

MONDAY AND TUESDAY JUNE 1ST AND 2ND 2015



GLEAM'15



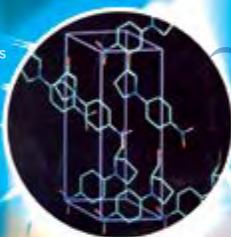
GAMES OF LIGHT WITH META-MOLECULES

COMMUNICATING, SENSING AND IMAGING

IN TRIBUTE TO JOSEPH ZYSS FOR HIS CONTRIBUTIONS TO THE FIELD



NANOPLASMONICS



MICROCAVITIES



PHOTONICS



SENSING



IMAGING



PARTIAL LIST OF INVITED SPEAKERS :

CHANTAL ANDRAUD (FRANCE)
DAVID ANDREWS (UK)
ADY ARIE (ISRAËL)
SOPHIE BRASSELET (FRANCE)
FRANCESCO MICHELOTTI (ITALY)
LUCIA PETTI (ITALY)
CHUCK SHANK (US)
MISHA SUMETSKY (UK)
MARIE-PAULE TEULADE-FICHOUE (FRANCE)
HERVÉ THIS (FRANCE)
DAVID YARON (US)

LOCATION:

ENS CACHAN, AUDITORIUM D.CHEMLA, INSTITUT
D'ALEMBERT AND LPQM

PROGRAMME

Monday, June 1., 2015

Morning

8h30 - 8h50 : Coffee

8h50 - 9h00 : Welcome address

SESSION 1 : Nano-imaging, nano-NLO and nanoplasmonics

Chuck Shank, Howard Hughes Medical Institute, Janelia Farm Research Campus, Ashburn, USA, « Bioimaging and excitation with sculpted light »

Sophie Brasselet, Fresnel Institute, Marseille, France, « Probing molecular organization down to super-resolution imaging with polarized microscopy »

Sébastien Bidault, ESPCI, France, « Building optical antennas with DNA »

10H25 - 10H50 : COFFEE BREAK

Marc Guillon, University Paris 5, France, « Optical Field Singularities for Super-Resolution Imaging »

Clément Lafargue, LPQM, IDA, ENS Cachan, France, « CARS imaging with comb lasers »

Lucia Petti, Institute of Cybernetics "E. Caianiello" of CNR, Pozzuoli, Italy, « 2D photonic quasi-crystals for nanobiosensing »

Eli Kapon, EPFL, Switzerland, « Tailored Quantum Dots for Integrated Quantum Photonics »

12H50 - 13H50 : LUNCH

Afternoon

Bruno Palpant, LPQM, IDA, Ecole Centrale de Paris, Châtenay-Malabry, France, « Ultrafast transient plasmonic-photonic coupling »

Timothée Toury, UTT, Troyes, France, « Irreducible formalism for nanoparticles optical properties description »

Bianca Sclavi, LBPA, IDA, ENS Cachan, France, « Fluorescent nano-objects for the study of bacterial physiology »

SESSION 2 : Microcavities

Misha Sumetsky, Aston University, UK, « Microresonator structures at the surface of an optical fibre »

David Andrews, University of East Anglia, Norwich (UK), « Finding the photon in photonics »

Mélanie Lebental, LPQM, IDA, ENS Cachan, France, « Non-linear wandering, from quantum chaos to micro-lasers »

16H40 - 17H00 : COFFEE BREAK

Special round table on « crossing frontiers and shaking institutions » : Physics and chemistry, technology and science, telecommunications and biology, research and institution. Moderator : Isabelle Ledoux-Rak

Maurice Bernard, Bernard Decomps, Claire Dupas, Jean-Yves MÉRINDOL, Hervé BIAUSSER, Jacques Biot, Muriel Touati, Keitaro Nakatani, Pierre-Paul Zalio .

GLEAM lecture by **Joseph Zyss**, LPQM, ENS Cachan, France « From Molecules to Meta-Molecules for Photonics and biophotonics : Symmetry, confinement, geodesics and scale considerations ».

Sciences and food for present and future

18h45-19h45: Hervé This, Agro Paris Tech, Paris, France « Interactive cooking »

DINNER COCKTAIL, MUSIC

Tuesday, June 2., 2015

Morning

8h00 - 8h30 : Coffee

SESSION 3 : Devices for Photonics and Sensing

Ady Arie, Tel Aviv University, Israël, « Studying nonlinear optics using the tools of atomic physics »

Francesco Michelotti, Università di Roma « La Sapienza », Rome, Italy, « Bloch electro-magnetic surface waves for early cancer diagnosis »

Bruno Le Pioufle, SATIE, IDA, ENS Cachan, France, « Microfluidic devices for the cell sensing and treatment »

10H05 - 10H30 : COFFEE BREAK

Chi Thanh Nguyen, LPQM, IDA, ENS Cachan, France, « High detection limit optofluidic sensors for chemical and biological applications »

Abdel El Abed, LPQM, IDA, ENS Cachan, France, « Producing microdroplets for NLO and biological applications »

SESSION 4 : Molecular Engineering for Photonics and Biophotonics

David Yaron, Carnegie Mellon University, USA, « Modeling the role of torsional motions in the photophysics of organic dyes and semiconductors »

Isabelle Ledoux-Rak, LPQM, IDA, ENS Cachan, France, « Beyond Molecular Engineering for nonlinear optics : from molecules to nanoparticles »

12H20 - 14H00 : LUNCH AND POSTER SESSION

Afternoon

Antoni Mitus, M. Jarema, G. Pawlik and J. Zyss, Wroclaw University of Technology, Poland and LPQM, IDA, ENS Cachan, France, « From EFISH to Multipolar orientation: a statistical physics approach »

Marie-Paule Teulade-Fichou, Curie Institute, Paris, France, « Triphenylamine dyes: When typical NLO materials meet biology »

Chantal Andraud, ENS Lyon, France, « Biphotonic probes for Near-IR biophotonics applications »

Frédéric Bolze, Strasbourg University, France, « From materials to biology: a journey inside molecular engineering of two-photon dyes and harmonophores »

15H50 - 16H20 : COFFEE BREAK

Rémi Métivier, PPSM, IDA, ENS Cachan, France, « Design of molecular and hybrid nanoparticles with photoswitchable optical properties »

Hubert le Bozec, Rennes 1 University, France, « Metal-based NLO chromophores: from tuning to switching the quadratic nonlinearities »

17H10 - 17H30 : CLOSING CEREMONY

Session 1.1

Nano-imaging, nano-NLO and nanoplasmonics

Monday, June 1. 2015

8:50 am

Chairperson : Eric Deprez

Bioimaging and Excitation with Sculpted Light

C.V. Shank

Janelia Farm Research Campus

19700 Helix Dr., Ashburn, VA, USA

Probing molecular organization down to super-resolution imaging with polarized microscopy

Sophie Brasselet*, Cesar Valades Cruz,

Haitham Shaban Ahmed, Alla Kress, Julien Savatier

Aix-Marseille Université, CNRS, Centrale Marseille, Institut Fresnel

Domaine Universitaire St Jérôme, Marseille, France

Building Optical Antennas with DNA

Sébastien Bidault*

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1 rue Jussieu, 75005 Paris, France

Bioimaging and Excitation with Sculpted Light

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Numerous advances have taken place in microscopy that have permitted optical microscopy beyond the Abbe limit. In this talk I will describe how ultrashort optical pulses in combination with dispersion can create optical fields of nearly any arbitrary shape that can be used to make bioimages with 20nm resolution. In addition such optical fields can be shaped to excite a single neuron in volume of interconnected neurons. I will describe a multifocal array using an echelle grating that provides flexibility in defining the field of observation.

Acknowledgements : The work described in this talk was performed in cooperation with Alipasha Vaziri and Jianyong Tang.

Probing molecular organization down to super-resolution imaging with polarized microscopy

Sophie Brasselet*, Cesar Valades Cruz,

Haitham Shaban Ahmed, Alla Kress, Julien Savatier

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Super-resolution microscopy techniques based on single molecules localization, benefiting from the sensitivity of fluorescence imaging, have brought significant improvement in nano-scale bio-imaging [1-3]. While super-resolution microscopy can guide interpretation through morphological observation in biomolecular assemblies *in vivo* with unprecedented level of precision, it is still a challenge to provide fine structural information at the molecular scale. Understanding the structural organization of bio-molecules by measuring locally their orientation could bring considerable complementary information, related for instance to the relation between cell filaments organization and their mechanical properties involved in fundamental biological processes.

In this work, we report a super-resolution polarization-resolved microscopy technique able to image molecular fluorophores' orientation in static and dynamic environments at single molecule level and nano-scale resolution. Using direct Stochastic Optical Reconstruction Microscopy (dSTORM) [5,4] in combination with polarized detection, fluorescence anisotropy images can be reconstructed at a spatial resolution of 30nm. We will present how this information can be used to extract the dynamical nature of the fluorophore orientational order and its statistical angular constraint. Based on a refined signal analysis technique which provides high accuracy in the estimation of molecular anisotropies, we report nano-scale orientational behaviors in actin stress fibers in fixed cells and *in vitro* structures such as amyloid fibrils and double stranded DNA [6]. We show that this method brings a superior level of information as compared to previously developed ensemble polarization dependent methods [7-9] by adding a quantitative knowledge on the fluorophore orientational flexibility, a parameter that is determining in the interpretation of fluorescence polarized responses when investigating bio-molecular structural organization.

References :

- [1] Hess, S.T. et al. (2007) Proc. Natl. Acad. Sci. USA 104:17370–17375
- [2] Shroff, H. et al. (2008) Nat. Methods 5: 417–423
- [3] Huang, B. et al. (2008) Science 319 :810–813
- [4] T J Gould et al., (2008) Nature Methods 5:1027-1030
- [5] Heilemann, M. et al. (2008) Angew. Chem. Int. Ed.Engl. 47:6172-6176
- [6] C. A. Valades Cruz, H. Ahmed Shaban, S. Monneret, N. Bertaux, J. Savatier, S. Brasselet, submitted
- [7] A. Kress, X. Wang, H. Ranchon, J. Savatier, H. Rigneault, P. Ferrand, S. Brasselet, Biophys. J. 105, 127 (2013)
- [8] J. Duboisset, P. Ferrand, H. Wei, X. Wang, H. Rigneault, S. Brasselet, J. Phys. Chem. B, 117 (3), 784 (2013)
- [9] M. Mavrikakis, Y. Azou-Gros, F-C. Tsai, J. Alvarado, A. Bertin, F. Iv, A. Kress, S. Brasselet, G.H. Koenderink and T. Lecuit. Nature Cell Biology 16, 322–334 (2014)

Building Optical Antennas with DNA

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Plasmon-based optical antennas have become ubiquitous in photonics with numerous biomedical applications (in sensing, imaging and therapy) and by allowing the design of optimized photo-detectors, light emitters and photovoltaic cells. DNA has recently emerged as the building material of choice to mass-produce plasmonic resonators with controlled geometries and chemical environments, allowing their reproducible coupling to single quantum emitters¹ and the dynamic modulation of their photonic properties.²

To enhance the fluorescence properties of single molecules, we assemble them in the centre of gold nanoparticle (AuNP) dimers, using a short DNA double-strand, which are obtained in large scale as a purified colloidal suspension (figure 1-a).³ Confocal luminescence lifetime measurements in microfluidic conditions demonstrate that these nanostructures are single photon-emitters with picosecond lifetimes (figure 1-b).¹ Furthermore, molecules with a dipolar transition moment parallel to the dimer axis can be selected with radially-polarized Laguerre-Gauss beams for antennas oriented perpendicularly to our sample plane.⁴ A conjunction of time-resolved luminescence and fluorescence correlation spectroscopy allows us to fully characterize the photophysical properties of these hybrid emitters that feature excitation cross-sections and decay rates enhanced by more than one order of magnitude with respect to isolated organic dyes.⁵

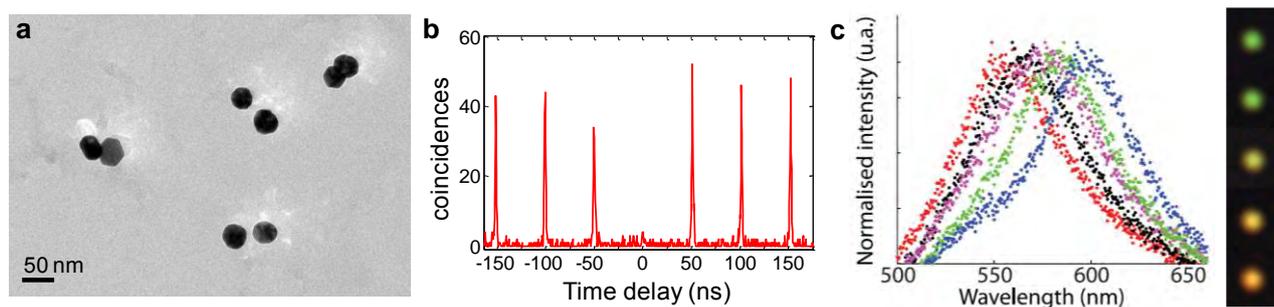


Figure 1: (a) Cryo-EM image of 40 nm AuNP dimers linked by a 30 base-pair DNA strand. (b) Photon antibunching from a single molecule in the center of a 40 nm AuNP dimer, that features a fluorescence lifetime of a few tens of ps. (c) Evolution of the scattering signal from a single 40 nm AuNP dimer, when increasing the salt concentration, measured with a confocal spectrometer (left) or a color camera (right).

Furthermore, the nanometer-scale sensitivity of plasmon coupling allows the translation of minute morphological changes in nanostructures into macroscopic optical signals. In particular, single nanostructure scattering spectroscopy provides a direct estimation of interparticle distances in gold nanoparticle dimers linked by a short DNA double-strand.³ This spectroscopic information can be inferred from simple widefield measurements on a calibrated color camera (figure 1-c).² This allows us to analyze the influence of electrostatic and steric interparticle interactions on the morphology of DNA-templated AuNP groupings. We apply this spectroscopic characterization to identify dimers featuring two different conformations of the same DNA template. In practice, the biomolecular scaffold contains a hairpin-loop that opens after hybridization to a specific DNA sequence and increases the interparticle distance.⁶ These results open numerous perspectives for the parallel colorimetric sensing of single biomolecules using dynamic plasmon rulers.

References:

- ¹ M. P. Busson, B. Rolly, B. Stout, N. Bonod, and S. Bidault, *Nat. Commun.* **3**, 962 (2012).
- ² L. Lermusiaux, V. Maillard, and S. Bidault, *ACS Nano* **9**, 978 (2015).
- ³ M. P. Busson, B. Rolly, B. Stout, N. Bonod, E. Larquet, A. Polman, and S. Bidault, *Nano Lett* **11**, 5060 (2011).
- ⁴ M. P. Busson and S. Bidault, *Nano Lett* **14**, 284 (2014).
- ⁵ M. P. Busson, B. Rolly, B. Stout, N. Bonod, J. Wenger, and S. Bidault, *Angew. Chem. Int. Ed.* **51**, 11083 (2012).
- ⁶ L. Lermusiaux, A. Sereda, B. Portier, E. Larquet, and S. Bidault, *ACS Nano* **6**, 10992 (2012).

