Appel à projets doc iSiM 2024

Amplification of molecule-induced chirality in CdSe nanoplatelets composite assemblies for magneto-chiral properties.

SPOTLESS

(seeking properties in nanoplatelets composite assemblies)

Summary of the project

The objective of this project is to manipulate optical dichroic properties of CdSe nanoplatelets by triggering their assembly into helicoidal stacks thanks to intercalated chiral molecules and magnetic coordination compounds. Stacked CdSe nanoplatelets are known to propagate an energy input along the direction of stacking. The assemblies we propose will thus lead to composite materials with synergetic magneto-optical properties.



ORBONNE

Benoit Fleury Sorbonne Université Institut Parisien de Chimie Moléculaire (UMR 8232) Campus Pierre et Marie Curie, 75005 Paris

Carreer and Education

2018: 2010-today:	Habilitation à diriger des recherches: Molecular and Hybrid Materials Maître de conférences, IPCM, Research group on molecular materials and spectroscopies (ERMMES)								
2008-2010:	Invited researcher, KIT Karlsruhe, Functional Molecular Nanostructures group of Prof. Mario Ruben								
2006-2008:	Post-doctoral fellow, CEA Grenoble, Integration of hybrid polyoxometalates into Flash memory devices, under the supervision of Dr. Gérard Bidan								
2003-2006:	PhD, <i>Grafting of molecular nanomagnets and coordination networks on Si(100)</i> , Université Paris-Sud, ICMMO, Orsay, under the direction of Prof. Talal Mallah and Dr. Vincent Huc								

Involvements in PhD supervisions: Since 2010, I supervised 3 PhD students: Y. Flores (2015-2018), M. Fuchs (2017-2020), L. Curti (2020-2023). I have been invited to 6 PhD juries outside IPCM (3 times as a "rapporteur" including 2 PhD abroad, and three times in France as an "examinateur").

<u>Research projects:</u> I have been involved as a partner in 2 Labex projects (2013 & 2016) and 2 ANR projects (2018-2023, hold by F. Ribot, LCMCP; 2023-2027, hold by B. Gallas, INSP). I hold 2 projects: Emergence SU (2015) and the ANR project HSP (2016-2021, LOMA in Bordeaux, LCMCP, INSP, ITODYS in Paris as partners).

<u>Foreign collaborations</u>: After a stay at the University of Twente (NL) in 2016, I developed a collaboration with Prof. N. Katsonis and T. Kudernac (today in Groningen) that lead to an excellence grant for Y. Flores and a Hubert Curien project Van Gogh for exchanges of students between the two groups.

<u>Scientific network</u>: Since 2010 I have been a member of the GDR "Magnetism and molecular commutation" and a member of the French association of molecular magnetism since 2020. In that frame, I co-organized the National Scientific Days of the association in 2022.

I have an ongoing collaboration with B. Abécassis (ENS Lyon) on the role of chiral ligands on the properties of nanoparticles of various natures (semi-conducting QDs, perovskites).

<u>Other responsibilities</u>: member of the Scientific Council of the Chemistry department since 2022 and member of recruitment juries (for assistant professors) in 2019 (SU) and 2023 (U. Paris XIII)

5 significant publications for this project

- Magnetic Imaging of Cyanide-Bridged Coordination Nanoparticles Grafted on FIB- Patterned Si Substrates. <u>Small</u>, **2008**, 4, 2240
- Soft Magnets from the Self-Organization of Magnetic Nanoparticles in Twisted Liquid Crystals. <u>Angew. Chem. Int. Ed</u>., **2014**, 53, 12446
- Versatile nano-platforms for hybrid systems: expressing spin-transition behavior on nanoparticles. <u>J. Mater. Chem. C</u>, **2015**, 3, 3350
- Enhancing the magnetic anisotropy of maghemite nanoparticles via the surface coordination of molecular complexes. <u>Nature Communications</u>, **2015**, 6:10139, DOI: 10.1038/ncomms10139
- Chiroptical properties of semiconducting nanoplatelets functionalized by tartrate derivatives. ACS Nano transferred to Langmuir, **2024**, under revision.



