SORBONNE UNIVERSITÉ

PROGRAMME INTITUTS ET INITIATIVES

Appel à projet – campagne 2021

Proposition de projet de recherche doctoral (PRD)

ISim - Initiative Sces et ingénierie moléculaires

Intitulé du projet de recherche doctoral (PRD): The Use of Organometallic CHEmistry for the Synthesis of chiRAL Nanocatalysts

Directeur.rice de thèse porteur.euse du projet (titulaire d'une HDR) :

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Unité de Recherche :
Intitulé : IPCM
Code *(ex. UMR xxxx)* : UMR8232

École Doctorale de rattachement de l'équipe (future école doctorale du.de la doctorant.e) : **ED406-Chimie Moléculaire Paris Centre**

Doctorant.e.s actuellement encadré.e.s par la.e directeur.rice de thèse (préciser le nombre de doctorant.e.s, leur année de 1e inscription et la quotité d'encadrement) : 1 (2019 50%)

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Intitulé : MONARIS "de la Molécule aux Nano-objets : Réactivité, Interactions et Spectroscopies"
Code *(ex. UMR xxxx)* : 8233

École Doctorale de rattachement : **ED388-ChimiePhysiqueChimieAnalytique ParisCentre**
Ou si ED non Alliance SU :

Doctorant.e.s actuellement encadré.e.s par la.e co-directeur.rice de thèse (préciser le nombre de doctorant.e.s, leur année de 1e inscription et la quotité d'encadrement) : 2 doctorants; 2019 et 2020; respectivement 40% et 100%

Initiative sciences et ingénierie moléculaires
SORBONNE UNIVERSITÉ

Appel à projets doc *iSiM* 2021

L'Initiative de Sciences et Ingénierie Moléculaires lance son deuxième appel à projets Doc (2 supports). Il a pour objectif de soutenir des collaborations entre **équipes de l'Alliance Sorbonne Université aux savoir-faire complémentaires** dans le but de développer une recherche d'excellence à l'échelle moléculaire. Ces projets devront **impérativement** être présentés par un minimum de **deux équipes différentes** de *l'Alliance SU*.

L'échelle moléculaire est revendiquée par beaucoup de disciplines: la chimie évidemment, mais aussi la physique, la biologie, la médecine, les géosciences etc... Notre but est de renforcer l'impact de la recherche de l'Alliance SU en concentrant les moyens sur quelques projets fédérateurs impliquant des compétences multiples autours des sciences et de l'ingénierie moléculaires.

La molécule correspond à l'échelle élémentaire et structurante de la matière, de l'atome au nano-objet, et se trouve de ce fait à la croisée de nombreuses préoccupations scientifiques et d'enjeux sociétaux primordiaux que sont la santé, l'énergie, l'environnement, l'information et ce dans un contexte d'économie circulaire. En effet, toutes les disciplines scientifiques expérimentales majeures s'appuient fortement sur les propriétés moléculaires pour analyser, comprendre, reproduire et manipuler la complexité de la matière. Une approche multidisciplinaire à l'échelle de la molécule précisément identifiée est donc essentielle pour relever des défis scientifiques majeurs autours de questions fondamentales ou appliquées telles que le biomimétisme, la photosynthèse artificielle, l'origine cosmique des briques moléculaires du vivant, la vie artificielle, le stockage et la transmission moléculaire et supramoléculaire de l'information, la catalyse, la modélisation théorique d'assemblages moléculaires complexes, les machines moléculaires…

The Use of Organometallic CHEmistry for the Synthesis of chiRAL

Nanocatalysts

THEORETICAL

Partner 1: IPCM

Marc Petit (IPCM -UMR 8232 was recruited at CNRS as a researcher in 2004 in the CEISAM unit in Nantes, where he worked for 6 years on the chemistry of metallophosphonates in order to develop biomaterials and supported catalysts. Since 2010, he has been carrying out research activities at the Parisian Institute of Molecular Chemistry (IPCM) where he develop, two main themes in the area of organometallic catalysis. One focuses on the activation of E-H bonds (with E = C, Si, B, H…) followed by the functionalization of unsaturated compounds using either cobalt complexes or niobium complexes. The other is focused on the synthesis of nano-objects by organometallic routes and their applications in catalysis and in the energy field. The major common concern to these thematic is the design and the use of simple, well-defined, easily accessible catalytic systems, usable without adding additives and more over easily reproducible. This work is based on an understanding of the reaction mechanisms whether in catalysis but also in the growth of nano-objects.

he is co-author of 54 international peer-reviewed publications including one book chapter and one patent. (h-index: 23) and of 34 oral communications including 15 invited talk.

