



TGSW2018

Session 4-1

Ensemble of Light with Molecules, Materials, and Life for Sustainable Society

(持続可能な社会の実現に向けた光と分子・物質・生命科学のアンサンブル)

Program and Abstract

September 22, 2018

Venue: Room 202B, Tsukuba International Congress Center

Symposium: Organized by University of Tsukuba



Program

Morning Session: Molecular Assembly (9:30-11:50)

9:30-9:35 Opening Remark (Yohei Yamamoto)

9:35-10:15 Prof. Amar Flood (Indiana Univ. USA)

Anions in Molecular Recognition, Switching, and Hierarchical Assembly

10:15-10:45 Dr. Katsuhiko Ariga (NIMS & Univ. of Tokyo, Japan)

Control of Molecular Machine, 2D Material, and Life at Langmuir Interface

(15 min. break)

11:00-11:30 Prof. Hyo Jae Yoon (Korea Univ. Korea), Gyu Don Kong, Junji Jin, Hyunsun Song,

Mixing for Good: Charge Tunneling across Large-area Molecular Electronic Devices based on Mixed Self-Assembled Monolayers

11:30-11:50 Prof. Tatsuya Nabeshima (Univ. Tsukuba, Japan)

Design, Synthesis and Novel Functions of BODIPY Derivatives

Lunch Break (11:50-13:00)

Afternoon Session : Soft Optics, Lasers, Terahertz, etc. (13:00-17:25)

13:00-13:40 Dr. Jer-Shing Huang (Leibniz Inst. Germany), Jhih-Yuan Chen, Zhan-Hong Lin, Soh Kushida, Yohei Yamamoto

Goos-Hänchen Shift and Plasmon Coupling of Whispering-gallery Modes in a Self-assembled Fluorescent π -conjugated Polymer Sphere on Ultra Flat Gold Surface

13:40-14:10 Dr. Yasuhiro Ishida (RIKEN, Japan)

Photonic Crystals Composed of 99% Water and 1% Inorganic Nanosheet

14:10-14:30 Dr. Takashi Nakanishi (NIMS, Japan)

Novel Soft Matter/Materials; Optoelectronically-active Alkyl- π Molecular Liquids

(15 min. break)

- 14:45-15:25 Prof. Maurizio Ferrari (CNRS, Italy)
Glass and Glass-Ceramic Photonic Systems: advances and perspectives
- 15:25-15:45 Dr. Tadaaki Nagao (NIMS, Japan), Thang D. Dao, Kai Chen, Satoshi Ishii, Robert P. H. Chang
Nanomaterials and Their Surface Functionalization for Infrared Plasmonics Applications
- 15:45-16:05 Prof. Yohei Yamamoto (Univ. Tsukuba, Japan)
Self-Assembled Organic/Polymeric Microlasers and Photoswitchable Arrays

(15 min. break)

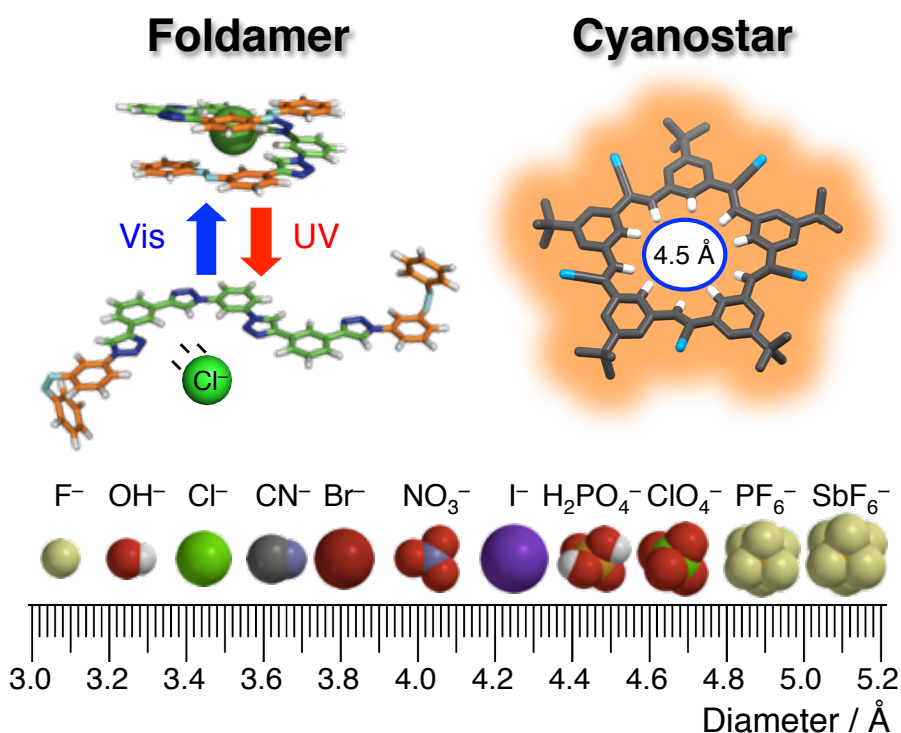
- 16:20-16:40 Dr. Fumio Sasaki (AIST, Japan)
Developments of organic semiconductor microcavities: from wafer processes to solution processes
- 16:40-17:00 Prof. Tatsuya Mori (Univ. Tsukuba, Japan), Yasuhiro Fujii, Yue Jiang, Leona Motoji, Suguru Kitani, Akitoshi Koreeda, Kentaro Shiraki, Yohei Yamamoto, Seiji Kojima
Terahertz Time-Domain Spectroscopy of Lyophilized Protein Lysozyme –Universal Dynamics of Disordered System in the Terahertz Region–
- 17:00-17:20 Mr. Mario Ziegler (Leibniz Inst. Germany)
Metastable Atomic Layer Deposition
- 17:20-17:25 Closing Remarks (Prof. Tatsuya Nabeshima)
- 18:00- Reception

