Tuesday, November 23th

Session Nano Gold by Young Researchers

10:50 - 11:20 Keynote

Nathalie LIDGI-GUIGUI, Sorbonne Paris Nord Univ. – LSPM, France

Abstracts

Keynote Speakers

Nathalie LIDGI-GUIGUI

Associate Professor (maîtresse de conférences) at University Sorbonne Paris Nord
LSPM Laboratory
Villetaneuse, France
nathalie.lidgi.guigui.fr
Twitter: @nlidgi

Biography
Nathalie Lidgi-Guigui is a nano-material researcher at the LSPM laboratory of the University Sorbonne Paris Nord. Her main interests go toward molecular plasmonics and contaminant detection.
She received her Ph.D. in 2005 followed by several post-doctoral experiences between 2006 and 2010. During the beginning of her research, she studied the growth of metallic nanostructures and used AFM to measure their interaction with (bio)molecules.
In 2011 she was awarded a lecturer position at the CSPBAT laboratory where she developed ultra-sensitive sensors based on Surface Enhanced Raman Scattering. In 2019 she joined the LSPM where she is working on nanostructuration processes for large scale surface enhanced Raman and Brillouin spectroscopy.

She has a long and enthusiastic experience in innovative teaching and outreach. To mention just a few of her project : «Recrue des Sciences» where the students were asked to make outreach projects. More recently, in 2018 she was invited in the team of «La Physique Autrement» where she developed an original project on clean rooms and nanofabrication. «The nano factory» soon became a board game. Her last project «The metamorphosis of materials» was designed with the purpose of explaining what a process is.

SCIENTIFIC OUTREACH: WHY AND HOW?

Teaching and educating to science are quite an old story. When looking back at how it was done in the past, an important split is observed in France. Before the 19th century, science was part of a general knowledge together with art and literature. Starting around 1850's science was not only separated from humanities but often opposed.

Science was seen as a universal language that could gather everyone when literature was reserved to highly educated people. Paradoxically science teaching was built in a highly discriminatory way, as shown by the low number of students in STEM fields coming from the working classes. This observation led to the development of science outreach.
In the first part of this talk we will see the reason why science outreach started. The second part of the talk will be focused on nowadays motivations for outreach. The diversity of media available in the 21st century offers a wide range of possibilities to communicate. We will consider some examples of recent outreach projects using traditional media such as books, newspaper or exhibition and more moderns one like social media, videos, games, art or smartphones.

Keywords: outreach; science education; media; gamification.

Thematic Session: Nano Gold by young researchers

Keywords: Gold nanoparticles – *N*-heterocyclic carbenes (NHC) – Mesoionic Carbenes (MIC)

Emergence of Mesoionic Carbenes for the Stabilization of Gold Nanoparticles

Porcheron Alexandre,[1,2] Ribot François,[1] Fensterbank Louis,[2] Mercier Dimitri,[3] Chanéac Corinne,[1] Chauvier Clément,[2] Hyppolyte Laura,[1,2], Bridonneau Nathalie[2]

1. *Sorbonne Université, CNRS, Laboratoire de Chimie de la Matière Condensée de Paris (UMR 7574), Paris, France*
2. *Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire (UMR 8232), Paris, France*
3. *PSL Research University, CNRS, Chimie ParisTech, Institut de Recherche de Chimie Paris (UMR 8247), Physical Chemistry of Surfaces Group, Paris, France*

Imidazolium-based *N*-heterocyclic carbenes (NHC)[i] have recently emerged as promising ligands for gold nanoparticles (Au NPs) formation[ii] because they form strong C–Au bonds stabilizing Au NPs over a wide pH and temperature range.[iii] The organic nature of NHCs can also be exploited to tune the reactivity or the properties of the nano-material. Nevertheless, the latter endeavor is often hampered by relatively complex synthetic procedures.

We report herein a new class of 1,2,3-triazolium-based mesoionic carbenes (MIC) [iv] that confers great stability to Au NPs but also benefits from simple synthesis through modular alkyne-azide "click" reactions.[v].The synthesis and characterization of various MIC and MIC-stabilized Au NPs will be presented and their stability discussed.

