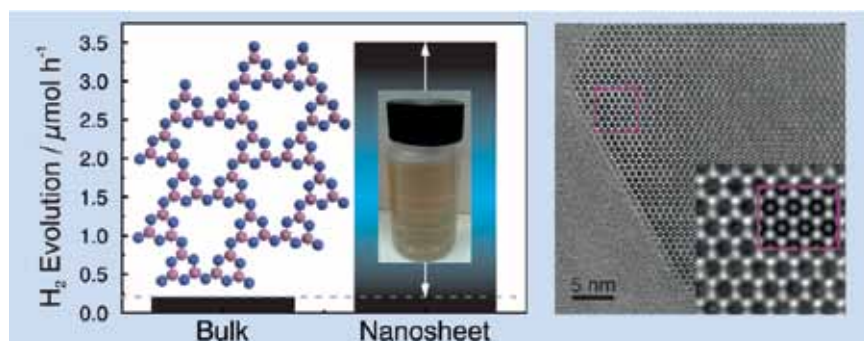
■ [www.cup.uni-muenchen.de/dept/ch/ac/lotsch](http://www.cup.uni-muenchen.de/dept/ch/ac/lotsch)

The economically viable conversion of solar energy into chemical fuels such as hydrogen requires the design of highly efficient semiconductor photocatalysts. A recent breakthrough in the development of abundant, metal-free photocatalysts has been achieved with amorphous carbon nitrides ( $\text{CN}_x$ ) referred to as "graphitic carbon nitride" or "Melon". Different optimization strategies have been employed to enhance the photocatalytic activities of amorphous Melon-type photocatalysts, including band gap engineering through doping, hybridization to form bulk heterojunctions, and by morphology control to increase the surface area and exposed active sites. We have recently

reported a new photocatalytically active member of the carbon nitride family – poly(triazine imide), PTI – which in contrast to heptazine-based Melon-type photocatalysts is built up by triazine building blocks and represents the first true 2D carbon nitride system. Unlike amorphous Melon, PTI is highly crystalline and therefore lends itself as an excellent model system to study its intrinsic catalytic properties and to explore the structure – activity relationship as a function of the exfoliation state.

PTI nanosheets were obtained by a one-step liquid exfoliation process in water, resulting in distinct negatively charged, 1-2 nm thick crystalline nano-

platelets of 60 nm lateral size, as verified by AFM and TEM. Through XRD and spectroscopic methods, a close structural relationship between the parent PTI and the nanosheets was confirmed. Solid-state NMR spectroscopy of  $^{15}\text{N}$  isotopically enriched nanosheets was used as a tool to indirectly probe the exfoliation process and elucidate the chemical changes occurring upon exfoliation, as well as to determine the thickness of the nanosheets after restacking. Photocatalytic tests using visible light demonstrate that PTI nanosheets show significantly enhanced photocatalytic activity for  $\text{H}_2$  evolution as compared to bulk PTI, which highlights the crucial role of morphology and surface area on the photocatalytic performance of carbon nitride materials.



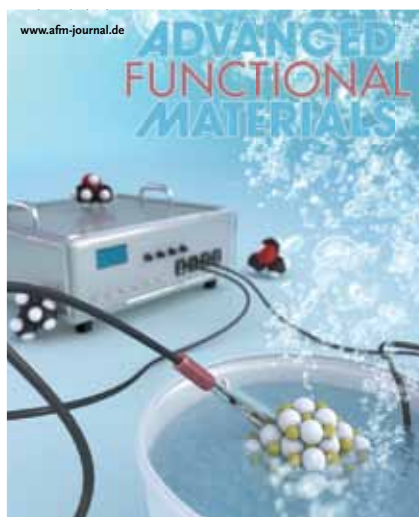
Left: Photocatalytic activity for  $\text{H}_2$  evolution after 3 hour illumination with  $> 420$  nm light of the Pt-doped PTI nanosheet suspension (inset) compared to the same concentration of dispersed bulk PTI using 10 vol% triethanolamine as sacrificial agent. Right: TEM image of an exfoliated ultrathin PTI nanosheet edge at higher magnification, viewed along [001], and corresponding simulation (JEMS;  $\Delta f = +50$  nm,  $t = 2.79$  nm; inset).

■ Katharina Schwinghammer, Maria B. Mesch, Viola Duppel, Christian Ziegler, Jürgen Senker, Bettina V. Lotsch: *Crystalline Carbon Nitride Nanosheets for Improved Visible-Light Hydrogen Evolution*; J. Am. Chem. Soc. 136, 1730-1733 (2014).

## ULTRASMALL DISPERSIBLE CRYSTALLINE NICKEL OXIDE NANOPARTICLES AS HIGH PERFORMANCE CATALYSTS FOR ELECTROCHEMICAL WATER SPLITTING

Prof. Dina Fattakhova-Rohlfing and Prof. Thomas Bein (LMU München, Department of Chemistry)

■ [www.cup.lmu.de/pc/fattakhova/](http://www.cup.lmu.de/pc/fattakhova/) ■ [bein.cup.uni-muenchen.de](http://bein.cup.uni-muenchen.de)



The CeNS scientists Dina Fattakhova-Rohlfing, Thomas Bein and their groups were the first to prepare ultrasmall, crystalline, and dispersible NiO nanoparticles with tunable size. These particles are promising candidates as catalysts for electrochemical water oxidation. Image: C. Hohmann/NIM, selected as a front cover of *Advanced Functional Materials*.

The development of sustainable and high performance energy conversion and storage technologies represents one of the most urgent goals of contemporary research. Hydrogen generation via electrochemical splitting of water holds the promise of providing a viable fuel from renewable energy sources. However, in order to reach competitive efficiencies, both

half reactions of water oxidation and reduction have to proceed at high rates. A significant challenge lies in finding stable and inexpensive catalysts for the water oxidation reaction, which was the major motivation of the cooperation project between the groups of Prof. Dina Fattakhova-Rohlfing and Prof. Thomas Bein.

Nickel oxide compounds are known as a promising class of catalytic materials suitable for electrochemical oxygen generation. In our project, a novel strategy was introduced to drastically enhance the catalytic activity of NiO via a synthetic bottom up approach where the resulting catalyst particles are only a few nanometers in size. Using a *tert*-butanol reaction route developed in our groups, very small nickel oxide nanocrystals were obtained with sizes tunable from 2.5 to 5 nm and a narrow particle size distribution. The crystals are perfectly dispersible even after drying, giving stable transparent colloidal dispersions. The structure of the nanocrystals corresponds to phase-pure stoichiometric nickel(II) oxide with a partially oxidized surface exhibiting Ni(III) states. The presence of these surface states could explain the efficient catalytic

behavior of the material in electrochemical water splitting experiments. Electrodes made by coating thin films of these nanoparticles show very high turnover frequencies for the oxygen evolution reaction in alkaline media. In quantitative terms, the nanoparticles of 3.3 nm in size demonstrate very high turn-over frequencies of 0.3 1/s at an overpotential of 300 mV for electrochemical water oxidation, thus even outperforming expensive rare earth iridium oxide catalysts.

The results of this project demonstrate the great potential of nanostructuring and nanoscaling for the development of efficient inexpensive electrocatalytic materials. Extremely high catalytic activity, high stability, abundance and low cost of the monocrystalline NiO nanoparticles developed in our groups make them environmentally and economically attractive options for water oxidation catalysis.

