AIM & SCOPE

The aim of this workshop will be to try to discriminate, from scientific knowledge all the way to societal implications, between facts based on actual demonstrations and understanding, shedding light inasmuch as possible onto the near future, and what pertains to obscuring extrapolations.

The ability to directly assess, manipulate, assemble and functionalize matter at the level of small scale atomic assemblies and beyond has opened-up an ongoing revolution which is bound to impact on every aspects of human life. Indeed, whereas successive ages of mankind have been labeled according to new generation of materials and their uses, from stone to silicon and onwards, we might very well be witnessing the emergence of a new "Nano age" or even a new "Nanobio age". In such a perspective, no domain of human activity would remain untouched and this new era is bound to encompass almost all knowledge-based activities, all the way to daily life and societal issues.

The main goal of the workshop will be to allow for a critical reappraisal based on an already significant and well established record track of successes and eventual pitfalls, if only to help push forward the domain and concentrate the effort towards relevant and better focused directions.

ORAL TALKS

Joseph ZYSS (French coordinator, ENS Cachan)
Seizo MIYATA (Japanese coordinator, Tokyo Institute of Technology)
Teruo OKANO (Tokyo Women’s Medical University)
Patrick COUVREUR (Université Paris XI, Chatenay-Malabry)
Fabrice CHARRA (CEA Saclay)
Thomas EBBESEN (ISIS, Université de Strasbourg)
Sophie BRASSELET (Groupe MOSAIC, Institut Fresnel, Marseille)
Yasuhiro KOIKE (Keio University)
Yasuo KITAOKA (Ministry of Economy, Trade and Industry (METI))
Ludovic JULLIEN (Laboratoire Pasteur, ENS Paris)
Jean-Pierre MAJORAL (Laboratoire de Chimie de Coordination, Toulouse)
Noritaka MIZUNO (University of Tokyo)
Kazunori KATAOKA (University of Tokyo)
Thierry LIVACHE (Institut Nanosciences et Cryogénie, Université Joseph Fourier)
Hiroyuki SASABE (Chitose Institute of Science and Technology)
Gérald DUJARDIN (ISMO, Université de Paris-Sud)
Junji WATANABE (Tokyo Institute of Technology)
Pascale SENELLART (Laboratoire de Physique des Nanostructures, Marcoussis)
Chihaya ADACHI (Kyushu University)
ORGANIZERS

Joseph ZYSS (Founding Director of d’Alembert Institute)
Seizo Miyata (Professor, Tokyo Institute of Technology)
Yoichi Nakatani (Director of JSPS Strasbourg Office)

ORGANIZING COMMITTEE

Keitaro Nakatani (Director of PPSM, ENS Cachan)
Marjolaine Vernier (Secretary General of d’Alembert Institute)
Satoko Tada (Deputy Director of JSPS Strasbourg Office)
Mina Saito (International Associate of JSPS Strasbourg Office)
Gaëlle Callouard (Secretary of d’Alembert Institute)
Isabelle Ledoux (Director of LPQM, ENS Cachan)
Malcolm Buckle (Director of LBPA, ENS Cachan)

PARTNERS
PROGRAM – December, Monday 12th

08:30 Welcome coffee

09:30 Opening session:
Prof. Jean-Yves MÉRINDOL (President, ENS Cachan)
Mr. Isao KISO, Ambassador, Japanese delegation of UNESCO
Prof. Yoichi NAKATANI, JSPS Strasbourg Office

Session 1 – Chairperson: Isabelle LEDOUX-RAK

10:00 Joseph ZYSS (French coordinator, ENS Cachan)
Some personal views on current challenges in nanoscale nonlinear optics

10:30 Seizo MIYATA (Japanese coordinator, Tokyo Institute of Technology)
Photonics polymer research based on Strategic Innovation Project

11:00 Teruo OKANO (Tokyo Women’s Medical University)
Intelligent Polymer Surfaces for Cell Sheet Tissue Engineering

11:40 Patrick COUVREUR (Université Paris-Sud, Chatenay-Malabry)
Nanomedicine for cancer treatment and theragnostic

12:20 Photo session

12:30 Lunch in Hall Villon

13:45 Coffee break + Poster session 1 in Hall Marie-Curie

Session 2 – Chairperson: Bruno PALPANT

14:30 Fabrice CHARRA (CEA Saclay)
Self-assembly: mastering photonic processes at nanoscale

15:10 Thomas EBBESEN (ISIS, Université de Strasbourg)
Light, Metal and Molecules

15:50 Sophie BRASSELET (Groupe MOSAIC, Institut Fresnel, Marseille)
Revealing nano-scale molecular processes in biology using polarized Optical microscopy

16:30 Coffee break

17:00 Yasuhiro KOIKE (Keio University)
New Generation Face-to-Face Communication Realized by Novel Photonic Polymers

17:40 Yasuo KITAOKA (Ministry of Economy, Trade and Industry (METI))
Japan's R&D Strategy of Nanotechnology

18:20 End
SESSION 3 – CHAIRPERSON: MALCOLM BUCKLE

08:30 Ludovic JULLIEN (Laboratoire Pasteur, ENS Paris)
Light driven behavior at nano- and microscales

09:10 Jean-Pierre MAJORAL (Laboratoire de Chimie de Coordination, Toulouse)
Functional dendrimers: from chemistry and biology to medicine

09:50 Noritaka MIZUNO (University of Tokyo)
Design of Highly Functionalized Polyoxometalate-based Nano-structured Catalysts by Hierarchical Three-dimensional Control of their Structures

10:30 Coffee break

11:00 Kazunori KATAOKA (University of Tokyo)
Supramolecular Nanodevices from Functionalized Block Copolymers for Molecular Therapy

11:40 Thierry LIVACHE (Institut Nanosciences et Cryogénie, Université Joseph Fourier)
Seeing biological events with plasmon resonance: from molecular binding to complex cellular interaction

12:20 Lunch in Hall Villon

13:30 Coffee break + Poster session 2 in Hall Marie-Curie

SESSION 4 – CHAIRPERSON: SOPHIE BRASSELET

14:15 Hiroyuki SASABE (Chitose Institute of Science and Technology)
New Era of Hyper-Structured Molecules

14:55 Gérald DÜJARDIN (ISMO, Université de Paris-Sud)
Quantum phenomena at the atomic-scale; from fundamental issues to a real atomic-scale technology

15:35 Junji WATANABE (Tokyo Institute of Technology)
Thermotropic liquid crystalline behavior of rigid-rod polysilane and its SmA layer formation with nano-scaled layer thickness of 10 to 200 nm corresponding to molecular length

16:15 Coffee break

16:45 Pascale SENELLART (Laboratoire de Physique des Nanostructures, Marcoussis)
Semiconductor deterministic bright sources of quantum light

17:25 Chihaya ADACHI (Kyushu University)
Challenges for novel organic light emitting devices

18:05 Closing remarks – Organizers
Prof. Joseph ZYSS (Professor, Director of D’Alembert Institute, ENS Cachan)
Prof. Seizo MIYATA (Professor, Tokyo Institute of Technology)
Prof. Yoichi NAKATANI (Director, JSPS Strasbourg Office)

18:30 End
How to connect to the WIFI network of ENS Cachan?

Two types of connection are available:

- "Guests" access: you profit from Internet access (http, https, ssh, VPN...), only your email address is required.
  
  http://public.ens-cachan.fr/anglais/index.html

- "Eduroam" Access: you profit from Internet access (http, https, ssh, VPN...), your credentials (the same you use in your establishment) are required. For more information:
  
  http://dsi-ext.ens-cachan.fr/eduroam/eduroamen.html

Comment se connecter au réseau WIFI de l'ENS de Cachan?

Deux types de connexions sont possibles :

- Accès "invité" : vous bénéficiez de l'accès Internet (http, https, ssh, VPN...), seule votre adresse électronique vous sera demandée.
  
  http://public.ens-cachan.fr/

- Accès "Eduroam" : vous bénéficiez de l'accès Internet (http, https, ssh, VPN...), dans ce cas seuls vos identifiants habituels (dans votre établissement) vous seront demandés. Pour plus d'informations:
  
  http://dsi-ext.ens-cachan.fr/eduroam/
LIST OF THE SPEAKERS

1st Session

Joseph Zyss
Institut d'Alembert – CNRS FR3242 / IFR121
Ecole Normale Supérieure de Cachan

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Phone: +33 1 47 40 55 63
E-mail: joseph.zyss@ida.ens-cachan.fr
www.ida.ens-cachan.fr

PRIOR APPOINTMENTS AND OTHERS

Joined CNET (Centre National d'Etudes des Télécommunications, research Laboratories of France Telecom) in 1974 and held various research positions in the Physics Division of the Optoelectronics branch of CNET in Bagneux. Head of the Département d'Electronique Quantique et Moléculaire at CNET (Molecular Quantum Electronics Department, 1988-1998).

Visiting scientist in various Laboratories such as: ATT-Bell Laboratories at Holmdel (July-August 1985), MIT-Department of Chemistry (summer 1991), Weizmann Institute (July-August 1992), Moved in 1998 to an Academic career at Ecole Normale Supérieure in Cachan.

Indian Institute of Science (Bangalore) as centennial Professor in 2010, Humboldt position at the Max Planck Institute for the Science of Light in Erlangen (since 2010)

EDUCATION AND CAREER

Born in Neuilly/S/Seine, France on 1/3/1950


AWARDS

IBM Prize in Physics awarded by the the French Physical Society (1987)
Incumbent of the Weizmann Institute Meierhof fellowship (1992)
Yves Rocard Prize of the French Physical Society (1996)
Fellow of the Optical Society of America (2000)
Humboldt award (France-Germany) 2010

RESEARCH INTEREST

Light-matter interaction in molecular media with emphasis on nonlinear processes with both fundamental and application oriented interests involving a combination of physics, applied physics and chemical physics cross disciplinary points of view.

Polymer based optoelectronics and related device technology; applications to optical communications; molecular engineering and nonlinear spectroscopy; parametric effects in crystalline structures and microcavities; coherent optical manipulation of molecular systems; advanced linear and nonlinear optical instrumentation and characterization methods. Introduction of the multipolar point of view in molecular
engineering and related classical and quantum models.

Main current interests: downscheduling of nonlinear optical processes to the micro and nanoscale towards nano-imaging and biophotonics. Polarization effects in multiphoton confocal microscopy. Electrooptic confocal microscopy for electric potential Imaging. Nonlinear effects from single semiconductor quantum dots and nanoplasmonic arrays.

Polymer based microcavity lasers and nonlinear dynamics: wave chaos, chaotic contours, control of the emission direction, spectrum interpretation in terms of orbits, applications to chemical sensing.

Some personal views on multidisciplinary challenges in Molecular Nonlinear Optics

Ongoing celebrations for the 50th anniversary of Nonlinear Optics provide a timely opportunity to review the domain of organic nonlinear optics from combined physics, chemistry (molecular engineering and materials science) and device technology viewpoints, pinpointing connections between these and highlighting current challenges into the future.

Molecular NLO exemplifies indeed the need of a multidisciplinary approach whereby physicists, chemists and life scientists are called to pool strength and cooperate towards jointly defined synergic goals, blurring therein sterile barriers between their respective backgrounds. The main goal of the D'Alembert Institute is to implement such an approach as mainly driven by the emerging multi-facetted field of "Nanobiophotonics".

Physics wise: the field has been traditionally divided between quadratic and cubic processes, each with its own chemistry and materials rationale and guidelines, with tensorial considerations, applicable consistently to fields and matter, at different scales, playing a pivotal role. This traditional breakdown reaches however its limits as we are now in an increasing position to implement strong coupling conditions and nonlinear dynamics situations which revive the domain and challenge the usual weak perturbation expansion scheme. Readily tailorable polymer based micro-cavity configurations, for lasing and NLO, are largely illustrate this new approach, thanks in particular to progresses in polymer based photonic technologies, having now reached nanometer precision and to the ensuing spectacular increase of linear and nonlinear figures of merits, such as towards micro-interferometry based sensors or electrooptic modulators.

Chemistry and Material wise, the domain has set the standards for a solid and durable collaboration between physicists and chemists, now over more than three decades, as illustrated from the onset of molecular engineering for NLO, onto the later extension from a dipolar to a multipolar frame and the ensuing wealth of material implementations and demonstrations at all scales, now based on unprejudiced hybridization of inorganic and organic components.

Technology and device wise, one of the most active domains is that of polymer based photonics by and large, whereby electro-optic modulators have gained over years in efficiency and stability, although this has not materialized in the market as yet. Spin-off's of this research is currently happening in other domains, such electro-optic imaging in bio environment, or polymer based lasers. In this domain, whereas electrical pumping is still ahead of us for purely organic structures, hybrid organo-mineral structures have successfully met this challenge and further progress and propositions, that may lead us from OLED's onto electrically pumped organic lasers, are being actively investigated.

The current revival of organic NLO and moreover of Bio NLO, is driven by the access to the micron- and nano-scales, in particular via a the "happy encounter" between NLO progress of life sciences and bio-imaging. Various versions of Biphotonic and Multiphoton Microscopes have now become common, sometimes "turn-key" instruments in almost any reasonably well equipped Life Science oriented laboratory.
This massive breakthrough can be viewed, at least to some extent, as a spin-off of Molecular NLO. Breaking the diffraction limits to ever smaller scales and preferably via simpler configurations, is a frontier challenge which attracts the imaging and NLO communities, with NLO and more generally “photonic labels” inheriting the earlier and current know-how in molecular NLO, but having to meet additional and inspiring requirements from life sciences.