Expertise

- Organometallic catalysis: Cobalt, Nickel Niobium…
- Surface functionalization: DNA chips, supported catalysts
- Synthesis of nanoparticles by organometallic approaches

Diploma

2002: PhD thesis at UPCM at Paris (Pr. M. Malacria): cycloaddition with cobalt complexes.
2004: CNRS position at Nantes (chargé de recherche)
2013: Habilitation to supervise PhD thesis (HDR)
2018: Research director at CNRS (Paris)

5 Selected Publications

- **Relaying asymmetry of transient atropisomers of o-iodoanilides by radical cyclizations**. M. Petit, A. J. B. Lapierre, D. P. Curran, *J. Am. Chem. Soc*., (impact factor: 14.612) **2005**, 127, 14994-14995.
- **Towards Zirconium Phosphonate-Based Microarrays for Probing DNA-Protein Interactions: Critical Influence of the Location of the Probe Anchoring Groups.** J. Monot, M. Petit, S. Lane, I. Guisle, J. Leger, C. Tellier, D.R. Talham, B. Bujoli*, J. Am. Chem. Soc.* (impact factor: 14.612) **2008**, *130*, 6243-6251.
- **C–H Activation/Functionalization Catalyzed by Simple, Well-Defined Low-Valent Cobalt Complexes**, B. J. Fallon, E. Derat, M. Amatore, C. Aubert, F. Chemla, F. Ferreira, A. Perez-Luna, M. Petit* *J. Am. Chem. Soc*, (impact factor: 14.612) **2015**, 137, 2448-2451.
- **Role of Oleylamine Revisited: An Original Disproportionation Route to Monodispersed Cobalt and Nickel** Nanocrystals A. Vivien, M. Guillaumont, L. Meziane, C.

Salzemann, C. Aubert, S. Halbert, H. Gérard*, M. Petit, * C. Petit* . *Chem. Mater.* (impact factor: 9.567) **2019**, 31, 960-968.

- **Simpler and Cleaner Synthesis of Variously Capped Cobalt Nanocrystals Applied in Semi-hydrogenation of Alkynes** A. Sodreau, A. Vivien, A. Moisset, C. Salzemann, C. Petit, * and M. Petit* *Inorg. Chem*. (impact factor: 4.825) **2020,** 13972-13978.

Partner 2: MONARIS

Caroline Salzemann (MONARIS -UMR 8233) is associate professor in general chemistry since 2008 in MONARIS laboratory. Her research areas consist in the rational elaboration of mono and bimetallic nanomaterials that could be integrated in catalytic and/or magnetic devices. She is interested in the understanding of the reduction/nucleation/growth mechanisms involved in colloidal syntheses. This approach is motivated by the ambition to move towards predictive syntheses by acquiring the knowledge necessary to master the various experimental parameters. Through her research, she has acquired an expertise in the elaboration of complex nanocrystals characterized by a low structural dispersion (size, shape, cristalliniyty, composition). The second aspect of her research consists in their organization in 2D and 3D assemblies by controlling the interparticle distance and the degree of order/disorder to modulate the physical (magnetic, optical) properties of the assemblies. Recently she has started to develop a new thematic on elaboration of metallic chiral nanocrystals with low structural dispersion for asymmetry catalysis and enantiomeric detection.

She is co-author of 26 international peer-reviewed publications including one book chapter and one patent. (h-index: 11) and of 35 oral communications including 4 invited talk and 9 poster presentations.

