

Appel à projets doc *iSiM* 2022

Understanding chirality transfer in gold nanocrystals:
a combined theoretical and experimental study

CHIRALor

Porteur : Prof. M. Calatayud (LCT)

Co-porteur : Dr. Hab. C. Salzemann (MONARIS)

Summary

In this project we aim at providing a rational behind the mechanism of chirality transfer in chiral gold nanoparticles, that have recently attracted much attention. An *ab initio* study will characterize the complex molecule-surface interface by screening target molecules and gold substrates, both chiral and non-chiral. The most promising systems will then be synthesized by wet chemistry, and characterized as regards their chiroptical properties.

Short CV Monica CALATAYUD

M. Calatayud (Almenara, Spain 1975) is **full professor** at Laboratoire de Chimie Théorique, SU (FR). Her research is focused on the **computational modelling of (nano)materials**, surfaces and interfaces, using *ab initio* methods to unravel the properties of the systems on the molecular level. She has investigated metals and metal oxide surfaces, adsorption and heterogeneous catalysis phenomena.

• Professional Preparation

- 2008: Habilitation Thesis at Université P. M. Curie, Paris, France
- 2001: PhD degree in Chemistry at Universitat Jaume I, Castelló, Spain
- 1997: Bachelor degree in Chemistry at Universitat Jaume I, Castelló, Spain

• Appointments

- 2020- Full professor Sorbonne Université (Paris, France)
- 2005-2020 Maître de Conférences (Associate Professor) UPMC (Paris, France)
- 2011-2016 Institut Universitaire de France **IUF** junior position (Paris, France)
- 2003-2004 Marie Curie Individual fellowship UPMC (Paris, France)
- 2001-2002 Post-Doc Université P. M. Curie (Paris, France)

• Selected Publications

A Multi-Scale Modelling of Aggregation of TiO₂ Nanoparticle Suspensions in Water
G. Mancardi, M. Alberghini, N. Aguilera-Porta, M. Calatayud, P. Asinari, E. Chiavazzo
Nanomaterials 12 217 (2022) [10.3390/nano12020217](https://doi.org/10.3390/nano12020217)

Nanoparticle Assembling through Click Chemistry Directed by Mixed SAMs for Magnetic Applications
M. Dolci, D. Toulemon, Z. Chaffar, J.-L. Bubendorff, F. Tielens, M. Calatayud, S. Zafeiratos, S. Begin-Colin, B. Pichon **ACS Applied Nano Materials** 2 (2019) 554 [10.1021/acsanm.8b02152](https://doi.org/10.1021/acsanm.8b02152)

Controlled selectivity for ethanol steam reforming reaction over doped CeO₂ surfaces: The role of gallium in avoiding coke formation
J. Vecchietti, P. Lustemberg, E. Fornero, M. Calatayud†, S. Collins, S. Mohr, V. Ganduglia-Pirovano, J. Libuda, A. Bonivardi **Appl. Catal B : Environmental** 277 (2020) 119103 <https://doi.org/10.1016/j.apcatb.2020.119103>

Platinum and platinum based nanoalloys synthesized by wet chemistry [10.1039/C5FD00002E](https://doi.org/10.1039/C5FD00002E)
C. Salzemann, F. Kameche, A. -T. Ngo, P. Andreazza, M. Calatayud, C. Petit **Faraday Trans.** 181 (2015) 19

Understanding How in situ Generated Hydrogen Controls the Morphology of Platinum Nanoparticles
N. Aguilera-Porta, M. Calatayud, C. Salzemann, C. Petit **J. Phys. Chem. C** 118 (2014) 9290 [10.1021/jp502174b](https://doi.org/10.1021/jp502174b)

• Research

Researcher ID: C-8308-2013	ORCID: 0000-0003-0555-8938
Citations: Author Identifier 0000-0003-0555-8938	
120 items	citations: >4700
	h-index: 42 (scholar)