Anions in Molecular Recognition, Switching, and Hierarchical Assembly

Amar Flood

Department of Chemistry, Indiana University

Anions are intimately related to the sustainable development of our society. The use of synthetic receptors to manage anions provides the means to support the safe production of food, energy and water. These include the overfertilization of crops with phosphate (H_2PO_4^-) for high-yield food production that contaminates waterways, hexafluorophosphate (PF_6^-) as the workhorse electrolyte in Li-ion batteries, and perchlorate anions (ClO_4^-), a rocket-fuel propellant, that infiltrates drinking water and damages human health. This talk will cover recent works tackling these anions with shape-persistent, and size-selective macrocycles, such as triazolophane [1], cyanostar [2], and tricarb [3], and with shape-dynamic and photoswitchable foldamers [4]. Hierarchical assembly involving anions will also be outlined, including those derived from the unexpected propensity for *anti*-electrostatic polymerization of phosphate [5].



References: [1] Liu *et al. Chem* **2017**, 3, 411427; [2] Lee *et al. Nat. Chem.* **2013**, 5, 704; [3] Lee *et al. Chem. Eur. J.* **2016**, 22, 560; [4] Hua *et al. JACS* **2010**, 132, 12838; [5] Fatila *et al. Chem. Sci.* **2018**, 9, 2863

Control of molecular machine, 2D material, and life at Langmuir interface

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Abstract: Here we propose a novel methodology “hand-operating nanotechnology” where molecular orientation, organization and even functions in nanometer-scale can be operated by our macroscopic (hand) operation. This concept can be realized at dynamic two-dimensional medium such as thin films at the air-water interface, i.e., Langmuir monolayer because this medium possess both features of bulk and molecular dimension. For example, we successfully manipulated molecular machines at the air-water interface upon bulk (10-100 cm size) motion of the entire monolayer and realized “capture and release” of aqueous guest molecules using molecular machine, steroid cyclophane (Figure 1). In addition, mechanically controlled chiral recognition of amino acid and discrimination of nucleosides by the supramolecular monolayer was successfully demonstrated. The concept has been also applied to indicator-displacement assay for sensor usage.

These examples demonstrate our new concept, manual nanotechnology so-called, hand-operating nanotechnology, with which we can manually control nano/molecular phenomena and functions by macroscopic mechanical force such as hand motions. Using hands for functional operation would be most environmentally friendly and least energy consuming technology.

In addition, recent accomplishments on cell differentiation control and 2D nanocarbon fabrication at Langmuir media will be presented.

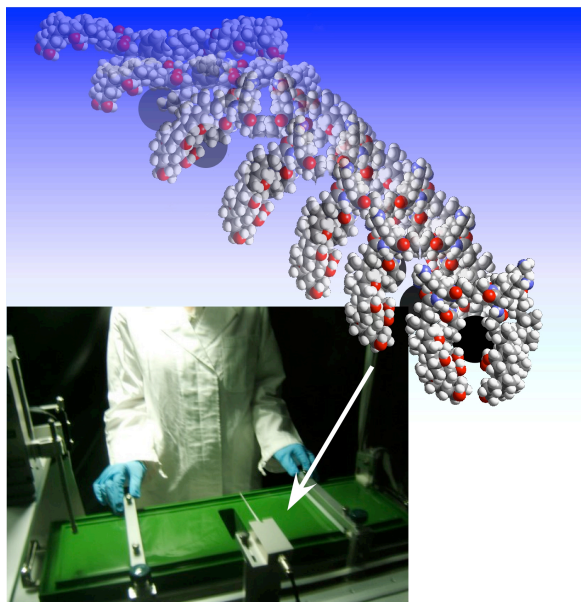


Figure 1. Manipulation of molecular machine by macroscopic mechanical motions.