Along these lines, we are witnessing an increasing hybridization at the nano-scale and above, between metals, semiconductors and molecular moieties, which tends to overcome the earlier and now obsolete confrontation between competing families of materials. Such multi-material, multi-functional and multi-scale hybridization provides a new enlarged basis towards the emergence of the new field of “NanoBioPhotonics” whereby nano-scale nonlinear optics, alongside electronics, magnetism and computer science is bound to play a crucial enabling role.
# 1st Session

## Seizo Miyata

**Tokyo Institute of Technology**

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## RESUME

### DATE AND PLACE OF BIRTH

May 28, 1941, Tokyo, Japan

### EDUCATION

1969 Graduate School, Chemistry Ph.D. Tokyo Institute of Technology

### EXPERIENCE

<table>
<thead>
<tr>
<th>Year</th>
<th>Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>1969–1970</td>
<td>Lecturer, Tokyo University of Agriculture &amp; Technology</td>
</tr>
<tr>
<td>1970–1986</td>
<td>Associate Professor, Tokyo University of Agriculture &amp; Technology</td>
</tr>
<tr>
<td>1982–1983</td>
<td>Visiting Professor, California Institute of Technology</td>
</tr>
<tr>
<td>1984</td>
<td>Visiting Researcher, AT &amp; T Bell Laboratories</td>
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<tr>
<td>1986</td>
<td>Professor, Tokyo University of Agriculture &amp; Technology</td>
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<tr>
<td>1994–1996</td>
<td>Vice President, Polymer Society, Japan</td>
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<tr>
<td>1995–1998</td>
<td>Member of Science and Technology Council, Ministry of Education</td>
</tr>
<tr>
<td>1995–2001</td>
<td>Dean, Graduate School of Tokyo University of Agriculture &amp; Technology</td>
</tr>
<tr>
<td>1997–1998</td>
<td>Vice President, The Society of Fiber Science and Technology, Japan</td>
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<tr>
<td>1999–2002</td>
<td>President, The Society of Fiber Science and Technology, Japan</td>
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<tr>
<td>2003–2005</td>
<td>Member of University Mobility in Asia and the Pacific</td>
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<tr>
<td>2001–2005</td>
<td>President, Tokyo University of Agriculture and Technology</td>
</tr>
<tr>
<td>2005–2010</td>
<td>Senior Program Manager, New Energy and Industrial Technology Department Organization</td>
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Photonics polymer research based on Strategic Innovation Project

Japan science and technology agency have launched a new program called strategic promotion of innovative research and development (S-Innovation). Projects chosen for the S-Innovation program are selected from among the research output of JST’s strategic and basic research programs, such as CREST, ERATO, Sakigake and SORST, which aim to create innovative new technologies, lead to the advancement of science and technology and the emergence of new industries. S-Innovation covers R&D themes from the aforementioned programs and is based on the seamless, long-term pursuit of R&D toward the practical application of novel technologies. It is envisaged that the innovation resulting from such technologies will form the foundations of future industries. Currently the program consists of four projects which are called iPS cells, organic electronics, photonics polymers and superconductivity system.

I am in charge of photonics polymer in which five themes are included such as high responsible organic photorefractive polymers conducted by Prof. Tsutsumi of Kyoto Institute of Technology, development of novel optical devices derived from nanostructure control of polymers by Prof. Watanabe of Tokyo Institute of Technology, ultra high density polymer memory by 3dimentional vector wave by Prof. Yatagai of Utsunomiya University, optical interconnecting devices by using nano-hybrid electro-optical polymers by Prof. Sugihara of Tohoku University and polymer quantum optics by Prof. Hakuta of University of Electro-Communication.

Each themes is funded approximately ¥100 M/year for ten years. Contents of each themes will be presented at the conference.
Intelligent Polymer Surfaces for Cell Sheet Tissue Engineering

Our research has been focused on constructing a novel form of co-culture consisting layered tissue structure. We first developed unique tissue culture dishes with the thermo-responsive polymer poly (N-isopropylacrylamide) (PIPAAm). The “intelligent surface” of these dishes possessed the hydrophobicity similar to regular tissue culture polystyrene dishes at 37°C. However, the surface reversibly became hydrophilic at a lower temperature and spontaneously released the cultured cells as a single layer without the need for trypsin or EDTA, thus leaving the cell layer with extracellular matrix (ECM) intact. All the cultured confluent cells were harvested as a single contiguous cell sheet from the thermo-responsive culture dishes and readily applied to other biological and non-biological surfaces. We here propose this novel system of cells and cell-layers arrangement called “cell sheet engineering.” We initiated human clinical studies of cell sheet engineering therapy using oral mucosal cell sheet for treatment of cornea epithelium deficient disease and recovery from endoscopic submucosal dissension surgery for esophageal epithelial cancer, and we also succeeded in treating cardio-mypathy using myoblast cell sheet. Therefore, cell sheet engineering is a highly promising tool for tissue engineering and regenerative medicine.
Even if new molecules are discovered to treat cancer diseases, the clinical use and efficacy of conventional chemotherapeutics is hampered by the following limitations: i) drug resistance at the tumor level due to physiological barriers (non cellular based mechanisms) ii) drug resistance at the cellular level (cellular mechanisms), and iii) non specific distribution, biotransformation and rapid clearance of anticancer drugs in the body. It is therefore of importance to develop nanodevices able to overcome resistance of cancer cells or tissues to chemotherapeutic treatments.

This is illustrated by the camouflage of doxorubicin into polyalkylcyanoacrylate nanoparticles, allowing to overflow the PgP detoxification capacity, thus inducing reversion of the multidrug resistance (MDR). The higher cytotoxicity of doxorubicin when loaded onto poly(isohexylcyanoacrylate) nanoparticles has been shown on the X/myc transgenic mouse model of hepatocellular carcinoma which mimics several steps of...
human hepatocarcinogenesis\textsuperscript{1}. Based on these data, a phase II multicentric clinical trial is currently performed on patients with resistant hepatocarcinoma or liver metastasis.

Another illustration of this approach is \textit{squalenoylation}\textsuperscript{2}, a technology that takes advantage of squalene’s dynamically folded conformation to link this natural compound to anticancer and antiviral nucleoside analogues in order to achieve the spontaneous formation of nanoassemblies (100–300 nm) in water without the aid of surfactants\textsuperscript{3}. When applied to the anti-cancer compound gemcitabine\textsuperscript{4}, this original concept was demonstrated to be able to overcome different mechanisms of resistance of gemcitabine\textsuperscript{5}, ie. deamination of gemcitabine by the blood deaminases, down regulation of nucleoside transporters\textsuperscript{6} and/or insufficient phosphorylation by the deoxycytidinekinases (dCK). Indeed, the squalenoylated gemcitabine nanoparticles were found (i) to be resistant to deaminases, (ii) to diffuse intracellularly independently of the presence of nucleoside transporters and (iii) to improve the phosphorylation of gemcitabin by dCK.

Finally, the use of nanohybrids constructed with metal organic frameworks (nanoMOFs) will be reviewed for their ability to encapsulate unprecedent high quantities of the anticancer compound busulfan\textsuperscript{7}.

Acknowledgement:

Part of this presentation benefits from the financial support of the European Council under the ERC Advanced Grant n°249835 “TERNANOMED”
Molecular Self-Assembly: Mastering Optoelectronic Processes at Nanoscale

Self-assembly techniques permit an accurate bottom-up control of matter organization at the nanoscale, through molecular-scale design of building blocks (the so-called tectons). The obtained supramolecular ordering is a determining factor for light absorption and emission processes. In particular, 3D molecular architectures are requested to control charge and energy transfer processes between molecule and substrate and between neighbouring molecules themselves. We present some general principles for off-plane self-assembly of molecular architectures on surfaces based on three-dimensional tectons. This is illustrated by three examples of realization of 3D nano-organizations designed in view of mastering specific photonic processes.[1]

The first one is about conjugated polymers designed so as to exploit weak inter-strand interactions to obtain a self-template effect leading to staggered organizations of well-aligned electronically-decoupled conjugated strands. The system is observed in-situ by scanning tunnelling microscopy and spectroscopy on
The next point is the exploitation of molecular self-assembly through interdigitation of side-chain. This permit the immobilization of isolated dyes inside the highly homogeneous 2D alveoli of a nanoporous self-assembled molecular matrices.[3] We will present also the rational design of 3D building blocks aimed at combining in-plane periodicity and off-plane dye protrusions.[4]

Finally, we will discuss 3D self-assembly in solution. As an illustration, we will detail the mechanisms of fluorescent labelling of DNA in terms of self-assembly of fluorophores on DNA considered as a 3D substrate.[5]

References:


Thomas Ebbesen is a Norwegian physical chemist born in Oslo in 1954. He was educated in the United States and France, receiving his bachelor degree from Oberlin College (USA) and his PhD from the Curie University in Paris. He then did research in both public and private institutions, in the US and in Japan, before returning to France in 1999 to build a new laboratory at the University of Strasbourg where he is currently professor and director of ISIS. The author of many papers and patents, Ebbesen has received awards for his pioneering research on nanostructured materials including the 2001 Agilent Europhysics Prize, the 2005 Prix France Telecom and the 2009 Quantum Electronics and Optics Prize of the EPS. He is a member of the Norwegian Academy of Science and Letters, the French Academy of Science and the Institut Universitaire de France.

Light, Metal and Molecules

Metal structures that resonate with electromagnetic waves and molecules or materials offer many interesting possibilities both in terms of fundamental science and applications. To illustrate this, we will focus on molecule – metal interactions and the role of surface plasmons. The possibility of coupling molecules to electromagnetic vacuum fluctuations which leads to hybrid states having strongly modified energies will be presented together with the important implications for molecular and material science.
Sophie Brasselet
Institut Fresnel - MOSAIC group
Université Aix-Marseille, CNRS

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Sophie Brasselet obtained her Ph.D in 1997 at University of Paris-Sud, France, on the study of multipolar molecules for nonlinear optical applications in polymers. She spent a two years postdoc at UCSD and Stanford University, USA, on single fluorescent molecules imaging in cells. After six years as an assistant professor at ENS Cachan, France, working on nonlinear microscopy and optical manipulation of single molecules, she is now a CNRS director at Institute Fresnel, Marseille, France. She is leading projects on the development of new schemes for nonlinear imaging in biological samples and in nanoplasmonics. Since 1997, she has been the co-author of 70 publications and 1 patent.

Research topics:

- Two, Three-photon and nonlinear microscopy imaging techniques using polarization and phase detections. Analysis of molecular organization at the nanometric scale in biological samples (cell membranes, tissues). Study of metal nano-structures supporting local enhancement of optical responses, diagnostics of mono-crystallinity in molecular and protein crystals.
- Single molecule spectroscopy at room temperature
- Pulse shaping in nonlinear microscopy applied to bio-imaging and nanoplasmonics.

Quantifying molecular order in biological samples using polarimetric muti-modal nonlinear microscopy

In addition to their interesting capabilities for bio-imaging, nonlinear optical contrasts involve rich excitation/emission processes based on multiple fields and therefore multiple polarization directions coupling. This opens the way to analysis of high order symmetry features in bio-molecular assemblies down to the nanometric scale, that are not accessible by linear optics tools [1].

We have recently developed a general polarimetric nonlinear microscopy technique able to circumvent the intrinsic limitations of fluorescence anisotropy, which is today the most widely used technique to measure molecular order information in biological samples. This polarimetric method, based on a variation of the incident fields polarization states combined with a polarized read-out of the emitted signal, allows retrieving information on local molecular angular distribution with no necessary a priori knowledge on its averaged orientation nor its shape.

We will demonstrate on several examples how this polarization-dependent nonlinear microscopy technique is able to measure quantitatively molecular order information in biological samples. Different contrasts will be described with emphasis on their specificities, either for incoherent processes such as
multi-photon fluorescence or for coherent harmonic generations. These specificities are illustrated in cells and tissues, where the contrasts are provided either from membrane markers (two-photon fluorescence) [2], from intrinsic mechanisms such as second harmonic generation (SHG) [3] or vibrational signatures using Coherent Anti Stokes Raman Scattering (CARS) [4]. Instrumental issues will be discussed, in particular on the diagnostics of polarization distortions due to complex samples such as tissues [3], or inherent to polarization-resolved microscopy [5].

References:
Yasuhiro Koike
Professor, Councilor, Keio University

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Phone: +81 (0)44 580 1562
E-mail: koike@appi.keio.ac.jp

Yasuhiro Koike was born in Tokyo, Japan. He received his B.S. in 1977, M.S. in 1979, and Ph.D. in 1982 in applied chemistry from the Graduate School of Engineering of Keio University, Yokohama, Japan. He was a visiting researcher with AT&T Bell Laboratories from 1989 to 1990. He has been Professor of Keio University since 1997. He developed the high-bandwidth graded-index polymer optical fiber “GI POF”, highly scattered optical transmission polymer “HSOT”, zero birefringence polymer, etc. He conducted Koike Photonics Polymer Project in the ERATO-SORST program of Japan Science and Technology Agency (JST) from 2000 to 2010. He also has been leading project entitled “Face-to-Face Communication Business by Ultra High-Speed Plastic Optical Fiber and High-Definition Photonics Polymer” in the FIRST program of Cabinet Office of Japan since March 2010. He received the International Engineering and Technology Award of the Society of Plastics Engineers in 1994, the Fujiwara Award in 2001, and an honor of Medal with Purple Ribbon in Palace in 2006. In 2007, he was conferred as an honorary doctorate from Eindhoven University of Technology.

New Generation Face-to-Face Communication Realized by Novel Photonic Polymers

Basic studies are undertaken to investigate how polarized waves or photons relate to various polymer chains (angstroms), their aggregation (several hundred angstroms), higher order structures, and huge heterogeneous structures, discovering the origins and intrinsic properties of light and polymer, we have proposed and demonstrated “photonics polymers” with new optical functions for applications in photonics fields such as world’s fastest Graded-Index Plastic Optical Fiber (GI POF) that achieved more than 40 Gbps data transmission for optical communication, Highly Scattered Optical Transmission (HSOT) Polymer for LCD backlight and zero-birefringence optical polymer for high quality display. Introducing these novel photonics polymer materials, we are proposing “Fiber-To-The-Display” concept, where GI POF network is directly connected to the high-definition display of homes and offices, by which breathtakingly realistic face-to-face communication can be realized.