Expertise

- Elaboration of mono and bimetallic nanomaterials for catalytic and/or magnetic applications: size, shape and crystallinity control
- 2D and 3D organisations: long-range order and modulation of the collective properties
- Elaboration of chiral nanocrystals

Diploma

2001-2004: PhD thesis at FHI at Berlin (Pr. J. Urban) in coordination with the LM2N laboratory (Paris VI- Pr. M.-P. Pileni)
Juillet 2019: Habilitation to supervise PhD thesis (HDR)

5 Selected 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 $ClCo(PPh_3)_3$ 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 $\{Mo_{132}\}$ 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), accepted august 2020, https://dx.doi.org/10.1021/acsnano.0c03366

Summary of the project

The aim of THEORETICAL project is to elaborate new chiral nanocatalysts for asymmetric catalysis, based on a mild and tunable NP-synthesis on 3d metals (Ni, Co, and Co-Ni). To reach that goal we will study two approaches: the first one deals with the anchoring of several families of chiral ligand on the surface of the NPs. The second approach is based on the elaboration of new intrinsically chiral NPs (Ni, Co, and Co-Ni) through breaking symmetry.

Scientific description (5 pages max.)

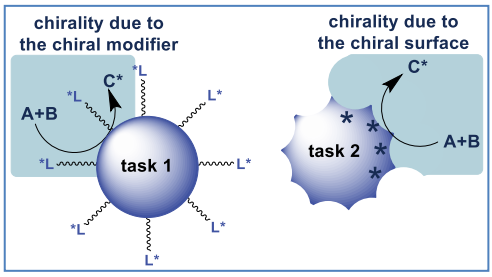
Objectives and description of the project

Enantioselective catalysis is one of the most efficient processes to access the chiral molecules needed in pharmaceutical industry.[1] Therefore the development of new chiral catalysts is a major challenge to tackle. In this field, homogeneous catalysis is the incontestable leader, as it allows catalyst modulation by tuning the ligand: researchers can perform an "easy" optimization of the reaction conditions, leading to high activity and enantioselectivities.[2,3] Despite these indisputable benefices, 80% of the most relevant industrial processes are still performed with heterogeneous catalysis, as it enables catalyst recycling, minimization of metal leaching, improved process handling and control as well as low cost.
To try to combine advantages of both the heterogeneous and the homogeneous catalysis, the so-call "homogeneous supported catalysis" strategy can be used: the soluble chiral catalyst is immobilized on a surface. The enantioselectivity thus arises from the action of the chiral catalyst and not from the surface. However, lack of both reactivity and selectivity were frequently reported compared to the native homogeneous catalyst, due to the steric hindrance and the problem of mass transport in the porous supports often preferred due to their high surface area.[4] More recently, nanoparticles (NPs) have proved to be a powerful alternative to classical supports as it allows a huge increase in the accessibility of the active site, maintaining the reactivity and selectivity observed in homogeneous catalysis. This is partially explained by the presence of corners and edges that constitute sites of weak coordination increasing the reactivity of the surface atoms.

Major drawbacks of NPs would be the harsh conditions required for their synthesis as well as their purification. Thus, by developing milder NP-synthesis conditions, huge improvements could be made in NP-supported catalysis. Recently we have shown that molecular chemistry, through the design of metallo-organic precursors, allows us to obtain NPs of Co, Ni and CoNi at room temperature (milder synthesis condition). Indeed, the nature of the precursor allows to finely control the reduction/nucleation/growth processes necessary to obtain NPs of low structural dispersion (size, shape, crystallinity).

In the context of heterogeneous catalysis based on NP with chiral ligands, the real role of the chiral ligands versus the metallic surface in the catalyst reactivity is still a remaining question, especially since a synergistic effect cannot be excluded. In particular the role of the crystallinity/morphology (related to the crystallographic surfaces exposed) can have a strong influence on the reactivity/selectivity. Actually, the main obstacle to the elaboration of NPs with a chiral shape is the high crystallographic symmetry of the metals that has to be broken. For small nanocrystals (less than 50 nm) such morphologies are very difficult to obtain by usual chemical colloidal synthesis as high mechanical constraints during the crystal growth are needed. **However molecular chemistry can constitute an alternative chemical way to design new chiral nanocatalysts (NCs)**.

In this project, organometallic chemistry synthesis will be used to design new nanocatalysts characterized by chiral surface or chiral morphology using either chiral modifiers or supramolecular assemblies. Their reactivity and efficiency (surface/crystallinity *vs* morphology) will be tested for enantioselective heterogeneous catalysis. Thus, the judicious association of surface reactivity of nanoparticles surface and the chirality of an appropriate designed ligand could provide the emergence of new catalysts for asymmetric reactions.



