International Associate Laboratory
LIA
NANO-SYNERGETICS

Photo-active Nanomaterials with Cooperative and Synergetic Responses

Report on 2017-2019 Activities

2nd Steering Committee
9th March 2020

Introduction

- The International Associate Laboratory on Photo-active Nanomaterials with Cooperative and Synergetic Responses (LIA Nano-Synergetics) is a “laboratory without walls” between research groups from École normale supérieure Paris-Saclay (ENS Paris-Saclay), Lille University, Centre national de la recherche scientifique (CNRS), Osaka University, Nara Institute of Science and Technology (NAIST), Kyoto University and Aoyama Gakuin University (AGU).

- After an assessment process, recognition as LIA was granted by CNRS in December 2016 with a financial support from 2017. With an official start on 1st January 2018, an agreement was signed in May 2018 for 2018-2021 between the 7 partner institutions, which support the activities of Nano-Synergetics. It is largely supported by an international action exchange scheme within Photo-Synergetics (2015-2019, Kokusai Katsudo Shien Han), a Grant-in-Aid for Scientific Research on Innovative Areas, Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

- French and Japanese researchers within Nano-Synergetics have significant records of collaborations from 2007 (bilateral projects and exchange of researchers and students). They were members of the International Research Group on PHoto-switchableE orgaNIC molecular systems & deviceS (GDRI PHENICS, 2008-2015) supported by CNRS. This context seeded a consortium based on mutual trust and respect, which gathers complementary skills.

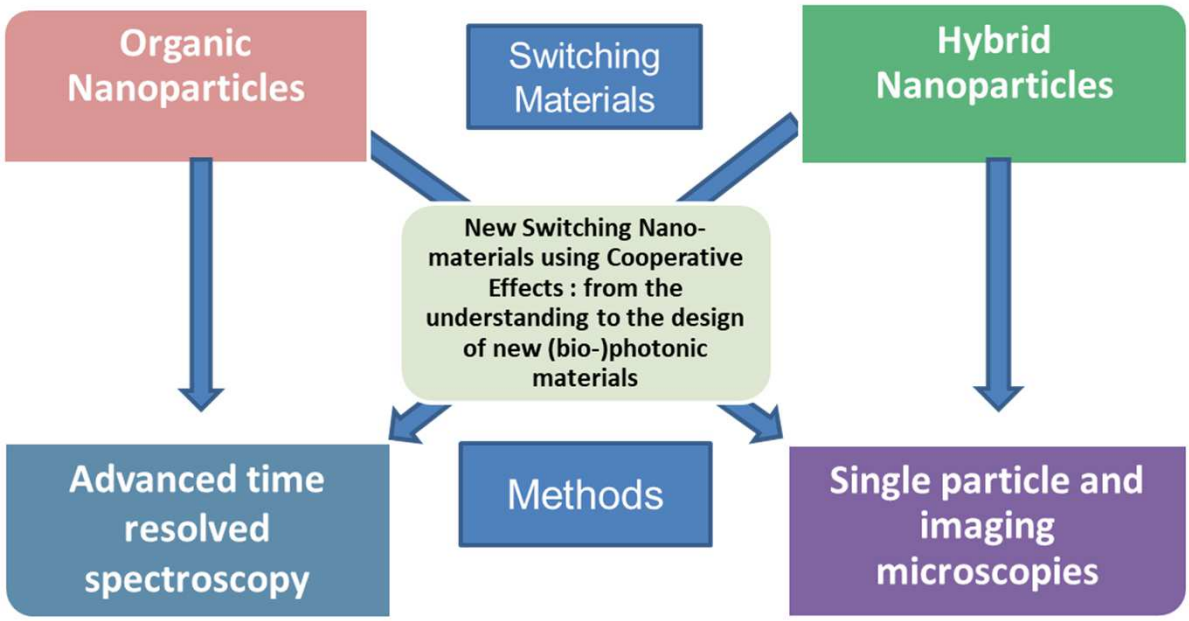
- The scientific goals of Nano-Synergetics are: creating novel photo-active materials exhibiting cooperative and amplified responses, and unravelling phenomena induced in switchable multimodal nano-objects. Indeed, understanding and mastering the nano-cooperative effects arising from the self-assembled units represent a novel approach to generate new nano-photonic materials with added value in terms of enhanced sensitivity and reactivity. Finally, the ambition is to gather complementary skills in the design, the synthesis and the fabrication of organic and hybrid materials, experimental and theoretical investigation methods (spectroscopy and microscopy), to achieve breakthroughs in the domain, with expected applications in optical data storage, multimodal bio-imaging, nano-motors “on-demand” drug delivery and anti-counterfeiting.