We have successfully demonstrated the 3D/4K display which increased the brightness and contrast by twice as the conventional backlight, and by zero-birefringence polymer dramatically improved the control of polarization phase and dissolves the mura problem at low fabrication cost. The latest results of this key technologies will be described in the presentation.
Yasuo Kitaoka

Fine Ceramics, Nanotechnologies and Advanced Materials Policy Planning Office, Manufacturing Industries Bureau, Ministry of Economy, Trade and Industry (METI)

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E-mail: kitaoka-yasuo@meti.go.jp

Yasuo Kitaoka obtained his Ph.D. from Osaka University in 1988 under the supervision of Professor T. Sasaki investigating green-blue light generation using organic and inorganic nonlinear crystals. He worked at Panasonic from 1991 to 2006, to develop visible light sources for the high-density optical disks, wherein he researched wavelength conversion devices using a LiNbO₃ crystal and crystal growth of nitride semiconductor materials such as GaN and AlN. He received the Best Paper Award of The Laser Society of Japan in 2000. In 2006, he was appointed professor at Osaka University and he joined the group of Prof. Mori in Osaka University to promote the NEDO (New Energy and Industrial Technology Development Organization) national project concerning liquid phase epitaxial growth of GaN crystals using a Na-flux method. His current research interests involve non-linear optical devices and the crystal growth of organic and inorganic functional materials. In 2010, he moved to the Ministry of Economy, Trade and Industry (METI) to make policy on nanotechnology and advanced materials.

Japan's R&D Strategy of Nanotechnology

I will talk about Japan's system and strategy for science and technology, and show the promotion for Nanotechnology and materials research. Japan promoted the 1st to 3rd Science and Technology (S&T) Basic Plans from 1996 to 2010. In the 3rd basic plan, 8 promotion areas were chosen and 4 areas of Life science, Information and communications, Environmental science, and Nanotechnology and materials are defined as prioritized areas. This year, we followed up the 3rd basic plan and constructed the 4th basic plan.

Next, we demonstrated the succeeded national projects and the recent topics in Nanotechnology and advanced materials in Japan. The remarkable progress of materials science and technology has led innovation in Japan's industrial development.

In Japan, the issue of stable supplies of critical metals and the Great East Japan Earthquake has reminded us that our advanced materials and device industries have huge influence on the global supply chain. In light of these recent crises, the importance of the continued development of the materials and device industries in Japan has become clear. It's expected that the necessity of Nanotechnology and materials for the development of new materials and substitute materials will increase especially in developing future energy policy.
Ludovic Jullien
Department of Chemistry, Ecole Normale Supérieure
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Phone: +33 (0)1 44 32 33 33
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Ludovic Jullien is Professor of Chemistry at the Université Pierre et Marie Curie (Paris) since 2011. He graduated from the Ecole Normale Supérieure (1986) and received his Ph.D. (1990) from the Université Pierre et Marie Curie. He is currently the chair of the Chemistry Department at the Ecole Normale Supérieure. His current major research interests are in Systems Chemistry, Biological Chemistry, Analytical Chemistry, Kinetics, Photophysically and Photochemically active organic probes, Reactivity-based analysis and separations, with results published in about 100 papers.

Light driven behavior at nano-and microscales

This lecture illustrates how light can be used to control the behavior of reactive systems both at the molecular and systemic levels.

The external control of biologically active substrates/media in a spatially and temporally precise manner has already strongly impacted many fields of Biology. Among the various triggers, light combines high specificity and absence of invasiveness together with easy implementation with conventional microscopes. I will first show how light can be used to photocontrol the function of various proteins in vivo. Then I will illustrate that light provides a convenient strategy to pilot the dynamical behavior of non-natural systems as well. In particular, our group has recently used light to build steady-state out-of-equilibrium concentration profiles in liquids and to unprecedentedly engineer light to chemical energy transfer by means of proton exchanges.
Jean-Pierre Majoral
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EXPERIENCE
1966    Assistant Professor, Toulouse University
1967     Attaché de Recherche CNRS, Toulouse
1972     Post-doc, University of East Anglia, Norwich (UK)
1973     Chargé de recherche, Maître de recherche, Directeur de Recherche second then first, then
           exceptional class, Emeritus, CNRS Toulouse
1999     Vice Director Laboratoire de Chimie de Coordination du CNRS
           Co-Director "Laboratoire Européen Associé" Lodz (Poland)-Toulouse (France)
2009     Scientific Director of the company « DENDRIS »
2010     Scientific Director (Institut MAScIR ,Rabat, Morocco)

AWARDS
1990     Award of the French Chemical Society, Division “Coordination Chemistry”.
1993     Award of the French Academy of Sciences.
1994     “Wittig Grignard” Award of the German Chemical Society.
1995     von Humboldt Foundation Award.
1997     Member of the European Academy of Sciences, Arts and Letters
1999     Member of the Academia Europeae
2000     Member of the Polish Academy of Sciences
2002     Catalan-Sabatier” Award of the Spanish Royal Society of Chemistry
2003     Le Bel Award of the French Chemical Society
2004     Fellow Royal Society of Chemistry (UK)
2005     Member of the Akademie der Wissenschaften, (German Academy of Sciences), Gottingen,
           Germany
2008     Grand Prix Emile Jungfleisch Académie des Sciences (France)

PUBLICATIONS  495

CONFERENCES TO WHICH INVITED
France:        172
Foreign:       280 (Conferences, Universities and research centres).

FIELDS OF INTEREST
Long standing interest on all aspects of phosphorus chemistry: low coordinated species, heterocycles,
macrocycles, cryptands, spherands, chiral ligands for catalysis, polymers, interactions between transition
metals and various unsaturated phosphorus derivatives. Two main topics are developed at the present time in Toulouse:

The first one concerns the characterization and studies of the physical and chemical properties of phosphorus containing dendrimers and related hyperbranched polymers with emphasize on applications from biology to material sciences. The second one concerns catalysis in water using monomeric, polymeric, or dendritic ligands is a recent investigated project of research.

Some other new research fields are investigated in Rabat: design of “smart” glasses (photochromic, electrochromic and thermochromic glasses), drug delivery with dendrimers, design and properties of hyperbranched polymers etc...

**Functional dendrimers: from chemistry and biology to medicine**

More and more applications of dendrimers are appearing in the literature covering many topics from biology, biomedicine, material sciences, catalysis. As a consequence such an appealing field of research implies to diversify the nature and the composition of existing types of dendrimers but also to propose the preparation of tailored new types of dendrimers which might be able to open new areas of investigations. Selected properties and applications of some of the phosphorus containing dendrimers we are currently working with will be presented and discussed.
Noritaka Mizuno received his Bachelor's degree in synthetic chemistry at the University of Tokyo in 1980. Then he started his research on the heterogeneous oxidation catalysis of heteropoly compounds at the University of Tokyo and received his Ph. D. in 1985. He continued the study of heterogeneous catalysis as a research associate at the same place. In 1989 he did a postdoctoral work with Professor Richard G. Finke at University of Oregon. In 1990, he returned to Japan as an Associate Professor at Catalysis Research Center, Hokkaido University. In 1994, he moved to the Institute of Industrial Science, the University of Tokyo, and then to the Department of Applied Chemistry of the same university, where he has been a full Professor since 2001. His research interests are mainly directed toward catalysis of metal oxide clusters such as heteropoly compounds and zeolitic materials and their syntheses. He has published about 240 original papers, 50 reviews, and 34 chapters in books.

Design of Highly Functionalized Polyoxometalate-based Nano-structured Catalysts by Hierarchical Three-dimensional Control of their Structures

Polyoxometalates (POMs) are a large family of anionic metal–oxygen clusters of early transition metals and stimulated many current research activities in broad fields of science including oxidation catalysis. We succeeded in the developments of highly atom-efficient and green oxidative functional group transformations by precise design and synthesis of novel POM-based molecular catalysts: The lacunary \( \gamma \)-SiW\(_{10}\)O\(_{34}\)(H\(_2\)O)\(_2\)\(^{4-}\) could catalyze the epoxidation of common alkenes, sulfides, and organosilanes using H\(_2\)O\(_2\) with high product selectivities and H\(_2\)O\(_2\) utilizations in homogeneous as well as heterogeneous manners. The divanadium-substituted \( \gamma \)-H\(_2\)XV\(_2\)W\(_{10}\)O\(_{40}\)\(^{n-}\) (X = Si or P) with the \{VO-(\(\mu\)-OH)\(_2\)-VO\} core could be synthesized and catalyze epoxidation and alkane hydroxylation with unique stereospecificities, diastereoselectivities, and regioselectivities. The aerobic oxidative alkyne-alkyne homocoupling efficiently proceeded with \( \gamma \)-H\(_2\)SiW\(_{10}\)O\(_{38}\)Cu\(_2\)(\(\mu\)-1,1-N\(_3\))\(_2\)\(^{4+}\). Various homoallylic alcohols could efficiently be epoxidized with \[\text{SeO}_4(\text{WO(O}_2\text{)})_2\]\(^{2-}\). Furthermore, we synthesized the organic-inorganic hybrid support by covalently anchoring N-octyldihydroimidazolium cation fragment onto SiO\(_2\). The above POM-based molecular catalysts could be immobilized onto the support via the stoichiometric anion exchange. The supported catalysts showed high performance for the oxidations without the loss of their intrinsic catalytic nature of the corresponding homogeneous analogues.

Kazunori Kataoka

Department of Materials Engineering, Graduate School of Engineering / Center for Disease Biology & Integrated Medicine, Graduate School of Medicine, The University of Tokyo

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http://www.bmw.t.u-tokyo.ac.jp/english/index.html

Kazunori Kataoka, Ph.D. is Professor of Biomaterials at Graduate School of Engineering, the University of Tokyo, Japan. He has been appointed joint position since 2004 from Graduate School of Medicine, the University of Tokyo as Professor of Clinical Biotechnology at Center of Disease Biology and Integrative Medicine. He received B.Eng. (1974) and Ph.D. (1979) from the University of Tokyo. Dr. Kataoka received several awards, including the Society Award from the Japanese Society for Biomaterials (1993), the Society Award from the Society of Polymer Science, Japan (2000), Clemson Award from the Society for Biomaterials USA (2005), Founder’s Award from the Controlled Release Society (2008), and the Science and Technology Prize awarded by the Minister of Education, Culture, Sports, Science and Technology, Japan (2010). He is a president of the Society of Polymer Science (2010-), Japan, a president-elect of the Controlled Release Society (2011-), Fellow of the American Institute of Medical and Biological Engineering (AIMBE) (1999-), and Fellow of Biomaterials Science and Engineering (FBSE) (2004-). He has been on the editorial board of twelve international journals, including Journal of Biomaterials Science, Polymer Edition (Editor), Biomacromolecules (Associate Editor), and Biomaterials (Associate Editor). His current major research interest is supramolecular materials for nanobiotechnology, particularly focusing on drug and gene targeting, and has published more than 400 papers.

Supramolecular Nanodevices from Functionalized Block Copolymers for Molecular Therapy

Nanotechnology-based medicine (Nanomedicine) has received progressive interest for the treatment of intractable diseases, such as cancer, as well as for the non-invasive diagnosis through various imaging modalities. Engineered polymeric nanodevices with smart functions play a key role in Nanomedicine, including drug carriers, gene vectors, and imaging probes. This presentation focuses present status and future trend of the development of polymeric nanodevices particularly for drug and gene delivery. Polymeric nanodevices with 10 to 100 nm in size can be prepared by programmed self-assembly of block copolymers in aqueous entity. Most typical example is polymeric micelles with distinctive core-shell architecture. Several micellar formulations of antitumor drugs have been intensively studied in preclinical and clinical trials, and their utility has been demonstrated. Compared with conventional formulations, such as liposomes, polymeric micelles have several advantages, including controlled drug release, tissue
penetrating ability and reduced toxicity. Critical features of the polymeric micelles as drug carriers, including particle size, stability, and loading capacity and release kinetics of drugs, can be modulated by the structures and physicochemical properties of the constituent block copolymers. The development of smart polymeric micelles that dynamically change their properties due to sensitivity to chemical or physical stimuli is the most promising trend, directing to the targeting therapy with high efficacy and ensured safety. Notable anti-tumor efficacy against intractable cancer, including pancreatic cancer, of DachPt-incorporated polymeric micelles with pH-responding property was demonstrated to emphasize a promising utility of Nanomedicine for the cancer treatment. Indeed, five different formulations of polymeric micelles loaded with anti-cancer drugs have already been in clinical trial worldwide, including Japan, Taiwan, Singapore, UK, France, and USA, featuring high utility of polymer-based therapeutics. Ref. M. Murakami, et al, Science Translational Medicine, 3, 64ra2 (2011).
Thierry Livache was born in 1964. He received his DEA of chemistry and his Pharmaceutical Doctorate from the University of Grenoble, France (Oligonucleotide chemistry for virus detection). He had been a senior scientist (DNA chemistry and molecular biology) in the R&D dpt at CISbiointernational (Gif-sur-Yvette, France) from 1990 to 1994 and biochip (Micam) project leader from 1994 to 1999 in the same company. In 2000, he moved to the CEA in Grenoble to be in charge of the bioassembling project at the fundamental research department. In 2003, he created the group CREAB involved in the joined unit SPram (CEA-CNRS-Grenoble University). The CREAB group involves 8 senior scientists, from CEA, CNRS or Grenoble University and currently 10 PhD students or postdocs. His current researches include the grafting and the micropatterning of biomolecules on surface for the construction of biochips and the development of associated analytical approaches including SPRimaging. The lab is also involved in clinical applications of these microsystems, from immunoassays to cell screening.

He founded the company Genoptics (SPR imaging) in 2002 and is currently scientific advisor of Horiba Jobin Yvon. He is a member of the commission P2N of the French National Research Agency (ANR). He also teaches at UJF and Phelma in Grenoble and at universities of SaoPaulo and HoChiMinh city.

Thierry Livache is the authors more than 70 publications or book chapters, 21 (14 licenced) patents and more than 50 invited conferences.

Seeing biological events with plasmon resonance: from molecular binding to complex cellular interactions

Microtechnologies have prompted the development of highly parallel devices allowing a high biological analysis throughput. Among them the DNA or protein microarrays which are a collection of systematically arranged probes grafted on a solid surface, can be used to interrogate a fluorescent labeled sample applied on the biochip (end point detection process). More recently, approaches such as SPRimaging involving label-free and real time detection processes have been developed and applied for the detection of molecular interactions, from simple DNA hybridizations to artificial tongue systems.