■ **K. Fominykh, J. M. Feckl, J. Sicklinger, M. Döblinger, S. Böcklein, T. Bein, D. Fattakhova-Rohlfing:** *Ultrasmall dispersible crystalline nickel oxide nanoparticles as high performance catalysts for electrochemical water splitting*; *Adv. Funct. Mater.* 24, 3123 (2014)



## POLYMERIZATION-BASED AMPLIFICATION FOR DETECTION AND IMAGING OF BIOMASS ENZYME ACTIVITY

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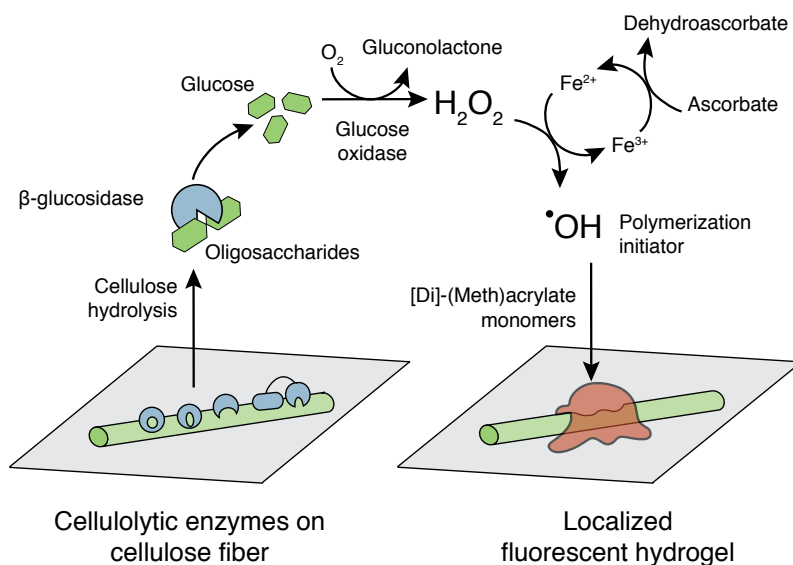
Understanding the process of biomass degradation by cellulolytic enzymes is of urgent importance for biofuel and chemical production. The goal of this project was to develop a novel and sensitive assay for studying the effectiveness of multi-component enzyme mixtures on lignocellulose. A hydrogel reagent signaling (HyReS) system was developed, which converts oligosaccharides produced during biomass hydrolysis into a fluorescent hydrogel. This system for assaying cellulolytic enzyme activity serves as a versatile platform on both soluble and insoluble substrates. When combined with total

internal reflection fluorescence microscopy, it provides a spatially resolved method for chemical imaging of biomass degradation in real time. The assay technology was patented in 2014 and featured on the cover of the Wiley journal ChemSusChem in October.

■ **K. Malinowska, T. Verdorfer, A. Meinhold, L.F. Milles, V. Funk, H.E. Gaub, and M.A. Nash:** *Redox-Initiated Hydrogel System for Detection and Real-Time Imaging of Cellulolytic Enzyme Activity*; ChemSusChem 7(10): 2825-2831 (2014)



ChemSusChem cover, October 2014, image: C. Hohmann/NIM.



A polymerization-based amplification system converts sugars produced during cellulose degradation into a fluorescent hydrogel. This signal-amplification cascade quantifies sugar production and localizes to sites of cellulose hydrolysis.

## RIBOSE-PROTONATED DNA BASE-EXCISION REPAIR: A COMBINED THEORETICAL AND EXPERIMENTAL STUDY

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■ [www.cup.uni-muenchen.de/pc/ochsenfeld](http://www.cup.uni-muenchen.de/pc/ochsenfeld)

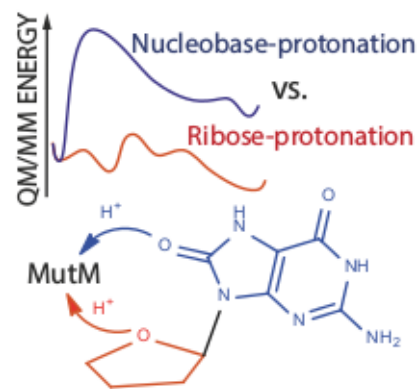
Prof. Thomas Carell (LMU München, Chemistry Department)

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Recent advances in linear-scaling quantum chemical techniques developed in the Ochsenfeld group, have made the electronic treatment of large biochemical systems computationally feasible. As part of the immense efforts to understand fundamental biological processes, accurate electronic structure calculations, specially hybrid quantum chemical/molecular mechanical (QM/MM) methods, provide valuable insights which are experimentally difficult to achieve, if not inaccessible. In their recent work, Sadeghian et al.<sup>[1]</sup> have investigated the base excision repair mechanism of the bacter-

ial enzyme, MutM, in catalyzing the removal of the oxidized guanine (8OG) from the DNA. In a joint collaboration between the Carell and the Ochsenfeld group, the base-protonated pathway propagated in the literature - a mechanism for which no direct evidence was provided earlier - was questioned for its validity. QM/MM calculations show that such a mechanism is not only unfavorable, but also contradicts new experimental data of the Carell-lab. Employing linear-scaling QM/MM calculations, a ribose-protonated reaction mechanism was proposed instead (Fig. 1), where the

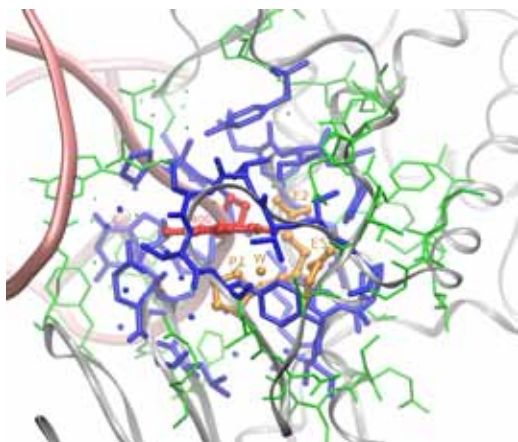
initial protonation of the lesion's ribose paves the path for an almost barrier-free cleavage of the glycosidic bond. Using QM-regions with more than 1000 atoms (Fig. 2), Sadeghian et al. estimate that a canonical guanine base is destabilized in the catalytic pocket of the enzyme by 20 kcal/mol compared with the 8OG lesion, hence



**Fig. 1:** Ribose-protonated 8OG-excision is preferred over the base-protonated mechanism.

explaining the lack of catalytic activity of MutM for undamaged bases. Overall, the combined theoretical and experimental investigation suggests that MutM relies heavily on early nucleobase selectivity during substrate interrogation and targets the ribose at the later catalytic stage.

■ **K. Sadeghian, D. Flaig, I.D. Blank, S. Schneider, R. Strasser, D. Stathis, M. Winnacker, T. Carell, and C. Ochsenfeld:** *Ribose-Protonated DNA Base Excision Repair: A Combined Theoretical and Experimental Study*; *Angew. Chemie Int. Ed.*, 53, 10044 (2014)



**Fig. 2:** The QM-region of the DNA-enzyme complex (1115 atoms) includes the 8OG lesion and the catalytic residues of MutM.

## A SMALL, VERSATILE AND MECHANICALLY PROBED LAB ON A CHIP

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Prof. Philip Tinnefeld (TU Braunschweig, Institute of Physical and Theoretical Chemistry)

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In synthetic biology, "understanding by building" requires exquisite control of the molecular constituents and their spatial organization. In collaboration with the strong research groups of Michael Nash, Diana Pippig and Martin Benoit and the projects initiated by Philip Tinnefeld the following experiments were successfully performed along this line.