- This project should also help both countries to keep their international status and recognized expertise in the highly competitive field of photo-switching.

- Another important role and target of Nano-Synergetics is to promote and give the opportunity for students of an international research-based training, attract talented students, and foster the next generation researchers. Also, for young researchers, it create favorable conditions for career launching and cooperation grant applications.

Scientific topics and goals

This project aims at designing and studying novel photo-active nanomaterials, based on organic photochromic molecular nanomaterials, exhibiting on nonlinear cooperative effects, multi-photon processes, and multifunctionality, thanks to the cross-expertise of Nano-Synergetics members laboratory.
Two main axes are targeted:
(1) the design, the synthesis and the fabrication of molecular systems and functional photo-active nano-assemblies, such as organic or hybrid nanoparticles, with the ability to switch between two states;
(2) the structural characterizations and photophysical and photochemical investigations of the photoreaction dynamics based on advanced spectroscopies: electron paramagnetic resonance (EPR), time resolved spectroscopies and microscopies (including single particle and imaging), combined with big data analyses.
As a general perspective, we intend to create novel photo-responsive molecular nano-materials that can be controlled by light and based on molecular cooperativity. These new multifunctional hybrid nano-materials can be applied for optical data storage, multimodal super-resolution bioimaging, “on-demand” drug delivery, nanomotors and anti-counterfeiting.



The scientific project of Nano-Synergetics is structured in 5 axes, corresponding to different properties of phenomena investigated. Each axis has a principal investigator (PI) from each country.

Axis 1: New photoswitchable organic fluorescent nanoparticles (NPs)
Axis 2: Charge transfer (CT) and aggregation-induced emission (AIE) photochromic NPs
Axis 3: Photomechanical effects
Axis 4: Multiphoton, upconversion in nanoparticles
Axis 5: Hybrid nanoparticles for magnetism and plasmonics