Beyond this molecular detection, interest complex system analyses such as direct cellular analyses has emerged during these last years. Indeed, qualitative and quantitative analysis of complex mixtures such as white blood cells is of major interest for both diagnostic and biomedical applications. In this way, a new approach of non-adherent cells capture was developed and used in conjunction with label free detection. We have recently shown that white blood cells ie B and T lymphocytes, can be efficiently separated and organized on micropatterned surfaces. Moreover, to ensure a cell sorting, different approaches of localized cell desorption were developed. Coupled with the detection of the cell secretions ie interferon, chemokines… it opens the field of the study of the immunological response at the individual cell level.
Lymphocytes organized on a surface patterned with specific antibodies

References:
Y Roupioz et al, Small, 5:1493-1497 (2009)
S Milgram et al Biosensors & Bioelect. 5:2728-32 (2011)
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Hiroyuki Sasabe received B.E., M.E. and Dr. E. degrees in applied physics from the University of Tokyo, Japan, in 1964, 1966, and 1972, respectively. He was a research scientist at Electrotechnical Laboratory, MITI (1966-1974), an associate professor at Tokyo University of Agriculture and Technology (1974-1983), a head of Biopolymer Physics Laboratory, RIKEN (1982-1999), and a professor at Chitose Institute of Science and Technology (CIST) (1999-2011), and became the president of CIST in 2002 for 8 years. After the retirement in 2011 he is a professor emeritus of CIST. He coordinated Frontier Research Program (FRP), RIKEN, during 1986-1991, and managed Nano-Photonics Materials Laboratory, FRP, during 1991-1999 as a head of laboratory. He also affiliated an adjunct professor of Graduate School of Saitama University (1989-1999), University of Massachusetts Lowell, USA, (1996-1998), Hokkaido University(1997-1999), Kwangju Institute of Science and Technology (1994-present), Hanyang University, Korea, (1999-present), and a guest professor of Peking University, China, (1995-present). His current research interests are hyper-structured molecules, organic ultrathin films, organic nonlinear optics, molecular- and bio- electronic devices, and organic semiconductor devices such as OLED and an organic laser.

New Era of Hyper-Structured Molecules

Hyper-structured molecules (HSM) are designed under the similar concept of ‘supramolecules’ proposed by Prof. Jean-Marie Lehn, but mostly focused on the self-organization of 3D structure by molecule itself and their electronic and photonic properties are also easily designed. Typical HSMs are dendrimers and/or starburst oligomers/polymers. 4 types of dendrimer structure are proposed: peripheral type, layer type, core type and block type. Some examples of molecular handling of HSM based on the near field optics (evanescent field interacting with molecules) and quantum effects in HSM and/or HSM 1D array are demonstrated in the presentation. We could actually confirm the energy transfer in a carbazole-anthracene type dendrimer and a Ru/Ni complex type dendrimer as light harvesting molecules. By tuning the molecular topology in chromogenic cyclic oligomers we could derive new photonic properties such as photorefractivity. We synthesized carbazole linear and/or cyclic oligomers and demonstrated their photorefractive properties. These molecules are considered as a ‘monolithic’ photorefractive molecule. Energy transfer inside the dendritic molecules leads to the light emitting diode (OLED) properties as demonstrated by Prof. Frechet’s group.

Recent tendency of HSM application in general is more oriented to the medical/pharmaceutical application such as drug delivery systems (DDS), which will be reviewed briefly.
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Institut des Sciences Moléculaires d’Orsay, Université Paris-Sud

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http://voyager.ppm.u-psud.fr/nanophysics.html

DATE AND PLACE OF BIRTH: November 5, 1950

ACADEMIC EXPERIENCE:

1971 : Ecole Normale Supérieure de Cachan
1974 : DEA de Physique Nucléaire à Orsay, Agrégation de Physique
1975 : Attaché de Recherche at CNRS
1978 : PhD thesis (Paris VI)
1982 : State thesis (Paris XI)
1982 : Chargé de Recherche at CNRS
1991 : Visiting Scientist at IBM Yorktown (USA)
1992 : Directeur de Recherche 2ème classe at CNRS
2002 : Directeur de Recherche 1ère classe at CNRS

RESEARCH AWARDS:

1998 : Nanotechnology price
2004 : Elected Fellow of the Institute of Physics

LEADERSHIP:

1994-2011 : Head of the « Molecular Nanoscience« group of the Institute for Molecular Science in Orsay (12 researchers)
1998-2000 : Member of the OFTA committee « Design and fabrication of nano-devices »
2004-2011 : Member of the OMNT committee on « Molecular electronics »
2006-2009 : Director of the PPF (Plan PluriFormation) of the University Paris XI « Individual Nano-Objects »
2006-2011 : Member of the board « Quantum molecular electronics » of the C’Nano Ile de France
2007-2011 : Member of the board « Nano-World » of the PRES Ile de France Sud
2008-2011 : Member of the committee « Network of near-field microscopies »

EDITORIAL BOARD:

2003-2007 : Member of the editorial board of J. Phys. C (IOP)
2002-2011 : Member of the editorial board of « Progress of Surface Science » (Elsevier)

INVITED TALKS:

65 invited talks at international conferences, 64 invited seminars at research institutions

Publications:

172 articles in international, refereed journals, 3100 citations, h factor : 30
Quantum phenomena at the atomic-scale; from fundamental issues to a real atomic-scale technology

The scanning tunneling microscope (STM) enables a large variety of quantum phenomena to be studied with an atomic-scale precision. For example, charge transport, electrical contact, current fluctuations, conductance and mapping of density of electronic states, whose influence are well known at the mesoscopic or macroscopic scale, can be investigated at the atomic-scale. Furthermore, inelastic electron tunneling enables vibrational and spin spectroscopy as well as optical and dynamical properties to be probed at the level of a single atom or molecule. Developing the compatibility of these new atomic-scale methods and techniques with material and device fabrication is certainly the biggest challenge for the next few decades.
Resumo

Nascimento: 28 de julho de 1948 em Ehime Prefeitura, Japão

Formação: Graduado do Instituto Técnico de Tóquio (Departamento de Química Polimérica) em 1970; Instituto Técnico de Tóquio, Doutor em Engenharia Química, 1975.


Interesse de Pesquisa: Estrutura e Propriedades Físicas de Polímeros Cristalinos Líquidos.
Pascale Senellart obtained her PhD in 2001 at Université Paris 6. Her PhD research was devoted to understanding the relaxation of cavity polaritons and demonstrating their bosonic nature [1].

Since 2002, P. Senellart is a permanent researcher within CNRS at the Laboratory for Photonic and Nanostructures (UPR20/CNRS, Marcoussis). Her main research activity is devoted to cavity quantum electrodynamics with single quantum dots. In 2005, her team demonstrated one of the first strong coupling regime for a single quantum dot in a microdisk cavity [2]. In 2008, she demonstrated a novel deterministic technology [3] leading to the scalable fabrication of bright single photon sources [5], strongly coupled quantum dot-pillar devices [6] and the brightest source of entangled photon pairs to date [7].

Part of her research activity is still devoted to the condensation of cavity polaritons, in collaboration with Dr. J. Bloch. In 2008, they demonstrated for the first time the possibility to create 0D condensates under non-resonant incoherent excitation [4]. Very recently, they demonstrated the creation and manipulation of 1D extended condensate exhibiting macroscopic spatial coherence.

P. Senellart has published over 70 articles in international journals, including Phys. Rev. Lett. (10), Nature (1), Nature Physics (1), Nature Materials (1), Appl. Phys. Lett (11). She has given more than 30 invited talks and a dozen seminars (Paris, Bremen, Cambridge, Munich, Warsaw, Gaithersburg…) on her main research activity since 2005. In 2011, she was awarded a Starting Grant from the European Research Council (ERC).

Selection of publications


A single semiconductor quantum dot (QD) is a promising system to achieve a solid-state source of single photons or entangled photon pairs. Controlling the radiative lifetime of a QD in the weak coupling regime (Purcell effect) is a way to make sure that the photons emitted by the QD are funneled into a cavity mode and efficiently collected. For the last few years, the main challenge has been to control both the spectral and spatial matching between a single QD and a cavity mode. We have developed an in-situ lithography technique that allows deterministically coupling a single QD to a cavity mode. Using this technique, we demonstrate the scalable fabrication of ultrabright sources of single photons or of entangled photon pairs. The same technique is also used to achieve on-demand strong coupling regime between a QD and a cavity mode. In this regime, we evidence optical non-linearities on a few photon scales.
Chihaya Adachi
Center for Organic Photonics and Electronics Research, Center for Future Chemistry, Department of Applied Chemistry, Kyushu University

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http://www.cstf.kyushu-u.ac.jp/~adachilab/index.html

Chihaya Adachi obtained his PhD degrees at the Kyushu University in 1991 on the research topics of organic electroluminescence. In 2005, he was appointed to Professor at the Center for Future Chemistry, Kyushu University and now he is the director of Center for Organic Photonics and Electronics Research (OPERA). His research interests include organic synthesis, device fabrication and optical and electrical device characterization of organic semiconductors. He has published about 201 papers, 58 reviews and 27 chapters in books.

Challenges for novel organic light emitting devices

Recently, in order to improve the exciton production efficiency at a singlet excited level ($S_1$) in OLEDs, we employed the mechanism of thermally activated delayed fluorescence (TADF). To realize high TADF efficiency, we need materials that have a small energy gap between $S_1$ and a triplet excited ($T_1$) levels ($\Delta E_{ST}$). $\Delta E_{ST}$ becomes smaller when the exchange energy that is overlapping between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is small. Therefore, the separation of the HOMO from the LUMO is crucial to enhance the up-conversion from $T_1$ to $S_1$ (RISC). Most recently, based on this conception, we developed a triazin derivative (PIC-TRZ) that realizes a small $\Delta E_{ST}$ of 0.1 eV and the OLED using PIC-TRZ for an emitting layer achieved a high external quantum efficiency of $\eta_{ext}=5.3\%$ that exceeds the theoretical limitation of $\eta_{ext}$ in conventional fluorescence OLEDs. In this study, to achieve higher EL efficiency using TADF, we developed a novel triazin derivative (PIC-TRZ2) having a nearly zero energy gap between $S_1$ and $T_1$, which was confirmed by the fact that fluorescence and phosphorescence spectra of PIC-TRZ2 shows exactly same 0-0 transition peak ($T=5K$). Furthermore, intense delayed fluorescence is confirmed in both the neat and a 6 wt%-PIC-TRZ2:1,3-bis(9-carbazoyl)benzene (m-CP) co-deposited film under photo-excitation at room temperature. In addition, the OLED using PIC-TRZ2 shows a high external quantum efficiency of $\eta_{ext}=7.9\%$ at 0.01 mA/cm² with delayed fluorescence.
LIST OF POSTERS

Day 1: 12th December 2011

(Odd Numbers)

1. Megumi Awata (Graduate School of Science and Technology, Keio University)
   An analysis of the correlation between the molecular structure of solvent and the mutual diffusion coefficient of solvent-polymer system

3. Yoshiki Mukawa (Graduate School of Science and Technology, Keio University)
   Optimization of the refractive index distribution of graded index polymer optical fiber by the coextrusion process

5. Yuji Kikukawa (Graduate School of Engineering, The University of Tokyo)
   Synthesis of Multinuclear-Zinc-Containing Polyoxometalates and Their Catalytic Properties

7. Yoshikazu Kumashiro (Institute of Advanced Biomedical Engineering and Science, Tokyo Women’s Medical University)
   Modulation of cell attachment and detachment on thermo-responsive polymeric surface

9. Takuma Yasuda (Department of Applied Molecular Science Division, Kyushu University, Center for Organic Photonics and Electronics Research)
   Development of Electro-Functional Octupolar π-Conjugated Liquid Crystals

11. Masaya Hirade (Center for Future Chemistry, Kyushu University)
    Small Molecular Photovoltaic Cells with Exciton Blocking Layer at Anode Interface for Improved Device Performance

13. Takehiko Ishii (Graduate School of Engineering, The University of Tokyo)
    Safe and effective gene delivery using spontaneously degradable engineered polyamino acid

15. Motoi Harada (Department of Organic and Polymeric Materials, Tokyo Institute of Technology)
    Regular undulation and polarization modulation on film surface of a planarly aligned SmC* polymer

17. Tao Wang (Université Paris-Sud)
    Electrical excitation of surface plasmons with the STM

19. Vasyl Shynkar (LPQM, Institut d’Alembert, Ecole Normale Supérieure de Cachan)
    Laser Induced pulsed Planck Imaging Microscopy

21. Elise Lepeltier (Université Paris-Sud, Châtenay-Malabry)
    Nanoassemblies of nucleoside analogues coupled to squalene and terpenes: Structural analysis

23. Amandine Bocheux (CEA)
    Local probe of the electronic properties in 3D self-assembled π-conjugated monolayers
25 : Rémi Métivier (PPSM, Institut d’Alembert, Ecole Normale Supérieure de Cachan)  
Photochromic nanomaterials: fabrication and photoswitching.