>**120 Publications:** 2 Review articles, 106 regular articles in peer-reviewed journals, 13 proceedings, 5 meeting abstracts, 2 Editorial, **3 book chapters** **Communications:** 15 invited lectures, 16 invited seminars, 50 oral communications **Editor:** of 2 special issues devoted to modelling catalytic processes: *J. Molec. Struct. Theochem* 903 (2009) *Catal. Today* 177 (2011). Editorial board of TCCM series-Springer. **Supervision** of 7 PhD, 7 postdocs, 12 Master **Research networks:** RIA H2020 Nanoinformatix, RIA H2020 Charisma, COST C18234, ANR CHIRNATIO

• Teaching activities

Besides **regular lectures** and lab courses for undergraduate and Master students (192 hours/year), I am involved in **international mobility programs:** Erasmus Mundus+ (EJM-TCCM, EJD-TCCM).

Short CV Caroline SALZEMANN

Caroline Salzemann (MONARIS -UMR 8233) est maître de conférences en chimie générale depuis 2008 à Sorbone Université. Ses domaines de recherche portent sur l'élaboration raisonnée de nanomatériaux mono et bimétalliques pouvant être intégrés dans des dispositifs catalytiques, optique et/ou magnétiques. Physico-chimiste, elle s'intéresse particulièrement à la compréhension des mécanismes de réduction/nucléation/croissance impliqués dans les synthèses colloïdales de nanoparticules. Cette approche est motivée par l'ambition de tendre vers des synthèses prédictives en acquérant les connaissances nécessaires à la maîtrise des différents paramètres expérimentaux. A travers ses recherches, elle a acquis une expertise dans l'élaboration de nanocristaux complexes caractérisés par une faible dispersion structurale (taille, forme, cristallinité, composition). Le second aspect de sa recherche consiste en leur organisation en assemblages 2D et 3D en contrôlant la distance interparticulaire et le degré d'ordre/désordre pour moduler les propriétés physiques (magnétiques, optiques) des assemblages. Depuis 2017 elle développe une nouvelle thématique sur l'élaboration de nanocristaux métalliques chiraux à faible dispersion structurale pour la catalyse asymétrique et la détection de molécules. Elle porte depuis octobre 2022 une ANR PRC, CHIRNATIO.

Elle est co-auteur de 28 publications internationales évaluées par des pairs, dont un chapitre de livre et un brevet. (h-index : 13) et de 35 communications orales dont 4 conférences invitées et 9 présentations de posters.

Expertise

- Élaboration de nanomatériaux mono et bimétalliques pour des applications catalytiques et/ou magnétiques : contrôle de la taille, de la forme et de la cristallinité
- Organisations 2D et 3D : ordre à longue distance et modulation des propriétés collectives
- Élaboration de nanocristaux chiraux

Diplomes

2001-2004 : Thèse de doctorat réalisée au FHI de Berlin (Pr. J. Urban) et au LM2N (Paris VI- Pr. M.-P. Pileni)

Juillet 2019 : Habilitation à diriger des recherches

Publications

- **Characterization and growth process of copper nanodisks**; C. Salzemann, I. Lisiecki, J. Urban and M.P. Pileni*; *Adv.Func.Mater.* (Impact Factor: 15.621) **2005**, 15, 1277.
- **Influence of hydrogen on the morphology of platinum and palladium nanocrystals** C. Salzemann, C. Petit ; *Langmuir* (impact factor: 3.683), **2012**, 28, 4835-4841
- **Synthesis of hcp Cobalt Nanocrystals Ferromagnetic at Room Temperature by Simple Mix of ClCo(PPh₃)₃ and Oleylamine**; L. Meziane, C. Salzemann, C. Aubert, H. Gérard, C. Petit and M. Petit, *Nanoscale* (Impact factor: 6.970), **2016**, 8, 18640
- **Binary Superlattices from {Mo₁₃₂} Polyoxometalates and Maghemite Nanocrystals: Long-Range Ordering and Fine-Tuning of Dipole Interactions**; R. Breitwieser, T. Auvray, F. Volatron, C. Salzemann, A.-T. Ngo, P-A. Albouy, A. Proust*, and C. Petit*; *Small* (Impact Factor: 10.856), **2016**, 12, 2, 220.
- **Chemical Evolution of Pt-Zn Nanoalloys Dressed in Oleylamine**; A. Zakhtser, A. Naitabdi*, R. Benbalagh, F. Rochet*, C. Salzemann*, C. Petit, and S. Giorgio, *ACS Nano* (Impact Factor: 14.588), **2020**, 15 (3) , pp.4018-4033.