The project is structured in 3 tasks

- Design of chiral modifier anchor at the NP surface: effect of crystallinity, morphology, nature of the metal
- Design of molecular chiral assemblies as templates to obtain nanocatalyst with a helical morphology
- Validation of the association (best synergistic effect) considering a model reaction

The first approach (chirality due to a chiral modifier) has been already used mainly with noble metal NPs such as palladium with pioneering results of Kobayashi, gold and platinum in hydrogenation and C–C coupling reactions.[5] However, increasing prices coupled with low natural abundance and toxicity issues limit their application for future development.[6] Due to their low cost, high abundance and unique reactivity intensively studied in homogeneous catalysis, first row transition metals are the natural candidates to replace them.[7] Given that transition metals in the same group often exhibit similar reactivity, it's not surprising that attention has been focused on cobalt as it shares a group with Rh and Ir. Indeed, Pericàs described the use of Co-NPs as support to anchor a chiral ruthenium catalyst for asymmetric hydrogenation of ketones.[8] The main advantage here is the use of magnetically decantable ligands to recover the functionalized NPs.[9] To the best of our knowledge no other asymmetric application has been reported using Co-NPs as the catalyst-support.
In the specific case of cobalt, different crystalline phases can be obtained (hcp and epsilon) that may exhibit different reactivities as well different morphologies.

Preliminary results: We recently took up this challenge by demonstrating that we could prepare hcp-cobalt NPs by a very simple procedure, starting from the $[ClCo(PPh_3)_3]$ cobalt complex in oleylamine (OAm) at 190°C. By just changing the reaction time, we are able to reach selectively 9 nm cobalt nanospheres or nanorods.[10] We proved moreover that this procedure can be applied to other metals as nickel and cobalt-nickel alloy were also accessible.[11] Moreover, and not the least, we just developed a brand new mild synthesis that allows the formation of mono-dispersed hcp-cobalt NPs at room temperature, capped with an easy-to-exchange tridecanol surfactant.[12] **We thus have the tools to face this challenge and produce various new chiral catalytic systems by tridecanol exchange.**

Second approach (chirality due to the chiral morphology). In the literature, the ligand adsorption can induce a reconstruction from achiral to chiral surfaces, which may even lead to morphological distortion. The chirality of the surface is maintained even after removal of the adsorbate.[13,14] However, for small particles (less than 50 nm) the surface relaxation to more stable achiral surfaces will be difficult to avoid. In order to easily modulate the chiral morphology of the NPs, we will use the simple procedure at room temperature we developed, considering new chiral precursors that can assemble into helical morphology. The molecular assemblies could then act as template to direct the nanocrystal growth. **Intrinsically magnetic chiral NPs is a great challenge in asymmetric catalysis as they are potentially recoverable by centrifugation or by magnetic filtration.**

TASK 1: CHIRAL SURFACE BY CHIRAL MODIFIER (IPCM-MONARIS)

This aim of this task is to design several chiral ligands to anchor the metallic surface of achiral nanocrystals in order to determine the best synergistic effect to assess activity, selectivity and efficiency.

1.1 DESIGN OF CHIRAL MODIFIER

The first step is the design of several chiral ligands from different families such as amine, phosphorus, *N*-heterocyclic carbenes (NHC), carboxylic or phosphoric acids. The chiral modifiers have two main roles: to introduce the chirality on the surface but also to modify the electronic properties of the metal and thus modulate its reactivity thanks to electron donating or withdrawing properties.

1.2 ACHIRAL NANOCRYSTALS SYNTHESIS

As the expressed metallic surfaces of the NCs are strongly related to the nanocristallinity and morphology, that consequently can have a strong impact on reactivity, different achiral nanocrystals will be elaborated. Hence comparative analysis will be performed to **study the influence of the i) nanocrystallinity (hcp vs ε):** Based on our recent discovery,[12] we will first use tridecanol to carry out a fast synthesis of 8-9 nm cobalt hcp NPs at room temperature then perform an easy exchange of this temporary surfactant. ε-Co NPs (non-compact structure) can be synthesized via a thermal decomposition of cobalt carbonyl.[19] **ii) nanomorphology (hcp spheres vs hcp nanorods):** We master the synthesis of nanosphere and nanorods, thus we will compare their reactivity and selectivity in catalysis. **iii) nature of the metal (Co vs Ni vs Co_xNi_{1-x}):** We will adapt the room-temperature-synthesis procedure to nickel NCs and cobalt-nickel alloys. We already demonstrated that such a synthesis is possible under thermal conditions (190°C), starting from the corresponding nickel complex.[11]