References :

[i] An overview of N-heterocyclic carbenes, M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485-496.
[ii] Carbene ligands in surface chemistry: from stabilization of discrete elemental allotropes to modidication of nanoscale and bulk substrates, A. Z. Zhukhovitskiy, M. J. MacLeod, J. A. Johnson, *Chem. Rev.* **2015**, *115*, 11503-11532.
[iii] PEGylated N-heterocyclic carbene anchors designed to stabilize gold nanoparticles in biologically relevant media, M.J. MacLeod, J. A. Johnson, *J. Am. Chem. Soc.* **2015**, *137*, 7974-7977
[iv] Application of 1,2,3-triazolydenes as versatile NHC-type ligands: synthesis, properties, and applications in catalysis and beyond, K. F. Donnelly, A. Petronilho, M. Albrecht, *Chem. Comm*. **2013**, 49, 1145-1159.
[v] For a recent development of click chemistry: Visible-light-mediated click chemistry for highly regioselective azide-alkyne cycloaddition by a photoredox electron transfer, Z.-G. Wu, X.-J. Liao, L. Yuan, Y. Wang, Y.-X. Zheng, J.-L. Zuo, Y. Pan, *Chem. Eur. J.* **2020**, 26, 5694-5700.

C'NANO 2020
The Nanoscience Meeting
TOULOUSE
Centre des congrès Pierre Baudis
December, 8, 9 and 10

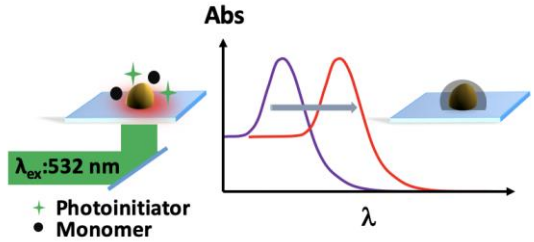
Thematic Session: Nano Gold by young researchers
Keywords: Photopolymerization, LSPR, Hybrid nanoparticles, Polymer

Photopolymerization at nanoscale on gold nanoparticles followed by plasmon resonance shift

Amine Khitous, Ching-Fu Lin, Farid Kameche, Jean-Pierre Malval, Dominique Berling, Olivier Soppera

1. *Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France*
2. *Université de Strasbourg, F-67081 Strasbourg, France*

Plasmon resonance of Au nanoparticle arrays is used to monitor photopolymerization at the nanoscale, by following, in situ, the optical response of the AuNPs during the light-induced polymerization process. [1] To demonstrate the interest of this approach, two configurations have been used which correspond to a resonant and non-resonant excitation regime between the photopolymer and the AuNPs used as nanoprobes. We show that this method allows not only to follow the evolution of the photopolymerization reaction at the nanoscale but also to highlight the near-field coupling effect responsible for the acceleration of the photoinduced reaction.[1,2] This methodology seems very interesting to study the photoinduced nanofabrication processes of metal/polymer hybrid nanoparticles and more globally as a methodology to study photopolymerization reactions at the nanoscale.[3,4]



References :
[1] A. Khitous, C.-F. Lin, F. Kameche, H.-W. Zan, J.-P. Malval, D. Berling, O. Soppera, *ACS Applied Nano Materials* **2021**, 4, 8770.
[2] F. Kameche, W. Heni, S. Telitel, L. Vidal, S. Marguet, L. Douillard, C. Fiorini-Debuisschert, R. Bachelot, O. Soppera, *The Journal of Physical Chemistry C* **2021**, 125, 8719.
[3] F. Kameche, W. Heni, S. Telitel, D. Ge, L. Vidal, F. Dumur, D. Gigmes, J. Lalevee, S. Marguet, L. Douillard, C. Fiorini-Debuisschert, R. Bachelot, O. Soppera, *Materials Today* **2020**, 40, 38.
[4] D. Ge, S. Marguet, A. Issa, S. Jradi, T. H. Nguyen, M. Nahra, J. Béal, R. Deturche, H. Chen, S. Blaize, J. Plain, C. Fiorini, L. Douillard, O. Soppera, X. Q. Dinh, C. Dang, X. Yang, T. Xu, B. Wei, X. W. Sun, C. Couteau, R. Bachelot, *Nature Communications* **2020**, 11, 3414.