Session 1.2

Nano-imaging, nano-NLO and nanoplasmonics

Monday, June 1. 2015

10:25 am

Chairperson : Sophie Brasselet

Optical Field Singularities for Super-Resolution Imaging

Marc Guillon*, Marco Pascucci, Marcel Lauterbach, Valentina Emiliani
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Rapid CARS Imaging with comb lasers

Clément Lafargue^{a,b*}, Ming Yan^{a,b}, Simon Holzner^{a,b}, Takuro Ideguchi^b, Theodor W. Hänsch^{a,b}, and Nathalie Picqué^{a,b,c}

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2D Photonic Quasi-Crystals for Nanobiosensing

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Tailored Quantum Dots for Integrated Quantum Photonics

Eli Kapon

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Optical Field Singularities for Super-Resolution Imaging

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Super-resolution imaging by Saturated Structured Illumination Microscopy (SSIM) [1] and Stimulated Emission Depletion (STED) microscopy [2] is obtained by using illumination patterns with zeros of intensity. In both cases, sub-diffraction information is obtained by saturating an optical transition (i.e. absorption or stimulated emission). The quality of the zeros of intensity is of primary importance to keep fluorescence ability in subdiffraction volumes. For wave-fields, zeros of intensity are associated with singular values of the phase and of the polarization orientation, so-called phase dislocations and polarization disclinations.

After a brief review of singularities used in the literature for super-resolution microscopy, we will discuss the possibility to use high numerical aperture speckle fields. In speckle fields, vortex phase dislocations naturally occur. As speckle fields naturally arise when coherent wavefields propagate through scattering media, the presented works will be discussed in the frame of super-resolution imaging in biological tissues.

References :

- [1] M.G.L. Gustafsson, PNAS 102 (37), 13081-13086 (2005)
- [2] K.I. Willig, S.O. Rizzoli, V. Westphal, R. Jahn and S.W. Hell, Nat. 440, 935 (2006)

Rapid CARS Imaging with comb lasers

Clément Lafargue^{a,b,*}, Ming Yan^{a,b}, Simon Holzner^{a,b}, Takuro Ideguchi^b, Theodor W. Hänsch^{a,b}, and Nathalie Picqué^{a,b,c}

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We report on a new concept of multiplex Raman spectroscopy, namely Dual-comb coherent Raman spectroscopy [1] simultaneously providing a high chemical specificity, multiple species detection, short measurement times and high acquisition rates. It may strongly benefit e.g. time-resolved spectroscopy of transient phenomena and hyperspectral imaging.

In the present experiment, Dual-comb coherent Raman spectroscopy main flaw, the poor refresh rate, is improved by one order of magnitude, with reasonable trade-offs, by using for one of the two comb generators a repetition frequency of 1 GHz, instead of 100 MHz (as in [1]). The spectra span more than a thousand reciprocal centimeters with a resolution only limited by the intrinsic width of the vibrational transitions of the liquid sample. The measurement time of a spectrum is of the order of a few hundreds of microseconds and the duty cycle of the acquisition of successive spectra can reach several tens of percent. We provide first experimental demonstration of our principle.

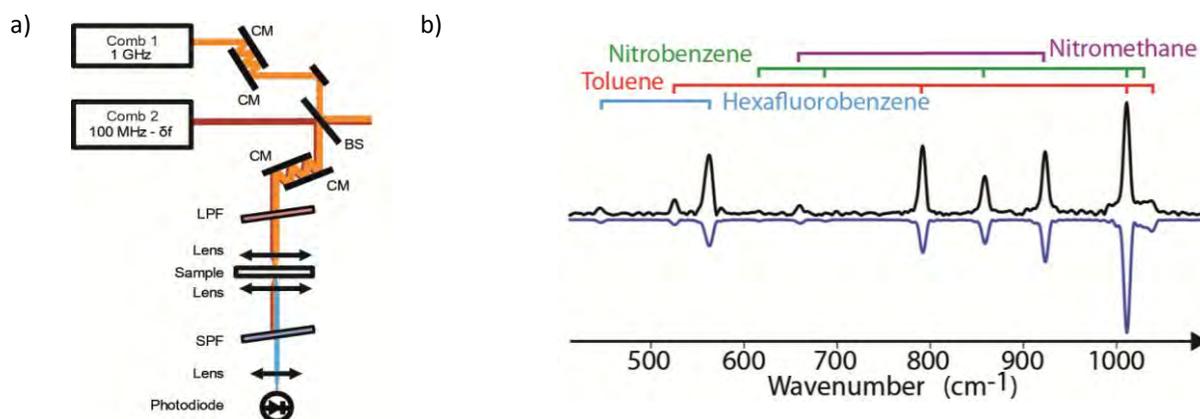


Figure 1 a) Experimental set-up. The beams of two laser combs with repetition frequencies of 1 GHz and 100 MHz-10Hz respectively are combined on a beam splitter. Pre-compensation for the second-order dispersion induced by the optical components of the setup is achieved with chirped mirrors. The combined beams are focused onto a liquid sample. Spectral filters isolate the CARS signal. The anti-Stokes radiation is forward-collected and focused on a silicon photodiode with a bandwidth of 100 MHz. b) Comparison of a spectrum recorded with the set-up of a) (black) and a spectrum recorded with two 100-MHz lasers (blue). For both spectra, the resolution is 8 cm^{-1} and the recording time is $167 \mu\text{s}$. The signal to noise ratio is 10 times lower with the 1GHz-100MHz system than with the two 100 MHz systems, consistently with energy-scaling expectations, but the refresh rate of successive acquisition is improved to 100 Hz, instead of 10 Hz.

References :

1 - Ideguchi T., Holzner S., Bernhardt B., Guelachvili G., Picqué N., Hänsch T.W., *Nature* **502**, 355-358 (2013).

2D Photonic Quasi-Crystals for Nanobiosensing

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The last decade has been characterized by artificial electromagnetic (EM) materials, including photonic crystals (PCs) and photonic quasi-crystals (PQCs), making these very attractive given that there are new possibilities to control the EM field in innovative way. Quasiperiodic crystals (QCs) are a new class of materials that have fascinating optical properties lying somewhere between those of disordered and period structures. With the use of PCs and PQCs, it is possible to synthesize novel artificial structures characterized by selective EM responses, which, in turn, undergo significant frequency shifts, in presence of biological material.

In the present work we studied artificial EM nanomaterials¹ to develop innovative plasmonic nanobiosensors based on Surface Enhanced Raman Scattering (SERS) substrates and working in the visible frequency band. Fabricated gold PQCs in a Thue Morse arrangement are proposed for the engineering of reproducible SERS substrates. Scanning electron microscopy, UV/Vis absorption spectroscopy, dark field microscopy and atomic force microscopy (AFM) are used to characterize the experimental structure. Using a molecular monolayer of pMA (p-mercaptoaniline) as a Raman reporter, we show that high values of SERS enhancement factors can be achieved in photonic structures.

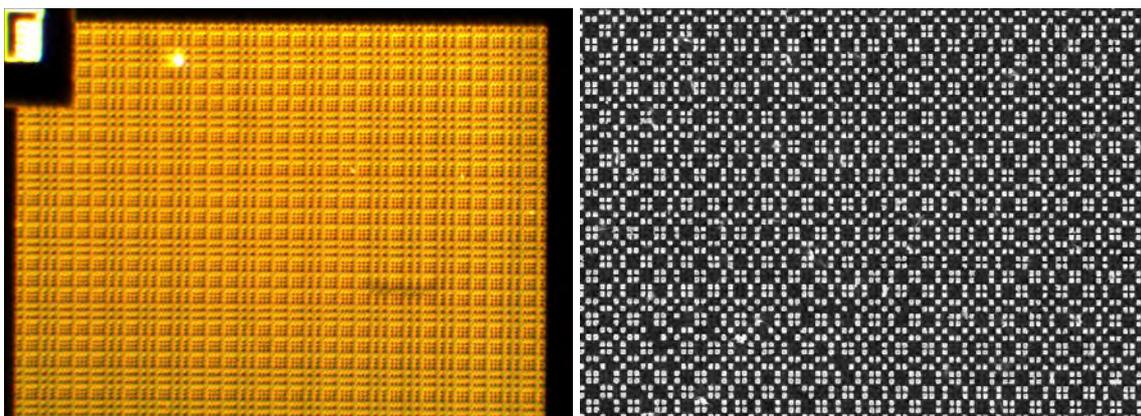


Figure 1 Bright field (left side) and scanning electron microscopy (SEM) images of the 2D Thue Morse quasi periodic array of 185 nm-side size and 60 nm-high Au nanoparticles on a quartz substrate (nearest center-to-center separation $\Delta = 79$ nm and filling factor $FF = 0.27$).

References:

[1] V. Caligiuri, L. De Sio, L. Petti, R. Capasso, M. Rippa, M. G. Maglione, N. Tabiryan and C. Umeton. *Advanced Optical Materials*, 2: 950–955. DOI: 10.1002/adom.201400203 (2014).

Tailored Quantum Dots for Integrated Quantum Photonics

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Semiconductor quantum dots offer unique linear and non-linear optical properties attractive for applications in quantum information technology and ultra-low power lasers. Radiative recombination of QD-confined exciton complexes yields atomic-like optical spectra, rendering them efficient solid-state sources of quantum light. Their small size and narrow spectral linewidths make them useful for very low power nonlinear optical switching, down to the single photon level. The high optical gain they provide should be useful for low power-consumption few-QD lasers, by integrating them into high Q-factor photonic cavities. More generally, QD-based single photon emitters, together with other optical elements and single photon detectors, can be combined to produce on-chip single photon devices for generating, processing and detecting non-classical states of light.

The realization of integrated photonic circuits utilizing semiconductor QDs as active elements requires an advanced QD technology, with which QDs with prescribed positions and optical spectra can be produced and integrated with photonic cavities and waveguides in a deterministic and reproducible way. One such promising approach relies on site-controlled InGaAs/GaAs pyramidal QDs grown on patterned (111)B GaAs substrates. Progress in controlling the optical properties of pyramidal QDs, using them for the generation of quantum light, and their integration with several types of photonic cavities is reviewed.

The pyramidal QDs are formed by organometallic vapor phase epitaxy (OMVPE) on substrates patterned with arrays of pyramidal pits [1], which brings about their inherent site control (practically <50nm alignment accuracy). Their self-formation mechanism relies on growth rate anisotropy and capillarity, different from most self-assembled QD systems, and this results in several important features relevant for integration and generation of quantum light: low inhomogeneous broadening (<5meV spread of exciton energy), control over emission wavelength by adjusting the growth rate and adatom fluxes [2], high in-plane symmetry (C_{3v} symmetry or higher) yielding polarization-isotropic emission and small fine structure splitting [3], and reproducible exciton emission spectra [4]. Emission of single- and bunched-photons and formation of QD-molecules by quantum-wire-assisted tunnel coupling [5] have been demonstrated with such dots. Integration of single- as well as multiple-QDs in photonic crystal (PhC) membrane cavities of different configurations has also been implemented. The removal of far-off-resonance coupling of cavity modes with QD excitons in these structures, due to the absence of wetting layers trapping parasitic multi-exciton states, permits the realization of a two-level-like solid state system for studying cavity quantum electrodynamics in the solid state. The role of phonons [6] and pure dephasing in QD-cavity coupling is thus revealed [6]. Simultaneous, deterministic coupling of several QDs in L_3 and L_7 PhC cavities to the same cavity mode is also evidenced by demonstrating the expected Purcell effect on QD emission polarization and intensity [7]. Prospects for realizing quantum networks using pyramidal QDs integrated with arrays of coupled photonic cavities will be discussed.

References:

1. E. Kapon et al., *Physica E* **25**, 288 (2004)
2. M. Felici et al., *Small* **5**, 938 (2009)
3. M.-A. Dupertuis et al, *Phys. Rev. Lett.* **107**, 127403 (2011)
4. C. Jarlov et al, *Appl. Phys. Lett.* **101**, 191101 (2012)
5. Q. Zhu et al., *Small* **5** (3), 329 (2009)
6. M. Calic et al, *Phys. Rev. Lett.* **106**, 227401 (2011); C. Jarlov et al., submitted (2015)
7. A. Lyasota et al., *J. Crystal Growth* **414**, 192 (2015)

Session 1.3

Nano-imaging, nano-NLO and nanoplasmonics

Monday, June 1. 2015

13:50 am

Chairperson : Lucia Petti

Ultrafast transient plasmonic-photonic coupling

B. Palpant^{1*}, X. Wang¹, R. Morea², J. Gonzalo²

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An irreducible formalism for the nonlinear optical properties of extended objects

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Fluorescent nano-objects for the study of bacterial physiology

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Ultrafast transient plasmonic-photonic coupling

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The remarkable optical properties of plasmonic nanoparticles can be modified on an ultrafast time scale following light pulse absorption. However, this ultrafast nonlinear response remains too low for being directly exploited in high-rate photonic processing. We demonstrate in this communication, both theoretically and experimentally, that the ultrafast transient coupling of the localised plasmon mode in gold nanoparticles (Au-NPs) and a localised photonic mode in a resonant microcavity can be used to tackle this challenge [1]. After design optimization, hybrid cavities have been elaborated by pulsed laser ablation [2]. Their transient optical response has then be measured by pump-probe spectroscopy [3]. A reversible and ultrafast optical signal modulation of more than 100% is achieved with a few picosecond recovery time by using a light pump fluence lower than 1 mJ cm^{-2} . This is ten times better than the performances of a plasmonic device reported earlier, based on non-locality in long gold nanorods [4]. Thanks to the coupling, the Au-NP transient optical response is enhanced by a factor of 30 to 40 and its spectral profile is strongly sharpened [5].

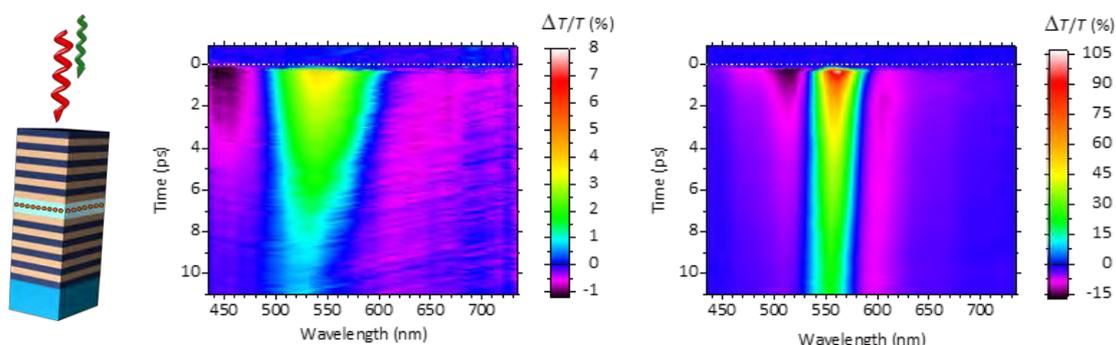


Figure: Scheme of the multi-layered hybrid cavity (left). Transient spectrum of photo-induced transmittance modulation for a bare layer of Au-NPs (middle) and the hybrid cavity (right).