Title: Mixing for Good: Charge Tunneling across Large-area Molecular Electronic Devices based on Mixed Self-Assembled Monolayers

Gyu Don Kong, Junji Jin, Hyunsun Song, Hyo Jae Yoon*

Department of Chemistry, Korea University, Seoul 02841, South Korea

Abstract

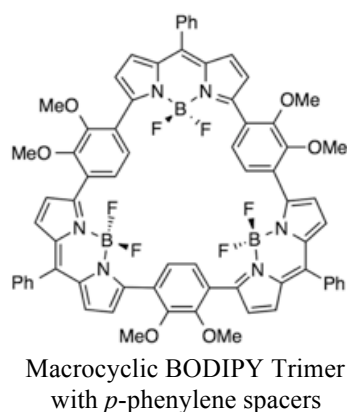
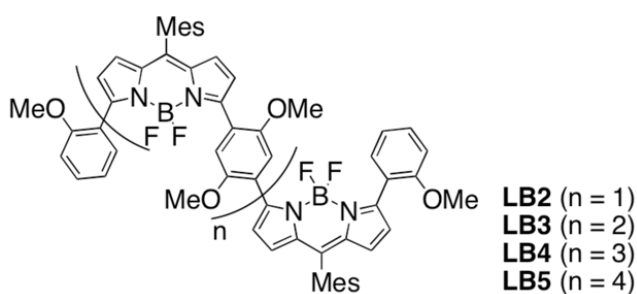
Molecular electronics promises miniaturization of electrical components into the molecular scale. An important goal in molecular electronics is to relate the rates of charge transport by quantum tunneling across device to chemical and electronic structure of molecule inside it. This goal is, however, difficult to achieve since the simplest molecular electronic device such as an electrode-molecule-electrode junction is even a complicated physical-organic system where the complexities arising from ill-defined molecule-electrode interfaces and from complicated molecular structure on surface often exist. In large-area molecular electronic devices, molecules are packed and disordered to some extent, and understanding how intermolecular interactions between molecules affect the performance of devices is a significant challenge. This presentation focuses on our recent effort to resolve this problem by harnessing mixed self-assembled monolayers to achieve molecular-level control of supramolecular structure on surface, and a junction platform based on liquid metal top-electrode to guarantee high-yield of working devices. We will show the synthesis and characterization of various pure and mixed monolayers composed of *n*-alkanethiolates of different lengths, or organic molecular diode (4,4'-bipyridine-terminated *n*-alkanethiolate) and non-rectifying *n*-alkanethiolates. The tunneling behaviors of these mixed monolayers as a function of the length difference between the molecules inside monolayers and their molar ratio will be discussed to evidence the supramolecular structural effect on the performance of tunneling devices.

Design, Synthesis and Novel Functions of BODIPY Derivatives

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Abstract: Dipyrroin-boron complex, BODIPY and its derivatives have been used as a sensor, a bioimaging tool, etc., because they exhibit excellent photophysical properties and photostability. However, applications of the BODIPY derivatives and analogs to functional host molecules that utilize a B-F unit as a binding site are interesting and important but still limited. Thus, we synthesized macrocyclic [1,2] and linear [3] BODIPY oligomers as a host molecule, in which the BODIPY units work as an emissive unit and a binding site for a guest through a new type of B-F...cation interactions. Uv-vis and fluorescence spectra of the cyclic and linear BODIPY derivatives were changed in the presence of a cationic guest. A macrocyclic BODIPY trimer bearing *m*-phenylene spacers exhibits high recognition ability to secondary ammonium salts, especially to protonated adrenaline through noncovalent interactions including CH- π interactions and hydrogen bonds between B-F and the ammonium protons. Other functionalized BODIPYs, chiral derivatives showing CPL, and BODIPY analogs [4-9] will be also discussed.



Reference:

- [1] N. Sakamoto, C. Ikeda, T. Nabeshima, *Chem. Commun.*, **46**, 6732 (2010).
- [2] T. Nakamura, G. Yamaguchi, T. Nabeshima, *Angew. Chem. Int. Ed.*, **55**, 9606 (2016).
- [3] N. Sakamoto, C. Ikeda, M. Yamamura, and T. Nabeshima, *Chem. Commun.*, 2012, **48**, 4818 (2012).
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- [5] N. Sakamoto, C. Ikeda, M. Yamamura, and T. Nabeshima, *J. Am. Chem. Soc.*, **133**, 4726 (2011).
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- [9] Y. Gobo, M. Yamamura, T. Nakamura, and T. Nabeshima, *Org. Lett.*, **18**, 2719 (2016).