C'NANO 2020
The Nanoscience Meeting
TOULOUSE
Centre des congrès Pierre Baudis
December, 8, 9 and 10

Thematic Session: (Nanoplasmonics, nanomaterials)
Keywords: (gold nanoparticles, seed-mediated growth process, colloidal assembly, plasmonics, chirality)

Colloidal assembly of anisotropic gold nanostructures and optical-plasmonic properties

A. Carone, D. Château, A. Désert, F. Lerouge, S. Parola

Functional and Photonic Materials, Laboratoire de Chimie, ENS Lyon, UCBL-CRNS, Lyon, France

Assembly of nanoparticles (NPs) is a hot and challenging topic in nanomaterials chemistry field since it is a promising "bottom-up" approach to control micro- and macro-scale structures and properties of materials.[1] Non-spherical and anisotropic NPs [2] and plasmonic systems [3] are of particular interest to reach new kind of assemblies with unique optical properties. However, easily fabricating such nanostructures -ideally with an up-scalable, low cost, reproducible and versatile process- is currently a huge challenge. We want to address this challenge by developing the colloidal synthesis and self-assembly of a class of gold nanoparticles. Recent efforts in our team have led to unprecedented improvement concerning the AuNPs colloidal synthesis: a large variety of pentatwinned AuNPs is nowadays easily obtainable, with high purity and monodispersity, and in high concentration.[4] Using pentatwinned AuNPs as building blocks, different methodologies have been explored to obtain peculiar nanostructures with interesting optical properties: (i) self-assembly of Au bipyramids (BPs) via chiral ligand (L-arginine and L-cysteine), (ii) via fine tuning of surfactant concentration (CTAB) in absence of any ligand and (iii) stabilization of obtained assembly by depositing of a thin layer of Ag on the nanoparticles surface. The methods employed resulted in original gold nanostructures with specific absorption behavior, like linear chains of self-assembled AuNP, and core-shell of Au@Ag aggregated NPs.
Finally, we will present our recent efforts to synthetize chiral building blocks using seed-mediated growth process in presence of amino acids (L-cysteine and L-glutathione) as a promising way to achieve chiral response.

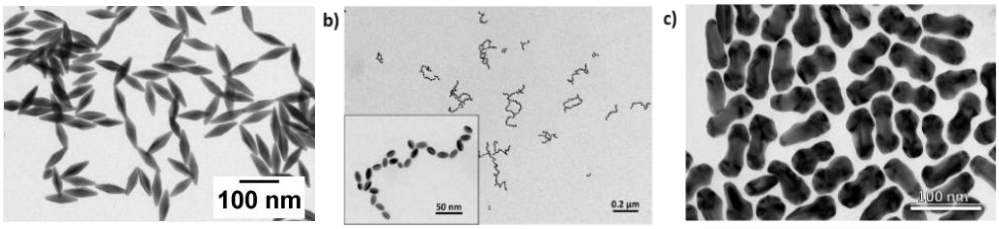


Fig.1 - TEM images of a) AuBPs, b) assembly of AuBPs with arginine, c) dumbbell-like AuNPs prepared with cysteine

References (max. 5):
[1] M. A. Boles, M. Engel, D. V. Talapin, *Chem. Rev*., **2016**, 116, 11220.
[2] T. Hueckel, S. Sacanna, *Elsevier*, **2018**, 4, 105-130; X. Bouju et al., *Advanced Materials*, **2018**, 30, 1706558; S.-Y. Zhang et al., *Chem. Soc. Rev*., **2014**, 43, 2301–2323.
[3] S.-W. Hsu et al., *Chem. Rev*., **2018**, 118, 3100–3120; S. Gwo et al., *Chem. Soc. Rev*., **2016**, 45, 5672-5716.
[4] D. Chateau et al., *ACS Applied Materials & Interfaces*, **2019**, 11, 39068.

C'NANO 2020
The Nanoscience Meeting
TOULOUSE
Centre des congrès Pierre Baudis
December, 8, 9 and 10

Thematic Session: Nano Gold by young researchers
Keywords: nanoclusters, gold, synthesis, n-heterocyclic carbenes

Gold nanoclusters synthesis and functionalization aiming at properties enhancement

ASILA Victoire,[1] PORCHERON Alexandre,[1,2] LESAGE Denis,[2] FENSTERBANK Louis,[2] RIBOT François,[1] CHANEAC Corinne[1]