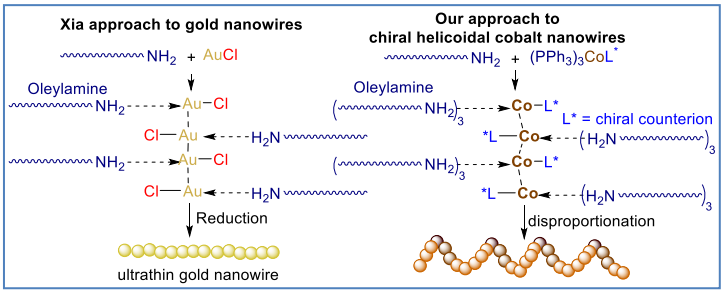
1.3 EXCHANGE LIGAND

For the achiral nanocrystals obtained by our mild synthesis using tridecanol as the surfactant, the ligand exchange should occur quite easily in order to anchor the chiral ligand.

TASK 2: CHIRAL MORPHOLOGY BY CHIRAL (SUPRA)MOLECULAR ASSEMBLIES (IPCM-MONARIS)

In this task, a molecular synthesis strategy will be designed to induce a chiral morphology of the metallic NCs to form Co, Ni and CoNi twisted nanorods

OAm is used as a shaping ligand/surfactant by promoting the elongation of the nuclei.[18-20] This mechanism is based on the formation of micelles in the solvent/surfactant system. Recently, hcp-cobalt, fcc-nickel and hcp-Co_xNi_{1-x} nanorods have been obtained through a kinetic growth in OAm (9h).[10,11] In the literature, the formation of ultrafine Au nanowires using an [(OAm)AuCl] complex is described: OAm has been shown to structure itself in solution to form tubular template by aurophilic attraction.[18] Based on this synthesis, we propose to transfer the strategy of the chiral counterion used in homogeneous catalysis[21] to synthetize chiral cobalt nanostructure.



2.1 CHIRAL (SUPRA)MOLECULAR ASSEMBLIES

We recently demonstrated that the complex [$ClCo(PPh_3)_3$] undergoes structuration in OAm like gold.[22] Thus, chiral deformation of linear assembly of OAm will be achieved by exchanging the chloride on the cobalt complex by a chiral counterion. The idea is to modulate the counterion to induce the formation of helical nanowires. We thus propose to screen first different acids that are known to induce helicoidal self-assembling such as glutamic acid or phospholipidic acid.[23] Another alternative would be at longer term to design specific surfactants such as a helicen with two amines on one side and long alkyl chains on the other. The IPCM already published a bimetallic helical structure[24] and we can imagine to use such structure with cobalt and to synthesize acids bearing a helical skeleton that can self-assembled in bigger structure.[25]

In addition, using our new room-temperature-synthesis of hcp–Co NPs in presence of an alcohol, and under kinetic control, we will easily control the anisotropy of shape of the NPs obtained. Thus we want to use chiral alcohols instead of tridecanol as the capping ligand. More

precisely we will focus on helicoidal structures bearing alcohols such as helixol[25] that can serve as host with their chiral cavity and control the "chiral growth" of the NPs.

2.2 Templated nanocrystal growth

The reduction of the metallic salt will be performed directly in presence of the chiral assemblies. In this case, the growth will be directed using the helical structure as template. As the inner growth of cobalt nanoparticles inside linear templates made of OAm leads to cobalt nanowires, due to their ultrathin cross-section we expect to be possible to maintain the morphological distortion linked to the chiral templates.

For each tasks, structural (1.4 and 2.3) and spectroscopic (1.5 and 2.4) characterizations will be performed. The structure of the NCs will be characterized by electronic microscopy (SEM, TEM) as well their chirality using circular dichroism in order to determine their asymmetric factor.