Goos-Hänchen Shift and Plasmon Coupling of Whispering-gallery Modes in a Self-assembled Fluorescent π -conjugated Polymer Sphere on Ultra Flat Gold Surface

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Abstract: Fluorescent π -conjugated polymer is semiconducting and can be electrically pumped to generate light. A method to create self-assembled almost perfect microspheres made of such polymer that support whispering-gallery modes (WGMs) has been developed by Yamamoto and coworkers [1]. Toward electrical pumping of the WGMs, contact with noble metals, such as gold could be necessary. To this aim, the influence of the substrate on the optical properties of the microsphere cavity needs to be well understood. Here, we theoretically and experimentally study the influence of atomically flat gold substrate [2] on the WGMs of the fluorescent π -conjugated polymer microspheres (Fig. 1a). We selectively excite different WGMs by controlling the position of the laser focal spot. Spectral shift and intensity change due to the gold substrate have been observed and explained. For the spectral shift, we found blue and red shift for the meridian TE and TM modes, respectively (Fig. 1b). We attribute the different spectral shift is due to the opposite sign of Goos-Hänchen shift of the WGMs. As for the intensity, we found that gold substrate enhances the spectral intensity. However, the intensity ratio of TE/TM is reduced because the TM modes couple into surface plasmons on gold surface via Otto-coupling configuration (Fig. 1c) [3]. Our work gains insight into the influence of gold substrate on the WGMs and provides important information for the realization of electrically pumped WGM lasers, which may provide a practical light source of plasmonic integrated optical nanocircuits [4-6].

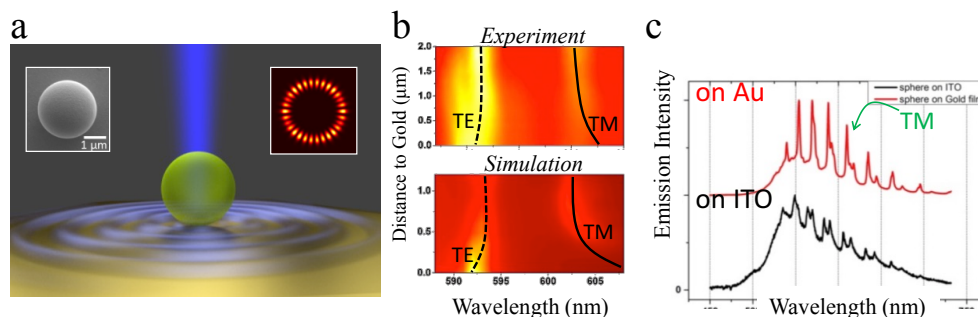


Fig. 1. (a) Illustration of the concept of this work. The left inset shows the SEM image of the sphere and the right one shows the simulated field distribution of the spheres in air. (b) Spectral shift of TE and TM obtained from experiment and FDTD simulations. The red shift of TM is due to the negative Goos-Hänchen shift. (c) Emission spectra of sphere on gold (upper, red) and ITO substrate (bottom, black).

Reference:

- [1] T. Adachi, L. Tong, J. Kuwabara, T. Kanbara, A. Saeki, S. Seki, Y. Yamamoto, *J. Am. Chem. Soc.* **135**, 870-876 (2013).
- [2] J.-S. Huang *et al.*, *Nat Commun.* **1**, 150 (2010).
- [3] P. Biagioni, J.-S. Huang, B. Hecht, *Rep. Prog. Phys.* **75**, 024402 (2012).
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- [5] Y.-T. Hung, C.-B. Huang, J.-S. Huang, *Opt. Exp.* **20**, 20342-20355 (2012).
- [6] W.-H. Dai, F.-C. Lin, C.-B. Huang, J.-S. Huang, *Nano Lett.* **14**, 3881-3886 (2014).

Photonic Crystals Composed of 99% Water and 1% Inorganic Nanosheet

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Abstract: Photonic crystals are ordered nanostructures with a periodicity of visible-light wavelength, which can control the properties of lights, such as exhibiting structural colors. If a fluid forms such a nanostructure, its structural color could be dynamically modulated by external stimuli. Indeed, some fish can dynamically change their colors by modulating the periodic distance of crystalline guanine sheets cofacially oriented in their fluid cytoplasm. In this presentation, we report that a dilute aqueous colloidal dispersion of negatively charged titanate nanosheets, which we have extensively studied in these years [1–6], exhibits structural colors [4,6].

In this particular colloidal dispersion, the nanosheets spontaneously adopt a cofacial geometry with an ultralong periodic distance of up to 675 nm due to a strong electrostatic repulsion. Because the periodic distance can be tuned over a wide range by the nanosheet concentration, the reflection wavelength can be modulated from UV to visible and even to near-infrared region up to 1,750 nm. The structural color becomes more vivid in a magnetic flux that induces monodomain structural ordering of the colloidal dispersion. The reflective color of the photonic water can be modulated over the entire visible region in response to appropriate physical or chemical stimuli.