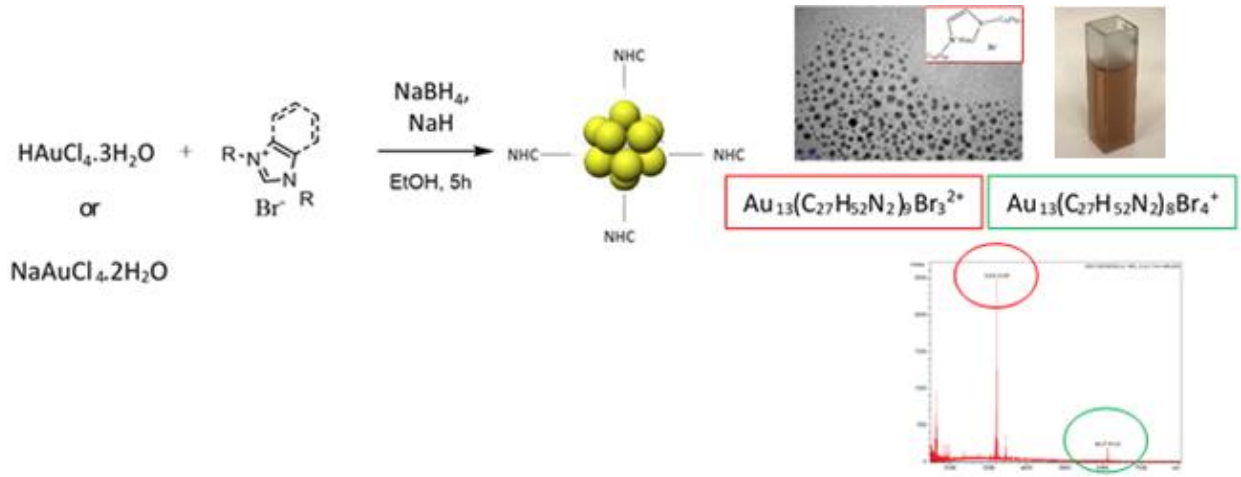
1. *Sorbonne Université, CNRS, Laboratoire Chimie de la Matière Condensée de Paris, UMR 7574, Paris, France.*
2. *Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, UMR 8232, Paris, France.*

Gold nanoclusters (Au-NCs) have been an attractive frontier of nanoparticle research due to their very small size (1-2 nm). Indeed, these smaller particles lose their metallic character and behave like molecular entities: they exhibit unique properties such as an enhanced catalytic activity and luminescence. [1] Recent works showed the stabilization of gold nanoclusters by N-heterocyclic carbenes (NHCs) through ligands exchange [2] and direct synthesis. [3] [4]

Our group interest is to develop new effective and simple synthesis methods of NHCs capped Au-NCs and to study more deeply the mechanisms behind nanoclusters formation. The syntheses are based on the use of imidazolium salts as NHC precursors, gold salts and $NaBH_4$ as reducer. The results showed that using $AuClPPh_3$ as a gold source produces a mixture of PPh_3 capped Au-NCs, NHC capped Au-NCs and Au-NCs capped by both type of ligands. Regarding Au-NCs with NHC at the surface, aging of the suspensions revealed that $Au_{11}(PPh_3)_7(NHC)Br^{2+}$ is stable since other NHC capped Au-NCs disappear over time. We also developed syntheses from $HAuCl_4.3H_2O$ and $NaAuCl_4.2H_2O$ that were able to produce $Au_{13}(C_{27}H_{52}N_2)_9Br_3^{2+}$ and $Au_{13}(C_{27}H_{52}N_2)_8Br_4^{+}$ NCs (figure 1). Finally, we are interested in the synthesis of hydrosoluble Au-NCs using a water soluble imidazolium salt to expand the possible applications of these particles.

We will focus on explaining the reactivity of the gold sources in regards to the ligand. We will also discuss the different synthesis methods and parameters that allow obtaining NCs instead of nanoparticles.