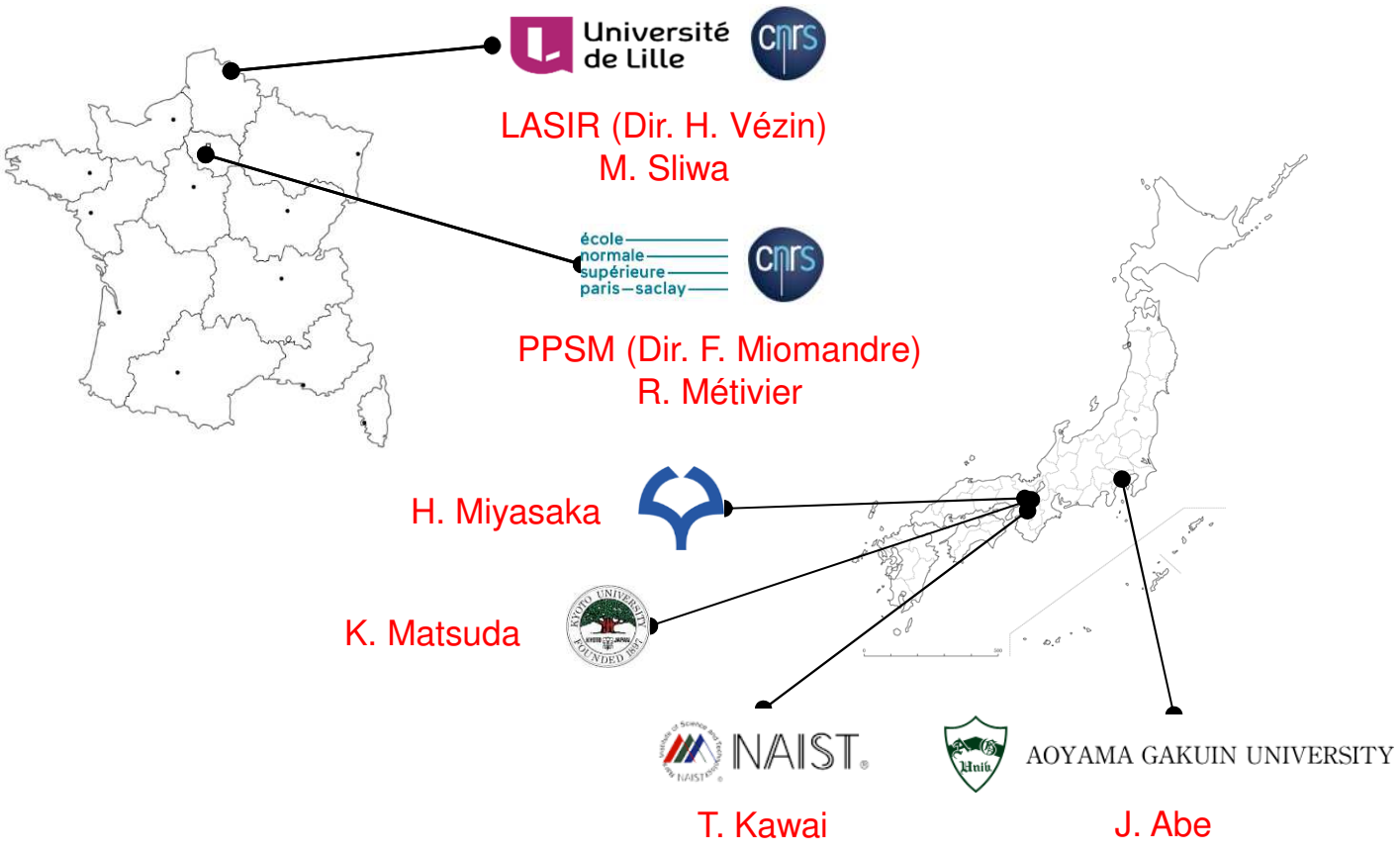
Structure & organization

Nano-Synergetics is coordinated by 4 researchers, 2 from each country. 6 partner institutions (3 from each country) are represented in the Steering committee. Also, 4 eminent scientists of the field accepted to advice Nano-Synergetics.
The 6 research groups, in France and in Japan, contribute. The total number of participating researchers is 31. In addition to ca. 20 PhD students, Master students from both countries are involved in the Nano-Synergetics projects.
The activities of the different research axes presented previously rely on the complementarity of manpower, know-how, equipment, etc., as summarized in the table on the next page. Extended collaborations, involving third parties are also active in Nano-Synergetics (see Scientific Achievements).

FRANCE		JAPAN
K. Nakatani *M. Sliwa*	Coordinator *Deputy Coordinator*	H. Miyasaka *T. Kawai*