Two new protein-tags were evaluated by Single-Molecule Force Spectroscopy (SMFS): The more than 100 amino acids large Dockerin-tag selectively binds to Cohesin with high affinity and thus allows molecules of interest to be repeatedly probed by an Cohesin-modified AFM cantilever.

The ybbR-tag with negligible size (11 amino acids) covalently

attaches to Coenzyme A at high coupling efficiency and specificity<sup>[1]</sup>. Both tags provide a rather non-invasive, yet versatile, general and robust way of adding a freely programmable and highly selective attachment site to virtually any protein or surface of interest. These tags not only improve the often complicated preparation for SMF and SMC&P<sup>[2]</sup> experiments but also their success. In particular the covalent ybbR-tag surface attachment now allows for measurements of single-molecule protein mechanical properties via the Dockerin tag on each molecule to perform thousands of pulling cycles using a single Cohesin-modified cantilever.

Combining this with a microfluidic platform (Figure) for on-chip expression generates a compact

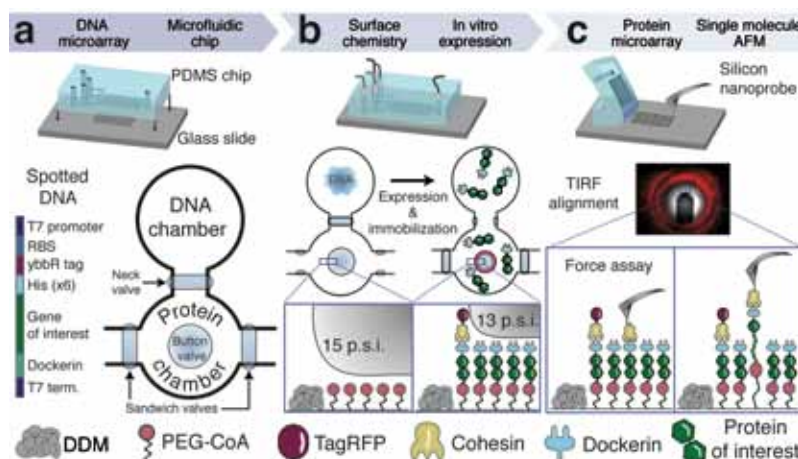
lab on a chip for SMFS measurements<sup>[3]</sup>. In contrast to (SMFS), the Molecular Force Assay (MFA), even parallelizes force measurements so that it can test even multiple proteins in a single experiment<sup>[4]</sup>.

All these abilities to synthesize and mechanically probe protein libraries enable high-throughput mechanical phenotyping.

■ [1] **D.A. Pippig, F. Baumann, M. Strackharn, D. Aschenbrenner, and H.E. Gaub:** *Protein-DNA Chimeras for Nano Assembly*; ACS Nano, Article ASAP, DOI: 10.1021/nn501644w (2014)

[2] **S.F. Heucke, F. Baumann, G.P. Acuna, P. Severin, S.W. Stahl, M. Strackharn, I. Stein, P. Altpeter, P. Tinnefeld, and H.E. Gaub:** *Placing individual molecules in the center of nanoapertures*; Nano Letters 14, DOI: 10.1021/nl401517a (2014)

[3] **M. Otten, W. Ott, M.A. Jobst, L. Milles, T. Verdorfer, D. Pippig, M.A. Nash, and H.E. Gaub:** *From Genes to Protein Mechanics on a Chip*; Nature Methods 11(11): 1127-1130 (2014)\*



Lab on a chip design, preparation, and function.

[4] K. Limmer, D.A. Pippig, D. Aschenbrenner, H.E. Gaub: *A Force-Based, Parallel Assay for the Quantification of Protein-DNA Interactions*;

PLOS ONE, DOI: 10.1371/journal.pone.0089626 (2014)

31

## LOW ENERGY ELECTRON MICROSCOPY OF THE DESORPTION OF MOLECULES FROM SOLID SURFACES

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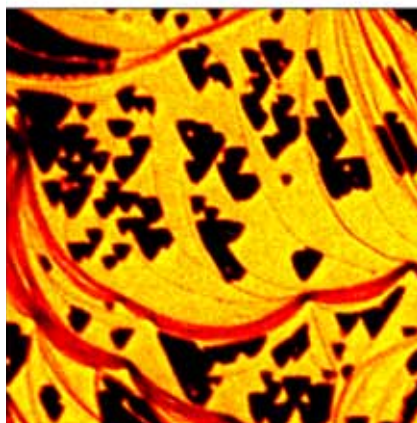
In heterogeneous catalysis chemical reactions take place on the surfaces of solids, e.g., for a typical industrial catalyst, on the surfaces of metal particles on an oxide support. A catalytic reaction consists of many, often complicated and unknown chemical steps, but in any case the last step is the desorption of the product molecules from the surface. This step regenerates the empty sites required for the further reaction. The desorption step is usually considered a purely statistical process, the rate of which only depends on temperature and on the number of product molecules present. On

the other hand, there is strong, albeit indirect evidence that this is not valid, and that, in contrast, the distribution of product molecules on the catalyst surface plays a role.

In this project it has been achieved to microscopically image a surface during desorption of molecules. The method used was LEEM (low energy electron microscopy), a technique similar to transmission electron microscopy, but in which the high-energy electrons of the electron microscope are slowed down in front of the sample surface. In this way the method becomes surface sensitive, i.e., only the top few atomic layers of the sample are imaged. The system investigated was a silver single crystal covered by oxygen atoms. When the temper-

ature of the silver sample was steadily increased, the oxygen atoms recombined to give O<sub>2</sub> molecules which desorbed from the surface, a process that was recorded by mass spectrometry. At the same time LEEM images were recorded. The LEEM images showed that the O atoms were not statistically distributed during desorption but formed small islands. By quantitatively analyzing the LEEM and mass spectrometry data it could be shown that the O<sub>2</sub> molecules exclusively desorb from the perimeters of the islands. That such effects exist had been assumed for a long time, but here they could be visualized for the first time. Such effects could be important ingredients to better model catalytic reactions.

■ S. Günther, T.O. Montes, M. A. Nino, A. Locatelli, S. Böcklein, J. Wintterlin: *Desorption kinetics from a surface derived from direct imaging of the adsorbate layer*; *Nature Communications*. 5, 3853 (2014)



LEEM image of an Ag(111) surface during desorption of oxygen. Field of view 4.8 µm. The oxygen atoms form small triangular islands that appear black. O<sub>2</sub> molecules exclusively desorb from the perimeters of these islands.