Laurent COOLEN

Born : 1981, student of ENS Paris : 2000-2004, PhD in Solid States Physics : 2006 Assistant professor (maître de conferences), Sorbonne Université : 2007 - ... Research at Institut de NanoSciences de Paris (INSP) Habilitation à Diriger les Recherches (HDR) : 2015 Group leader Nanophotonics and quantum optics (Nanopt), INSP : 2024 - ...

Research topics :

Semiconductor fluorescent nanoparticles Develop new methods for microscopic study of individual nano-emitters Energy transfer and collective effects in self-assembled chains of nanoplatelets (NPL) Nano-emitters coupled to photonic or plasmonic nanostructures Plasmonic application to photovoltaics (perovskite solar cells)

Research production :

50 peer-reviewed articles, 21 since 2018 Z. Ouzit et al., ACS Photonics 10, 421 (2023) J. Liu et al., J. Phys. Chem. A 125, 7572 (2021) J. Liu et al., ACS Photonics 7, 2825 (2020) J. Liu et al., Nano Lett. 20, 3465 (2020) F. Feng et al., ACS Photonics 5, 1994 (2018)

Collective blinking in nanoplatelet chains Method for single-emitter dipole analysis Dipole analysis on nanoplatelet chains Long range energy transfer in NPL chains Dipole analysis for single cubic NPLs

Research management :

Co-supervisoror for 1 thesis (C. Lethiec, 2011-2014, 7 papers) Supervisor for 4 PhD theses (Fu Feng, 2013-2016, 6 papers ; Jiawen Liu, 2017-2020, 8 papers ; Z. Ouzit, 2020-2023, 6 papers ; G. Baillard, 2021-2024, 1 paper) Co-supervisor for 1 post-doc (D. Zheng, 2022-2024)

Research contracts (principal investigator) :

ANR project Foenics (2021-2024, 316 k€ ; with ENS de Lyon) CNRS PICS international project (2014-2017, France-Vietnam, 18 k€) ANR project Ponimi (2013-2016, JCJC, 264 k€) C'Nano project NanoPlasmAA (2009-2012, 83 k€ ; with ESPCI)

Scientific reviewer/expert :

Member of the ANR panel CE30 (2023, 2024) PhD jurys : 8 jurys outside INSP since 2016, 5 as rapporteur Member of CNU (section 30, 2012-2019), board member (assesseur 2015-2019) Co-chairman DPC 16, abstract selection + guest editor J. Lumin (2016) Reviewer for ANR (2011, 2021, 2023), Labew PALM Paris-Saclay (2022), NCN (Poland, 2016) Recruitment committees : Maître de conferences (Paris 7 (2011), PhD grants (ED PIF, 2018) Scientific Council UFR de Physique (2022-...), Teaching council UFR de Physique (invited member, 2023 - ...), Laboratory Council (2013-2018)



Scientific description

Objectives and description of the project

The objective of this project is to manipulate the optical dichroic properties of CdSe nanoplatelets by triggering their assembly into helicoidal stacks thanks to intercalated chiral molecules and magnetic coordination compounds. Stacked CdSe nanoplatelets are known to propagate energy by FRET from a localized optical input along the direction of stacking.¹ The assemblies we propose will thus lead to composite materials with synergetic magneto-optical properties thanks to the coupling of energy levels between communicating NPLs and the intercalated coordination compounds.

CdSe nanoplatelets are semiconducting nanocrystals. The thickness of the platelets is controlled at the atomic layer scale (from 2 to 8 layers of Se atoms) during their synthesis.^{2–8} That results in 1D quantum confinement that provides CdSe nanoplatelets unique optical properties such as unparalleled spectrally sharp and monodisperse luminescence in the visible region at discrete wavelength corresponding to their thickness. These nanoparticles will be functionalised by chiral molecules that will play a triple role: (*i*) inducing chirality to the nanoparticles for dichroic optical properties, (*ii*) triggering the assembly of the nanoplatelets into helicoidal stacks to amplify the properties, (*iii*) induce paramagnetism for magneto-chiral properties.