Figure 1:



References

[1] X. Wan, J-Q. Wang, Z. Nan, Q. Wang, Science Advances, **2017**, 3,10, e1701823

[2] M. R. Narouz, K. M. Osten, P. J. Unsworth, R. W. Y. Man, K. Salorinne, S. Takano, R. Tomihara, S. Kaappa, S. Malola, C.T. Dinh, J. D. Padmos, K. Ayoo, G. J. Patrick, M. Nambo, J. H. Horton, E.H. Sargent, H. Häkkinen, T. Tsukuda, C. Crudden**,** Nature Chemistry**, 2019,** 11, 5, 419-425

[3] M. R. Narouz, S. Takano, P.A. Lummis, T. I. Levchenko, A. Nazemi, S. Kaappa, S. Malola, G. Yousefalizadeh, L. A. Calhoun, Kevin G. Stamplecoskie, H. Häkkinen, T. Tsukuda, C.M. Crudden, J. Am. Chem. Soc., **2019**, 141, 38, 14997-15002

[4] H. Shen, G. Deng, S. Kaappa, T. Tan, Y-Z. Han, S. Malola, S-C. Lin, B. K. Teo, H. Häkkinen, N. Zheng, Angewandte Chemie**, 2019,** online publication

Tuesday, November 23th

Session Nano Gold by Young Researchers

15:00 - 15:30 Keynote

Didier BOURISSOU, CNRS - LHFA, France

Abstracts

Keynote Speakers

Didier BOURISSOU

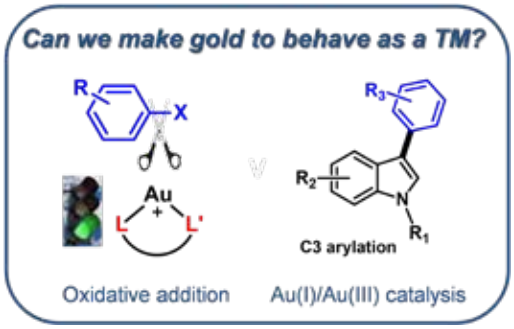
CNRS Research Director
LHFA Laboratory
Toulouse, France
https://www.lhfa.cnrs.fr/index.php/en/teams/lbpb-en/accueil-lbpb-en

Biography

Didier Bourissou studied chemistry at the Ecole Normale Superieure in Paris and obtained a PhD degree from Paul Sabatier University in 1998 under the supervision of G. Bertrand. He then worked with F. Mathey and P. Le Floch at the Ecole Polytechnique in Palaiseau as a research associate. He was appointed as a CNRS junior researcher in 1998. Since 2006, he holds a senior scientist position (Directeur de Recherche) at the CNRS and from 2006 to 2018, he has been Associate Professor at the Ecole Polytechnique in Palaiseau. He is Director of the Laboratory of Fundamental and Applied Heterochemistry at the University Paul Sabatier in Toulouse since 2011. His research interests concern new bonding situations and reactivity patterns arising from the main group elements, the transition metals and their interplay. He has pioneered ambiphilic ligands in the mid 2000's and developed the concept of □-acceptor ligands. Part of his research also deals with non-innocent pincer complexes and unusual behavior of the coinage metals, in particular gold. He is also interested in biodegradable polymers (ring-opening polymerization, organic and dual catalysis, drug delivery systems).

NEW BASIC ORGANOMETALLIC REACTIVITY OF GOLD: TOWARDS NEW APPLICATIONS?

With the aim to open new avenues in gold chemistry, we are exploring the basic structure and reactivity of coordination complexes. In particular, thanks to rationale ligand design, we have isolated key carbene complexes1 and challenged the presumed reluctance of gold to undergo oxidative addition,2 a pivotal transformation in many processes. Chelating (P,P) and hemilabile (P,N) ligands have been shown to readily promote the activation of C–I/Br and C–C bonds. The approach is amenable to Au(I)/Au(III) catalysis, without the need for an external oxidant or photoredox conditions.3 Such fundamental studies combining experimental work and DFT calculations extend the chemical space of gold and advance our understanding of the key factors controlling its behaviour. Besides their own interests, well-defined molecular complexes are also valuable models for nanoparticles, and the parallel with key intermediates and elementary steps presumably involved in heterogeneous catalysis with Au-NPs will be drawn.



References

[1] (a) Zeineddine, A.; Rekhroukh, F.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Angew. Chem. Int. Ed*. **2018**, *57*, 1306. (b) Pujol, A.; Lafage, M.; Rekhroukh, F.; Saffon-Merceron, N.; Amgoune, A.; Bourissou, D.; Nebra, N.; Boutignon, M.; Mézailles, N. *Angew. Chem. Int. Ed.* **2017**, *56*, 12264.