Scientific description

Objectives and description of the project

Chirality, defined as the absence of symmetry that leads an object not to be superimposed to its image in a mirror, is ubiquitous in nature on different scales, from (bio)molecules to plant growth to galaxy shape. The research of chiral inorganic nanomaterials has experienced a tremendous growth in the last years for applications in optoelectronic, biomedicine or catalysis¹. Despite recent advances in synthesis and characterization of chiral nanoobjects, the molecular mechanisms behind are still poorly understood, limiting the development of applications. In the present project we aim at establishing the fundamental rules that govern the interaction between molecule and surface leading to chiroptical gold nanocrystals (NCs).

A recent report shows that it is possible to synthesize chiral gold NCs by wet chemistry, through seed-mediated growth considering metal seeds of controlled size, crystallinity and morphology². In wet chemistry synthesis every species (ligand, molecules, ions) even the by-products are susceptible to adsorb on the surface of a NC modifying its surface energy, either by growth kinetics or thermodynamics. A valid strategy to imprint chirality consists in considering anisotropic colloidal NCs characterized by Miller's high-index facets, that can be stabilized to prevent their relaxation toward low-index facets. It is thus of utmost importance to understand the role played by the molecule-surface interface to tune the NC's chirality.

Very recently, chiral nano-arrows (NAs) have been obtained at MONARIS (Fig. 1A) from elongated tetrahexahedra seeds characterised by $\{hk0\}$ high-index facets, with L-cysteine, a common chirality imprinter. The HRTEM image of the NAs shows that the main surfaces evolve during the growth from high to compact low-index facets. However, the growth rate of (111) facets of the tips is different leading to a zig-zag morphology (Fig. 1B). The corresponding circular dichroism (CD) confirms the chirality transfer from the cysteine to the NAs (Fig. 1C, red). The study has been extended to other aminoacids close to the structure of L-cysteine to assess steric hindrance (L-penicillamine) and spaciation (L-homocysteine, see below). Interestingly, all the molecules anchor to the surface via a Au-S bond (confirmed by Raman), but the chirality transfer leads to different NA response (Fig. 1C). Indeed, intensity, and more surprisingly the sign of the CD, changes with the aminoacid used as well with their concentration during the synthesis. Concerning the nanomorphology, homocysteine gives similar NA to those with cysteine while rounded tips are obtained with the L-penicillamine more like dumbbells or bones. These intriguing results show the need for a deeper, thorough investigation to understand the chirality transfer mechanism.

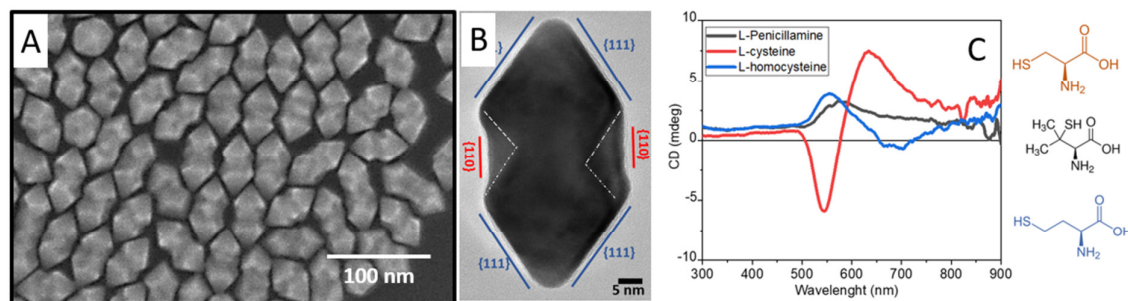


Figure 1 : (A) SEM-FEG image of Au chiral nanocrystals synthesized by successive seeding process in presence of L-cysteine. (B) corresponding HRTEM image. (C) CD spectra for NAs obtained using L-cysteine (red), L-penicillamine (black) and L-homocysteine (blue).