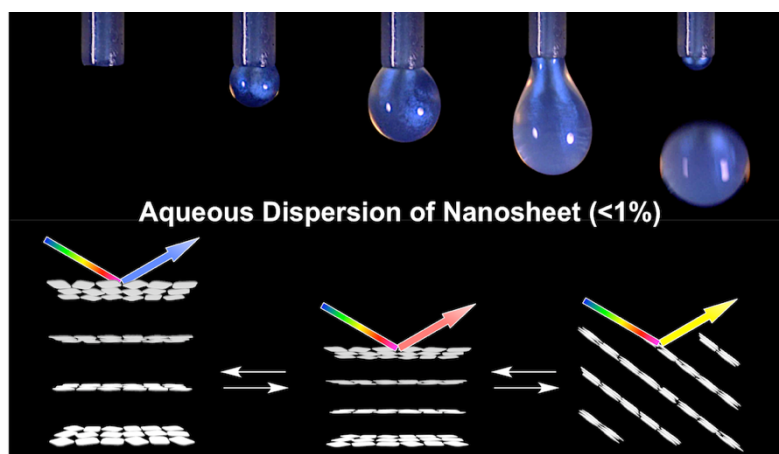


Fig. Pictures of the aqueous dispersion of titanate nanosheets (0.45 vol%) dropping from a thin capillary (upper) and its color modulation mechanism by tuning the periodic distance or the direction of the nanosheets in response to external stimuli.

Reference:

- [1] M. Liu *et al.* *Nature Commun.* **4**, 2029 (2013).
- [2] M. Liu *et al.* *Nature* **517**, 68 (2015).
- [3] Y. S. Kim *et al.* *Nature Mater.* **14**, 1002 (2015).
- [4] K. Sano *et al.* *Nature Commun.* **7**, 12559 (2016).
- [5] K. Sano *et al.* *Angew. Chem. Int. Ed.* **57**, 2532 (2018).
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Novel Soft Matter/Materials; Optoelectronically-active Alkyl- π Molecular Liquids

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Abstract: Our recent research interest is to develop novel ultimate-soft organic materials, i.e., room-temperature functional molecular liquids (FMLs) composed of a π -conjugated molecular unit bearing bulky, flexible branched alkyl chains (Figure 1). There are no charged units on the molecule, thus FMLs show a clear contrast with ionic liquids (ILs) in terms of functions in their liquid form. The studies of multi-color tunable luminescent liquids based on blue-color emitting, electron-donor type liquids^{1,2)} and uncommon phase phenomena with the photoconducting property of liquid fullerenes^{3,4)} are designed simply by controlling a balance of intermolecular interactions in the alkyl- π compounds, i.e., van der Waals and π - π interactions among adjacent molecules, or “alkyl- π engineering”⁵⁾. Here, the molecular design principle of FMLs based on an alkylated- π molecular systems, and their luminescent and optoelectronic properties as well as liquid phase control⁶⁾ are presented. The π -unit molecular component described in this paper will be naphthalene⁷⁾, anthracene^{2,6)}, pyrene⁸⁾, phthalocyanine⁹⁾. The latest our attempt such as supercooling phenomena of blue emitting liquid anthracenes⁶⁾ and development of liquids possessing spin-active nature synchronized with electrochromism⁹⁾ will be mainly discussed in the presentation.

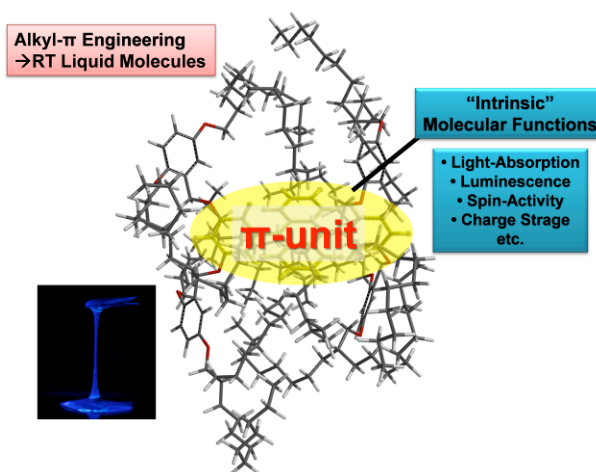


Fig. 1. A schematic drawing of alkyl- π functional molecular liquids and a photograph of typical blue emitting liquid.

Reference:

- 1) *Angew. Chem. Int. Ed.*, **2012**, *51*, 3391-3395. (Highlighted in *Nature*, **2012**, *484*, 9.)
- 2) *Nature Commun.*, **2013**, *4*, 1969.
- 3) *Nature Chem.*, **2014**, *6*, 690-696.
- 4) *J. Am. Chem. Soc.*, **2006**, *128*, 10384-10385.
- 5) *Chem. Commun.*, **2017**, *53*, 10344-10357. (Feature Article)
- 6) *Chem. Sci.*, **2018**, *9*, 6774-6778. (Hot Article, Backside Back Cover Page, Highlighted in *ChemSci Pick of the Week*)
- 7) *Phys. Chem. Chem. Phys.*, **2018**, *20*, 2970-2975. (Hot Article, Inside Front Cover Page)
- 8) *Sci. Rep.*, **2017**, *7*, 3416.
- 9) *Chem. Asian J.*, **2018**, *13*, 770-774.