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An irreducible formalism for the nonlinear optical properties of extended objects

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The use of an irreducible description has been very fruitful to understand and design molecular nonlinear emitters.

However, with the advent of nanotechnologies, physicists have been dealing with a new class of objects, nanoparticles for example, that behaves in a completely different fashion. The non-negligible spatial extension of those objects brings the necessity to extend the irreducible expansion for point object like molecules to spatially extended ones.

In this talk, an attempt to create such a formalism that necessitates not only a multipolar expansion of the response tensor but also of the electromagnetic fields will be presented. Throughout the construction of this formalism, the example of shaped-like nanostars belonging to the D_{3h} group of symmetry as a guiding light will illustrate the concepts discussed.

The ability to discuss and predict experiments with the help of a multipolar formalism is linked with the capacity to create models within it. Translational addition of multipoles helps to do so by providing a way to generate higher orders multipoles from translated ones.

The presentation will conclude on some propositions to discuss the frequency behavior of multipoles.

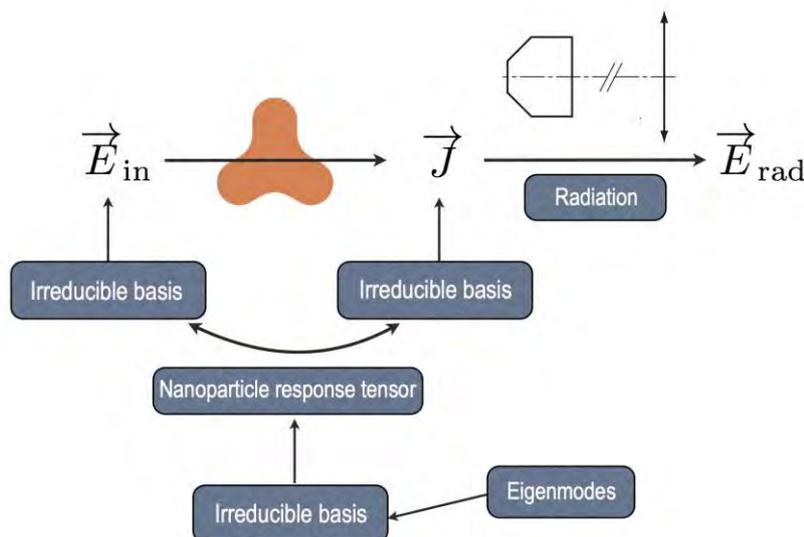


Figure : This diagram outlines the formalism that will be developed in this presentation. An appropriate irreducible basis is used to describe all the physical quantities, leading to a symmetry respectful formalism.

This work has been supported by the Conseil Régional de Champagne-Ardenne and the Nano'mat facilities.

Fluorescent nano-objects for the study of bacterial physiology

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We have developed novel fluorescent nano-objects that can be used for the study of bacterial physiology and for the design of biosensors used to detect the presence of pathogenic and antibiotic-resistant bacterial strains. These nano-objects include fluorescent, organic nano-particles and fluorescent polymer chains. The organic fluorescent nano-particles developed at the PPSM have several advantages compared to other fluorophores: they are stable in biological media and non-toxic to bacterial growth and they are very bright and do not blink, which are key properties for extended-time, single molecule tracking experiments. In addition, the side chains of these NPs are easily functionalized, which allows for direct coupling to antibodies to direct them to specific targets within a biological sample. The modification of the side chains with a pH sensitive fluorophore has resulted in the development of a pH-sensitive biosensor to detect the presence of bacterial growth. In addition, we have used fluorescent polymer chains (FPC) to efficiently label the bacterial cells. Different versions of these polymer chains are either internalized or remain fixed to the cell membrane, resulting in differential labeling (Figure 1). This approach can be used in the detection of the presence of bacteria by flow cytometry or microscopy. This provides a relatively low cost solution to bacteria detection compared to existing fluorophores.

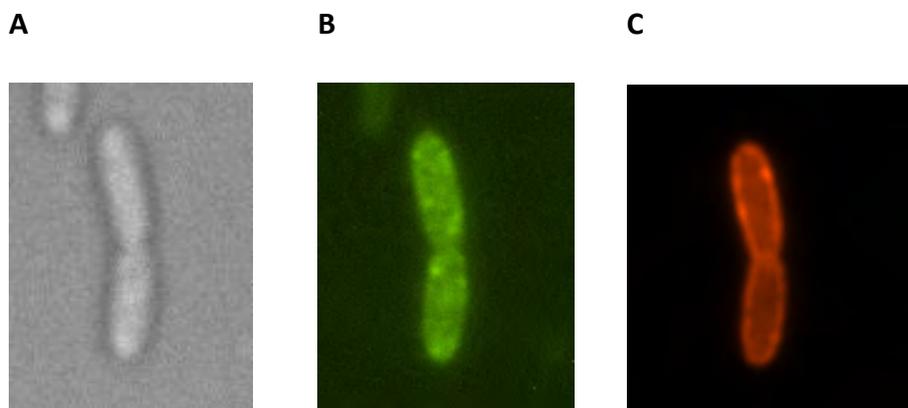


Figure 1. *E.coli* cells interacting with (B) negatively charged green fluorescent polymer chains (GFPC-) and (C) positively charged red fluorescent polymer chains (RFPC+).

Session 2

Microcavities

Monday, June 1. 2015

~ 3:10 pm

Chaiperson : Henri Benisty

Microresonator structures at the surface of an optical fiber

M. Sumetsky

Aston Institute of Photonics Technologies, Aston University

Birmingham B4 7ET, UK

Finding the Photon in Photonics

David L. Andrews*

University of East Anglia

Norwich Research Park, Norwich NR4 7TJ, United Kingdom

Non-linear wandering, from quantum chaos to micro-lasers

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Microresonator structures at the surface of an optical fiber

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Nanometer-scale local deformation of the optical fiber shape can cause strong localization of whispering gallery modes (WGMs) propagating along the fiber surface [1]. This effect is explored in Surface Nanoscale Axial Photonics (SNAP), the recently introduced platform for fabrication of high Q-factor resonant circuits at the surface of an optical fiber with unprecedented subangstrom precision [2, 3]. Usually, the fiber deformation is introduced by directional heating with a CO₂ laser. As examples of SNAP devices, Fig. 1(a) illustrates the structure of 30 coupled resonators, which is fabricated by periodic modulation of the silica fiber radius with 1.2 nm amplitude [2] and Fig. 1(b) illustrates a 2.8 nm high parabolic bottle resonator, the record smallest slow light device which performs the record dispersionless and low-loss delay of optical pulses [3]. To date, the SNAP technology was developed for silica fibers. However, the intriguing generalization of this technology for fibers composed of other optical materials, e.g., polymer [4] and multi-material fibers is anticipated.

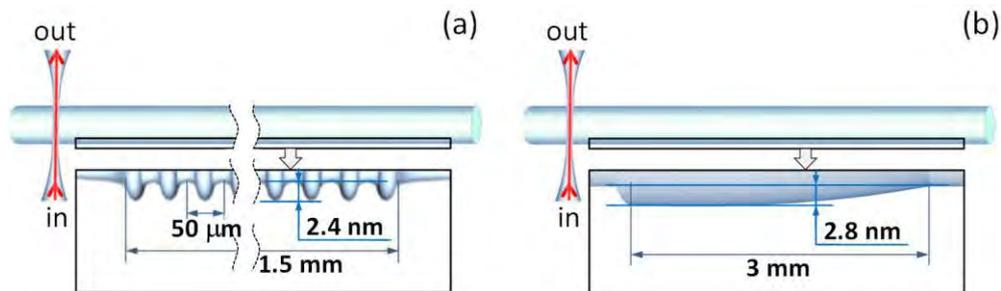


Fig. 1. Illustration of SNAP structures fabricated with subangstrom precision. (a) – 30 coupled microresonators [2]. (b) – Parabolic resonator [3]. Insets: magnified nanoscale fiber radius variation.

This presentation reviews the theory, experimental realization, and potential applications of SNAP microresonator structures. The slow axial propagation of WGMs in SNAP is described by the one-dimensional wave equation which has the form of the Schrödinger equation. In this equation, the energy is proportional to the variation of radiation wavelength and the potential is proportional to the effective fiber radius variation. For this reason, the SNAP platform allows us to mimic numerous quantum mechanical phenomena with light (tunneling, turning points, coupled periodic and aperiodic quantum wells (resonators), etc.). Potential applications of the SNAP technology in fundamental physics and optics include investigation of tunneling of light, Anderson localization, localized states in continuum, nonlinear photonics, optomechanics, atom trapping, and cavity quantum electrodynamics. The potential engineering applications include the SNAP-based microwave photonics, optofluidics, optical tweezers, sensors, gyros, lasers, and quantum processors.

Acknowledgement. The author is grateful to Professor Zyss for stimulating discussions of potential applications of the SNAP platform for fabrication of miniature polymer fiber based lasers and devices.

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Finding the Photon in Photonics

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The term 'photonics', originally proposed in the 1950's [1], and greatly boosted by the arrival of the laser shortly afterwards [2], now characterizes a huge sector of modern technology. Advances in photonics are continually bringing the fundamental nature and properties of the photon under fresh scrutiny; the state of knowledge even a quarter of a century ago is an uncertain guide to current understanding, and several current research topics would have been unheard of at that point in time. What we now understand about photons has become very much richer (though indeed less simple) than Einstein's original conception [3], and the need for fully photon-based representations of mechanism has never been greater – not only in the realms of nonlinear optics or plasmonics but even in connection with spontaneous emission [4-6].

Some of the most important recent advances in imaging, sensing and communications hinge upon discrete photon properties and interactions. The technology behind single-molecule imaging, which is now proving so important in a range of biological and medical applications, has an obvious basis in detecting specific photon events [7]. Sensors based on fluorescence energy transfer can achieve molecular recognition [8] as well as providing dynamical information on processes such as protein folding [9]; here there are energy and lighting applications too [10]. Elsewhere, the discovery that photons can be made to convey orbital, as well as spin, angular momentum [11] offers scope for greatly enhancing the information density in optical communications; the same attribute of photons can even be used for microfluidic applications [12]. Other emerging areas of application include nanomanipulation and all-optical switching.

This lecture outlines the numerous properties that characterize photons and their interactions, highlighting some of the recent discoveries, and giving a few clues to some of the puzzles that now need to be solved.

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Non-linear wandering: from quantum chaos to micro-lasers

Mélanie Lebental* and Joseph Zyss

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During this talk, I will review the different issues which were investigated in our group for a decade [1], from a strong collaboration with Richard Chang at Yale University in the beginning of the 2000' [2], to very recent results on three dimensional cavities [3]. In particular, the specific role of each PhD student of the group will be emphasized: Nadia Djellali, Sergey Lozenko, Iryna Gozhyk, Clément Lafargue, and Nina Sobeshchuk.

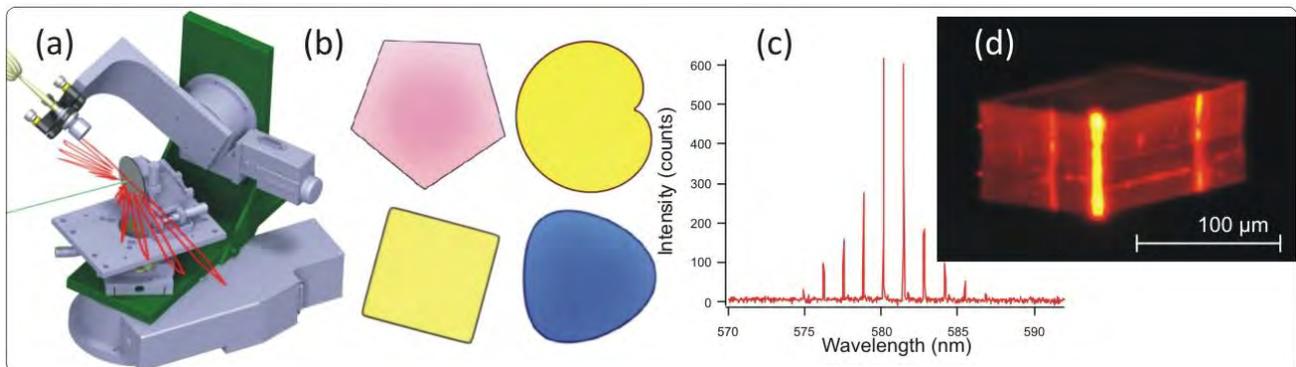


Figure 1: (a) Three dimensional goniometer. The sample is vertical; the green pump beam is incident from the left. An experimental emission diagram is superimposed in red. (b) Photographs in real color with an optical microscope of micro-lasers with various shapes. (c) Experimental laser spectrum from a cuboid. (d) Image with a zoom lens and a camera in real colors of a cuboid under pumping. The green pump is not visible. The image is duplicated by the substrate.

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Acknowledgements: We gratefully acknowledge all the students, PhD students, and post-doctoral fellows who worked – and are still working – with us.

Special GLEAM session

Monday, June 1. 2015

5:00 pm

Chairperson : Isabelle Ledoux-Rak

Round table "crossing frontiers and shaking institutions" :

Physics and chemistry, technology and science,

telecommunications and biology, research and institutions

Maurice Bernard, Bernard Decombs, Claire Dupas, Jean-Yves MÉRINDOL,
Hervé BIAUSSER, Jacques BIOT, Muriel TOUATI, Keitaro NAKATANI, Pierre-Paul
ZALIO

Moderator : Isabelle Ledoux-Rak

GLEAM Lecture :

Games of Light with Molecules, Meta-Molecules and Billiards: symmetry, shape, geodesics and scale

Joseph ZYSS

*Laboratoire de Photonique Quantique et Moléculaire, Institut d'Alembert,
Ecole Normale Supérieure de Cachan, 61 Avenue du Président Wilson,
94231-Cachan, France*

Interactive cooking (~ 6:45 pm)

Hervé THIS

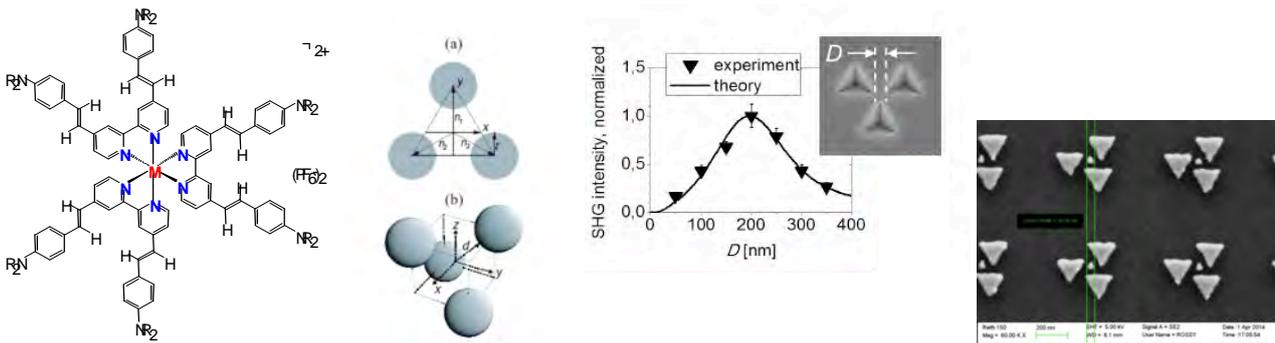
Agro Paris Tech, Paris, France

Games of Light with Molecules, Meta-Molecules and Billiards: symmetry, shape, geodesics and scale

Joseph ZYSS

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Symmetry considerations (e.g. Pierre Curie's visionary principle and Eugene Wigner's pioneering introduction of group theory in quantum mechanics) together with variational formulations (e.g. from Pierre Fermat to Maupertuis, from William Hamilton and Karl Jacobi to Richard Feynman) are two main cornerstones of physical sciences, upstream to specific scale and material implementations, in conjunction with statistical considerations (e.g. Ludwig Boltzmann's definition of entropy) to account for randomness. In spite of their different expressions, symmetry considerations and the variational principle are to some extent related, due to the equivalent variational expression of the spectral representation of mathematical-physics equations, eigen-spaces being closed and eventually irreducible with respect to the invariance group of the classical or quantum operator of interest. We will illustrate this interplay by some examples from our current research in micro-billiard lasers [1], a paradigmatic test-bed where geometric, physical and mathematic issues, some of which still open, are playing a joint role to determine the laser emission properties. We will refer to the Fagnano-Fermat theorem to illustrate the elegance and power of combining physical considerations (from Fermat's XVIIth century principle all the way to modern "transformation optics" and related geodesic-like solutions for propagation in tailored dielectric landscapes) with geometric ones (from Fagnano's XVIIIth century theorem to modern computer aided mathematical "unfolding" methods), implemented in XXIth century polymer based nano-technologies and laser physics.



