

## Symposium Single Molecule Spectroscopy of Nanoobjects (SYSM)

veranstaltet vom  
Fachverband Molekülphysik (MO)

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### Übersicht der Hauptvorträge und Fachsitzungen

(Hörsaal VMP 8 HS)

#### Hauptvorträge

SYSM 1.1	Do	10:30–11:10	VMP 8 HS	<b>Dynamics of Semiconductor Nanocrystals and Quantum dot- Dye Assemblies</b> — ●CHRISTIAN VON BORCZYKOWSKI
SYSM 1.2	Do	11:10–11:50	VMP 8 HS	<b>Ultrafast spectroscopy of nanoplasmonic systems</b> — ●MARKUS LIP- PITZ
SYSM 1.3	Do	11:50–12:30	VMP 8 HS	<b>Hot Brownian Motion and Photothermal Correlation Spectroscopy</b> — ●ROMY RADÜNZ, DANIEL RINGS, KLAUS KROY, FRANK CICHOS
SYSM 2.1	Do	14:00–14:40	VMP 8 HS	<b>Single Emitters Coupled to Optical Nano-Antennas</b> — TIM H. TA- MINIAU, FERNANDO D. STEFANI, ALBERTO GONZALEZ-CURTO, ●NIEK F. VAN HULST
SYSM 2.2	Do	14:40–15:20	VMP 8 HS	<b>Tracking of transport dynamics in living cells</b> — ●RALF BAUSINGER, CHRISTIAN JÜNGST, ANDREAS ZUMBUSCH
SYSM 2.3	Do	15:20–16:00	VMP 8 HS	<b>Photoswitching microscopy with subdiffraction optical resolution</b> — ●MARKUS SAUER, MIKE HEILEMANN, SEBASTIAN VAN DE LINDE
SYSM 3.1	Do	16:30–17:10	VMP 8 HS	<b>Fluorophores as optical sensors for local forces</b> — ●STEFAN MARAW- SKE, DENIS DÖRR, DANIEL SCHMITZ, AXEL KOSLOWSKI, YOU LU, HEL- MUT RITTER, WALTER THIEL, CLAUS A.M. SEIDEL, RALF KÜHNEMUTH
SYSM 3.2	Do	17:10–17:50	VMP 8 HS	<b>Single molecule studies of electronic excitation energy transfer: From transfer rates and mechanisms to manipulation</b> — ●THOMAS BASCHE
SYSM 3.3	Do	17:50–18:30	VMP 8 HS	<b>Femtosecond Time-Resolved Spectroscopy of Single Molecules</b> — ●RICHARD HILDNER, DAAN BRINKS, NIEK F. VAN HULST

#### Fachsitzungen

SYSM 1.1–1.3	Do	10:30–12:30	VMP 8 HS	<b>Single Molecule Spectroscopy of Nanoobjects I</b>
SYSM 2.1–2.3	Do	14:00–16:00	VMP 8 HS	<b>Single Molecule Spectroscopy of Nanoobjects II</b>
SYSM 3.1–3.4	Do	16:30–18:45	VMP 8 HS	<b>Single Molecule Spectroscopy of Nanoobjects III</b>

**SYSM 1: Single Molecule Spectroscopy of Nanoobjects I**

Zeit: Donnerstag 10:30–12:30

Raum: VMP 8 HS

**Hauptvortrag** SYSM 1.1 Do 10:30 VMP 8 HS  
**Dynamics of Semiconductor Nanocrystals and Quantum dot-Dye Assemblies** — ●CHRISTIAN VON BORCZYKOWSKI — Center for Nanostructured Materials and Analytics (nanoMA), Chemnitz University of Technology, Chemnitz, Germany

Semiconductor quantum dots such as silicon or CdSe show rich dynamics of exciton formation and relaxation which can be investigated by single molecule techniques. Dynamics are controlled by electron-phonon coupling and photo-induced charge (blinking) and/or energy transfer (FRET). In this contribution we will concentrate on the interplay of these processes. In general, this interplay can only be described properly by taking into account the spatial distribution of the exciton wave function. Moreover, we will show that the wave function can be probed by single dye molecules attached to the surface of a single quantum dot.