Scientific objectives. The surprising results obtained in the MONARIS synthesis motivate the present project. The main goal is to rationalize the mechanism of chirality transfer by identifying the role of the molecules and their interaction with the NCs surfaces leading to different chiroptical response. Specifically, we will characterize in detail the nature of the complex interface formed between selected molecules with the high-index and low-index

gold surfaces. To this end, we will use a theoretical approach that will provide an accurate description of the interface on the molecular level, accompanied by experiments.

Strategy. The complexity of the interfacial system requires a multitechnique investigation that disentangles the role of each factor involved. The strategy in the present project is to first model the surface-molecule interactions to extract the key features ruling their stability, then use that information to set new synthesis of chiral NCs with selected properties. Figure 2 schematizes the process and the systems to be studied.

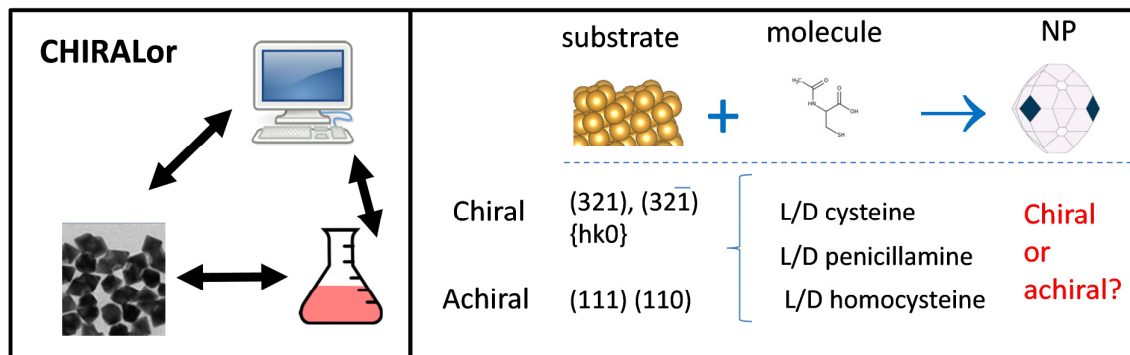


Figure 2. schematic representation of the strategy planned and the target systems to be studied

In particular, the binding molecule-surface will be accurately addressed to highlight

- steric hindrance of the anchoring group to form Au-S: L/D-penicillamine, which is a cysteine including CH₃ instead of H, will be used
- spaciacion between anchoring group and chiral group: L/D homocysteine, which is a cysteine containing a longer alkyl group, will be used

Intrinsically chiral surfaces will be modelled by *ab initio* quantum chemical calculations (periodic density functional theory DFT), as it has been reported to successfully describe similar systems. In particular the interaction of chiral aminoacids with regular gold terminations (110), (111)³, and more recently, high index terminations (521), (321), (17 11 9) with chiral ligands has been addressed.⁴ In the present project, such methodology will be used to i) identify stable chiral molecule-surface systems ii) characterize the gold-molecule interfaces interpret, complement and predict the chiroptical properties of the objects. The calculations will be followed by experimental synthesis and characterization of selected systems, to prove or discard the role of each factor in the stability of chiral gold NCs.

Originality. The scarce literature on intrinsic chiral gold NCs reveals the lack of fundamental knowledge on the mechanistic aspects for chirality transfer. The first chemical synthesis of chiral gold NCs is reported in 2018. Since then, few groups in the world have synthesized such objects by the adsorption of chiral ligands on low-index facets of gold nanocubes, nanotriangles or nanooctopods.^{2, 5} Actually, intermediate NCs characterized by high-index facets have been generated in situ in the chemical bath during the crystal growth from the low-index seeds. The first French publication on chiral surface around high-index facets gold bipyramides is from January 2022.⁶ **Our original hypothesis is that starting directly from controlled high-index facets NCs, and guided by the theoretical exploration of other candidate molecules, will allow an improved control on the crystal growth compared to a non-controlled *in situ* generation of high-index facets or from low-index NCs.** From the theoretical point of view, also few groups in the world apply quantum chemical description for the study of intrinsically chiral surfaces^{4a, 7}. They base their studies on published experiments carried out in different research groups. **Our project joins together both theory and experiment conducted by the same person, minimizing the reaction time to implement the results obtained from theory to synthesis and inversely.**