Steering Committee

Advisors:
D. Bassani
M. Irie
H. Masuhara
P. Samori



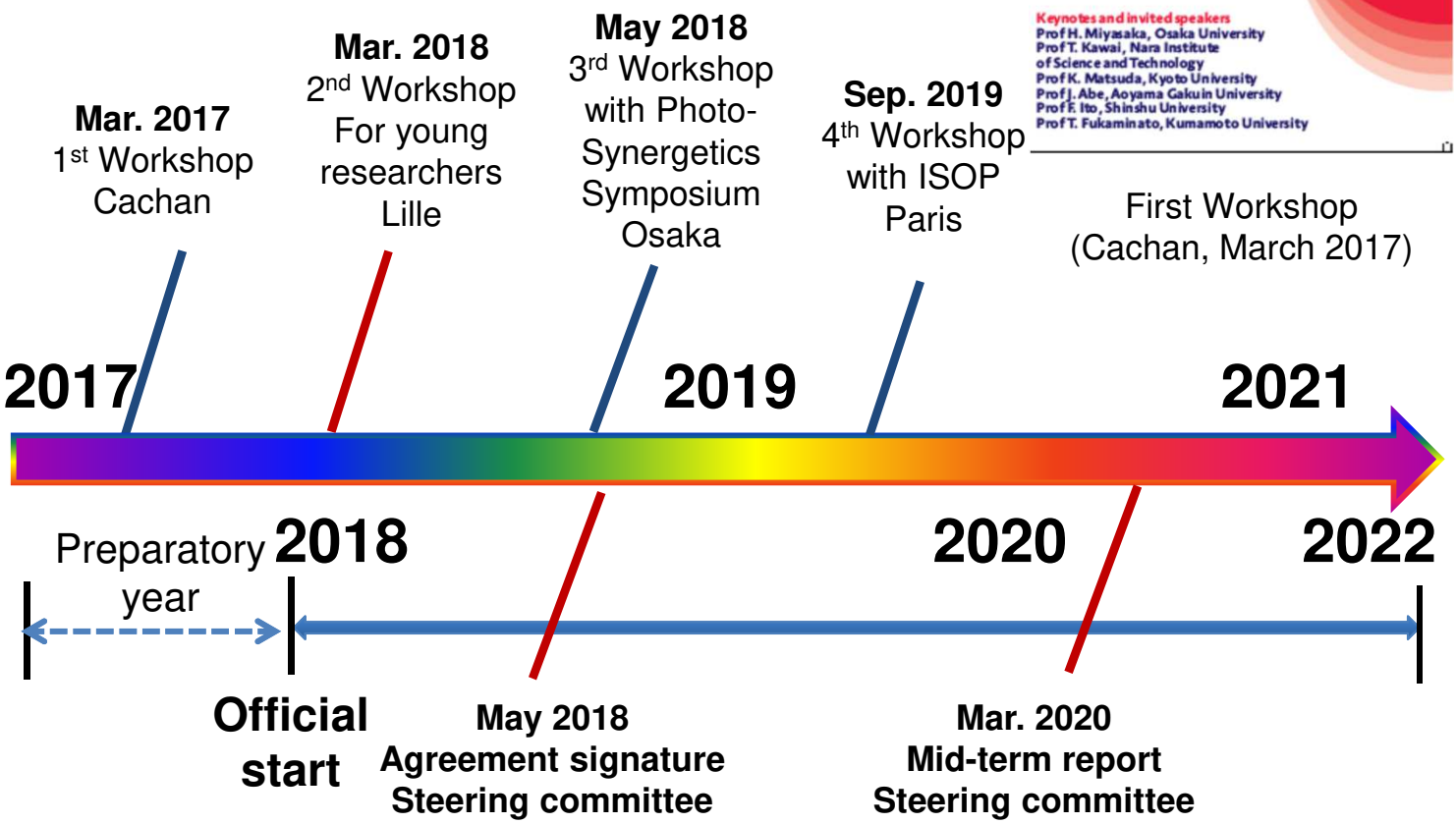
Structure & organization

	Researchers *PhD students*	Design, synthesis and fabrication of materials	Data analysis	Time resolved spectroscopy	Single particle / Imaging microscopies
PPSM (ENS Paris-Saclay, CNRS) Mechano-fluorochromism Plasmonics Switchable-nanoparticles Fluorescent materials	**11** ***6***	**X**			**X**
LASIR (Lille Univ., CNRS) Data Analysis Ultrafast nanoscopy EPR / NMR Super-resolution microscopy	**10** ***3***		**X**	**X**	**X**
H. Miyasaka (Osaka U.) Multi-photon ultrafast Spectroscopy & Single molecule spectroscopy	**4** ***2***			**X**	**X**
T. Kawai (NAIST) Charge-transfer molecules Circularly polarized luminescent (CPL) mechanoswitch	**4** ***2***	**X**			**X**
K. Matsuda (Kyoto U.) Supramolecular materials	**3** ***2***	**X**	**X**		
J. Abe (AGU) Fast photochromes & organic magnet	**2** ***2***	**X**		**X**	

Key events of Nano-Synergetics

For 2017-2019, as scheduled, annual meetings were organized in France and in Japan, a well as a ceremony for the signature in May 2018 in Kyoto (French General Consulate).
Budget allotted to Nano-Synergetics allowed an active participation of all the different partners to the 4 main workshops (see Mobility section for more details on the attendance). Graduate students and young researchers were given the opportunity to deliver oral presentations and to get acquainted with senior researchers of partner groups. Graduate students attending the workshops is close to 1/3 of the total participants.

First Workshop
(Cachan, March 2017)



Signature Ceremony
(Kyoto, May 2018)

4th Workshop
(Paris, September 2019)

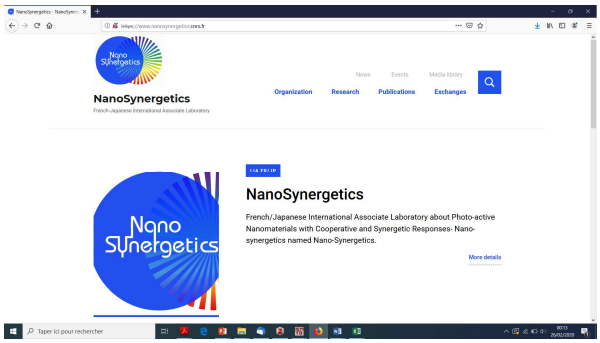
Key events of Nano-Synergetics

The possibility to organize some Nano-Synergetics workshops as satellites of important symposia is an opportunity to connect the members to the scientific community, and extend the web of collaborations. In these events, a large number of non-members of Nano-Synergetics attended the workshops, representing about half of the participants. As an example, in September 2019, the 4th Workshop was organized in Paris, as a satellite of International Symposium On Photochromism (ISOP), the most important international conference (every 3 years, 250 participants) in the field of photo-switching. French and Japanese members of Nano-Synergetics have a strong involvement in ISOP.
6 additional workshops involving some groups of Nano-Synergetics, as well as the participation of its members to symposia of partner projects can be mentioned (see below). Finally, during the Carrier Day at ENS Paris-Saclay in December 2017, French and Japanese members were invited to round tables to share their international experience to a wide student audience, and during the 2nd Workshop in Lille, the Embassy of Japan in France took the opportunity to present its mobility program.