[2] (a) Joost, M.; Zeineddine, A.; Estévez, L.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *J. Am. Chem. Soc*. **2014**, *136*, 14654. (b) Joost, M.; Estevez, L.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Angew. Chem. Int. Ed.* **2015**, *54*, 5236. (c) Zeineddine, A.; Estévez, L.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Nat. Commun*. **2017**, *8*, 565.

[3] (a) Rodriguez, J.; Zeineddine, A.; Sosa Carrizo, E. D.; Miqueu, D.; Saffon-Merceron, N.; Amgoune, A.; Bourissou, D. *Chem. Sci*. **2019**, *10*, 7183. (b) Rigoulet, M.; Thillaye du Boullay O.; Amgoune, A.; Bourissou, D. *Angew. Chem. Int. Ed*. **2020**, *59*, 16625.

Keywords: gold; reactivity; ligand; catalysis; bonding.

Excitation of multipolar surface plasmon modes offers new horizons in nano-localized surface chemistry.

Plasmonic excitation of metallic nanoparticles can trigger chemical reactions at the nanoscale. Such optical effects can also be employed to selectively and locally graft photopolymer layers at the nanostructure surface, and, when combined with a surface functionalization agent, new pathways can be explored to modify the surface of a plasmonic nanoparticle. Among these approaches, diazonium salt chemistry is seen as an attractive strategy due to the high photoinduced reactivity of these salts. In this work, we demonstrate that it is possible to trigger the site-selective grafting of aryl films derived from diazonium salts on distinct nano-localized area of single gold nanotriangles, by taking advantage of their multipolar localized surface plasmon modes. It is shown the aryl film will preferentially graft in areas where the electric field enhancement is maximum, independently of the considered excited surface plasmon mode. These experimental findings are in very good qualitative agreement with the calculations of the local electric field, using the finite-difference time-domain (FDTD) method. We believe that this plasmonic-based approach will not only pave a new way for the spatially controlled surface functionalization of plasmonic nanoparticles, but also provide a general strategy to attach distinct molecules to hot spot regions on a single nanoparticle, opening sensing multiplexing and fully optically controlled nano-scale patterning of various functional groups.

Co-author:
Kherbouche I. ; MacRae D. ; Geronimi Jourdain T. ; Lagugné- abarthet F ; Lamouri A. ; Chevillot-Biraud A. ; Mangeney C. and Félidj N.

C'NANO 2020
The Nanoscience Meeting
TOULOUSE
Centre des congrès Pierre Baudis
December, 8, 9 and 10

Thematic Session: Nano Gold by young researchers
Keywords: gold nanoparticle, diarylethene, plasmon, switching ratio, conductivity

Optical monitoring of the switching of diarylethene molecules grafted on gold nanoparticles

A. Dileseigres[1], Y. Prado[1], O. Pluchery[1]

1. *Institut des NanoSciences de Paris (INSP, UMR 7588), CNRS, Sorbonne Université, Paris, France*

Diarylethenes (DAEs) are photochromic molecules, they undergo reversible isomerization between two stable forms with distinct geometry, electronic structure, and absorption spectra. If both isomers are thermally stable, fatigue-resistant, highly sensitive, reactive in solid state and provide fast response: they can be considered for optoelectronic switches, memories, and actuators/molecular machines.[1]
Gold nanoparticles (AuNPs) were deposited on ITO, DAE molecules were grafted on the AuNPs, both used as electrodes and plasmonic antennas. Functionalization of the AuNPs by the DAEs was monitored with UV-visible spectroscopy for multiple AuNPs and with dark-field microscopy coupled to UV-visible spectroscopy for single AuNPs. The switching of DAE molecules grafted on AuNPs was measured by UV-visible spectroscopy[2] confirming the switching ability of the DAEs was preserved upon functionalization.
In fine, the goal is to study the optical properties of the DAEs in terms of switching ratio: can plasmonic effects contribute to reduce the asymmetry of the switching ratio? And the effect of the plasmon on the conductive properties of the DAEs: do electrons of the plasmon contribute to the conduction inside the DAE? To address that matter, conductive AFM measurements are envisioned.

References:

(1) Irie, M.; Fukaminato, T.; Matsuda, K.; Kobatake, S. Photochromism of Diarylethene Molecules and Crystals: Memories, Switches, and Actuators. *Chem Rev* **2014**, 104.
(2) Snegir, S. V.; Khodko, A. A.; Sysoiev, D.; Lacaze, E.; Pluchery, O.; Huhn, T. Optical Properties of Gold Nanoparticles Decorated with Furan-Based Diarylethene Photochromic Molecules. *J. Photochem. Photobiol. Chem.* **2017**, *342*, 78–84.