## SURFACE ACOUSTIC WAVES AS A POWERFUL TOOL FOR SEMICONDUCTOR NANOPHOTONICS

Prof. Achim Wixforth and Prof. Hubert Krenner (University of Augsburg, Institute of Physics)

■ [www.physik.uni-augsburg.de/exp1](http://www.physik.uni-augsburg.de/exp1)

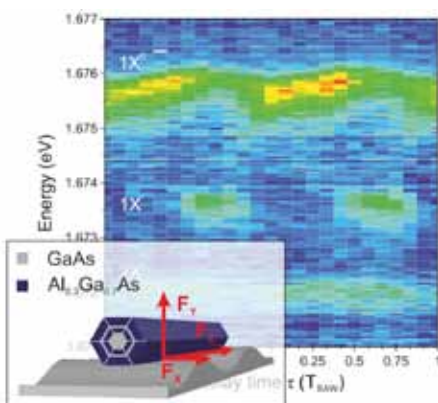
We study the influence of the dynamic electric and strain fields induced by a radio frequency surface acoustic wave (SAW) on the optical emission of single semiconductor nanowires. The investigated NWs consist of a GaAs core and an AlGaAs shell containing a 5 nm thick GaAs quantum well (QW). In addition to the emission of core and QW, we observe additional sharp emission lines at higher energies. The microscopic origin of these quantum dot-like emission centers (ECs) is currently controversially discussed as arising from precisely ordered faceted islands or randomly distributed alloy fluctuations and defects. We employ a stroboscopic photoluminescence spectroscopy (s-PL) technique to resolve the

full SAW-driven dynamics of the EC emission. In Figure 1 we present a s-PL scan of a single EC controlled by a  $T_{\text{SAW}}=5.15$  ns ( $f_{\text{SAW}}=194$  MHz) SAW. This data is recorded over two full acoustic cycles and clearly demonstrates two major effects: (i) Firstly, the EC's emission energy is tuned spectrally on a nanosecond timescale. This dynamic spectral tuning arises from a combined impact of the dynamic mechanical strain component of the SAW and its gyrating piezoelectric field via the deformation potential coupling and the Stark effect, respectively. (ii) Secondly, the observed emission lines, arising from radiative recombination of different excitonic occupancy states of the EC, exhibit distinct anti-correlated intensity oscillations during the acoustic cycle. The underlying mechanism is a previously unobserved dynamically triggered carrier extraction out of an optically active quantum emitter into a continuum of states (QW, core, surface) in the radial heterostructure. Using WKB-theory we identify quantum tunneling as the underlying mechanism and quantitatively reproduce the observed switch-

ing contrast. Based on this modeling we can further conclude that these ECs are randomly distributed and separated by at least 10 nm from any empty continuum of states. This in turn points towards a defect-related nature of the ECs for our NWs rather than ordered, near surface heterostructure QDs. Our findings not only provide a deeper understanding of the microscopic origin of these ECs, they also provide the previously missing element for full on-NW quantum state transfer protocols.

■ **M. Weiß, J.B. Kinzel, F.J.R. Schüle, M. Heigl, D. Rudolph, S. Morkötter, M. Döblinger, M. Bichler, G. Abstreiter, J.J. Finley, G. Koblmüller, A. Wixforth, H.J. Krenner:** *Dynamic acoustic control of individual optically active quantum dot-like emission centers in heterostructure nanowires*; Nano Letters 14, 2256-2264 (2014)

**M. Weiß, F.J.R. Schüle, J.B. Kinzel, M. Heigl, D. Rudolph, M. Bichler, G. Abstreiter, J.J. Finley, A. Wixforth, G. Koblmüller, H.J. Krenner:** *Radio frequency occupancy state control of a single nanowire quantum dot*; Journal of Physics D: Applied Physics 47, 394011 (2014)



Stroboscopic photoluminescence scan of single emission center recorded over two acoustic cycles demonstrating (i) dynamic spectral tuning of individual emission lines and (ii) programming of the EC's occupancy state by tuning the delay time  $\tau$ . Inset: Schematic of heterostructure NW modulated by a surface acoustic wave.

## TAILORING THE MORPHOLOGY OF MESOPOROUS TITANIA THIN FILMS THROUGH BIOTEMPLATING WITH NANOCRYSTALLINE CELLULOSE

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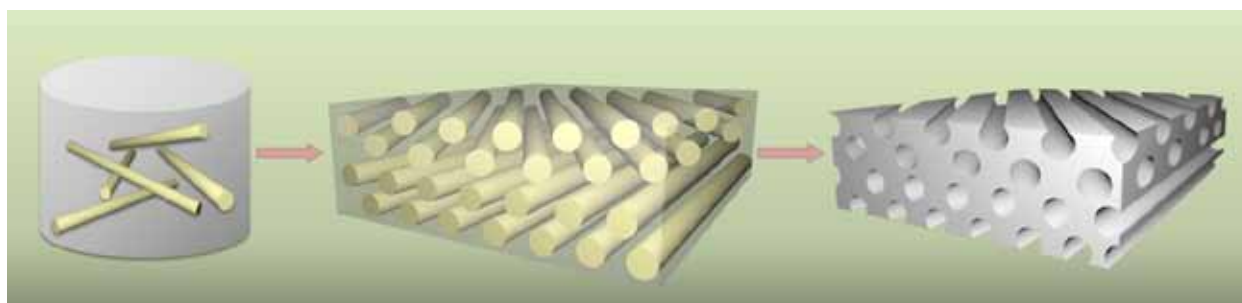
The group reports on nanocrystalline cellulose (NCC) as a novel shape-persistent biotemplating agent enabling the straightforward synthesis and tailoring of mesoporous titania thin films. Their strategy involves addition of purified cellulose nanocrystals to titania precursor solutions followed by direct film deposition on substrates and template combustion. The resulting titania networks are highly porous anatase morphologies having well-defined, narrow pore size distributions. The authors demonstrate the ease and effectiveness of this biotemplating method regarding both film processability and performance of NCC-derived porous scaffolds. The main advantages of the NCC template compared to the traditionally used 'soft templates' such as surfactant micelles include shape persistence, high temperature stability and tunable

nano-dimensions. It was shown that the combination of these features permits straightforward tailoring of the titania morphology by adjusting the composition of the precursor mixture and by applying post-deposition treatments. Comprehensive characterization reveals significant changes of NCC-templated titania surface area, pore size, pore anisotropy and dimensions of titania crystallites at different titania-to-template ratios in a precursor solution, and as a result of processing conditions. The thin films fabricated with the NCC biotemplating approach show very high activity in the photocatalytic NO conversion and in the degradation of 4-chlorophenol, outperforming Pluronic-templated mesoporous titania films. Furthermore, successful application of NCC replicated

titania networks as anodes in dye-sensitized solar cells was demonstrated.

The group anticipates that templating with nanoscale cellulose crystals has the potential to supersede conventional templating approaches towards porous titania thin films. Moreover, this synthetic approach can be easily generalized for the fabrication of crystalline mesoporous thin films of other oxides, thus offering promising prospects for the sustainable generation of porous oxides used in diverse applications.

■ **A. Ivanova, D. Fattakhova-Rohlfing, B.E. Kayaalp, J. Rathousky, T. Bein:** *Tailoring the Morphology of Mesoporous Titania Thin Films through Biotemplating with Nanocrystalline Cellulose*, J. Am. Chem. Soc., 136, 5930 (2014)



Synthesis approach for the NCC-templated mesoporous  $\text{TiO}_2$ .

## PLASMONIC DNA-ORIGAMI NANOANTENNAS FOR SURFACE-ENHANCED RAMAN SPECTROSCOPY

Prof. Tim Liedl (LMU München, Physics Department)

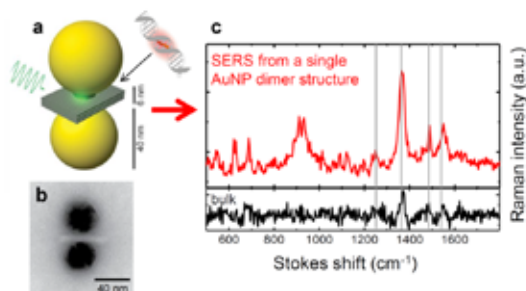
■ [www.softmatter.physik.uni-muenchen.de/liedl\\_group](http://www.softmatter.physik.uni-muenchen.de/liedl_group)

Dr. Theobald Lohmüller (LMU München, Physics Department) ■ [www.phog.physik.lmu.de](http://www.phog.physik.lmu.de)

We used DNA origami to arrange a plasmonic antenna system consisting of two gold nanoparticles, each 40 nm in diameter, mounted opposing each other with a distance of 6 nm. With this arrangement it was possible to perform Surface Enhanced Raman Spectroscopy (SERS) with molecules placed in the

small gap between the particles. Through plasmon-mediated enhancement of the electromagnetic field between the particles, the intensity of the SERS signal was strongly increased. Signatures of a number of fluorescent molecules and of DNA bases could be detected with high sensitivity.