Tsukuba Global Science Week (TGSW) symposium, session “Ensemble of Light with Molecules, Materials, and Life for Sustainable Society”.

Glass and Glass-Ceramic Photonic Systems: advances and perspectives

Lidia Zur^{1,2}, Thi Ngoc Lam Tran^{2,3,4}, Alessandro Chiasera², Yann G. Boucher^{5,6}, Alessandro Vaccari⁷, Francesco Prudeniano⁸, Damiano Massella^{9,2}, Cesare Meroni^{9,2}, Francesco Enrichi^{1,10}, Stefano Varas², Cristina Armellini², Andrea Chiappini², Alessandro Carpentiero², Maurizio Mazzola², Alexander Quandt¹¹, Dominik Dorosz¹², Anna Lukowiak¹³, Brigitte Boulard¹⁴, Daniele Zonta^{3,2,15}, Roberta Ramponi¹⁶, Giancarlo C. Righini^{1,17}, *Maurizio Ferrari^{2,1}

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Glass photonics is pervasive in a huge number of human activities and drive the research in the field of enabling technologies. Glass materials and photonic structures are the cornerstones of scientific and technological building in integrated optics. Photonic glasses, optical glass waveguides, planar light integrated circuits, waveguide gratings and arrays, functionalized waveguides, photonic crystal heterostructures, and hybrid microresonators are some examples of glass-based integrated optical devices that play a significant role in optical communication, sensing, biophotonics, processing, and computing. We present some recent results obtained by our consortium in rare earth doped photonic glasses and confined structures, in order to give some highlights regarding the state of art in glass photonics. To evidence the unique properties of transparent glass ceramics we will compare spectroscopic and structural properties between the parent glass and the glass ceramics. Starting from planar waveguides we will move to spherical microresonators, a very interesting class of photonic confined structures. Then we will present 1D-photonic crystals and opals allowing management of optical and spectroscopic properties. We will conclude the short review with some remarks about the more significant applications such as laser action and structural sensing and the appealing perspective for glass-based photonic structures.

The research activity is performed in the framework of COST Action MP1401 Advanced fibre laser and coherent source as tools for society, manufacturing and lifescience (2014-2018, ERANET-LAC FP7 Project RECOLA - Recovery of Lanthanides and other Metals from WEEE (2017-2019) and Centro Fermi MiFo (2017-2020) project. L.T.N. Tran acknowledges Vietnamese Ministry of Education and Training for her PhD scholarship.

Tsukuba Global Science Week (TGSW) symposium, session “Ensemble of Light with Molecules, Materials, and Life for Sustainable Society”.

Nanomaterials and Their Surface Functionalization for Infrared Plasmonics Applications

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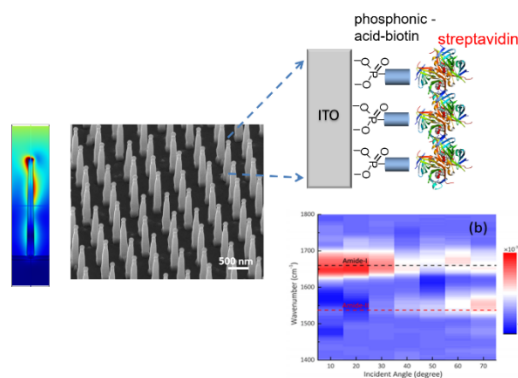
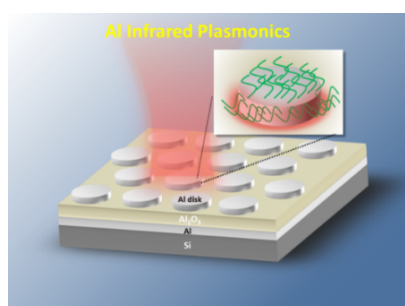
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Abstract

Surface-Enhanced Infrared Absorption (SEIRA) is a phenomenon that vibrational signals from trace amount of analyte or sub-monolayer molecules adsorbed on solid surfaces are dramatically enhanced in their intensities. By utilizing the localized surface plasmon resonances of infrared optical antennas and metamaterials, strong signal enhancement of molecules becomes operative in an effective manner to realize high sensitivity vibrational sensing. Recent developments in nanostructure fabrication techniques as well as their surface functionalization techniques have enabled us to propose and fabricate various types of advanced SEIRA nanodevices in nanophotonics and nano-biosensing field as well as in analytical chemistry. Moreover, recent advances in searching appropriate infrared plasmonic materials beyond noble metals have dramatically widened the possibilities to utilize low-cost base metal and conductive metal oxides for SEIRA applications. In this talk, I introduce the detection of dilute molecules and pathogenic enzymes in solution by *in situ* ATR-IR method using surface-functionalized Au nanogap broadband absorbers, as well as protein SEIRA sensing by surface-functionalized Al optical antennas and metamaterials. We also introduce our new approach utilizing infrared surface plasmons of single crystal ITO nanorod array covered with phosphonic acid to detect proteins with high specificity and sensitivity.