Feasibility. Risk assessment and management

The tools envisaged have been successfully used to investigate similar systems. *Ab initio* studies have shown that the L-cysteine patterns on chiral gold surfaces are robust, proving the adequacy of the methodology ^{4a}. However, only L-cys has been reported in detail, with models constructed on small unit cells ^{4b}. **We will push further by extending the study to different target molecules to reveal the role of steric hindrance and speciation in the binding molecule-surface, and by considering advanced theoretical techniques characterize chirality of those novel systems.** Two candidate molecules have been identified (L/D-penicillamine, L/D homocysteine) that lead to unexpected chiroptical properties, and that ideally fit in the structural models that can be computationally calculated.

The success of the project is based on the close dialogue between theory and experiment, this is why we search for a candidate that will carry out both calculations and synthesis.

Risks and remediation

1. calculations too demanding → we will ask for time in the French supercomputing center. Currently the group benefits of 1 M h/year, which could be increased for the study if needed. For the sampling of long range molecular configurations we will rely on a collaboration with P. Stishenko (Cardiff) started last year, who is a developer of the code SusMost ⁸ devoted to explore the configurational space of complex interfaces.
2. The risk on experimental synthesis is limited as it will be performed starting from the protocol already established at MONARIS and further adapted by considering different chiral molecules and/or reducing agent. We will use characterization techniques available to analyze the structure/properties of the objects obtained, and the reasons of the deviations observed.
3. **Find a candidate → the projects needs a candidate that masters theoretical tools but should also reproduce experiments as he/she will not have to develop new synthesis.** During the first months he/she will benefit from the knowledge of the actual PhD student Nada Khalfaoui Hassani (3rd year PhD thesis) who will be doing her postdoc near SU and will be able to ensure the transmission of all useful information. **Thanks to the ISIM funding of an M2 internship, the two PIs are currently supervising a student, M. Tabut, since beginning of February that is carrying out both the calculations and the synthesis, with promising results.** She has already reproduced the synthesis of chiral gold nanoparticles with cysteine and also successfully reproduced the recent calculations in ref. ^{4b}. If for some reason she cannot be hired, we will publish the job offer in doctoral school websites, psi-k, TCCM, GDR and personal networks to reach a maximum of potential candidates. We are confident that the dual skills of theory and experience developed in such projects will attract curious and ambitious candidates.

Position of the project within national and international context

As stated above, only few groups in the world conduct successful synthesis and theoretical characterization of chiral gold nanoparticles. In the last year, 2 key events happened

- the collaboration of the two PIs was strengthened by an ANR funding on chiral plasmonics. ANR CHIRNATIO, leads by C. Salzemann and involving M. Calatayud as responsible for the *ab initio* calculations. The project is devoted to the chiroptical properties of Au NCs and does not overlap with the present project. This confirms the scientific quality and potential of both the collaboration and the topic, but does not allocate resources for a joint PhD.

- an important paper by Ni et al.^{4b} was published, showing the enormous impact of associating theory and experiment in the field. In that work the role of high index chiral surfaces is highlighted for four-fold twisted objects. Also, the *ab initio* calculations are based only on L-cys, and the other molecules effects (solvent, reducing agent, surfactant, other potential chiral molecules) are ignored. Besides, the structural models only consider small areas with few molecules. In the present proposal we will push the limits by considering different objects, different chiral molecules and more realistic molecular assemblies obtained by advanced automatized theoretical sampling techniques.

In this context, we believe that our proposal is not only innovative but also very timely. A PhD would boost the research in the field and consolidate SU and ISiM as leading actors in the field of chiral NCs.