■ P. Kühler, E.-M. Roller, R. Schreiber, T. Liedl, T. Lohmüller und J. Feldmann: *Plasmonic DNA-Origami Nanoantennas for Surface-Enhanced Raman Spectroscopy*; *Nano Letters* 14, S. 2914-2919 (2014)\*



a) Scheme of the DNA origami nanoantenna with two 40 nm gold particles mounted. Molecules in the gap between the particles experience a strongly enhanced electromagnetic field if excited resonantly. b) Transmission electron microscopy image of an assembled nanoantenna. c) Raman spectroscopy signal of a DNA-intercalating dye detected from a single DNA origami nanoantenna (red). In comparison the signal measured in a concentrated solution of the same dye (black).

## DRUG DELIVERY WITH pDNA POLYPLEXES

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Prof. Ernst Wagner (LMU München, Pharmacy Department)

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The cationizable nature of "proton-sponge" transfection agents facilitates pDNA delivery in several steps. Protonated amines account for electrostatic DNA binding and cellular uptake, buffering amines mediate polyplex escape from acidifying

intracellular vesicles. As demonstrated with a sequence-defined library of oligo(ethan amino) amides containing selected oligoethan amino acids and histidines, the total protonation capacity as well as the cationization pH profile within the endoly-

sosomal range have critical impact on gene transfer. Building blocks with even numbered amine groups (Gtt, Sph) exhibited higher total endolysosomal buffer capacity than odd number (Stp) analogs. Within the endolysosomal range, Gtt has the

highest buffer capacity around pH 5, whereas Stp has its maximum around pH 7. Histidines increased the total buffer capacity, resulted in a more continuous cationization pH profile and greatly improved transgene expression *in vitro* and *in vivo*.

Using receptor targeted and polyethylene glycol shielded polyplexes, better endosomal escape and N100-fold enhanced transfection was detected.

■ **U. Lächelt, P. Kos, F.M. Mickler, A. Herrmann, E.E. Salcher, W. Rödl, N. Badgujar, C. Bräuchle, E. Wagner:** *Fine-tuning of proton sponges by precise diaminoethanes and histidines in pDNA polyplexes;* Nanomedicine 10, 35 (2014)

36

## EXTRACTION OF PHOTOGENERATED ELECTRONS AND HOLES FROM A COVALENT ORGANIC FRAMEWORK INTEGRATED HETEROJUNCTION

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**Prof. Dirk Trauner (LMU München, Department of Chemistry)**

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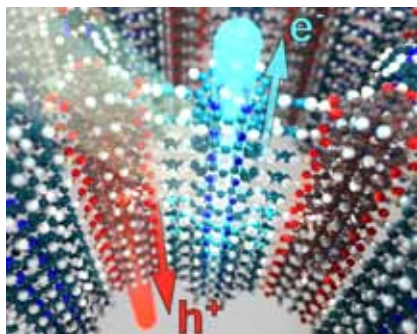
Covalent organic frameworks (COFs) offer a strategy to position molecular semiconductors within a rigid network in a highly controlled and predictable manner. The  $\pi$ -stacked columns of layered two-dimensional COFs enable electronic interactions between the COF sheets, thereby providing a path for exciton and charge carrier migration. Frame-

works comprising two electronically separated subunits can form highly defined interdigitated donor–acceptor heterojunctions, which can drive the photogeneration of free charge carriers.

The CeNS groups of Thomas Bein, Achim Hartschuh and Dirk Trauner reported the first example of a photovoltaic device that utilizes exclusively a crystalline organic framework with an inherent Type II heterojunction as the active layer. The newly developed triphenylene–porphyrin COF was grown as an oriented thin film with the donor and acceptor units forming one-dimensional stacks that extend along the substrate normal, thus providing an optimal geometry for charge carrier transport. As a result of the degree of morphological

precision that can be achieved with COFs and the enormous diversity of functional molecular building blocks that can be used to construct the frameworks, these materials show great potential as model systems for organic heterojunctions and might ultimately provide an alternative to the current disordered bulk heterojunctions.

■ **M. Calik, F. Auras, L.M. Salonen, K. Bader, I. Grill, M. Handloser, D.D. Medina, M. Dogru, F. Löbermann, D. Trauner, A. Hartschuh, T. Bein:** *Extraction of Photogenerated Electrons and Holes from a Covalent Organic Framework Integrated Heterojunction;* J. Am. Chem. Soc. 136, 17802-17807 (2014)



Light-induced generation of mobile electrons and holes inside a covalent organic framework that can travel along aligned molecular columns.



## CELLULAR SELF-ORGANIZATION ON MICRO-STRUCTURED SURFACES FOR HIGH-THROUGHPUT SCREENING

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■ [www.softmatter.physik.uni-muenchen.de](http://www.softmatter.physik.uni-muenchen.de)

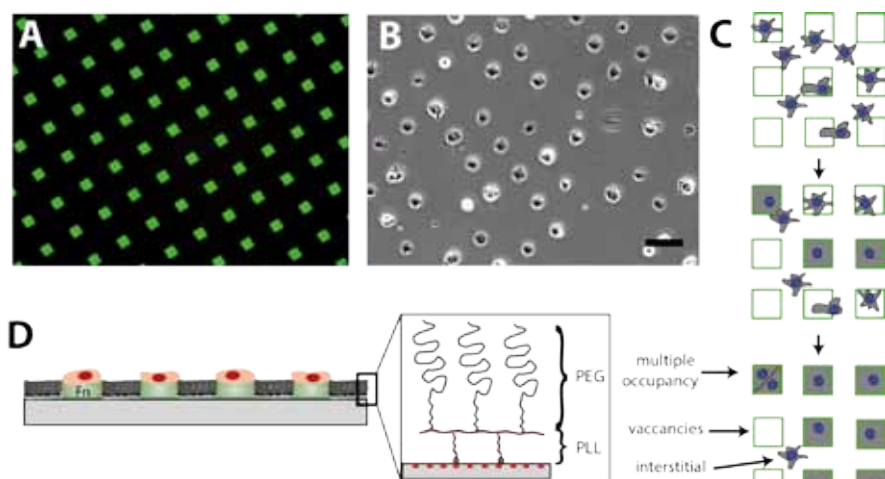
Micro-patterned surfaces are frequently used in high-throughput single cell studies, as they allow to image isolated cells in defined geometries. Commonly, cells are seeded in excess onto the entire chip and non-adherent cells are removed from the un-patterned parts via rinsing. In this project, a novel method to position cells via self-organization was developed. Substrates with regular arrays of protein coated islands in a PLL-g-PEG passivated background are generated. After seeding, cells randomly migrate on the passivated area and preferentially occupy adhesion sites. Using a

simple random-walk search model the time-to-order for a specific cell type with known motility can be optimized by rescaling the distances between the adhesion sites.<sup>[1]</sup> Using neutron reflectivity, the intercalation of protein in PEG layers can be addressed which leads to the partially migration on PEG surfaces. Protein repellence on PEG copolymers is mainly influenced by the underlying polymer-layer and secondly by the PEG density. The amount of adsorbed FN on PEGylated surfaces correlates with cell morphology and motion.<sup>[2]</sup> High throughput cell arrays have

potential for fundamental biophysical studies as well as biopharmaceutical screening applications. In ongoing work, single cell assays are used to study the expression kinetics of gene therapeutics and the timing of apoptosis inducing drugs. The approach allows for the assessment of the individual single cell kinetics for thousand of cells in parallel and hence yields a statistical view of cellular systems response. In particular, in the case of mRNA based delivery the distribution of GFP expression onset times and mRNA life times was measured.<sup>[3]</sup> The single cell analysis can be extended to multiple markers in different colors probing the correlation of events in cell signaling cascades.