Multi-scale implementations, over two decades, of general tensor symmetry considerations that have guided quadratic nonlinear optics, from the molecular scale with a propeller shaped organometallic molecular template [2,3] with chiral octupolar symmetry (left), onto 2-D and 3-D arrangements of spherical gold nanoparticles sustaining localized plasmons [4] (center left), and their further implementation by way of gold plated nano-pyramids etched in a GaAs semiconductor substrate, assembled in « meta-molecules » that exchange propagative plasmons [5] (center right), and chiral arrangements of gold nano-triangles [6] (right).

The combined power of tensor algebra with group symmetry considerations in order to conceive optically nonlinear entities and their organization schemes, onto their up-scaled revivals as "meta-molecules" bound by propagative plasmons, are illustrated in the Figure above and related considerations [4-6]. This research exemplifies a possible way towards a fast emerging age, whereby nano-photonics will emulate nano-electronics and vice-versa. Our quest for an ever deeper understanding of light-matter interactions towards their control at ultimate space-time scales, sustained by major social and economic demands, will continue to drive the field, throughout its fascinating and unfinished history of mutating paradigms.

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Session 3.1

Devices for Photonics and Sensing

Tuesday, June 2. 2015

10:30 am

Chairperson : Misha Sumetsky

Studying nonlinear optics using the tools of atomic physics

Ady Arie

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Bloch electro-magnetic surface waves for early cancer diagnosis

A. Sinibaldi¹, N. Danz², A. Anopchenko¹, P. Munzert², S. Schmieder³, R. Chandrawati⁴, S. Rana⁴, F. Sonntag³, A. Occhicone¹, L. Napione⁵, M. M. Stevens⁴ and F. Michelotti¹

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Microfluidic devices for the cell sensing and treatment

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Studying nonlinear optics using the tools of atomic physics

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Consider a three-wave mixing process such as sum frequency generation. If one of the waves (the "pump" wave) is much stronger than the two other waves and is nearly up-depleted in the nonlinear process, the nonlinear system can be modeled as a dynamical two-level system that couples between these two waves [1]. There are many systems that have a similar dependence – two-coupled pendulums, coupler between two single-mode waveguides or an atomic two-level system that are coupled by electromagnetic radiation. Hence, many tools that were developed for studying an atomic two-level system can be adopted for studying nonlinear optical processes. Specifically, the population in the ground and excited states, the detuning and the time coordinate have they analog counter-parts in nonlinear optics – the intensities of the two waves (at the two frequencies that are coupled), the phase mismatch between the interacting waves and the propagation coordinate in the nonlinear crystal, as illustrated in Fig. 1. Moreover, tools such as Bloch sphere representation and eigenvalue energy diagram, as well as processes such as adiabatic following can be readily implemented in nonlinear optics. Here, the adiabatic following process means that the phase mismatch is varied throughout the nonlinear crystal, starting from a highly negative value and ending with a highly positive value, and at a rate which is slow compared to the coupling rate between the interacting waves. This process can provide robust, broadband and highly efficient conversion from an input wavelength to an output wavelength. Indeed, conversion efficiencies approaching 100% and acceptance bandwidth of more than one octave were experimentally demonstrated.

The analogy between atomic physics and nonlinear optics can be further extended for the case of a three level system. The analog nonlinear optics system consists of two cascaded nonlinear processes. Here we can adopt concepts such as stimulated Raman adiabatic passage (STIRAP) and adiabatic elimination in order to have efficient energy transfer through an intermediate state which is kept dark throughout the entire process. This opens new opportunities for frequency conversion through intermediate frequency that is located in highly absorptive regions e.g. in the ultraviolet or the mid-infrared.

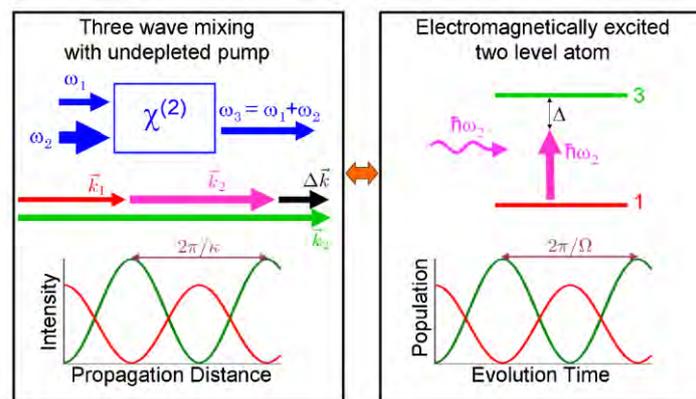


Figure 1 Illustration of the analogy between a three-wave mixing process and an electromagnetically excited two-level system.

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Bloch electro-magnetic surface waves for early cancer diagnosis

A. Sinibaldi¹, N. Danz², A. Anopchenko¹, P. Munzert², S. Schmieder³, R. Chandrawati⁴, S. Rana⁴, F. Sonntag³, A. Occhicone¹, L. Napione⁵, M. M. Stevens⁴ and F. Michelotti¹

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The increasing demand for non-invasive early detection of diseases has pushed the scientific community to develop more and more sensitive techniques to detect disease biomarkers in extremely low concentrations [1]. Among other techniques, optical label-free bio-sensing is considered to be the most promising tool for high throughput detection of biomolecules. Surface Plasmon resonance (SPR), operating in a variety of configurations, is commonly used in biology and pharmaceutical laboratories [2]. Among other label-free optical approaches [3, 4, 5] those based on the excitation of electromagnetic modes (Bloch Surface Waves - BSW) at the surface of one dimensional photonic crystals (1DPC) [6] were demonstrated as a practical route to enhanced resolution and constitute an attractive alternative to surface plasmon polaritons (SPP) [7].

The main advantages of BSW for bio-sensing, in comparison to SPR, lie in the favourable properties of the 1DPC such as the small absorption of the dielectric materials and the tunability of the layer thicknesses to operate in any wavelength range. Besides, the use of BSW in fluorescence-based bio-sensing does not suffer from quenching of the fluorophores emission at the 1DPC surface [8].

Here we report on the development of BSW biochips operating in an angular interrogation scheme and demonstrate their use for the detection of clinical biomarkers related to angiogenesis and early cancer development. We first describe the design and fabrication of BSW biochips and the layout of the optical reading instrument. Surface functionalization and methods for effective immobilization of proteins on the biochips are discussed. Experimental results of the assay are presented and compared to measurements obtained by other techniques.

This work was supported in part by the European Commission through the project BILOBA (www.biloba-project.eu; Grant agreement 318035). The authors gratefully acknowledge Dr. Emmanuel Maillart from HORIBA Jobin Yvon (France) and Prof. Federico Bussolino from the University of Torino (Italy) for fruitful discussions.

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Microfluidic devices for the cell sensing and treatment

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Since the last two decades we see the emergence of the microfluidic technology in the domains of biology, medicine and pharmacology [Whitesides '06] . Cell tissues and organized cell co-cultures were successfully reconstructed, using therefore microfluidic devices i) for the cell tissue production, like in the work of [Onoe '13] where functional cell fibers including extracellular matrix proteins are produced for the cell-tissue 3D patterning, ii) for the cell tissue characterization, like in the work of [Huh '10] where lung alveoles function mimicking biodevices were achieved for toxicological studies. Besides these cell tissue studies, the microfluidic technology also motivates many investigations for the characterization [Gawad '01] or treatment [Le Pioufle '00] [Dalmay '11] of circulating cells or even single cells [Huang '01] . To achieve such capabilities, sensing functions must be integrated on the microfluidic device, to characterize the cell(s) mechanically, electrically or optically while they are flowing or trapped for treatment purpose.

We recently developed a microfluidic device mimicking the sequestration function of the spleen, based on the mechanical properties of red blood cells (RBC), that might be altered due to parasit infection (*Plasmodium Falcifarum*, inducing malaria), or genetic disease (Sickle Cell Disease). In this device we reproduce both the fast circulation in the spleen (20% of RBC circulation), and the slow circulation (80% of RBC) through the red pulp and the inter-endothelium slits. Fluorescence marking of the altered RBC shows the selective trapping of mechanically altered RBC in the microfiltering microfluidic units mimicking the inter-endothelial slits [Picot '15] . Such mechanical sensing of the RBC rigidity will be a precious tool for pharmaceutical research.

The integration of electrical sensing functions within microfluidic devices is also a promising alternative for the real-time characterisation of cells. We develop a microfluidic platform for the electrical characterization of circulating cells [Trainito '15] . The method plays on the dielectric properties of the cell, trapping a single cell between electrodes by negative dielectrophoresis, and extracting the dielectric properties of its membrane and cytoplasm using a propagative rotary field.

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Session 3.2

Devices for Photonics and Sensing

Tuesday, June 2. 2015

10:30 am

Chairperson : Francesco Michelotti

High detection limit optofluidic sensors for chemical and biological applications

Chi Thanh Nguyen

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Producing and Manipulating Microdroplets for NLO and Biological Applications

Abdel I. EL ABED

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High detection limit optofluidic sensors for chemical and biological applications

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Optofluidic label-free sensors integrating optical microresonators are highly attractive for real-time, high sensitivity detection of chemical or biochemical species. The detection principle of these sensors consists in the measurement of the resonator effective refractive index change due to the interaction, at the vicinity of resonator surfaces, between the guided mode of the evanescent field and analyte. These sensors can display highly specific and ultrasensitive detection properties if their surfaces are functionalized to detect target molecules via surface binding detection mechanisms. Optical sensors are often integrated into a microfluidic circuit, forming an optofluidic cell, in order to control the analyte solution during measurements. In the domain of integrated photonic devices, polymer materials offer the advantages of low cost, easy fabrication, low scattering loss on waveguide sidewalls, and high coupling efficiency to optical fibres and waveguides. Moreover, for biochemical and chemical sensing, polymer surfaces can be easily modified to immobilize a wide choice of target molecules. Polymers are also compatible with microfluidic circuits, favouring the insertion of photonic circuits into optofluidic cells.

We report on the design, fabrication and performances of these optofluidic label-free sensors based on polymeric microresonators and microfluidic circuits. Particularly, two orthogonal polarizations TE and TM guided modes of sensor response are simultaneously measured in real-time continuous monitoring, which can give the possibility of detection of target molecules conformation change. The sensor response time can be reduced to 1 millisecond, providing a large possibility of real-time kinetic monitoring of biochemical reactions. Homogeneous sensing experiments performed with the sensors displayed a limit of detection of $2 \cdot 10^{-6}$ RIU, whereas surface sensing experiments performed using TAMRA-cadaverine as a test molecule, which can be quantified through fluorescence analysis, demonstrated a very low limit of detection of 0.22 attogram. A specific surface sensing of Cadmium ions in water, based on a specific binding between these ions and a ligand attached on the polymeric surface of the microresonator, displays a very low limit of detection of $5 \cdot 10^{-11}$ mol/L. The sensors, possessing a temperature resolution of sensing about several millikelvin, offer in parallel the possibility of real-time monitoring of reaction enthalpies.

Producing and Manipulating Microdroplets for NLO and Biological Applications

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Droplet-based microfluidics technology allows for the production and manipulation at KHz rates of highly monodisperse microdroplets, which are generally made of an aqueous solution dispersed in a continuous non-miscible inert fluorinated oil phase. Such microsystems proved to be very effective tools in many multidisciplinary scientific and technological areas: they may serve as independent micro-reactors, cargoes or optical biosensors.

A particular focus will be made on biological and NLO applications, which are based not only on the narrow size distribution and high throughput production features of such microsystems but also on the photo-activation of individual microdroplets. The later aspect appears to be largely under-explored, despite the fact that these photoactive microsystems may solve various technological problems, such as drug delivery and well-controlled chemical stimuli with high spatio-temporal resolution and high throughput screening of nonlinear molecules using either fluorescence or second harmonic generation measurements.

Session 4.1

Molecular Engineering for Photonics and Biophotonics

Tuesday, June 2. 2015

~11:10 am

Chairperson : Robert Pansu

Modeling the Role of Torsional Motions in the Photophysics of Organic Dyes and Semiconductors

David J. Yaron*, Matheus Tanha, Nicolae M. Albu, and Christian Legaspi
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Beyond Molecular Nonlinear Optics : from molecules to nanoparticles

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Modeling the Role of Torsional Motions in the Photophysics of Organic Dyes and Semiconductors

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In organic molecules with extensive π conjugation, the photophysics is often strongly influenced by coupling of electrons to torsional degrees of freedom. This strong coupling originates from the tendency of photoexcitation to alter the nature of the torsional potential. In addition to being essential for understanding phenomena such as the charge mobility of conjugated polymers, engineering of the torsional potential can aid design of molecules with desirable properties, such as dyes for bioimaging.

In conjugated polymers, the torsional potential is weak in the ground electronic state and increases substantially on photoexcitation. The low barrier in the ground state has the desirable outcome of imparting flexibility to the polymer chains, such that the materials are easily processed. However, this torsional flexibility leads to substantial disorder and wide spectral linewidths. A simple one-dimensional model will be presented that accounts for these linewidths through a competition between energy, which prefers planar structures, and entropy, which prefers non-planar structures. The strong increase in torsional potential on photoexcitation leads to rapid planarization in the excited state. A Brownian dynamics model of this excited-state relaxation reveals universal behaviors that apply across a wide range of polymer systems. Among these universal features is the presence of two timescales for the relaxation such that short-time and longer-time dynamics differ substantially¹. Similar to the planarization associated with photoexcitation, oxidation or reduction to form a charge on the polymer also increases the torsional potential and so leads to a planarized region. Our models (Figure 1) suggest that the solution-phase charge mobility, as measured by microwave reflectivity, is established by the stochastic motion of this planarized, charged region along the polymer chain¹. Models of electric-field induced quenching in organic LEDs will also be discussed².