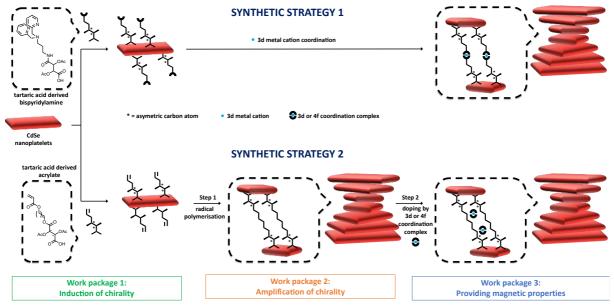


Figure 1: schematic over-view of the project

Two synthetic strategies will be followed in order to fulfil three work packages (figure 1). The starting common point in both strategies is the coordination of tartrate derivatives at the surface of CdSe nanoplatelets to induce chirality and chiroptical properties.

Synthetic strategy 1: assembly by coordination polymerisation

The tartrate ligands will be tailored so as to bear a second free coordination site able to link the nanoplatelets face-to-face thanks to metalation with paramagnetic transition metal ions.

Synthetic strategy 2: assembly by organic polymerisation

Step 1: The tartrate ligands will be tailored so as to bear an acrylate function in order to link the nanoplatelets face-to-face by radical polymerisation.

Step 2: Paramagnetic complexes will diffuse into the super-structure to complete the composite material.



Work Package 1 (WP1): Induction of chirality from chiral ligands to CdSe nanoplatelets (IPCM & INSP)

Task 1.1: Tartrate derivatives will be prepared in one step from commercially available (R,R) and (S,S) diacetyl tartaric anhydrides: (*i*) by amidification with bis(pyridin-2-ylmethyl)propane-1,3-diamine (strategy 1), and (*ii*) by esterification of commercially available 4-hydroxybutyl acrylate and 2-hydroxyethyl acrylate (strategy 2). All ligands will be prepared and characterized (¹H and ¹³C NMR, mass spectroscopy) at IPCM.

Task 1.2: Reacting Cd myristate, selenium and oleic acid in octadecene yields CdSe nanoplatelets whose thickness depends on the reaction conditions. After purification, the nanoplatelets are covered with oleate ligands and dispersed in non-polar solvents such as toluene or hexane.

Task 1.3: The oleate ligands covering the CdSe nanoparticles can easily be exchanged by other ligands in solution.⁹ Reacting an excess of molecules prepared in WP1 displaces the ligand exchange equilibrium towards the target hybrid nanoplatelets.

CdSe nanoplatelets will be synthesised and characterised by UV-visible and photoluminescence spectroscopies at IPCM and TEM on the microscopy platform of the Chemistry department. These techniques also allow the monitoring of the ligand exchange reaction.

Task 1.4: The luminescence properties of the nanoplatelets will be analysed at INSP, either in solution or at the scale of individual emitters by fluorescence microscopy. Their quality will be inferred from their quantum yield, emission intermittency (blinking) and dynamics (decay curves). The effect of the ligands will be analysed on the emission circular polarization (CPL). Work Package 2 (WP2): Amplification of chirality from chiral NPLs to diamagnetic assemblies - (IPCM & INSP)

Task 2.1: Following synthetic strategy 2, acrylate-terminated nanoparticles will be polymerised under UV irradiation (365 nm) using a photoinitiator. This polymerisation will lead to helicoidal superstructures made of stacks of chiral nanoplatelets (IPCM). The morphology of the stacks will be checked by TEM. Small angle X-ray scattering (SAXS) can also be performed at SU for the measurement of stacks length and inter-particle distances.

Task 2.2: At INSP, the luminescence of the platelet assemblies will be compared to the luminescence of the isolated platelets. The quality of the assemblies and platelet protection by the ligands will be probed through quantum yield or decay dynamics. The efficiency of energy transfer between platelets will be probed, as in ref. 1, by imaging the luminescence from a platelet chain excited in one spot and measuring the extension of the emission portion. The molecular assembly will offer the possibility to vary the distance between platelets via the length of the molecules. A strong effect $(1/d^2)$ of this distance is expected on the length of the energy transfer diffusion over the chain, so that propagation lengths up to 1 µm or more may be obtained.

Work Package 3 (WP3): Providing magnetic properties to chirality-amplified assemblies (IPCM & INSP)

Task 3.1: Following synthetic strategy 1, bis(pyridinylmethyl)amine-covered nanoplatelets will be reacted with different 3d metal ions to trigger their assembly by coordination chemistry. This reaction will lead to helicoidal superstructures made of stacks of chiral nanoplatelets with intercalated magnetic coordination complexes.