The website of Nano-Synergetics is now operating, and provides information on the project, as well as a twitter account.

Additional meetings to Nano-Synergetics Workshops

- July 2017, Univ. Strasbourg, GDRI PHENICS International Network Symposium
- December 2017, ENS Paris-Saclay, Symposium on Photo-active molecules and materials: synthesis, photophysics and modeling
- December 2017, ENS Paris-Saclay. Career Day, focus to Japan
- January 2018, Osaka Univ., Symposium on PhotoSynergetics, Grant-in-Aid for Scientific Research on Innovative Areas, MEXT, Japan
- May 2018, NAIST, Japan. ENS Paris-Saclay PPSM & NAIST-MS Bilateral Workshop for Photoactive and Nano-Synergetic Systems
- October 2019, Final International Symposium on PhotoSynergetics



Website (2018-)

www.nanosynergetics.cnrs.fr

News, Events, Publications, Exchanges…

NanoSynergetics (@NSynergetics)

Scientific achievements

For the 2017-2019 period, each group of Nano-Synergetics has published more than 10 peer-reviewed original articles per year. Within the 5 research axes, 7 publications co-authored between French and Japanese groups were accepted. They deal with state of art results, accepted in high impact factor journals (IF > 7 for 5 of them). These results could only be obtained with the joint expertise of Japanese and French groups, combining the synthesis of novel molecules and materials, and advanced spectroscopies, carried out by Ph.D students. They are first authors of the articles (see below, names are in red) who could work in a partner laboratory to achieve their research. During the same period, they were also about 20 co-authored oral and poster presentations in international conferences, with 2 poster prizes awarded to Ph.D students.

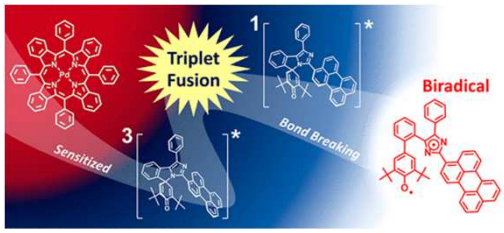
A focus on the last two articles is reported on the next page.

List of peer-reviewed original publications (2017-2019)

- A. Tokunaga, L. M. Uriarte, K. Mutoh, E. Fron, J. Hofkens, M. Sliwa and J. Abe, Photochromic Reaction by Red Light via Triplet Fusion Upconversion, J. Am. Chem. Soc. 2019 (IF 14.6)
- M. Louis, R. Sethy, J. Kumar, S. Katao, R. Guillot, T. Nakashima, C. Allain, T. Kawai, R. Métivier, Mechano-responsive circularly polarized luminescence of organic solid-state chiral emitters, Chem. Sci. 2019 (IF 9.5)
- R. Sethy, R. Métivier, A. Brosseau, T. Kawai, T. Nakashima, Impact of Optical Purity on the Light Harvesting Property in Supramolecular Nanofibers, J. Phys. Chem. Lett. 2018 (IF 7.3)
- K. Mutoh, M. Sliwa, E. Fron, J. Hofkens, J. Abe, Fluorescence modulation by fast photochromism of [2.2]paracyclophane-bridged imidazole dimer possessing a perylene bisimide moiety, J. Mater. Chem. C, 2018, 6, 9523-9531 (IF 6.6)
- R. Sethy, J. Kumar, R. Métivier, M. Louis, K. Nakatani, N. Mohan T. Mecheri, A. Subhakumari, K. G. Thomas, T. Kawai, T. Nakashima, Enantioselective light harvesting on self-assembled nanofibers, Angew. Chem. Int. Ed. 2017 (IF 12.2)
- F. Ito, J. Fujimori, N. Oka, M. Sliwa, C. Ruckebusch, S. Ito, H. Miyasaka, AIE phenomena of a cyanostilbene derivative as a probe of molecular assembly process, Faraday Disc. (cover picture), 2017 (IF 3.4)
- S. Brazevic, M. Sliwa, Y. Kobayashi, J. Abe, G. Burdzinski, Disclosing Whole Reaction Pathways of Photochromic 3H-Naphthopyrans with Fast Color Fading, J. Phys. Chem. Lett. 2017 (IF 8.7)

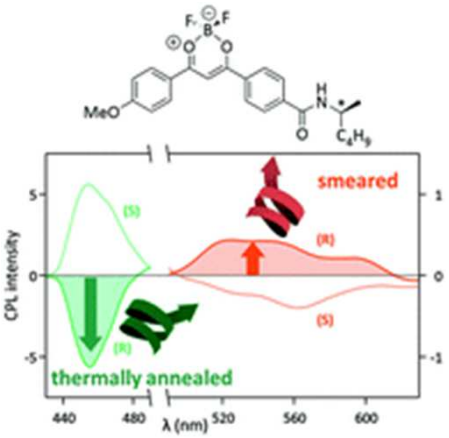
Scientific achievements

- A. Tokunaga, L. M. Uriarte, K. Mutoh, E. Fron, J. Hofkens, M. Sliwa and J. Abe, **Photochromic Reaction by Red Light via Triplet Fusion Upconversion**, J. Am. Chem. Soc., 141 (44), 17744-17753 (2019).