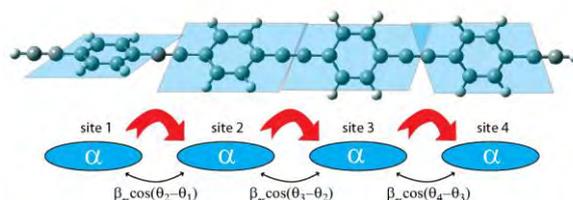


Figure 1 Site models, derived from quantum chemical calculations on oligomers, provide a computationally efficient description of electron-torsion coupling in conjugated polymers.

Torsional motions can also be used to design organic dyes for bioimaging applications. We have used computations to engineer molecules whose excited-state torsional potential has a local minimum at the planar structure and a global minimum at a twisted structure, with only the planar structure being fluorescent (Figure 2). Such dyes may act as fluorogens, which fluoresce only when bound to a protein because the rigidity of the protein environment prevents excited state relaxation to the twisted non-emissive structure. Design of dyes for detection of potassium ion, for use in neural imaging, will also be presented³.

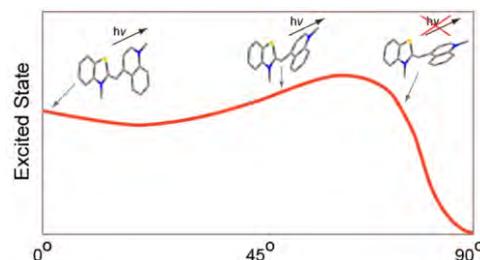


Figure 2 Excited state surface with a fluorescent planar and a nonfluorescent twisted structure.

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- 2) C.M. Legaspi, L.A. Peteanu, and D.J. Yaron *J. Phys. Chem. B* ASAP (2015).
- 3) M. Tanha, S.K. Chakraborty, B. Gabris, A.S. Waggoner, G. Salama, and D.J. Yaron *J. Phys. Chem A* **118**, 9837 (2014).

Acknowledgements: Funded by the US National Science Foundation

Beyond Molecular Nonlinear Optics : from molecules to nanoparticles

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The emergence of Molecular Photonics at the cross-road of physics, chemistry and device engineering has been triggered by an increasing demand in the domain of high bit rate telecommunications and of sensor applications. The wealth of molecular structures and the exploitation of their functional and structural flexibility open-up thoroughly renewed horizons in this domain.

Molecular material optimization for nonlinear optics is based on the elaboration of “molecular engineering” rules allowing for a reasonable prediction of microscopic NLO responses on the basis of various structural parameters such as π -electron conjugation and bond length alternation, electron donating and attracting strengths of substituents, and molecular symmetries. After the sophisticated and successful development of one-dimensional, dipolar molecules with high potential for huge bandwidth electro-optic devices, the decisive step in the story of molecular engineering has been triggered by a complete tensorial analysis of hyperpolarizabilities in terms of multipolar irreducible components, as proposed by J. Zyss in the early 90's. In particular, octupolar molecules, where symmetry constraints impose a cancellation of the dipole moment, have considerably extended the possibilities of molecular engineering of second order nonlinear optical molecules by enlarging the dimensionality of the charge transfer. This breakthrough immediately resulted in the investigation and synthesis of 2- and 3-dimensional NLO structures, and in the exploration of new types of molecules, this multipolar approach unveiling the high potential of metal complexes or lanthanide derivatives. Moreover, this new paradigm has triggered novel experimental and theoretical tools to be adapted to the non-polar character of octupolar molecules, such as Harmonic Light Scattering for the determination of hyperpolarizabilities, or optical poling to induce and control non-centrosymmetric organization of multipolar molecules in polymers. A few examples of this still ongoing story will be reported in this presentation.

This molecular engineering strategy is currently being challenged by the new avenues opened by Nanophotonics, where nano-objects may display huge NLO responses with various origins. Self-organized dendrimers and nanocrystals can be considered as “giant” supramolecular species, with, in some cases, a quasi-optimized acentric ordering resulting in very high β values. However, orienting these particles under electrical or optical fields in order to elaborate high performance NLO materials still remains a challenge. Another way to produce highly nonlinear nano-objects is based on metallic nanoparticles, their nonlinearity being mainly related to surface plasmon resonances. These NLO responses strongly depend on the nature, size and shape of these nanostructures, as illustrated by some examples of gold and platinum nanoparticles currently investigated in LPQM.

Session 4.2

Molecular Engineering for Photonics and Biophotonics

Tuesday, June 2. 2015

~2:00 pm

Chairperson : David Yaron

From EFISH to Multipolar orientation: a statistical physics approach

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Triphenylamine dyes: When typical NLO materials meet biology

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Biphotonic probes for Near-IR biophotonics

Chantal Andraud

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From materials to biology: a journey inside molecular engineering of two-photon dyes and harmonophores

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From EFISH to Multipolar orientation: a statistical physics approach

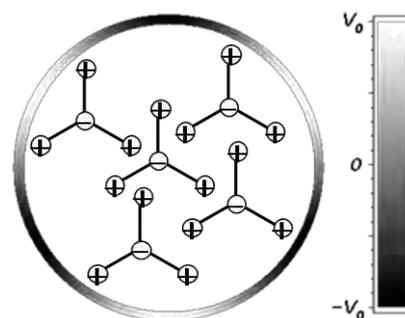
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The first generation of molecular engineering for non-linear optics has concentrated on polar conjugated molecules. The broader template of multipolar molecules was first proposed by Zyss [1-3], thus enlarging the pool of candidate nonlinear molecules and reviving the interface between chemists and physicists in the domain. A conceptual frame for a study of practical implementations of general electric-field-induced multipoling configurations which generalize the dipolar orientation schemes (EFISH) to multipolar orientation schemes (MEFISH) was recently formulated using a combined electro-static and statistical physics approach [4]. The concept of tailored multipoling cells that are enabling the coupling of the externally applied multipoling potential with any irreducible component of the molecular nonlinearity, each irreducible order corresponding to a different electrode design [4], whereas the earlier EFISH cell is limited to a projection of the dipolar component of the quadratic molecular susceptibility onto the poling vector field. This new concept needs adequate micro- and nano-scale implementation to provide efficient multipoling. This framework was used to study the conditions for an effective electric field poling of so-called “Y” shaped flat octupolar molecules in two dimensions [5-7]. Initial results were pointing at octupoling criteria that required unrealistic cooling conditions. In this paper we present more recent and elaborate results that show the possibility of improved poling conditions, based on analytical and numerical methods as well as Monte Carlo simulations. Both 2-D and 3-D octupolar molecules were studied in two- and three-dimension, the main issue being addressed here being the stability of the ground state non-centrosymmetric configurations. We have found that besides the role of the octupoling electric field itself intermolecular interactions, play an important role. We will present some specific poling schemes that demonstrate the possibility of efficient octupoling at realistic (e.g. liquid Nitrogene) temperatures.



Ground state of “Y” shaped model octupolar molecules in purely octupolar electric poling potential [7].

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Triphenylamine dyes: When typical NLO materials meet biology

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In view of the rapid developments of optical microscopies new fluorescent probes are constantly needed in particular IR-NIR probes compatible with intravital investigations.

In this context we launched a program aimed at the design of new fluorophores excitable in the IR range via a two-photon absorption (2PA) process. Based on the non-linear optical (NLO) properties of push-pull triphenylamines (TP), we engineered this chemical family to make it compatible with biological media and in particular cellular context. Several generations of 2 and 3 branched dyes bearing cationic e-acceptors (pyridinium, benzimidazolium) linked to the strong e-donor TP core via vinyl bonds has been synthesized.^{1,2} These compounds were shown to combine strong 2PA absorption and high affinity for AT-rich DNA grooves. In addition, of utmost importance is the switchable off/on fluorescence of the TP dyes that are virtually non-fluorescent in water and strongly emissive when immobilized in DNA which results in a strong contrast when imaging (Fig. 1).³

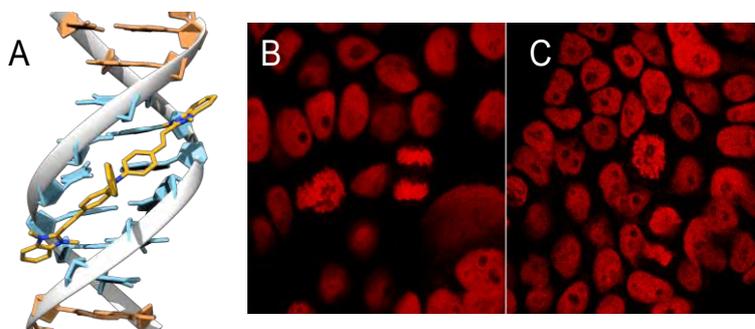


Figure 1 : A) Model of TP-2Bzim after docking in the minor groove of an AT-rich duplex. 2PA microscopy imaging of nuclear DNA in fixed HT29 cells at B) 1 μ M dye and C) 100nM dye (C); λ_{exc} : 800nm.

Finally we observed that the two-photon absorption cross-section of the dyes is dramatically enhanced once bound to DNA ($\delta=1080$ GM vs $\delta=110$ GM for the free TP-2Bzim compound).⁵ This is attributed to a tight fit of the TP-2Bzim molecule inside the minor groove of the DNA matrix, which induces geometrical rearrangements in the dye ground state and presumably in its excited state. This effect of the DNA matrix on the nonlinear absorption of a bound dye is revealed for the first time and paves the way for studying NLO processes in DNA. (WO 2008/055969, collaboration with. C Fiorini, F.Charra, CEA-Saclay).

More recently it was shown that in live cells the TP dyes are trapped in mitochondria. Upon IR-light excitation dye translocation to the nucleus is induced with concomitant induction of apoptosis.⁶ The TP dyes thus represent promising drug prototype able to kill cancer cell upon IR light activation (EP12306133.5.WO 09/13, collaboration with. P.Tauc, E.Deprez LBPA-IDA).

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- 6- R.Chennoufi et al. Submitted.

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Biphotonic probes for Near-IR biophotonics

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An ideal probe for *in vivo* biophotonics must fulfill many salient requirements, such as: high brightness in the biological transparency window, solubility in the physiological medium, non-toxicity, synthetic availability on relatively large scales, specificity and moderate cost. The main goal of this presentation is to illustrate our different recent approaches in order to reach these objectives. Then, we will show the main constraints of *in vivo* biophotonic and will present two of our recent results : (1) molecular engineering of chromophores with optimised properties for biphotonic imaging photo-dynamic therapy¹, (2) development of a method of hydrosolubilisation and biocompatibility of these biphotonic chromophores.²

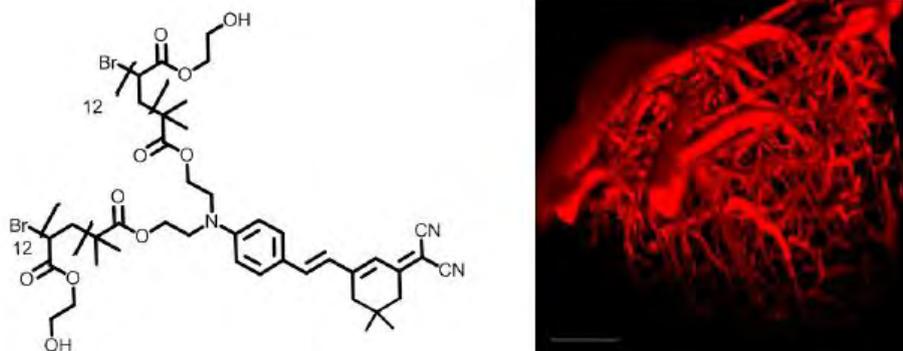


Figure 1. Example of fluorophore with a 3D image of the functional cerebral vasculature in the motor cortex of mice using two-photon laser scanning microscopy.

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From materials to biology: a journey inside molecular engineering of two-photon dyes and harmonophores

Jean-François Nicoud and Frédéric Bolze*

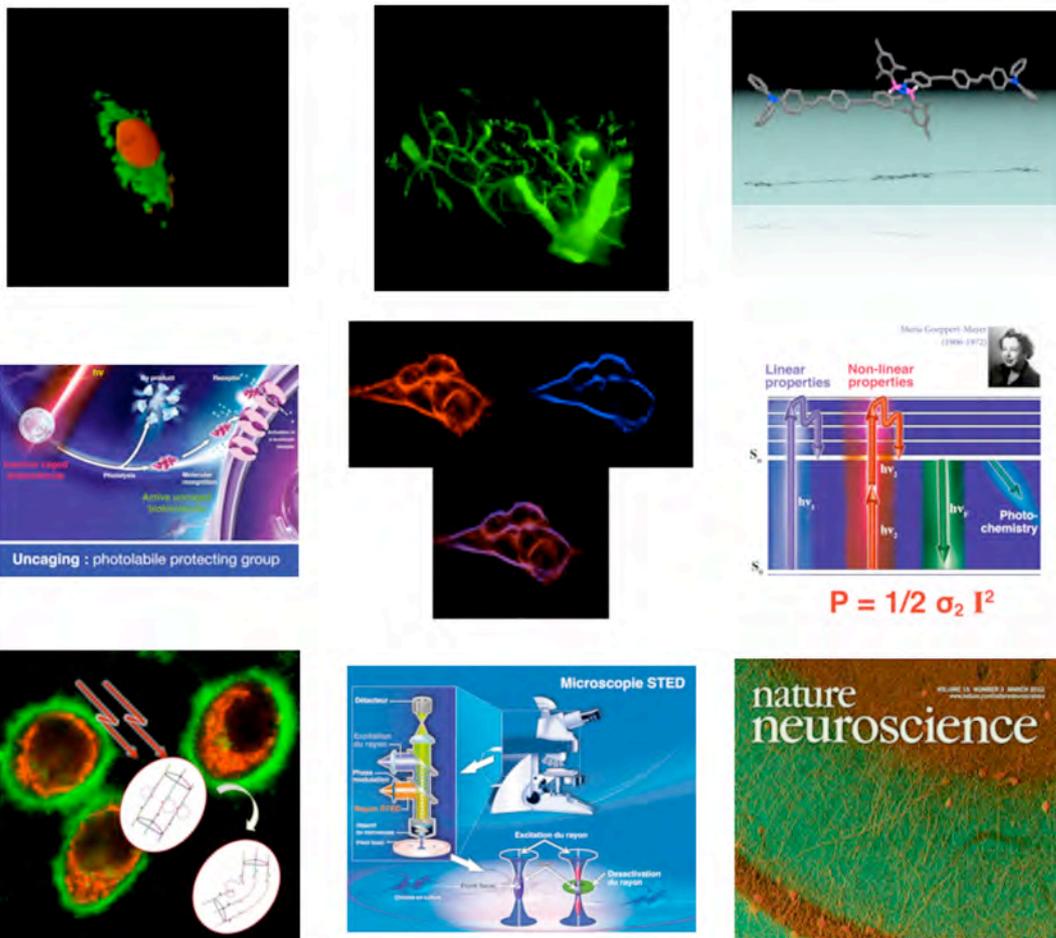
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The development of organic non-linear optical materials and their relevant molecular engineering started few decades ago, in particular in the telecommunication area. Thus a lot of very efficient molecules were designed and synthesized, that led to robust structure properties relationship. More recently, the development of biological microscopy pointed out that non-linear optics could lead to breakthrough in biological and medical sciences. Thus, many groups moved to the fascinating field of the uses of non-linear optics in microscopy.