Task 3: reactivity and selectivity (IPCM)

As shown by Glorius and others, NHC ligands are great candidates to increase the NCs reactivity and exploit them in catalysis.[16] However, once again, only one publication is related to the combination of 3d transition metal NCs (nickel)[17] and NHC, probably due to the difficult syntheses. There are thus plenty of possibilities for discoveries. We will then turn our attention towards an enantioselective approach by playing around the chirality within the best family of ligand.

Recently, we showed that our hcp-cobalt NPs stabilized with OAm were able to perform dehydrogenation of NH_3BH_3 with very high TON (turnover number) but also to hydrogenate ketones and semi-hydrogenate alkynes in excellent yields.[22] We will start by studying **the impact of the ligand properties vs NPs on TON and selectivity of hydrogenation reactions (3.1)** of alkynes, ketones, imines and aromatic compounds (using NH_3BH_3 or H_2 as the hydrogen source). Having developed a very fast synthesis of our NPs as well as a very fast exchange of the ligand, **we will run first a high throughput screening of the chiral ligand (3.2).** Due to the harsh reaction conditions and the difficult exchange of the surfactant in the syntheses reported in the literature, such a rapid screening has never being done in NP catalysis. **This is thus a real breakthrough for the application of NPs in catalysis (3.3) (enantioselective or not)**.

Feasibility. Risk assessment and management

As the synthesis of the different nanocatalysts: Co (two different phases), Ni and NiCo with different ratio of composition are mastered, the study of the reactivity (in hydrogenation for instance) can be run immediately. Moreover the room temperature synthesis that we developed[12] allows us to start right away the screening of the different ligands (chiral or not) and to establish their impact on the reactivity of the metal surface. By screening the numerous classes of ligands available, we will find at least a suitable one to carry out enantioselective analysis. The use of chiral counter-ions (task 2) is at higher risks. However counter-ion are well-known in our laboratory.[24] and the cationization of the $[ClCo(PPh_3)_3]$ has already been established in catalysis. Thus we can legitimately think that the transfer from the known gold metal[18] to the cobalt one will be feasible by screening the nature of the counter-ion. Finally, the templated nanocrystal growth appears to be the most challenging part in this project but again, the consortium has all the knowledge to conduct this task to success. Moreover for this task we have several possible approach that can attempted to reach success. It is worth underlying that this project can be valorized by publications and communications at each step.

Position of the project within national and international context

As mentioned in the main project, the main draw-back of chiral nano-catalyst is that the available synthesis described in the literature for non-noble nanoparticles are harsh and long. Thus screening of several ligand exchange or functionalization are time consuming and usually

never attempted. The groups of Chaudret and Glorius have shown scarce examples with palladium and gold in asymmetric catalysis but non-metal have never been applied. The only example is the one from Pericàs, however again the cobalt is just a support and the catalysis occurred at the ruthenium complex anchored on the nanoparticle. For the more challenging intrinsic chirality of the nano-catalyst, as previously mentioned only few very recent examples were published on gold nanoparticles and again non-noble metal have never been applied. Thus the project appears new and very challenging with only highly ranked international group working on such topic.

Position of the project in regard to the iSiM objectives

This project fits perfectly in the iSiM objectives as its aim is to control perfectly the formation and the application of a nano-object based on a molecular control of the synthesis. Indeed, herein we propose to associate the organic chemistry by designing ligands (chiral or not) and the organometallic chemistry by tuning the starting complex, in order to create rare and efficient chiral nano-catalysts. The ultima goal here is to obtain nano-catalyst with high turnover number, high selectivity, recyclable and having potentially other applications in magnetism and information storage due to their important anisotropy.

To succeed in this project**, the research consortium** combines two teams from SU: one specialized in organometallic chemistry and catalysis (**Partner 1)** and one specialized in NPs synthesis and characterization (**Partner 2**). This consortium relies on highly synergistic teamwork, and has potential for a broad impact. As all team members belong to Sorbonne Université, interactivity of the consortium will be facilitated. The *added value of this collaboration* is that each research group has an expertise in different fields, all being essential for the development and completeness of the project. The researchers each provide their own knowledge and internationally recognized long term proficiency in catalysis, organometallic, NPs synthesis and characterization, and magnetism. Moreover M. Petit and C. Salzemann already worked together on the first synthesis of hcp-cobalt NPs. Expertise of **Partner 1** in cobalt catalysis and chirality, combined with expertise of **Partner 2** in nanoparticles chemistry will doubtless allow important breakthrough in the field of chiral NP.