Acknowledgment: this project is funded by the ANR. Project PlasmoChrom ANR-18-CE92-0057 [2019-2022]

C'NANO 2020
The Nanoscience Meeting
TOULOUSE
Centre des congrès Pierre Baudis
December, 8, 9 and 10

Thematic Session: Nano Gold by young researchers
Keywords: Plasmonics, DNA Nanotechnology, Strong-coupling, Spontaneous emission

Reaching a strong coupling regime between fluorescent emitters and a gold plasmonic resonator with DNA

Jeanne Heintz[1], Elise Gayet[1], Nemanja Markesevic[1], Nicolas Bonod[2], et Sébastien Bidault[1],

1. *Institut Langevin, ESPCI Paris, Université PSL, CNRS, Paris, France*
2. *Institut Fresnel, Université Aix Marseille, CNRS, Centrale Marseille,Marseille, France*

DNA nanotechnology provides a flexible toolbox to produce hybrid nanostructures with a nanoscale control over the position and relative orientation of gold nanoparticles. In particular, this approach can be used to introduce a known number of dye molecules inside a plasmonic resonator made of two gold nanoparticles. In a weak electromagnetic coupling regime, DNA-templated gold particle dimers enhance the fluorescence rate of single molecules by more than two orders of magnitude, providing bright ultrafast single-photon sources with quantum yields above 50% [1]. However, it would be particularly attractive to increase the electromagnetic coupling strength in order to use such hybrid nanostructures as building blocks for quantum technologies at room temperature.

To produce hybrid nanostructures, in which a known number of dye molecules are strongly coupled to a plasmonic resonator, we produce 40 nm gold dimers featuring 5 ATTO647N molecules and we actively decrease the interparticle distance below 2 nm. Using scattering spectroscopy, we observe plasmon mode splitting in the longitudinal resonance of single 40 nm gold particles only when the spacing is below 2 nm [2]. The wavelength distribution of hybrid eigenmodes features an anticrossing behavior, typical of a strong-coupling regime, in excellent agreement with electrodynamic simulations. Furthermore, we demonstrate the influence of the planar facets of polycrystalline gold particles on the probability of observing this coupling regime, highlighting which geometrical parameters must be further optimized to reach single-molecule strong coupling at room temperature in a controlled and reproducible way.

References:

[1] S. Bidault et al, ACS Nano 10, 4806–4815 (2016)
[2] J. Heintz et al, ACS Nano 15, 14732-14743 (2021)

C'NANO 2020
The Nanoscience Meeting
TOULOUSE
Centre des congrès Pierre Baudis
December, 8, 9 and 10

Thematic Session: Nanochemistry & Nanoparticles, Nano Gold by young researchers, Nanophotonics & Nano-optics
Keywords: Gold nanoparticles, polyelectrolyte, polymer, self-assembly

Quench Assembly of Gold Nanoparticles With Quaternized Chitosan

F. Voisin[a], A. Balfourier,[a] F. Gazeau[a], J.M. Mallet[b], F. Carn[a]

[a]Laboratoire Matière et Systèmes Complexes (UMR 7057, Université de Paris-CNRS, Paris, France)
[b]Laboratoire des BioMolécules (UMR 7203, Ecole Normale Supérieure, département de chimie, Paris, France)

Gold nanoparticles (AuNPs) can behave as nanosources of heat under light irradiation with a frequency close to the surface plasmon. This property is commercially exploited for biomedical applications. Most of studies conducted so far have sought to maximize the heating power per NP at $\lambda > 700$ nm by adjusting the characteristics of individual NPs. As pointed by simulations [1], another option consists to assemble NPs in colloidal oligomers. This approach could allow the use of small NPs with small absorption cross-section but with good biodegradability compared to usual NPs.[2] Few experimental studies were done so far in this direction due to the difficulty to assemble NPs using biocompatible compounds in water.
I will present a strategy to assemble AuNPs in colloidal oligomers by electrostatic complexation with quaternized chitosan. This method has the advantage of using green and friendly compounds in aqueous media. First, I will describe the structure and the photothermal properties of the complexes obtained by equivolumic mixing in the different regions of the state diagram. I will show that neutral complexes, with the least colloidal stability, present the best optical and photothermal properties with a plasmon peak close to 750 nm, due to a minimized interparticle distance. Second, I will show that these neutral complexes could be stabilized, at different stages of their growth, by fast addition of polymer using a quench flow reactor allowing controlled mixing and delayed co-injection on a millisecond time scale. This method enables to rapidly produce stable suspensions of a few mL containing complexes with controlled aggregation number.