We succeeded to synthesize a new molecule (JP) that show an efficient high energy of upconversion light to drive a photochromic molecule that has a fast thermal back reaction. The femtosecond time-resolved absorption and fluorescence spectroscopy (FR) revealed that this photochromic reaction proceeds by the highly efficient singlet energy transfer from the annihilator unit to the photochromic unit. This strategy can be applied to the development of new NIR light responsive photochromic system for biological imaging.

- M. Louis, R. Sethy, J. Kumar, S. Katao, R. Guillot, T. Nakashima, C. Allain, T. Kawai, R. Métivier, **Mechano-responsive circularly polarized luminescence of organic solid-state chiral emitters**, Chem. Sci., 10 (3), 843-847 (2019).



In addition to photomechanical properties (light stimulus, mechanical response), novel organic materials (FR) showing mechanofluorochromic properties (mechanical stimulus, light response) were investigated, with promising applications in the field of circularly polarized luminescence (JP).

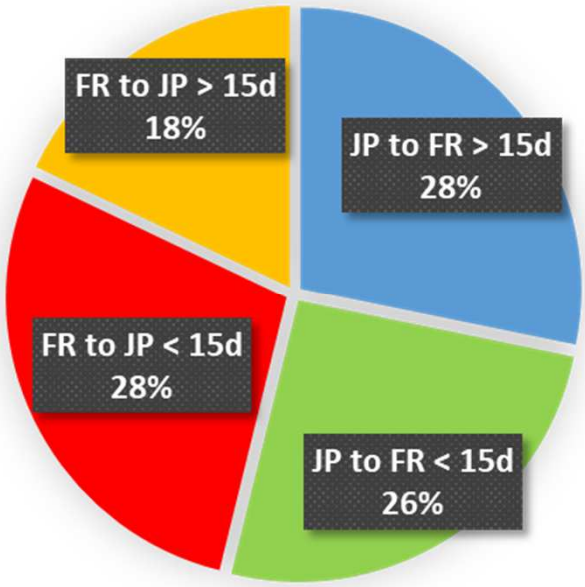
Mobility

Mobility have several purposes: participation to workshops, seminars, discussions on projects, brainstorming or experimental work on an equipment at a partner's laboratory. The mobility between the two countries is pretty well balanced, and long stays (> 15 days) represent almost half of the mobilities.

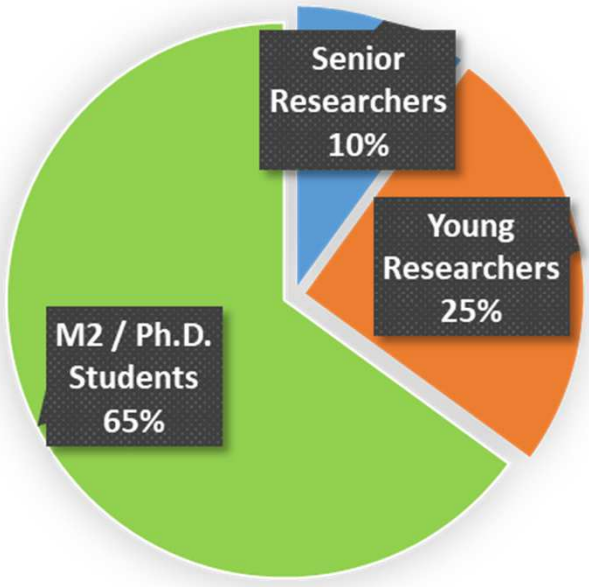
One important role played by Nano-Synergetics is to provide an added value to the research-based training of students, by giving them opportunities to work in new environments outside their home laboratory to get extra-experience and skills, in order to prepare them for the future. It aims also at attracting talented students (Master, Ph.D. students) and young researchers (post-docs, assistant professors or equivalent) in the concerned fields, and building sustainable relationship through the Nano-Synergetics network.

Hence, 90% of the long stays (> 15 days) concern students (65%) and young researchers (25%), giving them time to undergo experimental work, and brainstorming with the partners.