■ [1] P.J.F. Röttgermann, A.P. Alberola, J.O. Rädler: *Cellular Self-organization on Micro-structured Surfaces*; Soft Matter, doi:10.1039/c3sm52419a (2014)

[2] P.J.F. Röttgermann, S. Hertrich, I. Berths, M. Albert, F.J. Segerer, J.-F. Moulin, B. Nickel, and J.O. Rädler: *Cell Motility on Polyethylene Glycol Block Copolymers Correlates to Fibronectin Surface Adsorption*; Macromolecular Bioscience, doi:10.1002/mabi.201400246 (2014)



(A) Homogeneous patterned array of fibronectin (Fn) and labelled Alexa Fluor 488 fibrinogen. (B) After seeding, cells arrange themselves onto the protein-coated islands, obviating the need for any washing steps. Scale bar: 100  $\mu\text{m}$ . (C) During the self-organization process, optimal filling is compromised by defects such as multiple occupancies, vacancies and interstitial cells. Occupancy is quantified via order parameters. (D) Cartoon of the micro-structured surface: The PLL-PEG allows only for absorption of small protein amounts.<sup>[1]</sup>

[3] C. Leonhardt, G. Schwake, T. Stögbauer, S. Rappl, J.-T. Kuhr, T.S. Ligon, J.O. Rädler: *Single-*

*cell mRNA Transfection Studies: Delivery, Kinetics and Statistics by Numbers*; Nanomedicine:

Nanotechnology, Biology and Medicine. doi:10.1016/j.nano.2013.11.008 (2014)

## SOLUTION DEPOSITION-CONVERSION FOR PLANAR HETEROJUNCTION MIXED HALIDE PEROVSKITE SOLAR CELLS

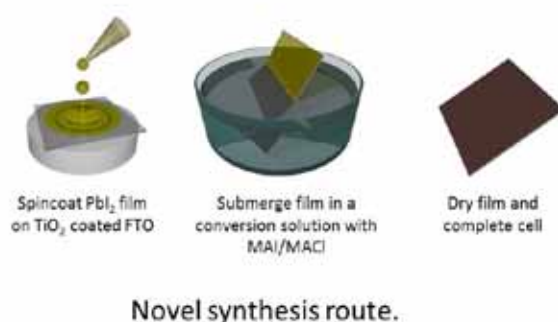
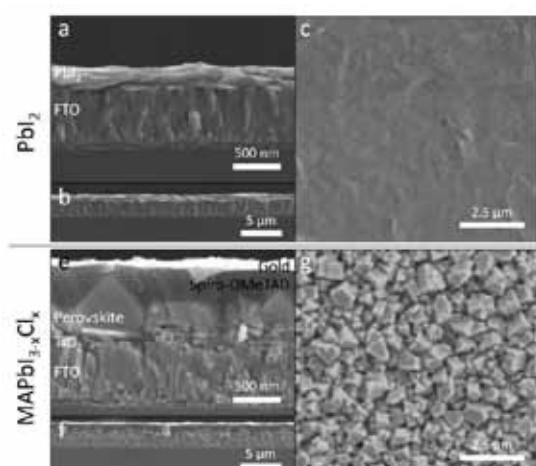
Prof. Thomas Bein (LMU München, Department of Chemistry) ■ [bein.cup.uni-muenchen.de](http://bein.cup.uni-muenchen.de)

Alkylammonium metal trihalide perovskite solar cells have recently attracted enormous interest. They can achieve very high power conversion efficiencies, already approaching poly-crystalline Si. Previously, record-breaking flat heterojunction devices have only been shown to operate efficiently when a Cl-I mixed halide perovskite was vacuum-deposited. In this project, we demonstrate a solution-based approach for a flat heterojunction, i.e. not requiring a titania scaffold, that matches the performance achieved with vacuum deposition (approaching

15% power conversion efficiency). The removal of the titania scaffold is an important advance which reduces series resistance losses. Our results greatly exceed the performance of previously reported solution-processed, planar heterojunction perovskite solar cells. Specifically, we show that planar  $\text{PbI}_2$  films can be fully converted within 5 minutes to the methylammonium(MA)-based  $\text{MAPbI}_{3-x}\text{Cl}_x$  perovskite structure by immersion in a heated solution mixture of MAI and MACl. We find that the presence of chloride critically impacts the lifetime of

photoexcited species in the active material resulting in greatly enhanced charge collection efficiencies, enabling almost complete sunlight capture and electron-conversion in 400 nm thick films.

■ P. Docampo, F.C. Hanusch, S. D. Stranks, M. Doblinger, J.M. Feckl, M. Ehrensperger, N.K. Minar, M.B. Johnston, H.J. Snaith, T. Bein: *Solution Deposition-Conversion for Planar Heterojunction Mixed Halide Perovskite Solar Cells*, Adv. Energy Mater. DOI 10.1002/aenm.201400355 (2014)



Electron micrographs of film synthesis steps and scheme for the synthesis of highly efficient  $\text{MAPbI}_{3-x}\text{Cl}_x$  perovskite films.

## DYNAMICS OF TRANSCRIPTION FACTORS

Prof. Don Lamb (LMU München, Department of Chemistry)

■ [www.cup.uni-muenchen.de/pc/lamb](http://www.cup.uni-muenchen.de/pc/lamb)

Prof. Philip Tinnefeld (TU Braunschweig, Institute of Physical and Theoretical Chemistry)

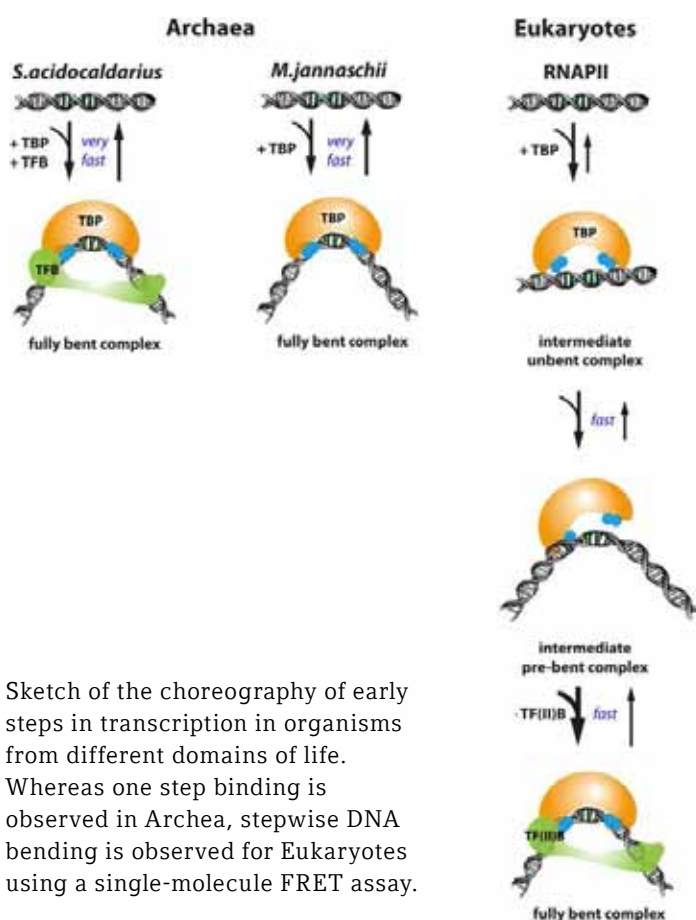
■ [www.tu-braunschweig.de/pci/research/tinnefeld](http://www.tu-braunschweig.de/pci/research/tinnefeld)