Task 3.2: The last step of synthetic strategy 2 consists in diffusing magnetic (3d or 4f) coordination complexes into the superstructures obtained in WP2 in order to get lamellar and magnetic helicoidal stacks of chiral nanoplatelets.

The same chemical characterisation methods as in work packages 1&2 will be employed. An in-depth study of the physical properties of the target assemblies will also be performed in order (*i*) to elucidate the consequences of combined chirality and magnetism on their optical properties and (*ii*) to detect a possible enhancement of these properties in comparison with the isolated nanoparticles.

Task 3.3: The emission polarization of the assemblies will be analyzed at the scale of a single chain, deposited on a glass substrate, and the circular polarization will be probed.

Task 3.4: Magnetic circular dichroism (MCD) on solutions of stacked particles can be performed at IPCM with the help of INSP by adapting a magnet on our CD spectrometer.¹⁰ If

needed, IPCM recently acquired a cryostat to be adapted to various spectrometers for lowtemperature measurements. In addition, element-specific contribution to these properties can also be measured by X-ray magnetic circular dichroism (XMCD) on the Deimos beam line at Soleil synchrotron since the ERMMES group of IPCM is expert in this technique.

Originality of the project

• Functionalisation of CdSe nanoplatelets with chiral ligands has been described with various thiolated molecules but leads to the loss of their luminescence and their CD spectra reveals moderate dissymmetry factors (*g*-factors $\approx 10^{-4}$).^{11–15} On the contrary, we recently demonstrated that the functionalisation of CdSe nanoplatelets with simple aliphatic tartrate derivatives (PhD thesis of L. Curti) keeps the luminescence of the particles and leads to exceptional *g*-factors (2.10⁻³).¹⁶

• Achieving long and stable stacks of CdSe nanoplatelets covered by native oleate ligands is difficult and somehow difficult to reproduce because the assembly is driven by weak interactions.^{17–20} The use of coordination links or covalent links to secure the assemblies has never been described and will help manipulating such superstructures for integration in future devices.

• Control of the chirality in assemblies of CdSe nanoplatelets has never been described since no source of chirality has never been introduced in such systems. The assembly of CdSe nanoplatelets in helicoidal stacks has been described by playing on the mechanical strain induced by the ligands on the nanoparticles, but this strategy leads to racemic mixtures.²¹ On the contrary, our approach is based on chiral molecules to induce such a stereoselectivity on the assemblies.

• Synergy between magnetism, chirality and optical properties belongs to molecular compounds, often at cryogenic temperatures.²² In our approach we expect enhanced properties thanks to the assembly process with regards to the properties of isolated hybrid nanoplatelets. Our approach towards hybrid and composite materials is thus disruptive since it can produce applicative nano-objects. Indeed, we aim at amplifying molecular properties at bigger scales in terms of size and temperature.

• Studying interactions between nanoparticles is often complex as it requires a good knowledge of the assembly of the particles. Self-assembled chains of platelets are a unique model system to analyze such mechanisms. The analysis of Förster transfer (FRET) in such systems, as pioneered in ref. 1, will take a new turn with the level of control offered by molecular methods of assembly. On a longer term (beyond the scope of this project), manipulation of FRET efficiency will afford fine probing of FRET effect on collective photoluminescence effects (such as collective fluorescence intermittency as demonstrated recently by the INSP group⁴⁴).

Feasibility. Risk assessment and management

From a general point of view, this project is new and ambitious. We are nonetheless confident in its success since synthetic difficulties have already been evaluated during L. Curti PhD (2019-2023) and a master internship in 2022. In addition, offering 2 alternative strategies for the chiral chain assembly mitigates the risk.

WP1 does not present any risk. Organic Chemistry implies one step reactions on the gram scale and without any tedious purifications. For instance, the esterification of tartaric anhydride has been achieved during the PhD of L. Curti at IPCM with several aliphatic alcohols. The same way, the synthesis and use of CdSe nanoplatelets has been studied at IPCM during the PhD of. L. Curti.¹⁶ CPL analysis at the single-emitter level requires certain technical care in order to correct setup depolarizing effects, but the INSP has an extensive experience of these matters.