Short stays (< 15 days) are more devoted to visits and discussion on on-going projects. It should also pointed that two LIA members participated to two Ph.D thesis jurys in France and Japan respectively (NAIST and ENS Paris-Saclay).



Share of mobilities:
Short (< 15 days) vs long stays (> 15 days),
France to Japan vs Japan to France



Share of long stays (> 15 days):
students,
young researchers (< 45 years old),
senior researchers

Mobility

As mentioned before (see Key events), Nano-Synergetics Workshops are important for the members, as they are places to communicate, and also disseminate the results. Thus, it is essential to have an important representation from both countries, and give a chance to students and young researchers to present their results by themselves. The table shows detailed figures of the participation of Nano-Synergetics members to the 4 main workshops.

		Total attendance	Nano-Synergetics members Attendance and number of presentations		
			From FR	From JP	Keynote / Oral / Poster
1st Workshop	FR	80	28	21	4 / 4 / 25
2nd Workshop	FR	100	25	14	4 / 16 / 21
3rd Workshop	JP	100	15	30	1 / 13 / 29
4th Workshop	FR	110	22	20	1 / 14 / N.A.

Highlight on some "Nano-Synergetics-bred" young researchers

- Marine LOUIS: She was a Ph.D. student at ENS Paris-Saclay from 2014 et 2017. In collaboration with NAIST, her work on stimuli-responsive materials led to 2 co-authored publications between PPSM and NAIST (Angew. Chem. Int. Ed. and Chem. Sci.). After spending two years in Germany, she started in 2019 a two-years Post Doctorate in NAIST supported by the JSPS.

- Ramarani SETHY: She was a Ph.D. student at NAIST from 2015 to 2018. She staid 2 times during 2 months at PPSM in 2017 to perform experiments of single particle microscopy and fluorescence lifetime for nanofibers. This led to 3 co-authored publication between NAIST and ENS Paris-Saclay (Chem. Sci., J. Phys. Chem. Lett., Angewandte). From 2019 she is a Post Doctorate at PPSM within the ERC Mechanofluorochromism..

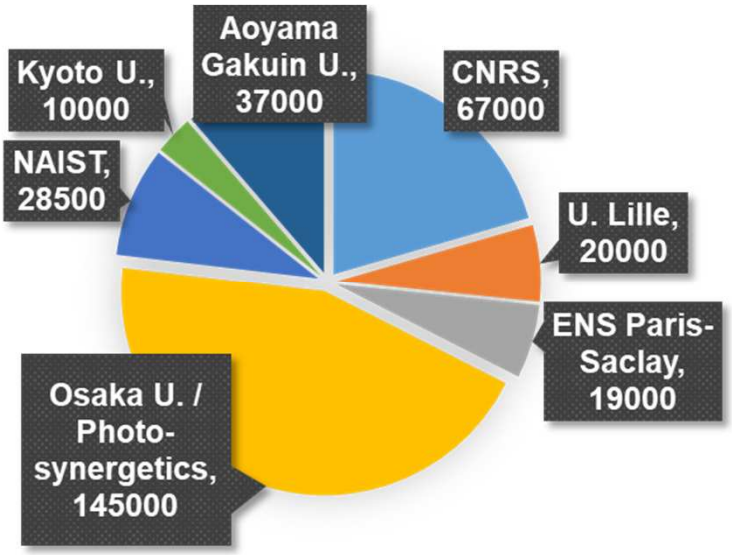
- Ayako TOKUNAGA: She was a Master student at Aoyama Gakuin University. She staid 2 times (2 weeks) in 2018 at LASIR to make some ultrafast experiments that are part of a co-authored publication in J. Am. Chem. Soc and a poster prize at an international conference. She continues her research as a Ph.D. student with a JSPS fellowship.

- Nicolas FABRE: He was BSc-MSc student at ENS Paris-Saclay and had several research experiences in Japan between 2015 and 2018 (collaboration PPSM-Kumamoto Univ.). During his Ph.D. at ENS Paris-Saclay, he spent 2 months at Aoyama Gakuin University in 2019 and another research stay is planned in 2020, to develop novel photoswitchable fluorescent materials based on negative photochromism.