Reference

- [1] T.D. Dao, S. Ishii, T. Yokoyama, T. Sawada, S. Ramu Pasupathi, K. Chen, Y. Wada, T. Nabatame, and T. Nagao, *ACS Photonics* **3**, 1271-1278 (2016).
- [2] Kai Chen, Thang Duy Dao, Tadaaki Nagao, *Scientific Reports* **7**, 440691(2017).
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Self-Assembled Organic/Polymeric Microlasers and Photoswitchable Arrays

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Abstract: Optical microcavities play an important role for the next-generation light technology. Recently, we succeeded in fabricating spherical microcavities from π -conjugated polymers (CPs) by simple self-assembly process (**Fig. 1a**).^[1] We found that the microcavities exhibit whispering gallery mode (WGM) resonant photoluminescence (PL) upon focused laser excitation, where PL generated inside the sphere is confined via total internal reflection at the polymer/air interface.^[2–12] The resonance occurs when the wavelength of the light is an integer multiple of the circumference of the microsphere. The CP-based microcavities have benefits to the conventional microcavities in the following points:

- (1) Simple and low-energy fabrication process to obtain well-defined microspheres
- (2) The microcavities act as both cavity and emitter
- (3) The microcavities possess high refractive index and photoabsorptivity
- (4) Potent use for electrically-driven WGM and laser oscillation.

In this presentation, recent results on the fundamentals of the self-assembly of the CPs, resonant PL from the CP microspheres, intra- and intersphere light energy conversion, optically-pumped lasing (**Fig. 1b**), and the future prospects to realize light- and electrically-driven WGM and lasing will be presented.

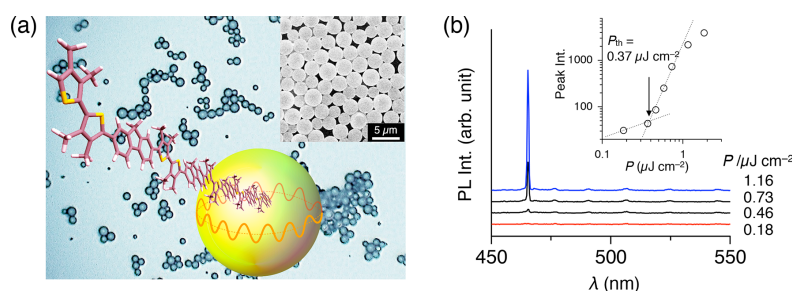


Fig. 1. Schematic representation of the self-assembled conjugated polymer microspheres, optical and SEM micrographs (a), and lasing spectra (b).

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Tsukuba Global Science Week (TGSW) symposium, session “Ensemble of Light with Molecules, Materials, and Life for Sustainable Society”.

Developments of organic semiconductor microcavities: from wafer processes to solution processes

Fumio Sasaki

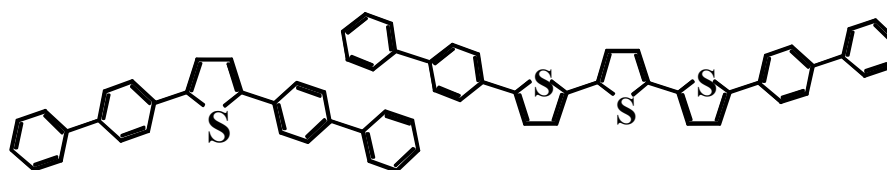
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Practical application of organic electronic luminescence (EL) is progressing steadily, and not only a small display but also large screen display product development is proceeding. Meanwhile, even in the field of lighting where higher brightness is required, a high brightness light source over 200 lm/W which far exceeds the fluorescent light has already been realized at the research level. The high brightness LEDs with high energy efficiency light sources are mainly made from a group III-V inorganic semiconductors. Furthermore, lighting applications of laser diode (LD) are also expected from the viewpoint of energy saving, because LD with the stimulated emission has higher energy efficiency than that of LED with the spontaneous emission. Recently, LD puts into practical use in the field of high performance headlights and laser projectors. However, LD with current injected lasing is realized only in inorganic semiconductor material systems. Many researchers have tried actively to realize current injected organic semiconductor lasers, but almost all of the trial have failed. More recently, reports on current injected optical amplification in light emitting transistors (LETs) using organic single crystals have been reported at the Japan Applied Physics Society. They used organic single crystal of thiophene/phenylene co-oligomers (TPCOs), examples of molecular structures are shown below. We have developed formation of microcavities by wafer process and realized reduction of optically pumped lasing in TPCOs. We will outline the formation of microcavities by wafer processes in TPCO organic semiconductor materials, and related topics of microcavity formations by solution processes including an organic/inorganic complex perovskite semiconductor material.