One of the first steps in protein biosynthesis is the binding of the transcription factor TATA-binding protein (TBP) to the promoter region of the gene that is to be transcribed. TBP recruits other factors such as the transcription factor B (TFB) and finally recruitment of the RNA polymerase. TBP and TFB/TF(II)B are highly conserved in both structure and function between the eukaryotic and archaeal domains of life although they

have to operate under vastly different conditions. To investigate the similarities and differences between the first steps in archaeal and eukaryotic transcription, single-molecule FRET was used. The authors could show that although the different TBPs are structurally homologous, the mechanism of their interactions is very different (see Figure). The eukaryotic TBP binds to the promoter DNA in a linear stepwise manner with

distinct intermediate steps and the fully bent conformation is stabilized by TF(II)B. In contrast, the interaction of the archaeal TBPs with DNA was even more dynamic. Two possible pathways for forming stable TBP-DNA complexes were observed. In one case, a stable fully-bent TBP-DNA conformation was obtained in the absence of TFB whereas, in a second species, a stable fully-bent TBP-DNA conformation was only possible with the assistance of TFB. This second pathway is observed for species with multiple basal transcription factors suggesting that specific TBP/TFB pairs are used to regulate different families of genes. Due to these novel insights, this paper was selected for F1000 prime. This work was a collaborative effort between four laboratories (Werner, Tinnefeld, Grohmann and Lamb) and was headed by Dina Grohmann, a junior group leader in the group of Philip Tinnefeld.

Sketch of the choreography of early steps in transcription in organisms from different domains of life. Whereas one step binding is observed in Archea, stepwise DNA bending is observed for Eukaryotes using a single-molecule FRET assay.



■ A. Gietl, P. Holzmeister, F. Blombach, S. Schulz, L.V. von Voithenberg, D.C. Lamb, F. Werner, P. Tinnefeld, and D. Grohmann: *Eukaryotic and archaeal TBP and TFB/TF(II)B follow different promoter DNA bending pathways*; Nucleic Acids Res 42, 6219 (2014)

## BIOACTIVITY AND CELLULAR UPTAKE OF DISTINCT NANOPARTICLES IN HUMAN ENDOTHELIAL CELLS

Prof. Achim Wixforth (University of Augsburg, Institute of Physics)

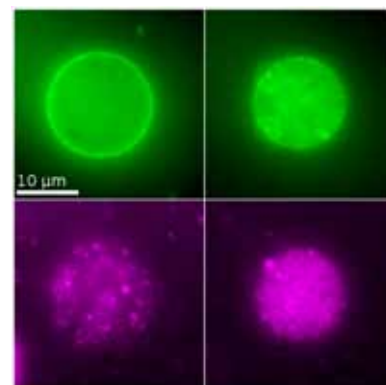
■ [www.physik.uni-augsburg.de/exp1](http://www.physik.uni-augsburg.de/exp1)

The uptake of nanoparticles into cells often involves their engulfment by the plasma membrane and fission of the latter. Understanding the physical mechanisms underlying these uptake processes may be achieved by the investigation of simple model systems which can be compared to theoretical models. Here, we present experiments on a massive uptake of silica nanoparticles by giant unilamellar lipid vesicles (GUVs). We find that this uptake process depends on the size of the particles as well as on the thermodynamic state of the lipid membrane. Our findings are discussed in the light of several theoretical models and indicate that these models have to be

extended in order to capture the interaction between nanomaterials and biological membranes correctly.

■ **C. Westerhausen, F.G. Strobl, R. Herrmann, A.T. Bauer, S.W. Schneider, A. Reller, A. Wixforth, M.F. Schneider:** *Chemical and mechanical impact of silica nanoparticles on the phase transition behavior of phospholipid membranes in theory and experiment.* Biophys J. 102, 1032-1038 (2012)

**F.G. Strobl, F. Seitz, C. Westerhausen, A. Reller, A.A. Torrano, C. Bräuchle, A. Wixforth, M.F. Schneider:** *Intake of silica nanoparticles by giant lipid vesicles: influence of particle size*



Lipid bilayer (DOPC) vesicle (green), 1min (left) and 10min (right) after the incubation with nanoparticles ( $r = 42\text{nm}$ , magenta). Obviously, vesicle membrane is consumed while particles are internalized.

*and thermodynamic membrane state;* Beilstein J. Nanotechnol. 5, 2468-2478 (2014)

## UNDERSTANDING SIZE-SHIELDING TRANSITION AND SEEBECK EFFECT IN THERMOPHORESIS

Prof. Dieter Braun (LMU München, Faculty of Physics) ■ [www.biosystems.physik.lmu.de](http://www.biosystems.physik.lmu.de)

The theory for thermophoresis in water is sketchy at best. The Braun lab could successfully extend and demonstrate that the previous capacitive model also works predicts thermophoresis correctly for the regime when the molecule becomes smaller

than the length scale of ionic shielding in the solution, the opposite regime to what was demonstrated before. Furthermore, the Seebeck effect in thermophoresis could be convincingly demonstrated without fitting parameters.

■ **M. Morasch, C. Mast, J. Langer, P. Schilcher and D. Braun:** *Dry polymerization of 3',5'-cyclic GMP to long strands of RNA;* ChemBioChem doi:10.1002/cbic.201300773 (2014)



## HIGHLIGHT ARTICLE FOR THE CHEMISTRY NOBEL PRIZE 2014 ON SUPER HIGH RESOLUTION MICROSCOPY

Prof. Christoph Bräuchle (LMU München, Chemistry Department)

■ [www.cup.uni-muenchen.de/pc/braeuchle](http://www.cup.uni-muenchen.de/pc/braeuchle)

Prof. Don Lamb (LMU München, Department of Chemistry)

■ [www.cup.uni-muenchen.de/pc/lamb](http://www.cup.uni-muenchen.de/pc/lamb)

The Nobel Prize in Chemistry 2014 was jointly awarded to Eric Betzig, Stefan Hell, and William E. Moerner "for the development of super-resolved fluorescence microscopy". The highlight article describes the development of the various techniques of super-resolved fluorescence microscopy, starting with the discovery of single molecule detection and following the different routes leading to photo-activated localization microscopy (PALM), stochastic optical reconstruction microscopy (STORM) and stimulated emission depletion (STED). Far-reaching current applications of this microscopy in biology and medicine are discussed.

■ L. Möckl, D.C. Lamb, C.