27 : Simona-Cristina Laza (Ecole Centrale, Châtenay-Malabry)  
Jeffamine induced self-assembly of gold nanorods

29 : Anu Singh (LPQM, Institut d’Alembert, Ecole Normale Supérieure de Cachan)  
Nonlinear optical properties of gold nanorods : the role of aspect ratio

31 : Xiao Wu (LPQM, Institut d’Alembert, Ecole Normale Supérieure de Cachan)  
UV beam-assisted efficient formation of surface relief grating on azobenzene polymers

33 : Camille Delezoide (LPQM, Institut d’Alembert, Ecole Normale Supérieure de Cachan)  
Label-free optofluidic biosensors based on polymeric microresonators

35 : Xuan Loc Le (LPQM, Institut d’Alembert, Ecole Normale Supérieure de Cachan)  
Fluorescent diamond nanoparticle, a stable marker for the functional study of dendritic spines of mouse cortical neurons in culture

37 : Radoslaw Kolkowski (LPQM, Institut d’Alembert, Ecole Normale Supérieure de Cachan)  
Semiconductor based nanoparticles for nanoscale NLO

39 : Gilles Clavier (PPSM, Institut d’Alembert, Ecole Normale Supérieure de Cachan)  
One-pot Synthesis of Pegylated Fluorescent Nanoparticles by RAFT Miniemulsion Polymerization using a Phase Inversion Process
LIST OF POSTERS

Day 2: 13th December 2011
(Even Numbers)

2: Sayaka Odajima (Graduate School of Science and Technology, Keio University)
Thermally Stable Graded Index Plastic Optical Fiber for In-Vehicle Network

4: Takahiro Kondo (Faculty of Pure and Applied Sciences, University of Tsukuba)
New insights into electronic structure of graphite-related materials in nano-scale probed with scanning tunneling microscope

6: Shintaro Itagaki (Graduate School of Engineering, The University of Tokyo)
Composites of Metal Nanoparticles and Heteropoly Acids for Reversible Hydrogen Storage as Protons and Electrons

8: Masamichi Nakayama (Institute of Advanced Biomedical Engineering and Science, Tokyo Women's Medical University)
Intelligent Nanomaterials Using Poly(N-isopropylacrylamide)-based Block Copolymers for Biomedical Applications

10: Kenichi Goushi (Center for Organic Photonics and Electronics Research, Kyushu University)
Organic light-emitting diodes using exciplex states to promote high reverse intersystem crossing efficiency

12: Kanjiro Miyata (Center for Disease Biology and Integrative Medicine, Graduate, School of Medicine, The University of Tokyo)
Design of Polymeric Nanocarriers for siRNA Delivery

14: Shiori Kihara (Department of Organic and Polymeric Materials, Tokyo Institute of Technology)
Spontaneous polarization ordering in nematic LC of polypeptide lyotropic solution.

16: Takayuki Sugiyama (Department of Organic and Polymeric Materials, Tokyo Institute of Technology)
Nematic-nematic phase separation from uniform nematic domain in polymer LC and low-molecular-weight LC mixture showing network lattice formation in pinning stage

18: Raphael Labruère (Institut Curie)
Branched self-immolative spacers for delay-controlled release of multiple substrates after photoactivation

20: Vasyl Shynkar (LPQM, Institut d'Alembert, Ecole Normale Supérieure de Cachan)
Nerve growth cones as sensing, amplifying and filtering modules: a single-molecule and microfluidic approach

22: Feriel Hamdi (SATIE, Institut d'Alembert, Ecole Normale Supérieure de Cachan)
Microtechnologies applied to the design of new tools for the cell therapies - electrofusion, nanoporation, cell sorting

26 : Marc Guillon (Université Paris V) Nanoscaled biological issues addressed with super-resolving STED microscopy

28 : Xiaoli Wang (Ecole Centrale, Châtenay-Malabry) Stationary and ultrafast transient optical responses of gold nanoparticle arrays

30 : Ludovic Caillat (Ecole Normale Supérieure de Chimie, Paris) Lanthanide doped functional nanoparticles for subdiffraction imaging and biophotonic labelling applications

32 : Qinggele Li (LPQM, Institut d'Alémber, Ecole Normale Supérieure de Cachan) Generation of sharper focal spot for super-resolution imaging and nanofabrication

34 : Sébastien Michel (LPQM, Institut d'Alémber, Ecole Normale Supérieure de Cachan) High-performance modulators for optical communications realized with a commercial side-chain DR1-PMMA electro-optic copolymer

36 : Marie-Pierre Adam (LPQM, Institut d'Alémber, Ecole Normale Supérieure de Cachan) STED superresolution fluorescence microscopy with NV color centers in diamond

38 : Fabien Boitier (LPQM, Institut d'Alémber, Ecole Normale Supérieure de Cachan) Femtosecond optical properties of two-dimensional layered perovskite semiconductors.

## Poster Abstract – № 1

An analysis of the correlation between the molecular structure of solvent and the mutual diffusion coefficient of solvent-polymer system

Megumi Awata, Makoto Asai, Azusa Inoue, Yasuhiro Koike

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Diffusion of a solvent in a polymer is one of the important phenomena in the industry. Recently, the phenomenon has been utilized as a method to produce a light-harvesting polymer such as a graded index plastic optical fiber (GI-POF). To fabricate a high-bandwidth GI-POF, it is necessary to optimize the refractive index profile within a core region of the GI-POF. In the coextrusion process, which has been proposed for mass production of GI-POF, the refractive index profile is formed using the polymer-solvent mutual diffusion in polymer melts. The refractive index profile can be controlled by adjusting the diffusion time and the diffusion temperature. We have reported that a molecular structure of a solvent significantly influenced on the refractive index profile. Therefore, there is a possibility that we control the refractive index profile by using a solvent with a molecular structure having a desired diffusion property. In this study, we investigated the influence of the molecular structure of solvent on diffusion in melted polymer doped with solvents. We measured the polymer-solvent mutual diffusion coefficients using various solvents and polymers. There was a apparent distinction between the mutual diffusion coefficients of melted polymethyl methacrylate (PMMA) doped with diphenyl sulfide (DPS), that of melted PMMA doped with dibenzothiophene (DBT) and that of melted PMMA doped with Diphenyl methane (DPM). From the results, we clarified that the mutual diffusion coefficient of solvent-PMMA system at melt state is influenced by the molecular structure, especially the rotation of the benzene ring within the molecule significantly. It is also discussed in the other polymer matrix.

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The purpose of this work is to fabricate a thermally stable GI POF for in-vehicle network. As novel base material of GI POF with high thermal stability, we selected poly(dicyclopentanyl methacrylate) (PDCPMA) with bulky side chain. We have successfully obtained the high $T_g$, high bandwidth and low loss PDCPMA-based GI POF. The measured $T_g$ at the core center in the PDCPMA based GI POF is 107 °C which is higher than that (90 °C) of PMMA based GI POF. The measured attenuation at 650-680 nm was less than 400 dB/km required for in-vehicle network. Moreover, the measured bandwidth of the PDCPMA based GI POF was 2.26 GHz for 18 m, high enough to enable a 1 Gbps transmission. We will discuss the attenuation increment of the GI POF during aging at 85 °C in details at the conference.

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Optimization of the refractive index distribution of graded index polymer optical fiber by the coextrusion process

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The graded index polymer optical fiber (GI POF) is a promising candidate for high speed communication medium for very short reach networks such as home networks and office local area networks. In order to maximize the bandwidth properties of GI POF, it is important to control the refractive index distribution of GI POF accurately. Recently, the coextrusion process has been proposed for mass production of GI POF. In this process, the forming process of refractive index distribution is expressed by the advection-diffusion equation which considers the dopant diffusion to the radial direction of fiber and polymer advection along the long axis of the fiber. Therefore, we investigated the general methodology to control refractive index profiles by numerically solving the advection-diffusion equation. Furthermore, poly(2,2,2-Trifluoroethyl Methacrylate) based GI POF with optimal refractive index distribution was fabricated by the coextrusion process.


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New insights into electronic structure of graphite-related materials in nano-scale probed with scanning tunneling microscope

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The physical and chemical properties of graphite-related materials such as carbon-nanotube, graphene and graphite are known to be significantly changed by the modification of its electronic structure and thus these materials have a large potential as the next-generation materials. Here, we report significant changes of the local electronic structure of the graphite surface (HOPG, Highly oriented pyrolytic graphite) induced by the nitrogen-doping, vacancy introduction, and potassium intercalation at the atomic resolution based on the measurements with the low-temperature scanning tunneling microscope (STM). In each case, local density of states near the Fermi level of graphite were found to be changed to appear the non-bonding electronic states and/or Landau levels even without external magnetic field.
Synthesis of Multinuclear-Zinc-Containing Polyoxometalates and Their Catalytic Properties

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Polyoxometalates are a large family of nanosized anionic metal–oxygen clusters of early transition metals and have a diverse range of applications such as catalysis, magnetism, biology, medicine, and material science. Since the synthesis of the divacant [γ-SiW_{10}O_{36}]^{8−} (SiW10) was reported,[1] SiW10 has been utilized as a "macroligand" to encapsulate multinuclear metal–oxygen cluster cores.

TBA_{4}H_{4}[γ-SiW_{10}O_{36}] (TBA-SiW10) (TBA = tetra-n-butylammonium) reacted with Zn(acac)_{2} (acac = acetylacetonato) in acetone to form a novel sandwich-type silicotungstate TBA_{4}[{Zn(OH)_{2}}(μ_{3}-OH)]_{2}[{Zn(OH)_{2}}_{2}](μ-HSiW_{10}O_{36})_{2}]·9H_{2}O (γ-Zn4).[2] Compound γ-Zn4 was built up of two SiW10 subunits sandwiching the tetranuclear zinc–oxygen cluster core [{Zn(OH)_{2}}(μ_{3}-OH)]_{2}[{Zn(OH)_{2}}_{2}]^{6+}. Also, TBA_{6}[{Zn}_{2}W(O)_{3}O_{5}]_{2}H_{4}(α-SiW_{9}O_{33})_{2}]·5H_{2}O (α-Zn4) and TBA_{6}[{Zn}_{2}W(O)_{3}O_{5}]_{2}H_{4}(β-SiW_{9}O_{33})_{2}]·7H_{2}O (β-Zn4) were synthesized by the solid-state thermally induced isomerization of γ-Zn4.[3] Compounds α-Zn4 and β-Zn4 consisted of two [SiW_{9}O_{33}]^{8−} subunits sandwiching the unprecedented distorted hexaprismane core [{Zn}_{2}W(O)_{3}O_{5}]^{7+}. The H_{2}O_{2}-based oxidation of secondary alcohols with these zinc-containing silicotungstates efficiently proceeded, and the activity and chemoselectivity were much different from those of tungsten-based catalysts including TBA-SiW10.

Figure 1. Polyhedral and ball-and-stick representations of the anion parts of (a) γ-Zn4, (b) α-Zn4, and (c) β-Zn4.

**Composites of Metal Nanoparticles and Heteropoly Acids for Reversible Hydrogen Storage as Protons and Electrons**

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Composites of metal nanoparticles and heteropoly acids (metal/HPAs) could store hydrogen (H$_2$) under ambient conditions ($P_{H_2} = 40$ kPa and $T = 308$ K). The H$_2$ storage rates increased in the order of Au/SiW < Ru/SiW < Pd/SiW < Rh/SiW < Ir/SiW < Pt/SiW ($SiW: H_4SiW_{12}O_{40}$) in accord with that of dissociative chemisorption energies of H$_2$ on the corresponding metals. The order of the amounts of H$_2$ stored in Pt/HPAs accords to that of the redox potentials of HPAs. The amount of H$_2$ stored in Pt/SiW was 0.46 mol mol$^{-1}$, and H$_2$ stored in the composite could quantitatively be released as H$_2$ without formation of H$_2$O. This is likely due to the redox potential of SiW located around 0 V (vs. NHE). The H$_2$ storage-release cycles with Pt/SiW could be repeated at least six times without an appreciable loss of its performance. The phase and the lattice constant of Pt/SiW as well as the Keggin structure of SiW were completely retained during the storage-release cycles. It was confirmed by UV/Vis and IR spectroscopy that H$_2$ is stored in SiW as protons and electrons.


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**Figure 1.**

a) Repeated H$_2$ storage-release performance of Pt/SiW and b) pictures of Pt/SiW and H$_2$ stored Pt/SiW (Pt/SiW-H$_2$).
Modulation of cell attachment and detachment on thermo-responsive polymeric surface

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Thermo-responsive polymeric surfaces can allow adhered cells and cell sheet to be spontaneously recovered by lowering temperature without proteolytic enzymes. In this study, hydrophilic thready micro-patterns were immobilized on the thermo-responsive surface for controlling a cell adhesion and proliferation. The following two studies using the patterned surface will be presented: (1) an acceleration of cell sheet fabrication, and (2) cell attachment and detachment control on the patterned surface for cell separation. In the first study, 3T3 cells adhered and proliferated at 37 ºC until confluent cell sheet on the patterned surface as well as the conventional thermo-responsive surface. The rate of 3T3 cell sheet detachment on the patterned surface after lowering temperature was approximately five times accelerated than that on the conventional thermo-responsive surface. In the second study, 3T3 cells, human umbilical vein endothelial cells (HUVEC), and HeLa cells were used for controlling the cell attachment and detachment. adhered 3T3 cells spontaneously detached themselves on the patterned surface after reducing temperature as mentioned above. On the other hand, HUVECs adhered on the patterned surface until 12 h incubation at 37 ºC, but the adhered HUVECs spontaneously detached themselves through the next 12 h incubation at 37 ºC. In addition, the attachment of HeLa cells was hardly observed on the patterned surface. Based on these results, we developed cell separation system using the patterned surface without any labels. In conclusion, the patterned surface in this study has a potential for breakthrough in the next generation of biomaterials.
Intelligent Nanomaterials Using Poly(N-isopropylacrylamide)-based Block Copolymers for Biomedical Applications

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Amphiphilic block copolymers are known to form nano-scaled multi-molecular assemblies (e.g., polymeric micelle) in aqueous media or phase-separated domains on solid interfaces. These unique polymer-based nanomaterials are utilized biomedical applications in biomaterial and drug delivery fields. Herein, thermoresponsive poly(N-isopropylacrylamide) (PIPAAm)-based block copolymers were applied for creating intelligent nanomaterials to control temperature-induced interactions with cells. First, thermoresponsive polymeric micelles as the tools of intracellular drug delivery were designed to achieve thermally induced cell adhesion and subsequent intracellular uptake by temperature changes across the lower critical solution temperature (LCST) of PIPAAm-based outer coronas. Second, thermoresponsive surfaces were prepared via a spin coating method with PIPAAm-based block copolymers on polystyrene substrates. Thermoresponsive polymer coated surfaces were optimized to regulate cellular adhesion/detachment by temperature changes across the LCST. Consequently, thermoresponsive surfaces were achieved to harvest contiguous sheet-like cellular structures, “cell sheets”, with their basal extracellular matrix proteins.