WP2 is innovative and presents more risk. In particular, we will dedicate time to optimise the experimental conditions during polymerisation, in particular concentration, in order to avoid reticulation that would lead to branched assemblies. In the worst case, bulk polymers or gels of nanoplatelets would be obtained. That case, even if not desired, would give nevertheless



interesting materials bearing the same properties as expected for the target super structures and would thus lead to original publications.

Regarding WP3, the risk of **task 3.2** is the possible difficulty of "doping" the super structures obtained after WP2 with coordination complexes. The choice of the complex (size, charge) will be studied as well as the synthetic conditions (concentration, temperature) in order to maximize the number of complexes to intercalate in the structure. The advantage is the use of the polymeric chiral matrix of CdSe nanoplatelets obtained in WP2. Indeed, such a matrix should be more stable than van der Waals-stabilised assemblies of nanoplatelets in a wider range of synthetic conditions.

The risk of **task 3.1** has been evaluated during a master internship in 2022. This preliminary work involved chiral tartrate derivatives on CdSe nanoplatelets terminated by nitrile ligands able to coordinate apical position of Co(II) phthalocyanines (CoPc). Helical assemblies of CdSe nanoplatelets were detected by TEM (figure 2) but the assemblies are short, probably because of the lability of the apical positions of the Co(II) ion, coordinated to weak nitrile ligands. This is why we chose a bispyridinyl amino ligand to be reacted with a 3d metal salt for a stronger chelate effect to stabilise the assembly. In addition, one could fear the quenching of CdSe luminescence by the intercalated magnetic 3d ions. In the case of CoPc mentioned above, the presence of the Co(II) complex was confirmed by UVvisible spectroscopy and the luminescence was nevertheless maintained. This is why we will use Co(II) complexes at first for this

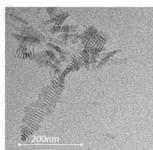


Figure 2: helical assembly of CdSe nanoplatelets with chiral ligands and CoPc complexes. The stack is 237nm long with a 3 nm inter-particle distance.

WP. **Tasks 3.3 and 3.4** are not risky since IPCM and INSP are equipped with adequate spectrometers and microscopes. It will nevertheless be time consuming to optimise sample preparation and results interpretations.

Position of the project within national and international context

Light has been shed on semi-conducting nanocrystals this year thanks to the award of the Nobel prize in Chemistry for the discovery and synthesis of quantum dots. These nanoparticles now spread their light from Q-LED televisions and LED lamps, and can also guide surgeons when they remove tumour tissue. Since the first experiments of Yekimov, Brus and Bawendi in the 80's and 90's, CdSe chemistry has been a field of intense development until nanoplatelets have been described for the first time in 2008.²³ Our project is therefore at the core of a brand new and hot domain with several international groups intensively producing publications. Some of these groups are French and IPCM and INSP both benefit from an ongoing collaboration at ENS Lyon with the group of B. Abécassis who realized the world premiere of assembling NPL chains in 2013 and is still the leading expert in this field, allowing recent breakthroughs^{1,44} on inter-nanoparticle FRET coupling by the INSP-ENS Lyon collaboration. Intense exchanges were recently born between L. Coolen at INSP and B. Fleury at IPCM, revealing the need of both communities to enrich each other. Indeed, the optical properties of CdSe nanoparticles strongly depend on their surface. Molecular chemists can thus bring a strong input in the domain by designing and synthesising new ligands and assembly protocols for these nanoparticles. On the other side of our project, magneto-chiral effects also attract the attention of the international community since they are not fully understood from a fundamental point of view while already proving to be at the origin of magneto-chiral dichroism (MChD) and Chirality Induced Spin Selectivity (CISS). These two phenomena are both attracting interest for their applications in enantio-separation or enantioselective synthesis.

MChD is the dichroic property of chiral magnetic compounds excited by non-polarised light and the control of this dichroism by the direction of an applied magnetic field.^{22,24,25} This property has been proposed as the cause of homochirality of of amino-acids on Earth.^{26,27} In particular, reverse MChD²⁶ was demonstrated recently by the photochemical enantiomerization of tris(oxalate)chromate(III) under magnetic field: this experiment demonstrated the generation of an enantiomeric excess (*e.e.*) by irradiation of a racemic mixture with unpolarized light aligned with the magnetic field, the sign of the *e.e.* being determined by the relative orientation of the light and the magnetic field.