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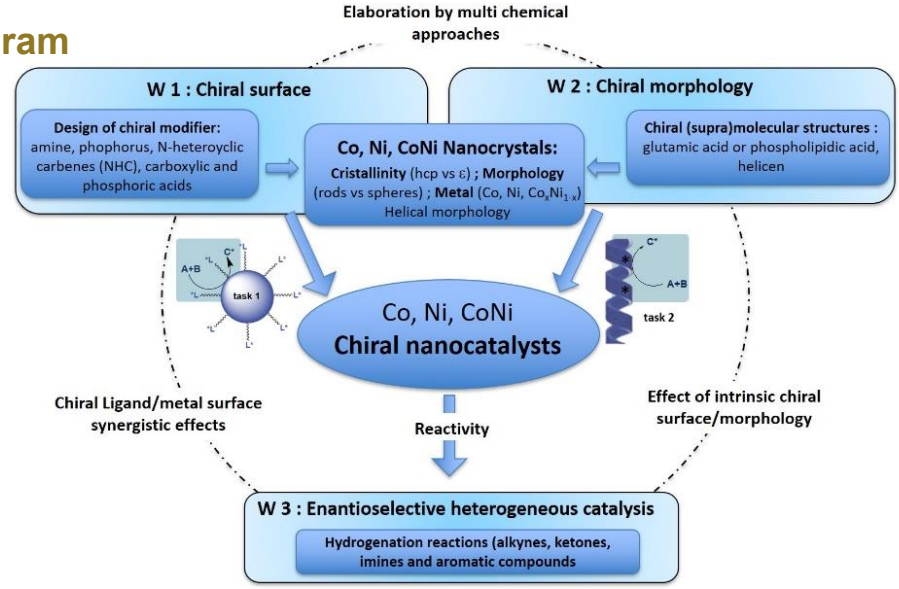
Work program



Workpackage and tasks		Year1				Year2				Year3			
10/01/2021 to 09/31/2024		3	6	9	12	15	18	21	24	27	30	33	36
1	**Chiral surface**												
1.1	Design of chiral modifier												
1.2	Achiral nanocrystal synthesis												
1.3	Exchange ligand on NPs												
1.4	Structural characterizations												
1.5	Chiral characterizations												
2	**Chiral morphology**												
2.1	(supra)molecular assemblies												
2.2	NCs templated growth												
2.3	Structural characterization												
2.4	Chiral characterization												
3	**Reactivity**												
3.1	Impact of the ligand properties *vs* NPs on TON & selectivity (hydrogenation reactions)												
3.2	High throughput screening of the chiral ligand												
3.3	Evaluation of chiral NPs chiral in catalysis												

Persons in charge: Partner 1: IPCM (UMR 8232) at SU; people involved: **M. Petit**, PI of the project, in charge of project coordination and management (WP0) as well as metal (Co and/or Ni)-complex synthesis and use of NP in catalysis, **M. Barbazanges** in charge of helicene chemistry and chiral counterion strategy and **C. Desmarets** for the characterization of the chiral constructs obtained. **Partner 2: MONARIS** UMR CNRS 8233 at SU and people involved are **C. Salzemann** and **N. Goubet**, in charge of NP synthesis and characterization).

Coordination and Management: *Person in charge: Marc Petit (Project Coordinator)*: This proposal is based on the pooling of complementary skills and knowledge in NP synthesis, characterization and asymmetric catalysis towards the development and utilisation of new chiral nanoparticles. As all the partners belong to Sorbonne Université, coordination will be simplified. Weekly meetings focusing on the progresses will be held within the interested people, in accordance with the development of the project. On a monthly basis, a short meeting between all the members will be organized, in order to present the recent results and discuss on the course of the project. In addition, the doctoral candidate will be expected to fill monthly progress reports, and to present his/her research every three months in the group research meeting. The doctoral candidate will be offered the possibility to attend at least one international conference to present his/her results.