We will begin the story by the description of the research works on the molecular engineering of organic materials for quadratic and cubic non-linear optics, mainly for second harmonic generation (SHG) and optical limiting. Then, we will describe the evolution of this research that led to the use of these dyes for biological applications, in particular in two-photon excited microscopy. These studies have permitted the emergence of a new thematic, consisting in the design of two-photon sensitive photolabile protecting groups for neurosciences. Thus, efficient systems called "cages" were designed and synthesized, and recently, a home coming to material sciences is ongoing...

Finally, we will conclude with the description of the revival of old dyes that were prepared for quadratic non-linear optical properties (SHG) and which, after decades of shelf life, were found useful and efficient in two-photon microscopy.



Session 4.3

Molecular Engineering for Photonics and Biophotonics

Tuesday, June 2. 2015

~4:20 pm

Chairperson : Marie-Paule Teulade-Fichou

Metal-based NLO chromophores: From Tuning to Switching the Quadratic Nonlinearities

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Design of molecular and hybrid nanoparticles with photoswitchable optical properties

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Design of molecular and hybrid nanoparticles with photoswitchable optical properties

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The field of advanced photoactive nanomaterials, with photoswitching capabilities, is extremely active and has been attracting ever-growing interest in recent years in many research fields for their potential applications in biological sensors, targeted medicine, high-resolution imaging, and innovative materials science. We report here on the design, fabrication and spectroscopy of photoswitchable emissive nanoparticles, based on novel dyad molecules, advantageously combining photochromic and fluorescent moieties.[1]

Three different strategies to achieve enhanced photoswitchable fluorescent nanomaterials are presented, based on fluorescent and photochromic molecular compounds (see figure): (1) photochromic-fluorescent nanoparticles obtained either by the reprecipitation method or by laser ablation; (2) photoswitchable emissive silica nanoparticles synthesized through surface grafting procedure; (3) core-shell multicomponent hybrid nanosystems fabricated from molecular derivatives and gold nanorods.[2]

In these various systems, the emission signal could be successfully and reversibly switched ON and OFF by light. A thorough study involving structural characterizations, steady-state and time-resolved spectroscopy measurements, from the ensemble level down to the single nanoparticle level, allowed us to quantify the switching efficiency, demonstrate unique size-dependent and nonlinear photoswitchable fluorescent properties, and decipher the processes driven at the nanoscale (intermolecular energy transfer, plasmonic interactions) leading to amplification effects.

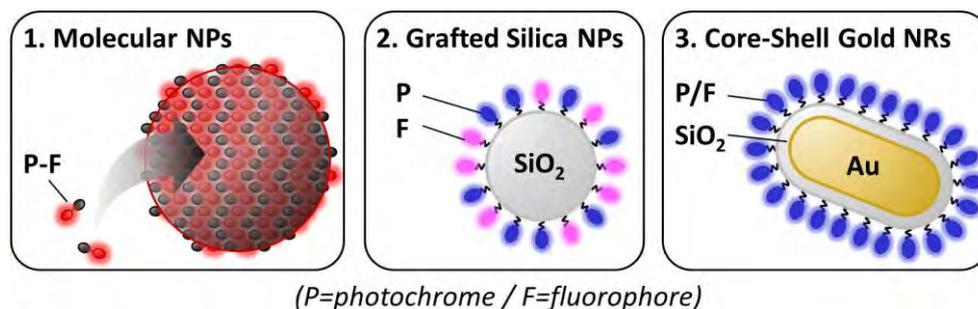


Figure 1 Three classes of designed photoswitchable fluorescent nanosystems.

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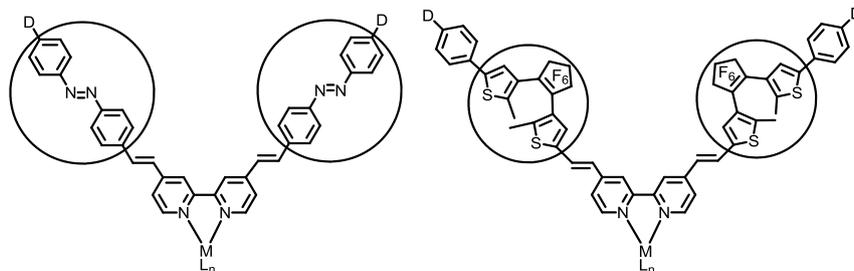
Metal-based NLO chromophores: From Tuning to Switching the Quadratic Nonlinearities

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Metallo-organic compounds are of particular interest for the design of new chromophores with large nonlinear optical (NLO) susceptibilities. Our research group has been involved for the past twenty years in the study of the NLO properties of functionalized oligopyridine metal complexes.¹ These ligands are excellent building blocks for the construction of dipolar² and octupolar³⁻⁵ (octahedral or tetrahedral) complexes. The combination of transition metals and ligands featuring photochromic units is also receiving much attention and opens up new perspectives for the design of metal-based photoswitchable molecules. We will describe some of our works made in the area of photochromic organometallic compounds which have been used for the photo-induced orientation of NLO chromophores in polymer films, as well as for the photoswitching of the quadratic NLO properties. To this purpose we have designed new functionalized bipyridine ligands featuring either azobenzene⁶⁻⁸ or dithienylethene (DTE)⁹⁻¹⁴ groups giving rise to multi-photochromic metal complexes.



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Poster Session

Tuesday, June 2. 2015

12:20 am

Entrance hall of the D'Alembert Institute

1- Anomalous Behavior in Self-induced Holographic Memories

Riccardo Castagna^{1,2*}, Andrea Di Donato³, Luca Nucara^{4,5}, Daniele E. Lucchetta², Ji-Hua Xu¹, Francesco Vita², P. Spegni², Luigino Criante^{2,6}, Davide Ceratti⁷, Andrey Shalit⁸, Francesco Simoni²

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2- Ortho-Sulfonamide Azobenzenes as Novel Ligands for the Synthesis of Photoswitchable Organometallic Complexes

Claire Deo^a, Nicolas Bogliotti^a, Rémi Métivier^a, Pascal Retailleau^b, Joanne Xie^a

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3- Fabrication of plasmonic gold nano-structures on glass substrate by thermal annealing technique

Minh Thanh DO, Quang Cong TONG, Isabelle LEDOUX-RAK, and Ngoc Diep LAI*

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4- Immobilization of gold nanoparticles functionalized by luminescent electroactive complexes

Laetitia Guerret¹, Fabien Miomandre¹, Jean-Frédéric Audibert¹, Marc Lepeltier²

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²ILV – Université Versailles-Saint Quentin, 45 Avenue des Etats-Unis 78035 VERSAILLES, France

5- Modelling and analysis of the sensitivity in 2D photonic crystal tapered microcavity

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6- Electro-Optical Microscope for cell biology

Z. Hayat¹, A. El-Abed¹, J.P. Barbot², A. Marty³, L. Mir⁴, C. Lafargue^{1*}, B. Le Pioufle² and J. Zyss¹

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7- Nano-scale engineering and nonlinear imaging of chiral plasmonic assemblies

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8- Mechanofluorochromic Materials: Synthesis and Photophysical Properties of Carbonyl Substituted Difluoroboron β -Diketones dyes.

Marine LOUIS, Arnaud BROSSEAU, Clémence ALLAIN, Rémi METIVIER

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9- Second harmonic generation from silver nanoparticles in aqueous solution with different protective agents

Hoang Minh Ngo, Isabelle Ledoux-Rak*

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10- Precisely embedding a single gold nanoparticle into polymeric photonic structure by LOPA-based direct laser writing

Dam Thuy Trang NGUYEN, Mai Trang DO, Quang Cong TONG, Hoang Minh NGO, Isabelle LEDOUX-RAK, and Ngoc Diep LAI*

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11- Photoswitchable and multicolor fluorescent-photochromic nanoparticles

Corentin PAVAGEAU¹, Maeva BOREL¹, Pei YU², Keitaro NAKATANI¹, Rémi METIVIER¹

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12- Fluorescent nano-objects for the study of bacterial physiology

Yang Si^{1,3}, Yayang Tian¹, Jean-Frederic Audibert¹, Gilles Clavier¹, Rachel Méallet-Renault², Bianca Sclavi^{3*}

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13- Realization of polymer-based 2D or 3D arbitrary form micro-resonators by low one-photon absorption direct laser writing technique

Quang Cong TONG, Bernard JOURNET, Isabelle LEDOUX-RAK and Ngoc Diep LAI*

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14- Modelling the oscillation frequency drift of an optoelectronic oscillator based on a vector network analyzer

VO Tien Tu, PHAM Toan Thang, Isabelle LEDOUX-RAK, Bernard JOURNET*

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Anomalous Behavior in Self-induced Holographic Memories

Riccardo Castagna,^{1,2,*} Andrea Di Donato,³ Luca Nucara,^{4,5} Daniele E. Lucchetta,² Ji-Hua Xu,¹ Francesco Vita,² P. Spegni,² Luigino Criante,^{2,6} Davide Ceratti,⁷ Andrey Shalit,⁸ Francesco Simoni²

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We report on photo-polymerization processes of multi-acrylate-based thin films deposited on transparent slides.^[1,4] Such a process allows the storage of information encoded by writing wavelength (λ_w), angle of incidence (θ_w) and polarization state of an impinging laser beam. This information is easily derivable by the optical far-field pattern obtained when the polymerized sample is irradiated with a probe beam having a different wavelength (λ_r) and/or angle of incidence (θ_r) from the writing one. After polymerization, the transmission far-field pattern shows parallel lines or concentric rings when the probe wavelength is the same used for the writing process or a different one, respectively. Moreover and unexpectedly, the center of the diffraction rings forms an angle $\Delta\theta$ with the direction of the transmitted beam whose sign depends on the sign of $\Delta\lambda$. The phenomenon depends on the interference generated in the microscope glass slide and recorded in the polymeric material, as experimentally shown and confirmed by numerical simulation analyses, and allows wavelength and angular multiplexing. These findings have applications in several technological fields, such as (a) high-density multiplexed optical data storage, (b) security-coding, (c) micro-lenses technology, (d) fast and real-time analysis for polymerization degree in photo-polymerization processes.

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Ortho-Sulfonamide Azobenzenes as Novel Ligands for the Synthesis of Photoswitchable Organometallic Complexes

Claire Deo^a, Nicolas Bogliotti^a, Rémi Métivier^a, Pascal Retailleau^b, Joanne Xie^a

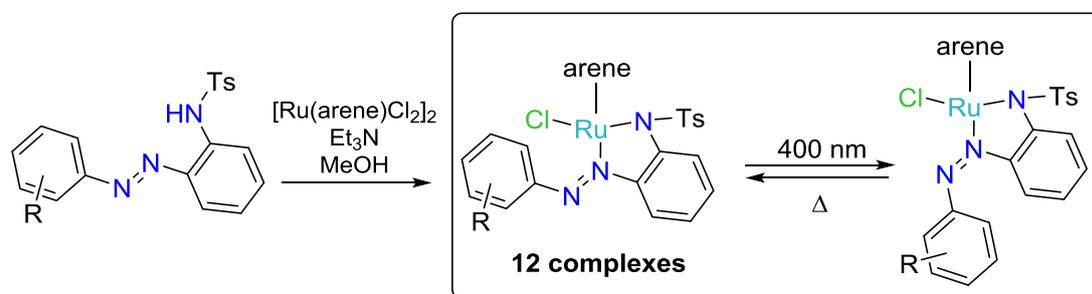
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In the aim of preparing new photo-responsive chemical systems, organometallic complexes incorporating azobenzene ligands represent an interesting class of compounds as they combine both the electronic, magnetic and catalytic properties of the metal center and the photo-isomerization behaviour of the azobenzene moiety. However, in contrast to the considerable amount of organometallic complexes bearing azobenzene ligands reported to date,¹ examples in which the coordinated azobenzene unit remains photoswitchable are rare.²

We have synthesized a series of *o*-sulfonamide azobenzene ligands and their corresponding (η^6 -arene)ruthenium(II) complexes which undergo reversible (*E*) to (*Z*) photo-isomerization upon irradiation at 400 nm. The synthesis of these novel ligands and their corresponding (η^6 -arene)ruthenium(II) complexes, as well as the influence of azobenzene substituents, arene group and solvent on their spectroscopic properties and photoswitching behavior will be presented.



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1) For recent examples, see: S. Dougan et al., *Inorg. Chem.*, **2006**, *45*, 10882-10894; J. Pratihari et al., *J. Organomet. Chem.*, **2009**, *694*, 3401-3408; M. Moustafa et al., *Organometallics*, **2013**, *32*, 2552-2557.

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Fabrication of plasmonic gold nano-structures on glass substrate by thermal annealing technique

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In this work, we present throughout the fabrication of plasmonic Au nano-structures on glass substrates by a combination of magnetron sputtering technique and thermal annealing process. The Au material was first deposited onto glass substrate at controlled sputtering times, resulting in desired film thicknesses. The Au films were then annealed in ambient conditions at different temperatures, approaching the glass transition temperature of glass substrate (560°C). All samples, before and after annealing, were characterized by different techniques, such as scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction, and UV-VIS spectroscopy. The initial sputtered films exhibit different morphologies and optical properties, which depend strongly on their thickness. Thermal annealing process promoted the modification in morphology of the initial film, from continuous surface toward isolated Au islands, leading to a qualitative enhancement of plasmonic resonance. Figure 1 shows SEM images and UV-VIS spectra of Au structures obtained before and after annealing at 500°C for 30 minutes for different samples obtained with various sputtering times. This thermal annealing method can be further developed by combining with optical lithography techniques in order to fabricate applicable plasmonic structures.