The CISS effect consists in filtering spins of electrons transferring through a chiral media. The corollary is that if electrons come from a magnetic electrode and are therefore already polarized, they can interact only with one handedness of molecules enabling the chiral resolution of a racemic mixture. Thus, the CISS effect is a simple, inexpensive and generic method for enantio-separation. It was first described in 1999²⁸ and became established in 2011.²⁹ Since this second paper, the field is expanding fast and both extensive experimental and theoretical studies are carried by various groups. In particular, associating peptides and CdSe quantum dots has been proved to allow magnetic field-controlled photoemission and light-controlled spin transport.³⁰ To face such fast progresses the international communities of chirality and magnetism gather their results on a didactic and dedicated website.³¹

Position of the project in regard to the iSiM objectives

This project is molecule-centred. It strongly depends on chiral organic ligands and magnetic coordination complexes. In this project, the molecules aim at structuring nanoplatelets into supra-particular nano-objects. The molecules will also bring properties since we seek a synergy between optical properties (absorption and luminescence) of CdSe nanoplatelets on the one side and chirality and magnetism of molecules on the other side. The induction of chirality in semiconducting nanocrystals, combined to their outstanding optical properties, represents a way to access a new manifold of possible applications, such as stereoselective synthesis,³²⁻³⁴ chiral recognition,³⁵ biosensing,³⁶⁻³⁹ asymmetric catalysis and display devices.^{40,41} In addition, it could also address the question of the cosmic origins of the molecular bricks of living organisms since a strong synergy between chirality, optical and magnetic properties can result in MChD. The quest of these properties lies beyond the scope of this project and should be explored on our compounds thanks to a wider consortium. In addition, organizing the assemblies we propose through this project on solid substrates would be on a longer term the initial step towards a room-temperature photospintronics device.³⁰ The success of this project would thus be an asset for a subsequent proposal in another call at the national or European level.

Highlight partners complementarity

The goup of L. Coolen developed various methods to analyze the radiation of individual luminescent nano-emitters by fluorescence microscopy and showed that CdSe/CdS nanoplatelets present an asymmetric emission in terms of polarisation.^{42,43} His recent work dealt with linear assemblies of nanoplatelets achieved at ENS Lyon.¹ He showed that these systems present a very fast energy transfer (a few ps) leading to the energy diffusion along a hundred of platelets. This energy transfer plays a crucial role on the luminescence properties of the assemblies: quantum yield, multi-excitonic cascades, photon antibunching etc. The understanding of this energy transfer would guide the development of new opto-electronic systems. Nanoplatelets assemblies bearing a controlled chirality have never been reported in the literature and open new perspectives in this domain.

The research activities of Benoit Fleury are focused on the study of confined molecular systems at interfaces and polyfunctional molecular and hybrid systems. He belongs to the ERMMES group (molecular materials and spectroscopies), which has an international visibility on coordination chemistry. B. Fleury's work in this group revolves around two intersecting axes: the integration of magnetic molecules into composite materials on the one hand and, on the other hand, the exaltation of molecular properties to the macroscopic scale.

As a result, for this project dealing with the synthesis of hybrid and composite materials with optical properties, the partners have chosen to associate the competencies in Physics of L. Coolen who is expert in the measurement of CdSe nanocrystals properties to the competencies in Chemistry of B. Fleury who is specialized in the synthesis of hybrid nanoparticles.

Bibliography

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Research program

WP	WP1				W	P2		W	P3	thesis and papers	
Task	1.1	1.2	1.3	1.4	2.1	2.2	3.1	3.2	3.3	3.4	redaction
Semester 1											
Semester 2											single particles
											single particles
Semester 3											
Semester 4											diamagnetic
											assemblies
Semester 5											
											no romo gnotio
											paramagnetic assemblies
											assemblies
Semester 6											
											thesis redaction
											and
											defence

This Gantt diagram presents an over-view of the scheduled research program.

WP1 being riskless, all synthesis will be performed on-demand all along the project duration.

WP2 will require a focus attention on longer time scales in order to optimize chemical reactions and physical measurement conditions.

WP3 will be time demanding in order to optimize chemical reactions, physical measurement conditions and cross-checking results between different physical methods.

Enough time will also be dedicated to papers redaction to disseminate results about individual particles and their assemblies. The last semester will mainly be dedicated to the PhD thesis redaction and defence preparation.