References :

1- B. Khlebtsov *et al.*, *Nanotechnology* **2006**, *17*, 5167
2- A. Balfourier *et al.*, *PNAS* **2020**, 117, 103

C'NANO 2020
The Nanoscience Meeting
TOULOUSE
Centre des congrès Pierre Baudis
December, 8, 9 and 10

Thematic Session: Nano Gold by young researchers
Keywords: ultrasmall gold nanoparticles, pre-nucleation clusters, growth mechanism, nucleation, crystallization

Ultrasmall nanospheres and ultrathin nanowires: growth mechanism study

E. Yildirim[1], R. K. Ramamoorthy[2], L.-M. Lacroix[1], P. Roblin[2], I. Rodriguez-Ruiz[2], S. Teychené[2], G. Viau[1]

1. *Université de Toulouse, Laboratoire de Physique et Chimie des Nano-Objets, UMR 5215 INSA, CNRS, UPS, 135 avenue de Rangueil, F-31077 Toulouse cedex 4, France*
2. *Laboratoire de Génie Chimique, Fédération de Recherche FERMaT, Université de Toulouse, CNRS, INP, UPS Toulouse, France*

Ultrasmall gold nanoparticles and ultrathin nanowires find applications in catalysis or in transparent electronics. The syntheses of gold nanoparticles (NPs) consisting in the reduction of hydrogen tetrachloroaurate(III) ($HAuCl_4.3H_2O$) in solution of oleylamine (OY) in hexane by addition of tri-isopropyl silane (TIPS) at room temperature (Eq.1) are very simple to carry out and offer a great variety of shape and atomic structure by varying the OY and TIPS concentrations [1]. The reason invoked for this atomic structure was the strong confined growth and the significant contribution of surface effect to the atomic configuration.One challenge is to unveil the precise role of OY that can act both as ligand for Au(III) and Au(I) complexes and as capping agent for the final Au(0) NPs.

$$HAuCl_4 + \frac{3}{2}R_3SiH + \frac{5}{2}C_{18}H_{35}NH_2 \rightarrow Au(0) + \frac{3}{2}R_3SiCl + \frac{5}{2}C_{18}H_{35}NH_3^+Cl^- \qquad \text{Eq. 1}$$

With the stoichiometric ratio OY/Au = 2.5, very fast reactions were observed with large excess of TIPS giving spherical particles with a diameter of 2 nm and an icosahedral structure. The reaction is slower when the TIPS concentration is decreased, favoring bigger nanoparticles with fcc structure. The SAXS results indicate that at initial times, there is a very rapid transformation of initial Au(III)/Au(I) pre-nucleation clusters (PNCs) directly into ultrasmall Au(0) nanoparticles [1]. With low TIPS concentration, an intermediate lamellar phase is observed that is not involved in the nucleation step but act as reservoir for the nanoparticles growth.

With large excess of OY (OY/Au = 20), the reaction is very slow and gives ultrathin nanowires (diameter <2 nm) and a length of several micrometers. XAS results showed that the coordination chemistry changed with OY in the Au(III) coordination sphere, decreasing the reactivity of the precursors. Oleylammonium chloride and OY are attached at the surface of nuclei as a bilayer favoring the growth in 1D direction [2]. The perspective of this work is the synthesis of bimetallic Au-Ag nanoparticles.

References:

[1] R. K. Ramamoorthy, E. Yildirim, E. Barba, P. Roblin, J.A. Vargas, L.-M. Lacroix, I. Rodriguez-Ruiz, P. Decorse, V. Petkov, S. Teychené, G. Viau, *Nanoscale*, **2020**, 12, 16173-16188

[2] A. Loubat, M. Impéror-Clerc, B. Pansu, F. Meneau, B. Raquet, G. Viau and L.-M. Lacroix, Langmuir, **2014**, 30, 4005–4012