**Hauptvortrag** SYSM 1.2 Do 11:10 VMP 8 HS  
**Ultrafast spectroscopy of nanoplasmonic systems** — ●MARKUS LIPPITZ — 4th Physics Institute, University of Stuttgart, Stuttgart — Max-Planck-Institute for Solid State Research, Stuttgart

The strong interaction of a metal nanoparticle's free electrons with light –the particle plasmon resonance– allows us ultrafast experiments on single metal nanoobjects. In this talk, some examples of such experiments will be presented.

A pump pulse heats the electron gas in a thin silver film. When being arranged in a Bragg structure, such films make it possible to switch the transmission of a probe pulse on a picosecond timescale.

The pump pulse also triggers mechanical oscillations of the whole metal nanostructure. As the Mie resonance depends on particle size, elastic properties of single nanoparticles can be probed all optical.

Already the presence of a plasmonic nanowire modifies the local optical density of states. This is found back in the luminescence lifetime and intensity of self-assembled GaAs quantum dots depending on the distance to the wire.

**Hauptvortrag** SYSM 1.3 Do 11:50 VMP 8 HS  
**Hot Brownian Motion and Photothermal Correlation Spectroscopy** — ●ROMY RADÜNZ<sup>1</sup>, DANIEL RINGS<sup>2</sup>, KLAUS KROY<sup>2</sup>, and FRANK CICHOS<sup>1</sup> — <sup>1</sup>Molecular Nanophotonics Group, Institute of Experimental Physics I, University Leipzig, Linnestra\sse 5, 04107 Leipzig, GERMANY — <sup>2</sup>Soft Condensed Matter Theory, Institute of Theoretical Physics, University Leipzig, Vor dem Hospitalore 1, 04103 Leipzig, GERMANY

We introduce a new technique for the measurement of tracer dynamics, called photothermal correlation spectroscopy, which is sensitive to single metal nanoparticles down to a radius of 2.5 nm with a time resolution of a few microseconds. The method is based on a fluctuation analysis of a heterodyne photothermal scattering signal, which is recorded in a simple confocal microscopy setup. It exploits the same principles as fluorescence correlation spectroscopy but targets the use of extremely photostable, non-fluorescent, nano-sized tracers as a replacement of fluorescent probes. To validate our approach, we verify that the Stokes-Einstein relation holds for heated diffusing gold nanoparticles, with an effective viscosity and temperature predicted by a semi-quantitative analytical model. This example of hot Brownian motion promises to shine new light into diffusion problems under thermal non-equilibrium as it is important for the heat conduction in nano-fluids. In summary, the presented method together with the photostability and the low size dispersion of gold nanoparticles provides large potential for broad applications especially in the field of high throughput biological screening.

**SYSM 2: Single Molecule Spectroscopy of Nanoobjects II**

Zeit: Donnerstag 14:00–16:00

Raum: VMP 8 HS

**Hauptvortrag** SYSM 2.1 Do 14:00 VMP 8 HS  
**Single Emitters Coupled to Optical Nano-Antennas** — TIM H. TAMINIAU<sup>1</sup>, FERNANDO D. STEFANI<sup>1</sup>, ALBERTO GONZALEZ-CURTO<sup>1</sup>, and ●NIEK F. VAN HULST<sup>1,2</sup> — <sup>1</sup>ICFO - the Institute of Photonic Sciences, Mediterranean Technology Park, 08860 Castelldefels (Barcelona), Spain — <sup>2</sup>ICREA - Institutió Catalana de Recerca i Estudis Avançats, Spain

We show how both excitation and emission of individual molecules is controlled by coupling to resonant optical nano-antennas. In these studies the single molecule approach is particularly effective as both position and orientation of the single absorber/emitter are well-defined. As a single absorber the molecule probes the local antenna field and here we show optical fields spatially localized within 25 nm at 514 nm wavelength for an 80 nm long Al resonant monopole antenna. Next the enhancement of the radiative and excitation rates is treated, particularly how the angular emission of the coupled system is highly directed. Clearly the dominant antenna mode determines the angular emission and arbitrary control over the main direction of emission is obtained, regardless of the orientation of the emitter. Finally a nano-Yagi-Uda antenna is discussed affording enhanced rates, strong unidirectional emission and, in reciprocity, efficient nano-focusing. The directivity is even more increased by the presence of a dielectric substrate, making such antennas a promising candidate for compact easy-to-address planar sensors at the single molecule level.