Position of the project in regard to the iSiM objectives

This project puts the molecule in the center of the study: different types of molecules play different roles (surfactant, chiral template, reducing agent...) and interact in different manners with the surfaces, leading to a final product with its own properties. In particular, we use target molecules selected to assess the properties from an accurate description of the Au-S bond: steric hindrance and bond-chiral group spaciation. Such approach perfectly fits with the chemist's strategy of a rational design by experimental and computational experiments.

Our project spreads the scope of iSiM in the field of chirality. The ubiquity of chirality ensures a wide projection of the results in domains like enantiomeric catalysis, electro-optic devices, astrochemistry or biomedical applications, already funded by iSiM and potentially accessible for CHIRALor. Ultimately, the PhD candidate will increase his/her job opportunities in (non)academic sectors thanks to the complementary experimental and computational skills, outlining the role of iSiM in the accessibility of young researchers to the job market.

Highlight partners complementarity

The project associates two complementary teams :

- M. Calatayud (LCT laboratoire de Chimie Théorique) expert in modelling surfaces, interfaces and nanomaterials with *ab initio* techniques. She has successfully described complex metal-organic molecule interfaces such as Au and Ag self-assembled monolayers of organic amine and thiol molecules⁹.
- C. Salzemann (MONARIS) expert in the synthesis of metal nanoparticles by wet chemistry. Currently she supervises a PhD thesis carried out by N. Khalfaoui (in 3rd year) devoted to the development of protocols to synthesize and characterize gold enantiomeric nanoparticles with plasmonic properties.

The two partners have successfully worked in the past on the control of size and shape of Pt NCs. They supervised together a Master student, N. Aguilera-Porta, who carried out both the calculations and the synthesis of the materials. They have 2 common publications, refs¹⁰ and¹¹. They currently co-supervise a M2 internship (M. Tabut) funded by iSiM.

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Research program

Step 1: elaboration of a surface-molecule map from theoretical calculations

We will develop an accurate mapping of molecule-surface interactions by quantum chemical calculations. The substrate will be modelled by (a)chiral gold terminations (see Figure 2), in interaction with the key molecules used in the synthesis: L/D-cysteine but also L/D penicillamine and L/D homocysteine. The interaction energy, the role of geometry, molecular form (protonated/deprotonated depending on the pH), solvent and coverage will be systematically investigated. Single adsorption and coadsorption will be calculated, and large assemblies of molecules will be obtained with Grand Canonical Monte Carlo sampling techniques (SusMosT program⁸). The surface energy, that ultimately determines the shape of the NP, will be obtained by the Wulff construction after collecting the data for all the combinations molecule-surface. The electronic structure will be investigated (charge transfer, oxidation states of molecule and surface) to characterize the reduction and growth processes. Periodic DFT as implemented in the VASP code will be employed. The computational settings (functional, pseudopotential, cutoff, dispersion correction, implicit solvent...) will be carefully chosen after comparison with available experimental and literature results for L-cysteine/gold^{4a}.

Step 2: synthesis and characterization of selected gold NCs

The systems exhibiting optimal adsorption features (strength, surface structure, coverage) according to step 1 will be selected to be synthesized. The current protocol will be adapted to emphasize the role of the reducing agent, the stepwise addition of seeds, the composition of the reaction bath and conditions (p, T, solvent). The products of the different syntheses will be characterized by HRTEM microscopy, circular dichroism, FT-IR/Raman spectroscopy, XPS, to obtain information about morphology, chirality and interface structure.

Step 3: analysis of the results

The results obtained from theory and experiment will be carefully compared to build a coherent scenario. New calculations and syntheses will be conducted based on those results to check the validity of the hypotheses.

The success of the project is based on the close dialogue between the partners at every step. We will organize regular meetings to discuss results and take decisions. The calculations will be carried out at LCT (access to local cluster and French GENCI supercomputing center). The experiments will be conducted at MONARIS.

	Year 1		Year 2		Year 3	
Step 1 map of molecule-surface interactions from DFT calculations	x	x				
Step 2 synthesis and characterization of selected Au NCs			x	x		
Step 3 analysis and summary of the results					x	
Writing PhD, defence						x