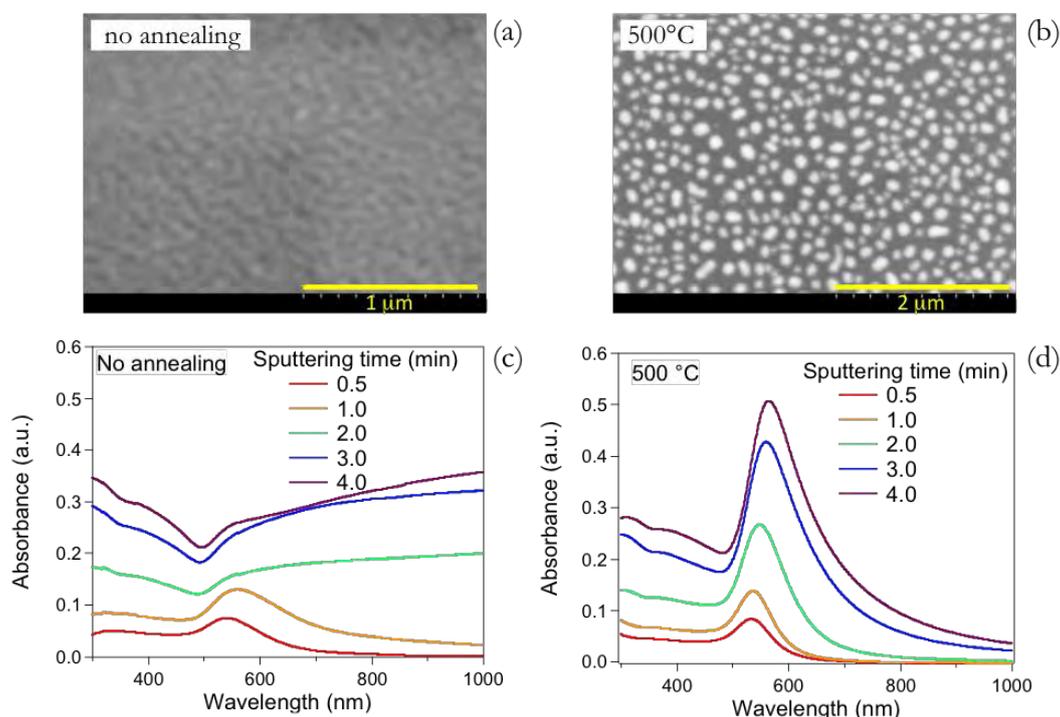


Figure 1: Scanning electron microscope images of Au structures obtained before annealing (a) and after annealing at 500°C for 30 minutes (b). Corresponding UV-VIS spectra of Au structures obtained with various sputtering times: (c) no annealing and (d) annealing for 30 minutes at 500°C.

Acknowledgements: The authors acknowledge Mr. Arnaud Brosseau and Mr. Joseph Lautru for their help in AFM and SEM measurements, respectively. Minh Thanh DO also thanks the Idex Paris Saclay for the master scholarship.

Immobilization of gold nanoparticles functionalized by luminescent electroactive complexes

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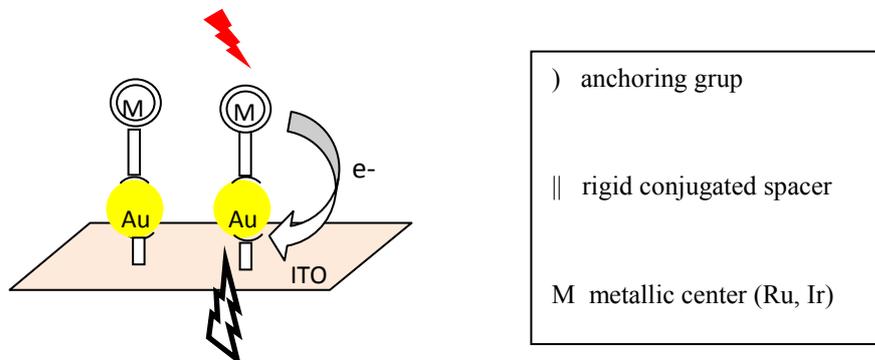
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Gold colloidal nanoparticles (NP) are the subject of many investigations due to their outstanding optical properties associated to chemical stability and biocompatibility that make them attractive targets for sensors and biomedical applications[1]. In the field of photophysics and electrochemistry, gold NP can be used as platforms to incorporate at their outer surface luminescent and redox active molecular compounds like ruthenium or iridium complexes. The interaction of the plasmonic properties brought by the NP and the absorption and emission properties of the complex leads to quenching or enhancement effects depending on various parameters like the distance of the spectral overlap[2]. Moreover the luminescence can be electrochemically tuned by changing the redox state of the metal as we recently demonstrated[3].

In the present study, we have tested different ways for covalently grafting the gold NP on the surface of ITO (see scheme below) and then incorporate the luminescent electroactive complex, to design electrodes made of functionalized gold NP arrays that can be used further in electrofluorochromism investigations (fluorescence microscopy under electrochemical monitoring)[4].



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Modelling and analysis of the sensitivity in 2D photonic crystal tapered microcavity

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In this work, we design a new Infiltrated liquid sensor based on a 2D photonic crystal waveguide incorporating a microcavity to sense small refractive index changes. The refractive index (RI) sensor is formed by a point-defect resonant cavity in the sandwiched waveguide with triangular lattice of air holes (index profile of silicon slab $n_{Si}=3.42$ and air $n_{air}=1$). The properties of the sensor are simulated using the finite-difference time-domain (FDTD) algorithm and the plane wave expansion (PWE) method (RSoft Photonic Suite). Sensors based on photonic crystal (PhC) waveguides incorporating microcavities have many advantages in compactness, high sensitivity and quality (Q) factor, easy extension to sensor arrays and various choices of materials, and capability of parallel measurement [1-4]. On the other hand, a tapered-shift structure along the line defect increases the quality factor of the microcavity [5]. So, the proposed RI sensor is formed with two waveguide couplers and a microcavity in the PhC with a triangular lattice of air holes, as shown in Fig.1. The microcavity is formed by change of the size of 14 air holes in the centre of the line defect. The hole's radii are: $r_A=200$ nm, $r_B=180$ nm. The sensing principle is based on the shift of resonance wavelength λ_0 , which occurs due to the change in RI of the sensor when the PhC's air holes are full of homogenous liquid. Several liquids with refractive indices ranging from 1 (the air) to 1.4 were studied and showed that the best sensitivity of 475 nm/RIU and limit of detection of 0.01 RIU can be achieved (Fig.2). The resonance wavelength is found to be a linear function of the refractive index in the range under study. The sensor is appropriate for detecting homogeneous media.

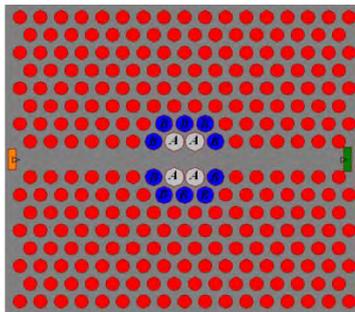


Fig.1. The proposed RI sensor.

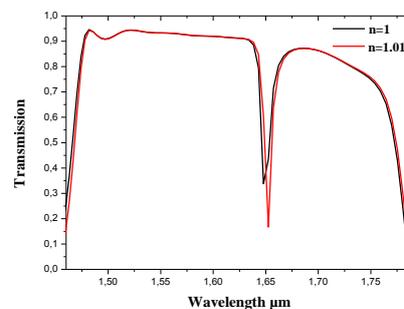


Fig.2. Transmission spectra of the RI sensor for TM polarization for $n=1$ and $n=1.01$.

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Electro-Optic Microscopy (EOM) for cell biology

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We propose to develop a new imaging modality for biology, based on the Pockels effect, providing quantitative physical information of structural and functional nature on cells and tissues. This non-invasive, bio-compatible and low-cost approach is based on nonlinear optical properties that are depending on statistical sub-micrometer organization schemes for an ensemble of molecules or nanoparticles embedded in the sample of interest. This method may allow for instance to study the structure of a cell membrane, at the molecular scale, under the application of an electric field (electro-permeation phenomenon) and thus takes on an important biological and clinical interest. Another domain of application that will be addressed is the all-optical detection of neuronal action potentials.

The set-up is based on a highly sensitive interferometric scheme allowing to detect the phase shift induced by the Pockels effect at the focal point of the microscope objective. Under the application through the sample of a quasi-static electric field, a quadratically nonlinear material experiences a linear change of its refractive index, known as the Pockels effect. Based on a quadratic response of the electrons in the systems to the combined optical and electrical field, the Pockels effect requires a breaking of centro-symmetry, which is intrinsic to the ferroelectric phase in oxide crystals [1,2] or to molecular crystals of adequate symmetry [3]. This condition can also be satisfied in statistically oriented molecular assemblies, such as biological membranes, which are generating considerable interest in biophysics and life sciences. The proof of principle of PLEOM microscopy has already been demonstrated experimentally [1-4].

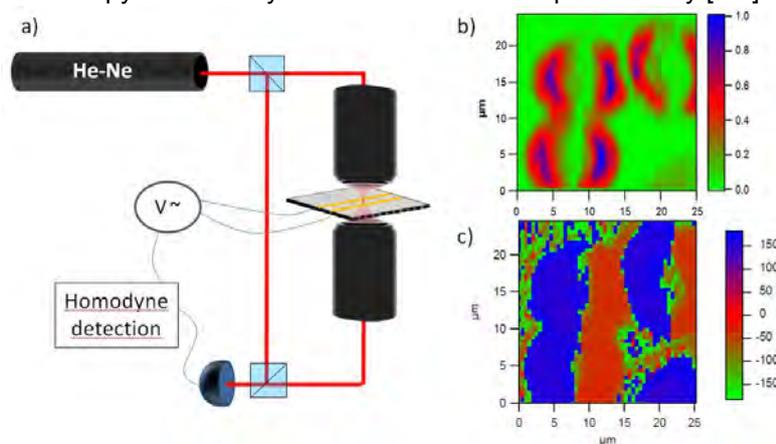


Figure 1 a) schematic principle of the EOM. b,c) EOM amplitude (resp. phase) images of PC12 cells.

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Nano-scale engineering and nonlinear imaging of chiral plasmonic assemblies

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Plasmonic nanostructures are well known for their strong interactions with light, leading to the enhancement of many different optical phenomena. Among them, a spectacular enhancement of the chiroptical effect can be observed. The differences in the interactions of chiral plasmonic nanomaterials with left-handed and right-handed circularly polarized light can be orders of magnitude larger than such differences in organic compounds. Further improvement can be achieved by switching from linear to nonlinear optical phenomena, such as second-harmonic generation (SHG) [1].

We use polarization-resolved two-photon microscopy to investigate the giant nonlinear chiroptical effect in chiral non-centrosymmetric gold nanostructures. Our samples are composed of triangular gold nano-prisms arranged into two-dimensional chiral patterns over a glass substrate. The individual nanostructures follow a 2-D octupolar design where chirality is introduced by way of breaking the mirror symmetries by interaction with adequately set lateral entities, while keeping the overall three-fold symmetry. Large chiroptical effect in SHG have been observed in experiments and confirmed by numerical simulations. Contrary to recently investigated nano-materials, such as the super-chiral surfaces studied by Valev *et al.* [1], our nanostructures constitute independent sub-wavelength super-chiral nano-objects, which can be arranged to form microscopic watermarks. We demonstrate efficient read-out of such watermarks using nonlinear microscopy.

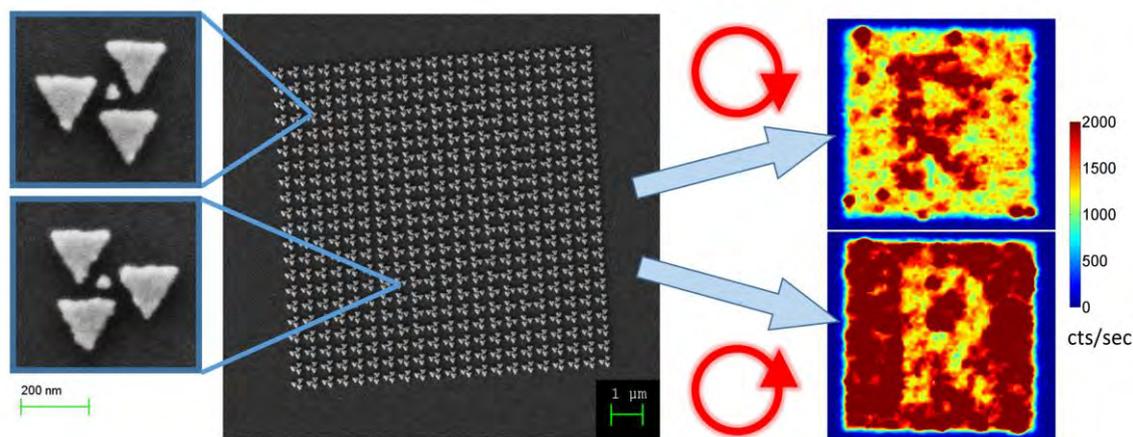


Figure 1 On the left: SEM image of the watermark composed of "left" and "right" enantiomers of a gold nanostructure; on the right: images obtained using two-photon microscopy using right-handed (top) and left-handed (bottom) circularly polarized light for excitation.

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Mechanofluorochromic Materials: Synthesis and Photophysical Properties of Carbonyl Substituted Difluoroboron β -Diketones dyes.

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Mechanofluorochromic (MFC) materials are a class of “smart” materials characterized by a modification of their emission wavelength, in the solid-state, when submitted to external mechanical stimuli (compressing, smearing, shearing). Since their first discovery, about a decade ago [1], they have acquired significant interest in particular for their possible use as mechanical sensors [2]. We decided to focus on the difluoroboron β -diketone dyes family, already known to exhibit significant solid-state emission as well as MFC [3] and to functionalize them with new carbonyl substituents to investigate the effect of those substituents on solid state fluorescence and MFC.

We synthesized a short series of difluoroboron β -diketone derivatives which all demonstrate MFC behaviour. The synthesis of those novel compounds along with their photophysical properties, in solution as well as in bulk solid and films deposited on glass, will be presented.

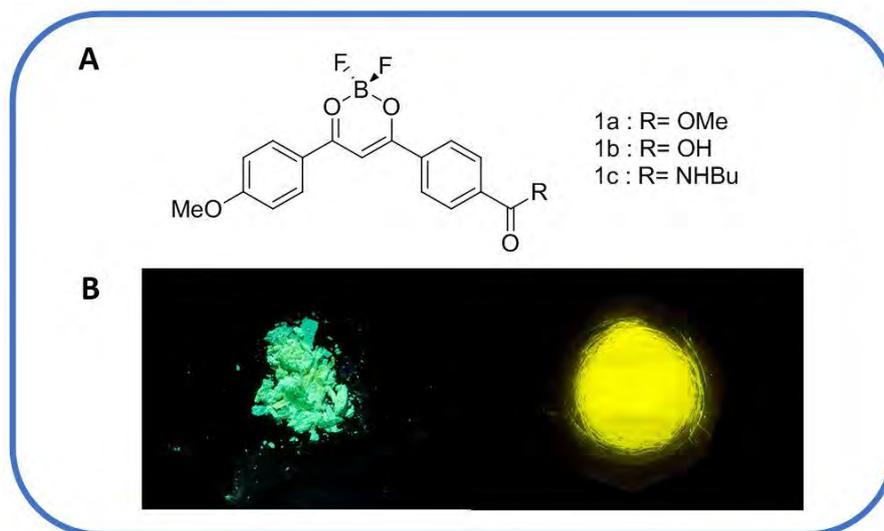


Figure 1. A. MFC dyes synthesized. **B.** Fluorescence of **1c** before (left) and after (right) smearing

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Second harmonic generation from silver nanoparticles in aqueous solution with different protective agents

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Nanometer-sized metallic colloidal particles with plasmonic resonances in the visible range are widely investigated for their attractive optical properties as sensors, for imaging and cancer treatment. Second harmonic generation (SHG) has emerged over the last decade as a powerful technique to measure the first hyperpolarizability tensor (β) of metallic nanoparticles [1]. Their second-order nonlinear optical properties are remarkably high. In this work, silver colloidal solutions have been synthesized by a simple and quick method in aqueous solutions with different protective agents (PVA, PVP). The first hyperpolarizability β values of Ag per atom and per particle for nanospheres at 1064 nm have been measured by Harmonic Light Scattering. Silver nanoparticles, which possess intense visible region surface plasmon absorption bands, prove to be excellent nonlinear scatterers.