**Hauptvortrag** SYSM 2.2 Do 14:40 VMP 8 HS  
**Tracking of transport dynamics in living cells** — ●RALF BAUSINGER<sup>2</sup>, CHRISTIAN JÜNGST<sup>1</sup>, and ANDREAS ZUMBUSCH<sup>1</sup> — <sup>1</sup>Department Chemie, Universität Konstanz — <sup>2</sup>Department Physik, Universität Konstanz

During the last decade, ultrasensitive microscopy has become one of the most important tools in biophysics. In this talk, two different microscopy techniques and their biophysical application will be presented. With fluorescence excitation, sensitivities down to the single molecule

detection limit can be achieved. As an example of single molecule sensitive microscopy in live cells, single particle tracking of individual nanocarriers will be shown. Polyethyleneimine (PEI) based gene carriers are among the most efficient synthetic vectors for the delivery of DNA into the cell nucleus. We use highly sensitive fluorescence microscopy and single particle tracking methods for the investigation of the particles' paths from the plasma membrane to the nucleus. Active actin polymerization around the particle supports its cell entry and Rab protein accumulation initiates the fast vesicular transport on microtubules. It will be shown how trajectories of this bidirectional transport process are segmented by a numerical algorithm separating different modes of motion. Diffusion analysis of these segments then allows to retrieve the distribution of the intracellular transport velocities. In the final part of the talk we will present new data on the modulation of the intracellular transport behaviour of single particles depending on their enzymatic functionalization.

**Hauptvortrag** SYSM 2.3 Do 15:20 VMP 8 HS  
**Photoswitching microscopy with subdiffraction optical resolution** — ●MARKUS SAUER, MIKE HEILEMANN, and SEBASTIAN VAN DE LINDE — Applied Laser Physics and Laser Spectroscopy, Bielefeld University, Universitaetsstr. 25, 33615 Bielefeld, Germany

We introduce a general approach for multicolor subdiffraction-resolution fluorescence imaging based on photoswitching of standard organic fluorophores. Photoswitching of ordinary fluorophores such as ATTO520, ATTO565, ATTO655, ATTO680, or ATTO700, i.e. the reversible transition from a fluorescent to a nonfluorescent state in aqueous buffers exploits the formation of long-lived triplet radical anions through reaction with reducing agents such as  $\beta$ -mercaptoethylamine and repopulation of the singlet ground state by reaction with molecular oxygen. Thus, the lifetime the different fluorophores reside in the fluorescent state can be easily adjusted by the excitation intensity and the concentration of the reducing agent. We demonstrate the potential of multicolor photoswitching microscopy with subdiffraction-resolution

on cytoskeletal networks and molecular quantification of proteins in the inner mitochondrial membrane with  $\sim 20$  nm optical resolution.

### SYSM 3: Single Molecule Spectroscopy of Nanoobjects III

Zeit: Donnerstag 16:30–18:45

Raum: VMP 8 HS

**Hauptvortrag** SYSM 3.1 Do 16:30 VMP 8 HS  
**Fluorophores as optical sensors for local forces** — •STEFAN MARAWSKE<sup>1</sup>, DENIS DÖRR<sup>1</sup>, DANIEL SCHMITZ<sup>2</sup>, AXEL KOSLOWSKI<sup>3</sup>, YOU LU<sup>3</sup>, HELMUT RITTER<sup>2</sup>, WALTER THIEL<sup>3</sup>, CLAUS A.M. SEIDEL<sup>1</sup>, and RALF KÜHNEMUTH<sup>1</sup> — <sup>1</sup>Department of Molecular Physical Chemistry, Heinrich-Heine-University Düsseldorf — <sup>2</sup>Department of Organic and Macromolecular Chemistry, Heinrich-Heine-University Düsseldorf — <sup>3</sup>Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr

In this work we designed a custom-tailored oligopara\*phenylenevinylene (OPV) derivative, which according to previous theoretical studies was expected to show a significant change in geometry if an external force is exerted. Thin foils made of PVC stained with OPV have been prepared. By applying uniaxial force the foils were stretched. Three major optical effects were observed simultaneously. At first, the fluorescence anisotropy increased, which indicates a reorientation of the fluorophores within the matrix. Second, the fluorescence lifetime decreased by approximately 2.5 %. Finally we observed a blue shift in the emission spectrum by about 1.2 nm. To relate the observed spectroscopic changes to the underlying changes in molecular properties, quantum-chemical calculations have been performed. Both the observed blue-shift of fluorescence and the reduced lifetime of OPV under tensile stress are consistent with the results of the semiempirical calculations. Our study proves the feasibility of fluorescence-based local force probes for polymers under tension.

**Hauptvortrag** SYSM 3.2 Do 17:10 VMP 8 HS  
**Single molecule studies of electronic excitation energy transfer: From transfer rates and mechanisms to manipulation** — •THOMAS BASCHE — Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz

Electronic excitation energy transfer plays a key role for the functioning of natural light-harvesting complexes and light-emitting devices. In recent years single molecule spectroscopy of molecular aggregates has provided new insights into the fundamentals of this process. In order of increasing structural complexity we have studied simple molecular dimers and multichromophoric aggregates and (conjugated) polymers. It will be shown that the combination of frequency selective single molecule spectroscopy and confocal fluorescence microscopy at 1.4 K is a unique tool to study energy transfer in these systems. In particular, from the line widths of single molecule excitation spectra rate constants of energy transfer can be deduced directly. Detailed analyses shows that for several cases the mechanism of energy transfer cannot be described by the simple Förster model (dipole-dipole coupling). Furthermore, novel single molecule pump-probe experiments will be presented which allow for redirecting the excitation energy flow in in-

dividual molecular aggregates.

**Hauptvortrag** SYSM 3.3 Do 17:50 VMP 8 HS  
**Femtosecond Time-Resolved Spectroscopy of Single Molecules** — •RICHARD HILDNER<sup>1</sup>, DAAN BRINKS<sup>1</sup>, and NIEK F. VAN HULST<sup>1,2</sup> — <sup>1</sup>ICFO - Institut de Ciències Fotòniques, Mediterranean Technology Park, 08860 Castelldefels (Barcelona), Spain — <sup>2</sup>ICREA - Institutio Catalana de Recerca i Estudis Avancats, 08015 Barcelona, Spain

We present a study of the femtosecond dynamics of single molecules embedded in an inert polymer matrix at room temperature employing a fluorescence detected double pulse excitation scheme. By controlling the delay time between the excitation pulses as well as the relative phase between the electric fields of the pulses we are able to manipulate the excited state population probabilities of single molecules. An analysis of these data based on the optical Bloch equations for two- and three-level systems allows to retrieve the dephasing time of single molecules directly in the time domain. In addition the transition dipole moments (absorption cross sections) and thus the Rabi-frequencies can be determined from these data. We found dephasing times between 25 – 50 fs and the transition dipole moments were distributed between 0.8 and 16 D.

SYSM 3.4 Do 18:30 VMP 8 HS  
**Restricted Conformation Dynamics of Single Functionalised Perylene Bisimide Molecules** — CHRISTIAN VON BORCZYKOWSKI, •DANNY KOWERKO, JÖRG SCHUSTER, and STEFAN KRAUSE — Center of nanostructured materials and analytics, TU-Chemnitz, 09107 Chemnitz

Perylene bisimide molecules offer a large diversity of applications in science and technology due to its outstanding possibilities to introduce functional substituents both at the imide nitrogen and at the carbocyclic scaffold in the so called-bay area. The bay groups give rise to complex intramolecular conformational dynamics that can be uncovered by multiparameter single molecule spectroscopy in different matrices and on via functional pyridyl groups surface attached molecules. Synchronous analysis of polarisation, spectral and lifetime fluctuations also at low temperatures allows for discrimination between changes in orientation and conformation [1]. Discussion of our results in the scope of models reported in current literature gives a deeper insight to conformational interconversion processes and its consequences for radiative and non-radiative fluorescence decay rates.

[1] D. Kowerko, J. Schuster, C. von Borczykowski, Mol. Phys. 2009, (acc.)