Poster Abstract – Nº 9

Development of Electro-Functional Octupolar π-Conjugated Liquid Crystals

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Liquid crystals are unique soft materials that combine molecular order and fluidity. Use of specific liquid-crystalline (LC) nanostructures has recently attracted much attention for the fabrication of electronic and optoelectronic functional molecular assemblies. Herein, we present experimental studies toward the realization of ambipolar conductive columnar materials by one-dimensional (1D) self-organization of octupolar π-conjugated LC molecules.

We have designed and synthesized a new series of propeller-shaped octupolar π-conjugated molecules, in which 3-fold electron-donating arms are attached to the electron-accepting triazine core. This molecular design offers a possibility for the donor and acceptor electron-active constituents to stack individually in coaxial concentric shells to provide 1D hole and electron transport pathways in the columnar nanostructures. Time-of-flight measurements have revealed that the octupolar materials are indeed capable of transporting both holes and electrons in the columnar LC phases. Moreover, it has been found that the transport of electrons is more than 100-times faster than that of holes. The desirable electronic structures responsible for ambipolar properties have been studied.

Poster Abstract – Nº 10
Organic light-emitting diodes using exciplex states to promote high reverse intersystem crossing efficiency

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We demonstrate that organic donor and acceptor interfaces give rise to a small energy gap between the singlet and triplet exciton levels ($\Delta E_{ST}$) of generated exciplexes. $\Delta E_{ST}$ can be determined from the exchange energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in a molecule, which is decreases exponentially with increasing the HOMO–LUMO separation distance. The exciplex is a well known electron transition from the LUMO of an acceptor to the HOMO of a donor. The electron-hole separation distance corresponds exactly to the distance between the donor and acceptor molecules, because the HOMO and the LUMO in exciplexes are mainly located on the donor and acceptor molecules, respectively. Therefore, the intermolecular excited states should provide a smaller exchange energy compared to that of intra-molecular excited states, resulting in the triplet levels being very close to the singlet levels. Our observations show that a high reverse intersystem crossing (ISC) efficiency of 86.5% can be realized using exciplexes, which leads to high efficiency for radiative-exciton production through a singlet excited state. By taking advantage of the highly efficient reverse ISC, we demonstrate a pronounced enhancement of electroluminescence efficiency under electrical excitation.
Small Molecular Organic Photovoltaic Cells with Exciton Blocking Layer at Anode Interface for Improved Device Performance

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To enhance the device performance of organic photovoltaic (OPV) cells, prevention of exciton quenching at metal electrodes is an important issue, and recent conventional OPV cells have used an exciton blocking layer (ExBL) such as bathocuproine (BCP) at acceptor/cathode interfaces to prevent exciton quenching. For the anode/donor interfaces, many materials have been used as an anodic buffer layer. In particular, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has been commonly used as an anodic buffer layer, while the PEDOT:PSS layer is well-known as an exciton quencher. In this study, we introduced an ExBL into an anode/donor interface, resulting in a significant enhancement of power conversion efficiency ($\eta_{PCE}$).

We fabricated a device, with a structure of ITO/PEDOT:PSS/tris[4-(5-phenylthiophen-2-yl)phenyl]amine (TPTPA, X nm)/tetraphenyldibenzo[π]periflanthene (DBP, 20-X nm)/C₆₀ (50 nm)/BCP (10 nm)/Al (100 nm). The reference device (X = 0 nm) showed short circuit current density ($J_{SC}$) of -5.61±0.08 mA/cm², $V_{OC}$ of 0.92±0.01 V, fill factor (FF) of 0.72±0.01, and $\eta_{PCE}$ of 3.88±0.06%. The enhancements of $J_{SC}$ and $\eta_{PCE}$ were achieved by inserting a TPTPA layer, and the device performance was gradually enhanced with increasing thickness of the TPTPA layer. In particular, a device with a 10 nm-thick TPTPA layer showed the maximum OPV performance with $J_{SC}$ = -7.15±0.25 mA/cm², $V_{OC}$ = 0.93±0.01 V, FF = 0.74±0.03, and $\eta_{PCE}$ = 5.04±0.21%, with the best $\eta_{PCE}$ value of 5.25%. From the action spectra, we observed that the incident photon to current efficiency (IPCE) around 500–600 nm, corresponding to the absorption region of the DBP layer, was enhanced by inserting the TPTPA layer. To estimate the exciton blocking effect of the 10 nm-thick TPTPA layer, we compared the photoluminescence (PL) intensity of the DBP layer deposited on a TPTPA layer with and without a PEDOT:PSS layer. Here, we obtained almost the same PL intensities between these two samples, indicating that the 10 nm-thick TPTPA layer completely suppressed exciton quenching against a PEDOT:PSS layer. From these results, we conclude the combination of the exciton blocking and the exciton confinement into a thin DBP layer by a TPTPA layer effectively enhanced the device performance.
Design of Polymeric Nanocarriers for siRNA Delivery

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Small interfering RNA (siRNA)\textsuperscript{1} has been attracting a great deal of interest as a novel genetic drug, because it can induce the sequence-specific, strong gene silencing, i.e., mRNA degradation, in the cytosol, based on the RNA interference (RNAi)\textsuperscript{2} mechanism. Toward clinical applications of siRNA, a variety of siRNA carriers have been developed for delivery into the cytosol of target cells. Nevertheless, there are no clinically approved formulations of siRNA therapeutics so far, due to the insufficient delivery efficiency. In the present study, cationic poly(amino acid) derivatives are synthesized and then applied for construction of polyion complexes (PICs) with siRNA for successful siRNA delivery. Especially, stabilization approaches of siRNA PICs are explored by fine-tuning the structures of cationic poly(amino acid)s\textsuperscript{3,4} as well as siRNA\textsuperscript{5}, because high complex stability is intensely needed for protection of siRNA from enzymatic degradation and also for enhanced cellular uptake of siRNA under harsh in vivo conditions.

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Safe and effective gene delivery using spontaneously degradable engineered polyamino acid.

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Gene delivery using cationic polymers has attracted much attention due to their potential advantages such as capability of plasmid DNA (pDNA) condensation, ease of large-scale production, and reduced immunogenicity. Recently, we reported that polyplexes from poly[N-[N’-(2-aminoethyl)-2-aminoethyl]aspartamide](PAsp(DET)) consist of biocompatible polyamino acid backbone and flanking ethylenediamine units in the side chain introduce transgenes efficiently with minimal toxicity, resulting successful safe gene transfection in animal models. We revealed that the pH-selective cellular membrane destabilization caused by PAsp(DET) plays a key role of efficient endosomal escape of the polyplex into the cytoplasm. Very recently, we additionally found that a kind of polyaspartamide including PAsp(DET) showed non-enzymatic and spontaneous degradation even in physiological buffer solution. The unique degradation was specifically observed in the combination of polyasparagine backbone and specified side-chain structure, in which the degradation velocity was strongly dependent with the side-chain structure. The acute toxicity issue of polycations has often been taken up in this field. However, cumulative toxicity of the polycations after transfection is another point of regard. Here we focused on that the biodegradable nature of PAsp(DET) surely contributes to safe gene transfections. we would represent the unique self-degradation mechanism and the advantage of spontaneously biodegradable PAsp(DET) by the result of sustained in vitro transgene expression, cellular homeostasis, cytotoxicity, and in vivo cytokine induction by comparison with non- (or less-) degradable polycations.

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### Spontaneous polarization ordering in nematic LC of polypeptide lyotropic solution

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Polypeptides and aromatic polyesters are known to possess a huge dipole moment along the polymer chain as a result of the accumulation of carbonyl dipole. Because of such a polar rod-like conformation, these materials can spontaneously form polar nematic liquid crystal (LC). In this study, we investigated the second harmonic generation (SHG) response from lyotropic LC solutions of poly (γ-phenyl alkyl glutamate) racemic mixtures using benzyl alcohol as the solvent. Here, poly (γ-phenyl alkyl glutamate)s are denoted as nPG, where n is corresponding to the outer alkyl carbon number as shown in Figure. The LC solution of nPG exhibited a polar-to-nonpolar nematic transition upon increasing the temperature. Polar-to-nonpolar nematic transition temperature, $T_c$, depended on the molecular weight of nPG, the concentration of the LC solution and the outer alkyl carbon number, n.

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### Poster Abstract – № 15

**Regular undulation and polarization modulation on the film surface of a planarly aligned SmC* polymer**

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Chiral smectic C (SmC*) in a main-chain type polymer exhibits undulations on its glassy film surface; these undulations are produced by the helical assembly of constituent polymer conforming SmC* structure. In this study, we have observed clear surface morphology of SmC* film by atomic force microscopy (AFM) image and confirmed that the repeating length (ranges in 200 – 700 nm) in AFM corresponds to the helical pitch of SmC*. This modulation is caused by the spontaneous polarization of each smectic layer; its direction is parallel to the layer and perpendicular to the tilt direction of molecules within a layer, and rotates around the helical axis. By clarifying the relative direction of the spontaneous polarization to the tilt direction of mesogens, we described how the polymers are accommodated to produce such a regular undulation and polarization modulation.
Nematic–nematic phase separation from uniform nematic domain in polymer LC and low-molecular-weight LC mixture showing network lattice formation in pinning stage

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In this study, we investigated the LC/LC phase separation dynamics from the uniformly aligned nematic phase. The phase separation proceeded in three stages in the following order; the early spinodal decomposition (SD) stage, later SD stage and pinning stage. In the final pinning stage, an ordered honeycomb network structure was formed wherein the low-molecular-weight LC-rich phases were accommodated within hollow microcells of the polymer LC-rich phase. The size of the network lattice was varied from 2 to 8μm by varying the weight fraction of the mixtures and the decomposition temperature.
Electrical excitation of propagating surface plasmons with a scanning tunneling microscope (STM)

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Surface plasmon light emission from noble metal surfaces stimulated by a STM tip has been studied in the past several decades. This light emission phenomenon is believed to be due to the inelastic tunneling of the electrons between the STM tip and the sample surface [1]. Electrical excitation of propagating SPP, using inelastic electron tunneling from the tip of a STM would have unique advantages such as very local excitation down to picometer scale [2] and no background light from the excitation source. By combining a STM with an inverted optical microscope in a controlled atmosphere, we successfully excited propagating surface plasmons on a thin gold film deposited on glass substrate with a STM tip and detected it by leakage radiation microscopy in the image plane and the Fourier plane [3]. We also checked the spectra of the surface plasmons. This technique can be easily transformed to other nanostructures (such as nanowires, nanoparticles, nanoholes and so on) to examine their surface plasmons properties very locally. This technique also give us an opportunity to find a bridge between nano-electronics and nano-optics.

References
Poster Abstract – N° 18

Branched self-immolative spacers for delay-controlled release of multiple substrates after photoactivation

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Controlling gene expression in space and time is a much sought after goal in biology. Inducible gene expression systems have been used but they remain limited by the technology associated to the inducer delivery. Ideally, the latter should be noninvasive, fast, local, and tunable. We want to implement a technology fulfilling all those criteria. It makes use of light to release a biologically active inducer upon photoactivation of a non-active precursor distributed in the organism after appropriate conditioning. This technology is based on self-immolative spacers that rely on an elimination reaction involving electron reorganization on an aromatic ring. In this model studies, light is used both to initiate the activation of spacer self-immolation and to observe the progress of the elimination leading to the release of fluorescent reporters. In this poster, we will present the synthesis and the kinetic study of a spacer releasing two reporters.

Poster Abstract – N° 19

Laser Induced pulsed Planck Imaging Microscopy

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Synthetic probes and endogeneous chromophores have long history of use in optical microscopy. However, very low quantum yield absorbers that are prevalent among endogenous chromophores typically undergo fast non-radiative decays, thus, limiting their use due to poor sensitivity of measurements. One recent solution proposed to use stimulated emission microscopy based on the fact that stimulated emission can be fast enough to compete with such non-radiative decays. Here, we demonstrate a much simpler strategy that we term Laser-Induced pulsed Planck Imaging Microscopy (LIPIM). In this approach, the absorption of a short light pulses by sub-microscopic absorbers leads to the emission of sub-microsecond thermal Planck light pulses that can be used in microscopy. We demonstrate the possibility of generating with organic probes such stable visible spectrum Planck pulses, having controlled optical temperature and spectral characteristics. A theoretical model of heat dynamics is proposed to support our observation that such pulsed heat emission does not destroy the sub-microscopic absorbers. We demonstrate a first application of LIPIM using scanning as well as wide-field microscopy for imaging of potential precursors of melanoma metastasis in tissue or blood samples.
### Poster Abstract – N° 20

**Nerve growth cones as sensing, amplifying and filtering modules:**

**a single-molecule and microfluidic approach.**

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In the last twenty years an important effort has permitted the identification a number of molecules involved in GC motility and signalling, but the detailed description of the protein network involved in neuronal response is still to be done. Precise characterization of the temporal and spatial dynamics of this protein network is crucial for understanding essential aspects of the chemotaxis of cellular system, such as the sensitivity to weak signals (often below 1-2% on cellular scale) and adaptation needed to answer on a large range of signal concentration. Our study of the GC response to GABA attractive signal demonstrated the existence of amplification mechanism relying on the formation of polarity at the GC membrane [1]. To address questions on gradient sensing, its amplification and filtering, we developed a new approach combining guidance cue gradient formation with single molecule imaging technique of the GABA receptors labelled by quantum dots (QD) (Figure 1). A classical micropipette-based gradient formation technique was substituted with a microfluidic device, which permits the quantitative study of the response of many growth cones under well-controlled stimulation. For that purpose, we developed a new approach to microchannel fabrication by soft-lithography method: sticking the microchannel onto glass coverslip with cells cultured on it [2]. The advantage of the proposed technique is that it eliminates the need of culturing cells in closed microcircuits. Further working on the GABA gradient stability for GC stimulation in the microchannel, we built a new two-compartment microfluidic device with introduced compartment separating membrane. This notion permits to create a stable guidance cue gradient during many hours, to have an easy pressure control by external controller, and what is more important, to avoid the pressure created by flow. We took advantage of this new device to determine the amplification and filtering response of nerve GCs during GABA directional sensing. By measuring the polarization of GABAA receptors at the GC membrane, we found that: (i) GCs are able to non-adaptively amplify external gradients, with a dependence on the ligand concentration determined by the saturable response of chemoreceptors, (ii) GCs act as low-pass temporal filters with a cut-off frequency independent of stimuli conditions. Furthermore, we used computational modelling of the receptor lateral dynamics and activation to quantitatively explain our experimental findings. Thereby, we directly bridge the gap between the properties of signalling molecules and the systems level behaviour. The optical and microfluidic techniques used in our assay should be of great interest for a large majority of research group interested in axonal guidance and chemotaxis, as it opens new prospects for the study of the GC response to complex patterns of one or multiple cues.