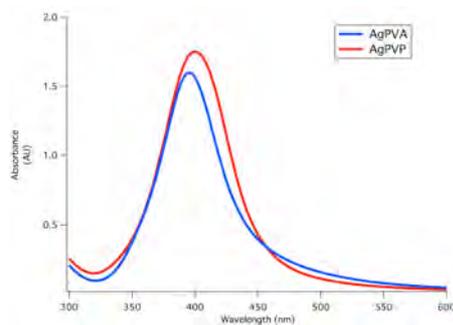


Figure 1. UV-Vis Absorption spectra of synthesized AgNPs.

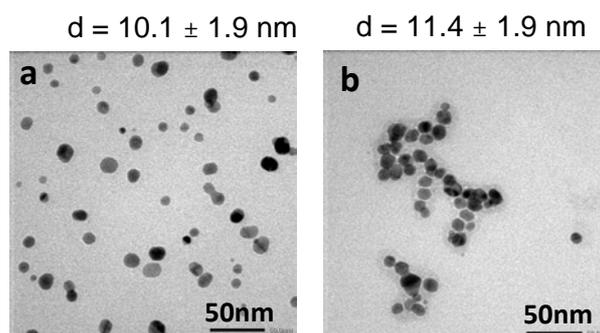


Figure 2. TEM image of AgNPs: (a) AgPVA, (b) AgPVP.

Table 1. The first hyperpolarizability (β) of Ag per atom and per particle.

Sample	Size Dia. (nm)	Volume (nm ³)	N _{Ag} per particle	Particle Conc.	β per particle (β) (10^{-26}) esu	β per Ag atom (β') (10^{-30}) esu
AgPVA	10.1	539.5	31442	4.0E-9	1.58	88.9
AgPVP	11.4	775.7	45213	2.8E-9	1.81	85.2

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Precisely embedding a single gold nanoparticle into polymeric photonic structure by LOPA-based direct laser writing

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We have precisely positioned and embedded a single gold nanoparticle into a desired polymeric microstructure using a simple and low cost technique called low one-photon absorption direct laser writing (LOPA DLW), with a two-step process: (i) determination of the position of a gold nanoparticle by using ultra-low excitation power (μW), and (ii) fabrication of the structure containing Au NP with high excitation power (mW). Figure 1(a) shows a part of the fluorescence image obtained at the first step, in which two individual Au NPs corresponding to two yellow marks are well identified with a precision < 20 nm. The fabrication step was performed by an excitation power of 3.8 mW since the absorption of SU8 photoresist at the excitation wavelength (532 nm) is very low. Figure 1(b) shows a SEM image of two fabricated structures consisting of micropillars arranged in a hexagonal configuration, where a single Au NP is embedded in the central pillar, and figures 1(d) and 1(e) show the zoom in of the central area. It can be clearly seen that the structure was well fabricated. However, instead of a pillar as expected, a microsphere was created at the position of the Au NP. The formation of the microsphere can be explained by the localized surface plasmon resonance of the Au NP at 532 nm - wavelength. Furthermore, the sample was placed back to the LOPA setup and the fabricated structure was characterized by measuring the fluorescence signal. Figure 1(c) shows the fluorescence image of the two corresponding fabricated structures. The image confirms the existence of a single gold NP in the structure and a six-fold fluorescence collection enhancement as compared to that obtained by a NP in unpatterned film [1]. The coupling of the NP and the photonic structure has been further confirmed by the numerical calculation using FDTD method.

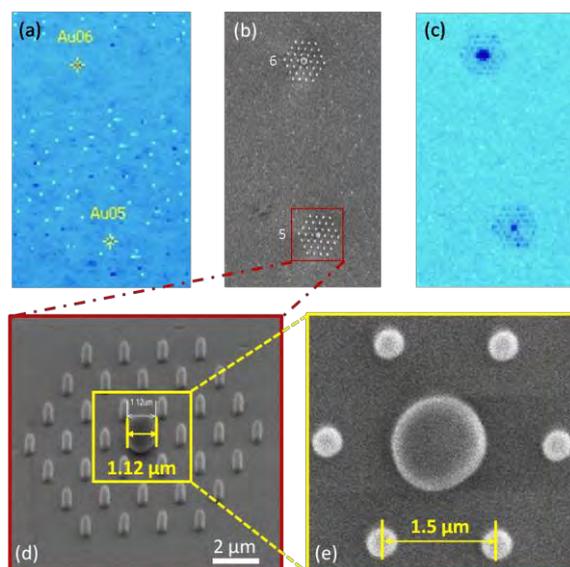


Figure 1: (a) Fluorescence image of gold nanoparticles before fabrication. (b) SEM image of fabricated structures, each contains a gold nanoparticle at the center. (c) Fluorescence image of corresponding fabricated structures. (d)-(e) Zoom in images of a fabricated structure containing a single gold nanoparticle.

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Photoswitchable and multicolor fluorescent-photochromic nanoparticles

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Development of new optical devices, such as optical memories, biocompatible fluorescent switches or well designed probes for optical sub-diffractive imaging, represents a considerable interest in the field of nanotechnologies.

In this presentation, we describe the synthesis of photochromic diarylethene families (DAE) and the combination with dicyanomethylene (DCM) fluorophores embedded in silica core – surfactant shell nanoparticles.^{[1][2]} Photophysical properties of “nano-photo-switches” hybrids have been studied by absorption and fluorescence spectroscopy in order to characterize their light-controllable optical properties and unravel the multiple Förster resonance energy transfer (FRET) processes between the fluorescent and photochromic moieties.^[3]

Figure 1 Target dyes and expected multiple energy transfer processes (FRET).

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Fluorescent nano-objects for the study of bacterial physiology

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We have developed novel fluorescent nano-objects that can be used for the study of bacterial physiology and for the design of biosensors used to detect the presence of pathogenic and antibiotic-resistant bacterial strains. These nano-objects include fluorescent, organic nano-particles and fluorescent polymer chains. The organic fluorescent nano-particles developed at the PPSM have several advantages compared to other fluorophores: they are stable in biological media and non-toxic to bacterial growth and they are very bright and do not blink, which are key properties for extended-time, single molecule tracking experiments. In addition, the side chains of these NPs are easily functionalized, which allows for direct coupling to antibodies to direct them to specific targets within a biological sample. The modification of the side chains with a pH sensitive fluorophore has resulted in the development of a pH-sensitive biosensor to detect the presence of bacterial growth. In addition, we have used fluorescent polymer chains (FPC) to efficiently label the bacterial cells. Different versions of these polymer chains are either internalized or remain fixed to the cell membrane, resulting in differential labeling (Figure 1). This approach can be used in the detection of the presence of bacteria by flow cytometry or microscopy. This provides a relatively low cost solution to bacteria detection compared to existing fluorophores.

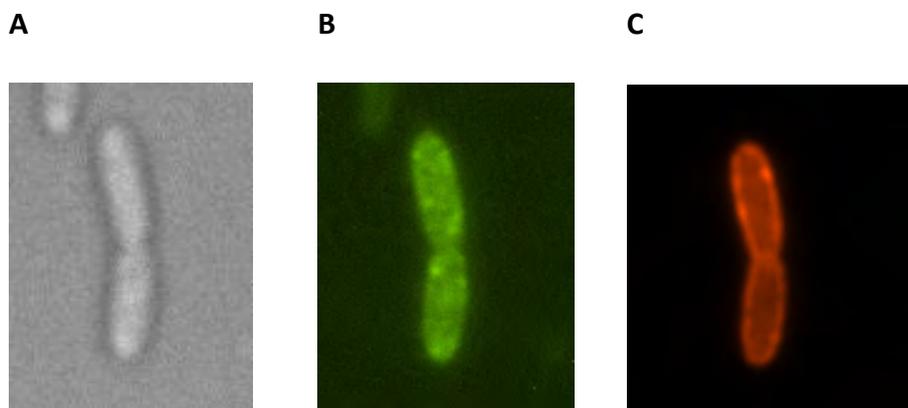


Figure 1. *E.coli* cells interacting with (B) negatively charged green fluorescent polymer chains (GFPC-) and (C) positively charged red fluorescent polymer chains (RFPC+).

Realization of polymer-based 2D or 3D arbitrary form micro-resonators by low one-photon absorption direct laser writing technique

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In this work, we demonstrate the use of low-one photon absorption (LOPA) - based direct laser writing (DLW) technique to fabricate desired 2D and 3D micro-resonators (MRRs) and waveguides structures. Figure 1(a) illustrates the experimental setup of the LOPA-based DLW technique. A laser beam is tightly focused into the sample by a high numerical aperture (NA) objective lens (OL). Thanks to the use of such high NA OL, the light intensity at the focusing area is increased by a factor of about 10^8 times, allowing compensate the ultralow absorption effect of the photoresist at the excitation wavelength, and resulting in a local efficient polymerization effect of photoresist. A few milliwatts of a continuous green laser is enough to realize desired structures in a commercial SU8 photoresist [1].

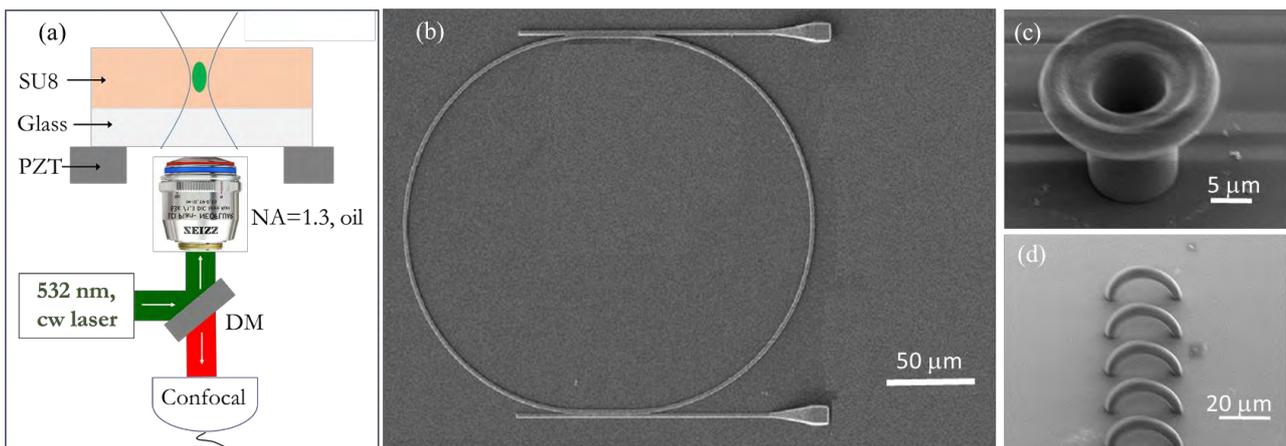


Figure 1 : (a) Illustration of the LOPA-based DLW experiment used to fabricate desired 2D and 3D micro-resonators. PZT: piezoelectric translator; DM: dichroic mirror; NA: numerical aperture of microscope objective. (b-d) SEM images of a 2D micro-ring-coupled waveguide (b), a 3D micro-ring (c) and 3D waveguides (d), realized on SU8 photoresist with various sizes and shapes.

In order to fabricate desired MRRs, we first pre-designed structures and optimized their optical properties by using Finite Difference Time Domain (FDTD) numerical calculation. Different structures have been numerically simulated showing that polymer-based MRRs possess interesting properties and they can be used for many applications. We then fabricated corresponding structures in SU8 photoresist by using LOPA-based DLW. Figure 1(b) shows, for example, a 2D micro-ring coupled to waveguides, where the ends of each waveguide are fabricated with a 3D taper in order to easily couple the light into/out of the waveguide. Figures 1(c) and 1(d) show a 3D micro-ring and 3D curved waveguides (rainbow), respectively. These structures are very promising, as compared with traditional 2D structures. Indeed, in terms of optical properties, a 3D micro-ring possesses a high Q-factor, and for practical uses, a curved waveguide allows easy coupling.

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Modelling the oscillation frequency drift of an optoelectronic oscillator based on a vector network analyzer

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In his classical topology [1] an opto-electronic oscillator (OEO) is a delay line oscillator: the oscillation frequency is determined by the length of the optical fibre. A RF filter selects the desired frequency among the frequency comb corresponding to the phase condition of the oscillations. The effective index of the optical fibre depends on temperature, therefore long term temperature variations induce a frequency drift which can be a problem specially for sensing application such as refractive index measurement [2]. In this work we present a study on the frequency drift during time, resulting from the change in the propagation time across the optical fibre. For that a second loop has been added to the classical OEO topology. A vector network analyser (VNA) is introduced in order to measure the phase-shift of a second modulating signal applied to the electro-optic modulator leading to the propagation time determination.

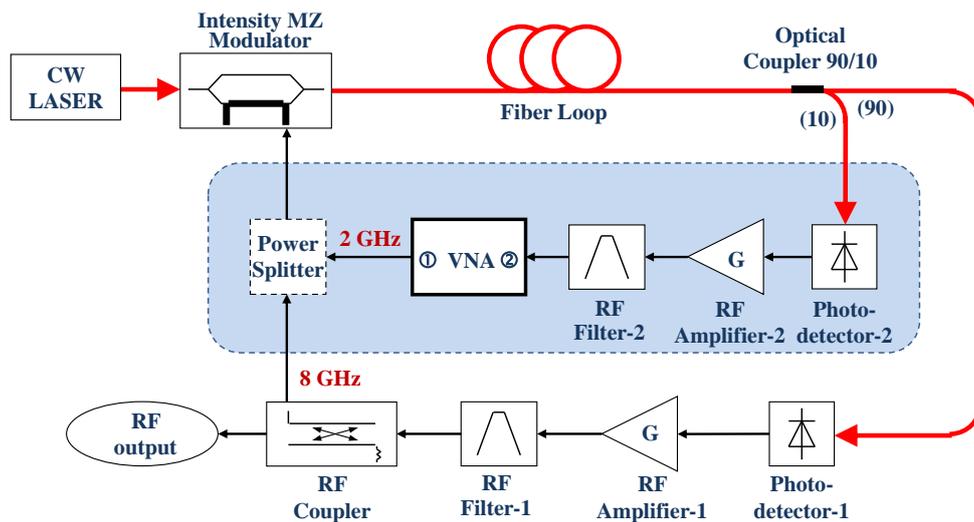


Figure 1: Vector network analyser based system for detection of the OEO frequency drift resulting from the optical fibre temperature variations.

The study is conducted for approximately 10 hours, with three different lengths of the optical fibre and in two different experimental conditions concerning the temperature of the fibre. All the experiments show the close correlation between frequency drift and phase of the S_{21} parameter, and the experimental results are in a good agreement with the theoretical calculation. Finally a modelling of the frequency drift calculated from the S_{21} phase can be used for a calibration of the oscillation frequency, which is fundamental in case of long-term applications. Nevertheless, there is still some residual frequency fluctuations of more than approximately 1 kHz after the correction, limiting the resolution of refractive index measurements to 10^{-2} in long-term applications instead of the 3×10^{-3} one in case of short-term applications. Future work should be reducing these fluctuations and improving the OEO topology.

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