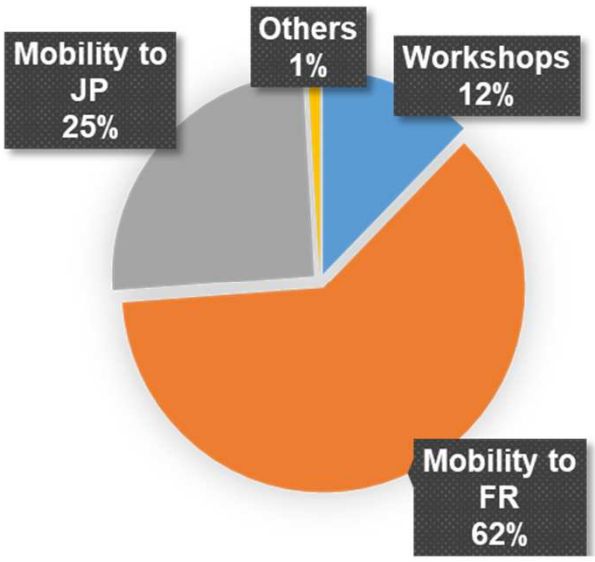
Financial report

Total budget (2017-2019) for mobility (research stays and travels to LIA workshops) and organization of workshops is about 325 000 EUR. It should also be mentioned that running costs of the different equipments and consumables (including chemicals) were supported by each laboratory's funds, provided by their institutions and funding agencies (MEXT "Kakenhi", ANR…).

CNRS part includes specific funds for Nano-Synergetics (47 000 EUR) and support from funding agencies. Univ. Lille part also includes specific funds for Nano-Synergetics (10 000 EUR). Contributions are also provided in the form of invited professorship (for ENS Paris-Saclay) and student grants (e.g. Ph.D grant from Région Hauts de France in Univ. Lille contribution). Osaka Univ.'s part includes PhotoSynergetics (Grant-in-Aid for Scientific Research on Innovative Areas, MEXT). Osaka Univ. (including PhotoSynergetics funds) and CNRS are the main contributors with respectively 44% and 22% of the budget.



Resources for mobility and organization of workshops
(does not include running costs nor consumables)
Contributions of the partner institutions



Expenses:
mobility and workshop organization

The large PhotoSynergetics funds can be correlated to the importance in the expenses of the mobility to France (62%), where most Nano-Synergetics Symposia took place. When mobility to Japan (25%) is added, we can conclude that the major part of the budget was used for mobility (87%). Organization costs of workshop represent 12%.

Perspectives

- As substantiated by the co-publications, the collaboration frame of Nano-Synergetics has helped progressing on the finding and the property characterization of novel photo-active molecular systems, and developing new topics, such as mechanical effects (as response or trigger), circularly polarized light-emission, etc. Introducing these phenomena in fields of applications such as bio-imaging is a development planned with the use of photo-switchable proteins. Another possible development to be discussed for the next years is the introduction of data sciences methods.

- An additional outcomes, not developed in this report, are positive side effects of Nano-Synergetics: through the strong connexions and the strategic positions of the partners, some projects came up with extended French-Japanese collaborations, where third parties (in France, Japan or elsewhere) contributed to the progress of the project.

- Nano-Synergetics is taking advantage of recently settled agreements between partner institutions, which facilitate mobility. In this scope, the first NAIST – Univ. Paris-Saclay double degree Ph.D student (Oct. 2019-) has started her work on supramolecular materials with enhanced circularly polarized luminescence. Other starting PhD students on hybrid nanoparticles, funded by CNRS (under review, fluorescent protein & metallic nanoparticles) or Univ. Lille & Région Hauts de France (fluorescent proteins & up conversion nanoparticles), could be candidates for Ph.D double degrees between other partners of Nano-Synergetics.

- Another possible development would be to cross-fertilize this French-Japanese cooperation by implementing mirror laboratories, with a dedicated researcher to Nano-Synergetics activities. In France, one possible settlement is the ENS Paris-Saclay new premises.

- Concerning the action plans for 2020, first, the annual workshop will be held as a satellite conference of IUPAC Photochemistry (July 2020, Amsterdam). Several mobilities have already been carried out or are planned. A researcher from Kyoto Univ. (K. Higashiguchi, in January) stayed in PPSM, and at least two visits from France to Japan (M. Sliwa in March and K. Nakatani in Spring, with delegations of their respective institutions) are planned. 5 students mobilities are also planned (including one pre-master), among them one funded by JSPS Summer Program and another by Univ. Paris-Saclay mobility program, reinforcing Nano-Synergetics' role as a breeding ground for future scientists.

Agreements signed between partner institutions of Nano-Synergetics

2014 (renewed in 2019)
- NAIST – ENS Paris-Saclay

2016
- Osaka Univ. (GS Eng. Science) – ENS Paris-Saclay
- NAIST – Univ. Lille

2017
- Kyoto Univ. – ENS Paris-Saclay

2020
- Kyoto Univ. – Lille Univ.
- Osaka Univ. (GS Eng. Science) – Univ. Lille