References:

Prodrugs are pharmacologically inactive compounds that yield therapeutically active metabolites upon exposure to the biological environment. When prodrugs self-organize in nanoparticles, their supramolecular structure is expected to be an important parameter for the pharmacological efficacy of the drug delivery system.

In this context, *squalenoylation* is an original and promising concept to design new nanomedicines. It consists in linking squalene (a natural lipid, precursor of cholesterol’s biosynthesis) to a polar drug in order to obtain an amphiphilic compound able to spontaneously give rise to nanoassemblies in water. It has been previously shown that the squalenoyl prodrug of Gemcitabine, an anticancer nucleoside analogue, displayed higher anticancer activity than gemcitabine against various leukemia and pancreatic cancer models. Remarkably, this compound self-organized in water as nanoassemblies exhibiting a reverse hexagonal structure [1].

In the present study, different nucleoside analogues (thymidine, inosine…) have been covalently coupled with squalene and then to terpenoids of different lengths (farnesyl, geranyl…) to determine the influence of the nature of the nucleoside and of the hydrophobic chain on the supramolecular organization of the nanoassemblies. Structures have been characterized using small and wide angles X-ray diffraction and electronic microscopy (cryo-TEM). A diversity of structures was observed, depending both on the polar headgroup and on the hydrophobic tail which clearly affected the packing parameter.

References:

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Microtechnologies applied to the design of new tools for the cell therapies - electrofusion, nanoporation, cell sorting

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The application of an electric field on living cells allows the handling or the treatment of cells or cell components. It is indeed possible to trap or move a cell thanks to DiElectroPhoresis force, or to permeabilize the cell membrane thanks to pulses of electric field. Micro and nanotechnologies, permit the fabrication of cell biochips that allow to envision the application of extreme fields or extreme field gradients. Two applications are developed:

Cell Electrofusion: the topology and time sequencing of the electrical field can permit to force the contact between two cells and the fusion of their cytoplasmic membrane. This might have important application for instance for the immunotherapy of cancer, where dendritic cells have to be fused with cancerous cells for the reactivation of the immune system. We work on the design and fabrication of biochips that will permit to optimize the electrofusion.

Nanoporation: while electric pulses of few microseconds duration and around 1 kV/cm ("micropulses") permit the poration of the cytoplasmic membrane of cells, shorter pulses (few nanoseconds) with higher amplitude (up to 200 kV/cm) permit to affect the intracellular membranes. We work on the design and fabrication of biochips that are capable to deliver these nanopulses.

Acknowledgement
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Local probe of the electronic properties in 3D self-assembled pi-conjugated monolayers

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Self-assembly of linear π-conjugated molecules, having mutual non-covalent interactions, is of particular interest for the patterning of surfaces at the molecular level [1]. Not only these planar structures can lead to quite complex lateral organizations, but their three-dimensional derivatives also pave the way towards different applications such as molecular sieving or single-molecule electronic or photonic devices relying on functionalized moieties decoupled from their metallic substrates [2].

To this aim, we have studied the self-assembly of different conjugated molecules forming three-dimensional architectures simultaneously with the resulting local electronic properties by Scanning Tunneling Microscopy at the solid-liquid interface at room temperature. Beyond the self-organization aspects, we have evidenced some specific electronic properties directly linked to the 3D nature, by scanning synchronously samples at different tunnel biases.

First, regioregular poly(3-alkylthiophenes) have been deposited on HOPG. They form a 2D well organized lamellar structure with 3-fold oriented monodomains in which the orientation of the alkyl chains is tilted compared to the one of the conjugated backbone [3]. Depending on the experimental conditions and on the polymer structure, a second layer can be formed. Thanks to the simultaneous scanning at different biases, electron tunneling responses specific to the second layer has been evidenced and analyzed.

Second, intrinsically multistory tectons based on [2.2]paracyclophane pillars have been employed to obtain a 3D structure. In this example, the first level ensures a stable lateral organization on HOPG [4], whereas the upper level permits the introduction of various functional moieties. Through bias-dependent imaging, distinct behaviours have been detected which are now linked to their 3D intramolecular structure and more specifically to the electronic couplings between the benzyl rings forming the pillar structure.

References
Photophysical studies of nanoscale properties of hybrid solar cells materials


In the frame of the MYOSOTIS project granted by the ANR, we study the photophysical properties of the different constituents of organic solar material. Samples* are composed of an intimate mixture of P3HT, a photo-conducting polymer, and CdSe nano-particles of different shapes and surface functionalization. A photo-induced charge separation occurs at the frontiers of the two materials. In our team, we monitor the efficiency of the charge separation from a loss of this process: the remaining luminescence that arises from a part of the solar energy that is not converted to separate charges.

The goal is to cross-correlate the optical properties (absorption, luminescence yield,...) with the structural and chemical properties of the sample: i.e. correlate the emission yield with the degree of crystallinity of the P3HT measured from its dichroism; with the doping level measured from a specific absorption of the CdSe nano-particles; and with the coupling between the two phases measured from the fluorescence lifetime of the Qdots.

The research topic of our team relies on the study of luminescent sample via advanced and under-development microscopy techniques. In addition to the spectrum, the intensity, the fluorescence lifetime and their temporal dynamics will be studied to gain valuable information on the interactions between molecule/nanoparticle and P3HT fibers or films. The studies of samples of different composition, growth and preparation procedures were conducted at ambient and low temperatures by using not only conventional spectrometers but also on our optical microscope that enables traditional characterizations together with wide-field lifetime imaging (fluorescence imaging and FLIM) and AFM, conducting to at least 4 different possible types of quantitative imaging modes. The challenge is to scout the limits and potentialities of the quantitative measurements of absorbance, dichroism and fluorescence in imaging mode under a microscope. The protocols for these measurements and the image processing software have been on purpose validated and optimized.

*: collaboration SPrAM-CEA Grenoble and ICS Strasbourg where the samples are prepared.
The development of novel optical devices, such as light-driven optical memories or biocompatible nanophotoswitches, attracts considerable interest in the growing field of cutting-edge technologies involving nanomaterials. We report here on the design of photoswitchable organic or hybrid nanomaterials, and a wide variety of fabrication methods to produce original and efficient light-triggered nanodevices.

First, nanorods of a photochromic salicylidene-aniline derivative were obtained by the laser ablation technique.[1] Particle size and distribution can be varied by changing the laser fluence and exposure time. Interestingly, these nanorods exhibit second harmonic generation properties and show reversible photoswitching associated with intermediate rate of thermal back reaction compared to solution and bulk solid.[2]

As a second example, light-induced self-assembled nanorods and nanowires of a simple dithienylethene derivative were obtained under UV light irradiation in aqueous dispersion and redissolved under green light. Reversible and fatigue-resistant optical switching in the nanoparticle state was demonstrated.[3]

A third example consists of photoswitchable fluorescent organic nanoparticles, based on a molecular compound bearing fluorescent and photochromic moieties, which were successfully obtained by the reprecipitation method. The emission intensity can be reversibly switched ON and OFF by light irradiation and intermolecular energy transfer was shown to be responsible for a considerable amplification effect of the quenching process.[4]

A last family of hybrid nanosystems involving silica nanobeads and core-shell gold nanorods covered by a thin silica layer was fabricated. Photochromic and fluorescent dyes were chemically grafted on the surface. Extensive spectroscopic studies reveal the unique and efficient interplay between photochromic, fluorescent, and plasmonic subunits at the nanoscale.

References:
**Poster Abstract – N° 26**

**Super-resolution STED microscopy**

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Fast stimulated emission depletion (STED) microscopy allows imaging in living cells with a temporal resolution of 35ms and a spatial resolution of about 60nm. It is envisaged here to upgrade our STED microscope to beam scanning to allow such fast scanning and in vivo imaging. Furthermore we are going to implement two color channels. Several collaborations with scientists interested in various biological questions were started.
Jeffamine induced self-assembly of gold nanorods

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The self-assembling of metallic nanoparticles functionalized with stimuli-responsive molecules became in the last years one of the main research themes in the field of nanotechnology. The increasing interest in the self-assembling of such nano-hybrids is due to its potential use in the construction of functional nano/micro-systems for sensing, photonics, biomolecular electronics, etc¹.

One of the main factors determining the final geometry of the resulting assembly is the nanoparticle's shape. In present, between the anisotropic metallic nanoparticles, there is considerable interest for gold nanorods (GNRs) due to their potential for bidirectional ordering². Moreover, the two plasmon resonances of the GNRs together with their capability for the light-heat conversion make them good candidates to be used as optically controlled nanometric heat sources³.

This work presents our results concerning the directed self-assembly of GNRs by functionalization with a thermo-responsive polymer⁴. Our findings show that the modification of the nanorods ends with amino-terminated poly(EOx-st-POy) Jeffamine lead to the selfassembling of GNRs into long one-dimensional nanostructures.

Figure 1 Nanorods chain obtained by self-assembly of GNRs functionalized with poly(EOx-st-POy) Jeffamine.

References:
Stationary and ultrafast transient optical responses of gold nanoparticle arrays

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Noble metals confined at the nanoscale exhibit the well known localized Surface Plasmon Resonance associated with the enhancement of the local electromagnetic field in the particles. The plasmon resonance is very sensitive to the shape, size and spatial arrangement of the particles, which may influence the spectral position, width and amplitude of the resonant absorption. Besides, the inter-particle electromagnetic coupling also plays an important role, so the nanoparticle aggregates with controllable dimensions have attracted great interest.

We have studied experimentally and theoretically plasmon coupling effects in ordered 50-nm gold nanoparticle arrays with different inter-particle distances. This study shows that the plasmon band red-shifts and the volumic absorption at resonance decrease when the inter-particle distance in the direction parallel to the incident field polarization decrease; the plasmon band blue-shifts and the volumic absorption at resonance decreases when the inter-particle distance in the orthogonal direction decreases. At last, the ultrafast transient optical responses of the arrays are shown and analyzed.

References

Nonlinear optical properties of gold nanorods: the role of aspect ratio

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Among novel research orientations in nonlinear nanophotonics, some of the most stimulating challenges are the development of efficient strategies for the investigation of metallic nanoparticles with strong surface plasmon resonances resulting in huge second harmonic emission in solution.

The SPR frequency depends not only on the metal, but also on the size and shape of the nanoparticle, the dielectric properties of the surrounding medium and inter-nanoparticle coupling interactions, thus imparting a unique tunability to the nanoparticle optical properties. Spherical Au nanospheres offer very limited tunability of their SPR frequency. Therefore, they are not suited for NIR applications. However, changing the shape of Au nanoparticles from spheres to rods results in the emergence of a new SPR band at longer wavelengths in addition to the plasmon band around 520 nm. This second mode arises from electron oscillation along the nanorod-long axis, its resonant wavelength displays a strong red shift with increasing aspect ratio thus allowing easy optical tunability in the desired NIR region.

In this work we explore the quadratic NLO properties in solution of very small gold nanoparticles with different shapes, ranging from spherical ones to nanorods with high aspect ratios. These particles are elaborated using an original synthesis method based on radiolysis, allowing a good control of the nanorod aspect ratio depending on the initial composition of the reacting medium. HLS measurements carried-out at 1.06 µm show high first-order hyperpolarizability (β) values for nanospheres and nanorods, with a significant enhancement of the quadratic NLO response when increasing the aspect ratio, for the same number of gold atoms. HLS depolarization factors D also display a strong dependence with the nanoparticle aspect ratio.

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Lanthanide doped functional nanoparticles for subdiffraction imaging and biophotonic labelling applications

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One the challenge of the 21st century is to understand the cellular machinery. The main problem is that diffraction limits the lateral resolution. For the first time, we propose the use of the up-conversion present Rare Earth doped nanoparticles to break the diffraction barrier. Rare Earth doped nanoparticles are recognized since few years as potential optical nanoprobes for biological imaging, due to their high photostability [1], well adapted for, long time observations and biocompatibility [2]. Another advantage concerns ability to convert near infra-red radiation into visible one, (depending on the dopants), allowing to improve the signal to noise ratio of images, to increase the tissue penetration, to suppress the problem due to photobleaching. The most efficient infra-red to visible up-conversion is achieved with Yb\(^{3+}\)- Er\(^{3+}\) as dopants which involves a two photons process, in this case, green and red emissions are obtained, while, Yb\(^{3+}\)-Tm\(^{3+}\) co-doping involves three and four photons processes leading to observe blue emissions under infra-red excitation. The intensity up-conversion varies as I_{exc}^n with the excitation power [3] (n being the process order i.e. the number of infra-red photons involved in the process). A reduction of the fluorescent spot size is expected due to the non linear by a factor compatible with the square root of the number of photons involved in the excitation process. As an example, for two-photons process observed with Yb\(^{3+}/\)Er\(^{3+}\) with only an power 10 µW as three photons and four photons process obtained under 20µW and 5µW respectively. The results of our experiments, conducted at room temperature, give evidence the enhancement of the lateral resolution, opening up, new possibilities, especially for a very low cost imagery with high resolution.