**Bräuchle:**

*Super-resolved Fluorescence Microscopy: Nobel Prize in Chemistry 2014 for Eric Betzig, Stefan Hell, and William E. Moerner; Angew. Chem. Int. Ed. 53(51), 13972 (2014)*

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THESES

**Kathrin Bader:** Optical investigation of charge carrier dynamics in photoactive materials (LMU, A. Hartschuh)

**Bernhard Böller :** Dissoziation von Kohlenmonoxid auf der Co(0001)-Oberfläche - eine *in situ*-Studie mit dem Rastertunnelmikroskop (LMU, J. Wintterlin)

**Stefano Duca:** Emergence of Cooperation by Group selection (LMU, E. Frey)

**Katy Erlich:** Integration of a Functional Enzyme into Single Molecule Cut & Paste (LMU, H. Gaub)

**Benedikt Ewald:** Timing heterogeneity, synchronisation and post-transcriptional regulation of the *Escherichia coli* Colicin E2 operon (LMU, M. Opitz)

**Timon Funck:** Chirale plasmonische Nanostrukturen mit schaltbarer optischer Aktivität (LMU, T. Liedl)

**Pirmin Ganter:** Synthesis and characterization of  $M_nP_2O_{5+3n}^{n-}$   $M=Sb(n=1, 3), Ta (n=1)$  nanosheets and studies towards novel 2D materials on the basis of Zintlphases (LMU, B. Lotsch)

**Florian Gartner:** Dynamic of fitness waves and adaption in well mixed systems (LMU, E. Frey)

**Irene Grill:** Design and ultrafast optical characterization of a graphene-based nanocavity for NL-PL enhancement (LMU, A. Hartschuh)

**Martin Grundei:** Random phase approximation - grid refinement, weight derivatives and dispersion effects (LMU, C. Ochsenfeld)

**Ann-Kathrin Henß:** Untersuchungen zur Synthese von freistehendem Graphen ausgehend von dünnen Ni(111)-Filmen (LMU, J. Wintterlin)

**Hendrik Hintz:** Postsynthetic modification of amino-functionalized metal-organic frameworks (LMU, T. Bein)

**Josef Hirte:** Optically Induced Lipid Phase Transitions: A GISAXS Study (LMU, B. Nickel)

**Marina Hoheneder:** Optoelectronic characterization of  $MoS_2$  (TUM, A. Holleitner)

**Stefan Holler:** Lipid membranes on sensing surfaces studied by x-ray reflectometry (LMU, B. Nickel)

**Maria Hoyer:** Statistical Kinetics of Actin Filament Nucleation studied with Zero-Mode Waveguides (LMU, D. Lamb)

**Philipp Jäker:** Systematic study of late transition metal diselenides in electrocatalytic water-reduction (LMU/MIT, D. Fattakhova-Rohlfing/Y. Shao-Horn)

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**Markus Mittenzweig:** Manipulating Min protein patterns (FU Berlin/Université Pierre et Marie Curie, Paris, P. Schwille/D. Baigl)

**Sebastian Müller:** Characterization and application of a commercial microscope system for complementary spectroscopy methods (LMU, A. Högele)

**Julia Nachtsheim:** Einfluss der Dezellularisierung und GAG Verdauung auf die viskoelastischen Eigenschaften von Gelenknorpel (TUM, O. Lieleg)



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**Pia Ringer:** Subcellular Dynamics and Force Transduction of Focal Adhesion Protein Talin1 and Talin2 (Universität Tübingen, C. Grashoff)

**Janina Roemer:** Nucleation of C70 aggregates on pentacene thin films for nano structuring organic interfaces (LMU, B. Nickel)

**Gökcen Savasci:** Quantum-Chemical Investigations on a Hydrazone-Based Photocatalytically Active Covalent Organic Framework (LMU, C. Ochsenfeld)

**Johannes Schlipf:** Novel structuring of organic thin films for improved absorption and performance in organic solar cells (TUM, P. Müller-Buschbaum)

**Hendrik Schlomberg:** Synthesis of a Novel Donor-Acceptor Molecule for Organic Solar Cells (LMU, T. Bein)

**Christoph Schreiber:** Characterizing Cell Motility and Transmigration on Ring Shaped Micro Patterns (LMU, J.O. Rädler)

**Maria Schwarzl:** Pursuit of a horde of prey: excluded volume and intelligent species (Universität Potsdam, R. Metzler)

**Richard Schwarzl:** Alterungseffekte und anomale Diffusion (Universität Potsdam, R. Metzler)

**Christina Sondermann:** Thermal condensation of carbon nitride films deposited by femtosecond-PLD (LMU, B. Lotsch)

**Katalin Szendrei:** 1D photonic crystals based on 2D nanosheet materials as optical humidity sensors for touchless positioning interfaces (LMU, B. Lotsch)

**Phillip Taenzler:** Quantum Chemical Investigations of the Nuclear Magnetic Resonance Properties of the Hydrogen Bond Network in Photoactive Yellow Protein (LMU, C. Ochsenfeld)

**Matthias Thubauville:** Localizing Non-Orthonormal Orbitals by Minimizing Powers of the Orbital Variance (LMU, C. Ochsenfeld)

**Benedikt v. Bronk:** Transcriptional Regulation and Heterogeneity in Colicin E2 Expression (LMU, M. Opitz)

**Tobias Verdorfer:** A Versatile Cellulase Activity and Localization Assay (LMU, M. Nash/H. Gaub)

**Andreas Vetter:** Interferometric detection of cell activity on periodic nano structures (LMU, J.O. Rädler)

**Sigurd Vogler:** Cholesky-decomposed density MP2 energy gradients with the resolution-of-the-identity approximation (LMU, C. Ochsenfeld)

**David Volbers:** Real-Time Interferometric Cell Ensemble Analysis (LMU, J.O. Rädler)

**Benedikt von Bronck:** Transcriptional Regulation and Heterogeneity on Colicin E2 Expression (LMU, J.O. Rädler)

**Philipp Walker:** Dimerization Measurements of the Protein "MeCP2" - DNA Loop Formation and Rupture Events Measured with Magnetic Tweezers (LMU, H. Gaub)

**Bernd Waschnek:** Experimental Investigation of Quantum Point Contacts with Transport and Optical Spectroscopy (LMU, A. Högele and S. Ludwig)

**Matthias Weiß:** Optische Untersuchungen an Halbleiterquantenstrukturen in Nanodrähten (Universität Augsburg, H. Krenner)

**Peter Zehetmaier:** Synthesis of nanostructured LiCoO<sub>2</sub> as a cathode material for lithium ion batteries (LMU, D. Fattakhova-Rohlfing)

**Thomas Zettl:** DNA Tile-Based Ion Channels (LMU, T. Liedl)

**Daniela Zitnanska:** Hydrothermal synthesis of hexaferrites (LMU/ Siemens Corporate Technology, D. Fattakhova-Rohlfing/ Dr. R. Karmazin)

**Christian Argyo:** Tailoring Properties of Multifunctional Mesoporous Silica Nanoparticles for Controlled Drug Delivery (LMU, T. Bein)

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**Hetvi Gandhi:** Early events in cytokine receptor signaling (TU Dresden, P. Schwille)

**Jan T. Glückert:** Optical spectroscopy of individual single-walled carbon nanotubes in an electric gate structure (LMU, A. Högele)

**Matthias Handloser:** Optical Investigation of Charge Carrier Dynamics in Organic Semiconductors and Graphene for Photovoltaic Applications (LMU, A. Hartschuh)

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**Ramona Hoffmann:** Electron microscopy investigations of the coccoliths of the calcareous algae *Emiliania huxleyi* and *Calcidiscus leptoporus* (LMU, C. Scheu/W. Schmahl)

**Stephan Hug:** Covalent Triazine Frameworks: Structure, properties and applications in gas storage and energy conversion (LMU, B. Lotsch)

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