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Terahertz time-domain spectroscopy of lyophilized protein lysozyme -universal dynamics of disordered system in the terahertz region-

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Disordered materials show universal dynamics in the terahertz region, i.e., the so-called boson peak (BP), and it is recognized as one of the unsolved problems in glass physics [1]. The BP universally appears at the THz region in the spectrum of the density of states divided by the squared frequency. The spectrum deviates from the Debye model for a crystalline system, and has been experimentally and theoretically investigated for several decades [1,2]. Recently, we pointed out that the BP in the infrared spectrum appears in the representation of $\alpha(\nu)/\nu^2$ [2-4], where $\alpha(\nu)$ is the absorption coefficient, although this fact is well known to past researchers.

On the other hand, in the self-similar disordered structure, such as a polymer glass and proteins, it is expected to exhibit the fractal dynamics called a *fracton*. The fracton will appear above the boson peak frequency [6,7], because the dynamics relates the inter-molecular vibrations of the monomer structure of the self-similarity materials. However, there are few studies of the fracton by far-infrared spectroscopy, because the theoretical understanding of how the terahertz light and fracton modes couple has not progressed. In this study, we propose how to detect fractal dynamics by terahertz spectroscopy using the protein lysozyme as an example.

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Metastable atomic layer deposition

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An important feature of atomic layer deposition (ALD) is the fact that the coating that has been deposited is conformal to the substrate surface. Therefore, pre-patterned substrates are usually used for the fabrication of 3D nanostructures using ALD. Here, we present a new method to generate 3D silver-silica nanostructures using plasma enhanced atomic layer deposition (PEALD) of silica with tri-dimethyl-amino-silane (TDMAS) and oxygen plasma as precursors. Unlike the conventional ALD, the coating of MS-ALD is not conformal to the substrate surface. Rather, the 3D nanostructures are self-assembled because of side-reactions. The geometry of the formed nanostructures can be easily adjusted by tuning the deposition parameters, such as dose time of both precursors and cycle numbers. By doing so, we observed nanoporous and microporous sponge-like structures as well as nanowire like structures with feature sizes of up to 10 μm (Fig. 1). This talk gives an overview over diverse generated structures. In addition a suggestion for the growth theory is given.

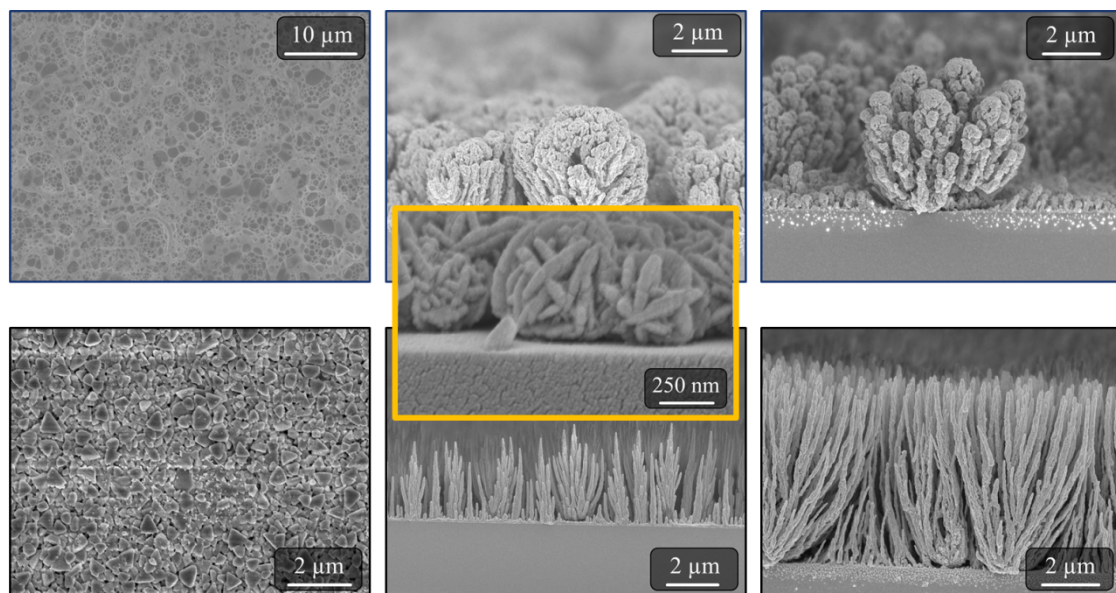


Figure 1: SEM images of diverse structures generated using MSALD and an enzymatically generated nanoparticle as template (center)

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