References
UV beam-assisted efficient formation of surface relief grating on azobenzene polymers

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Azobenzene-containing polymers attract much attention as materials for many applications such as holographic data storage, active waveguide and electro-optic modulator, as well as generation of new light wavelengths. Irradiation of thin azopolymer films with an interference pattern of coherent light can induce not only photoorientation of chromophores throughout the volume of the material (birefringence grating) but also a controlled modification of the film surface, called surface relief gratings (SRG). Such polymer-based SRGs are very useful for many interesting applications, such as DFB laser, functionalized grating, waveguide coupler, etc. In this work, we demonstrate a new technique to optimize the formation of SRGs. The method is based on the assisting of an UV beam (355 nm) on the cis-form to trans-form isomerization process, which allows to improve the SRG formation speed and quality. The effect of polarization of both writing (532 nm) and pumping (355 nm) beams were also investigated, and we found that the best SRG can be obtained when the polarization of the UV assisting beam is parallel to that of the writing beams. The SRG modulation depth is enhanced from several nanometers to several hundreds nanometers. This work is useful to understand the formation of the SRG on azobenzene polymer materials and is interesting for different applications as polymer-based photonic devices.
Optical microscope is an extremely important tool for many applications in different domains, including physics, biology, information storage, medical and material science. The key parameter of such instrument is the tightly focused optical spot owing to the use of a high numerical aperture (NA) objective lens (OL). In this work, we first theoretically investigated the intensity distribution of the focusing spot as a function of different parameters, such as NA of OL, polarization and intensity distribution of the input beam. These theoretical predictions were then compared and agreed well with the experimental results obtained by realizing fluorescent images of Gold nanoparticles, with different OLs. Furthermore, we demonstrated that the combination of an azimuthally (or radially) polarized laser beam with an amplitude or/and a vortex mask, allowed to reduce the focusing spot along lateral direction as the small size of 0.41λ, which is much smaller than the result obtained from the case of circular polarized light beam (0.54λ). These results are important and interesting for different applications, in particular for our related works such as optical data storage, nanoimaging and nanofabrication.
Vertically coupled polymer microresonators for optofluidic label-free biosensors

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Optofluidic label-free biochemical sensors integrating optical microresonators are highly attractive for real-time, high sensitivity detection of chemical or biochemical species. In this paper we report on the design and fabrication of polymeric microracetracks optical resonators for optofluidic label-free biosensing. In the domain of optical integrated devices, polymer materials offer the advantages of low cost, easy fabrication, low scattering loss on sidewalls of waveguides, and high coupling efficiency to optical fibres and waveguides. Moreover, for biochemical sensing, polymer surfaces can be easily modified to immobilize a wide choice of target molecules. Polymers are also well compatible with microfluidic circuits, facilitating the insertion of photonic circuits into optofluidic cells. The vertical coupling configuration, in which resonators are vertically coupled to the buried bus waveguide, presents several advantages in comparison with the lateral coupling configuration, particularly in the context of optofluidic biosensors. Polymeric microracetracks were fabricated using the SU-8 negative photoresist and the CYTOP fluorinated polymer, using a combination of a simple near UV lithography and reactive ion etching technology. Vertically coupled microracetracks immerged in deionized water display high Q-factors (> 35000) and finesse up to 25. Surface sensing experiments performed with these microresonators using TAMRA-cadaverine as a test molecule, which can be quantified through fluorescence and radioactivity analyses, demonstrated a very low detection limit of 0.22 attograms.
High-performance modulators for optical communications realized with a commercial side-chain DR1-PMMA electro-optic copolymer.

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Several high-performance polymeric electro-optic modulators have been demonstrated in the last decade. Most of them have been elaborated using specific electro-optic polymers designed for their exceptional electro-optic response and their thermal stability. However, these materials are not available yet as fully commercial products. We report the high performance of electro-optic modulators made of a commercial side-chain electro-optic copolymer DR1-PMMA as the active core material and of a passive epoxy polymer NOA73 as cladding material. The electro-optic polymer used in these modulators is a Disperse Red 1- poly-methyl-methacrylate (DR1-MMA) side-chain copolymer with relative molar concentrations of DR1-substituted (resp. MMA unsubstituted) groups equal to 30 % (resp. 70%). We have designed, elaborated and tested various modulator architectures, such as phase, conventional Mach-Zehnder, push-pull Mach-Zehnder and loop structure push-pull Mach-Zehnder modulators, in order to optimize their figure of merit $V_\pi L$ measured at the 1550 nm telecommunication wavelength. A push-pull Mach-Zehnder modulator with 2 cm-long electrodes and an inter-electrode distance of 8.8 µm displays a half-wave voltage of 1.92 V at 1550 nm, corresponding to a figure of merit of 3.84 V.cm. This result was obtained with a moderate poling electric field of 75 V/µm applied to the core of the modulator waveguide. We report here the best figure of merit that has ever been observed in a modulator realized with a commercial side-chain electro-optic polymer.
Fluorescent diamond nanoparticle, a stable marker for the functional study of dendritic spines of mouse cortical neurons in culture.

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Neurons display dendritic spines plasticity and morphology anomalies in numerous psychiatric and neurodegenerative diseases. These changes are associated to abnormal dendritic traffic that can be evidenced by fluorescence microscopy [1,2]. We use fluorescent diamond nanoparticles (fNDs) of size<50 nm to monitor this traffic.

Their fluorescence stems from embedded nitrogen-vacancy (NV) color centers, which are perfect photostable emitters, allowing for long-term cellular tracking [3]. It was shown that fNDs are spontaneously internalized by endocytosis [4] in various cell lines in culture and that their intracellular motion can be tracked on long-term scale [5].

Here we show that bare fNDs can be used to monitor dendritic traffic in mouse cortical neurons maintained in a primary culture.

The neurons are extracted from the cortex of mouse embryos (embryonic day 14), dissociated and incubated with a fNDs aqueous suspension. They are then placed in culture in LabTek dishes, and observed live about 24 hours after, using a home-made fluorescent microscope in a wide-field total internal reflection fluorescence (TIRF) configuration.

We recorded motion of fNDs along the dendrites proving that they are spontaneously taken in charge by molecular motors. We also transfected the cortical neurons to identify the compartments involved in this traffic.

References
The Nitrogen-Vacancy color center in diamond is a perfectly stable emitter in the red and near-infrared spectral region. It is perfectly suited for Stimulated Emission DEpletion microscopy (STED), a technique of microscopy below the diffraction limit and which requires a high power laser beam. The later usually yields to a rapid photobleaching of the dye, limiting the applications.

We build such a STED setup for NV center superresolution imaging, relying on the combination of continuous wave lasers (at 532 nm for the fluorescence excitation and at 735 nm for the stimulation). We will present raster scans of samples containing single emitter and displaying an optical resolution of 50 nm. We will use this setup to image the macromolecular organization in neuron dendritic spines to probe the synapse plasticity in the context of neuronal disorder.
Semiconductor based nanoparticles for nonlinear optics

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Nanoparticles exhibiting efficient non-resonant nonlinear optical properties such as second harmonic generation (SHG) have attracted considerable attention due to their potential applications in multiphoton microscopy. Their main advantages over classical fluorescent nanoprobes are: long-term photostability of the emission (no blinking), no saturation of the nonlinear response up to very high excitation power, ultrashort response time providing coherence with the incident optical field (hence - the possibility of the interferometric detection), and high sensitivity to the angle of incident beam polarization, which enables to probe the orientation of single nanoobjects. It has recently been demonstrated, that the orientation of crystal lattice of single CdTe/CdS core/shell quantum dots (QDs) [1] and CdTe/CdS rod-on-dot (RD) hybrids [2] can be efficiently determined based on the polarization response of the second-harmonic emission. In case of RD nanostructures, the measured polarization response exhibit mixed octupolar-dipolar character, which can be explained by a pointwise additive model of the second-order susceptibility tensors associated to the nanoparticle components. Based on this model, it is possible to decompose the polarization response into the contribution of CdTe, CdS and the interaction cross-term, which appears to be crucial for the resultant polarization response pattern as well as for the enhancement of SHG emission. Thanks to the small size (below 10 nm) of these semiconductor based nonlinear scatterers and their relatively strong second-harmonic signal, these nanostructures are highly promising candidates for multiphoton bioimaging.

References:
Ultrafast carrier dynamics in organic-inorganic perovskite quantum wells

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Optical properties of hybrid organic-inorganic materials have attracted much attention for years thanks to their potential applications in optoelectronics devices. The idea is to combine the properties both of inorganic materials (band engineering, high mobility) and of organic materials (low cost technology, high luminescence quantum yield at room temperature). In this context, organic-inorganic perovskites, having a chemical formula \((\text{R-NH}_3)\text{M}X_4\) where \(\text{R}\) is an organic chain, \(\text{M}\) is a metal and \(X\) a halogen, represent a natural hybrid system. When deposited by spin coating, the molecules self-organize to form a multiple quantum wells structure where excitons have binding energies of several hundreds of meV. The quantum wells luminescence is observed at room temperature, and its energy can be tuned from the UV to the visible simply by changing the chemical formula of the molecule [1]. This kind of perovskites has been studied both for applications in optoelectronics and for fundamental studies. For instance, it has been inserted in planar microcavities and the strong coupling regime has been achieved at room temperature [2-4]. In order to go further, a better understanding of the electronic structure of these quantum wells is necessary [5-6]. For instance, in a way to investigate stimulated processes in these microcavities, a good comprehension of excitonic interactions is needed. However, there is a lack of information on the dynamics and on the carrier interactions in these structures.

We present here preliminary results on the ultrafast carrier dynamics in \((\text{C}_6\text{H}_5\text{C}_2\text{H}_4-\text{NH}_3)\text{PbI}_4\) perovskite quantum wells. The exciton dynamics is investigated through a two colors femtosecond pump/probe experiment. The excitation is achieved thanks to the fourth harmonic of the idler of an OPA at 1kHz. The probe beam consists in a white light pulse. It allows to perform transient absorption spectra. The cross correlation of the pump and probe pulses at a given wavelength is of the order of 100 fs. In the small perturbation regime, a \(\sim 100\) ps relaxation time of the excitons is measured. By increasing the excitation density, both the dynamics and the transient spectra are modified showing a first evidence of carrier – carrier interactions in these quantum wells.

References
One-pot Synthesis of Pegylated Fluorescent Nanoparticles by RAFT Miniemulsion Polymerization using a Phase Inversion Process

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In the last decade, fluorescent nanoobjects have received increasing interest for their high potential in biology and biochemistry. They are especially attractive for sensing, imaging and biomedical applications. Recent works in controlled radical polymerization (CRP), allows the use of amphiphilic macromolecular RAFT agents and miniemulsion in order to both stabilise the nanoparticles and control the polymerisation of hydrophobic monomers.

Based on this methodology we developed a new strategy to design fluorescent nanoobjects where the fluorophore is copolymerised in the hydrophobic centre of the polymeric micelle. The approach to obtain fluorescent nanoparticles of well-defined chain lengths and sizes, via a miniemulsion process in water is based on a phase inversion, without the use of surfactants and hydrophobic cosolvent. In our study, we chose a hydrophilic PEO-b-PAA-TTC-C₁₂ (poly(ethylene oxide)-b-poly(acrylic acid)-trithiocarbonate) macroRAFT agent in order to reach pegylated biocompatible and pH-sensitive auto-stabilized fluorescent nanoparticles. It is used to control the copolymerization of styrene with a fluorescent BODIPY (BODPY-methacrylate, BDPMA) based monomer in miniémulsion (see scheme). BODPY was chosen as fluorophore since it exhibits attractive spectroscopic characteristics such as emission spectra tuneable from green to red and high fluorescence quantum yields.

The particles present a 60nm diameter and a narrow size distribution and are stable at pH>5. Their fluorescence colour is close to that of the monomer. Timed resolved fluorescence anisotropy reveals a fast interchromophore energy hoping. The presence of carboxylic groups at the exterior of the nanoobjects allows for their transformation into nanosensors by reaction with various molecules and macromolecules bearing an amine. The first results of such functionalisations with pH sensitive chromophores and proteins will be presented. The short distance between those peripheral groups and the hydrophobic heart of the nanoparticle allows for a modulation of fluorescence of the BODIPY by a FRET process which depends on the colour of the pH sensitive molecule.
Monitoring Aggregation Process and Optimization of the Fluorescence Properties of BODIPY Derivatives in Solid State

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Our aim is to develop fluorescent organic nanocrystals (in sol-gel or suspensions) as sensors for biological or environmental purposes. Nanocrystals have intermediate properties between molecules and microcrystals. They are extremely bright objects whose fluorescence can be modulated through energy transfer \textsuperscript{[1]} \textsuperscript{[2]}. In the past years we have developed a redox based oxygen titration with rubrene nanocrystals\textsuperscript{[1]} and a sensitive copper (II) ion sensor based upon latex particles\textsuperscript{[2]}. In order to improve the response of our systems, we need to get a better sensitivity designing highly fluorescent molecules in the solid state. BODIPY chromophores have a high absorption cross section\textsuperscript{[3]}. Those dyes are hindered in order to avoid $\pi$-$\pi$ stacking which is a known major cause of fluorescence inhibition in the solid state.

The results of fluorescence lifetime (FLIM) imaging will demonstrate the ability of such molecules to emit efficiently in solid-state\textsuperscript{[3]}\textsuperscript{[4]}. We will first focus on 4 new hindered BODIPY dyes (see schemes above). The chromophores were designed to shift their absorption and emission wavelengths to the red. [2.2]paracyclophane (PcP) was grafted on the BODIPY core as well as alkyl chains of various length to force the molecules away one from each other. The spectroscopic and electrochemical properties in solution will be presented.

Absorption, emission and FLIM were done on drop-casted films of the fluorophores. The addition of alkyl substituents (-Me, -Et, $n$-Pr) next to PcP group clearly affects the emission properties in solid state: the dyes display sharper emission bands than in solution and their relative fluorescence quantum yield increases with the number of carbons in the alkyl chain. FLIM analysis reveals complex decay profiles.

We will also introduce recent progresses in the formulation of nanoparticles from another Bodipy derivative. Indeed using a microfluidic device we managed to produce size-controlled nanoparticles with luminescent properties. Those properties will be discussed after detailed spectroscopic analysis of PMMA films doped with the Bodipy molecule.

References: