Design of functional nanostructures *via* chirality induction

Emilie POUGET

e.pouget@cbmn.u-Bordeaux.fr

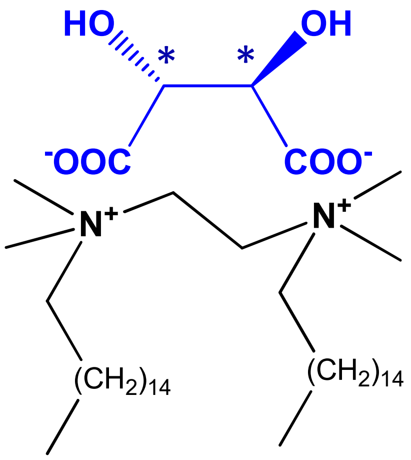
Institute of Chemistry & Biology of Membranes & Nanoobjects
(UMR5248 CBMN)
CNRS –Bordeaux University - Bordeaux INP

XiNOA, Bordeaux, November 2021

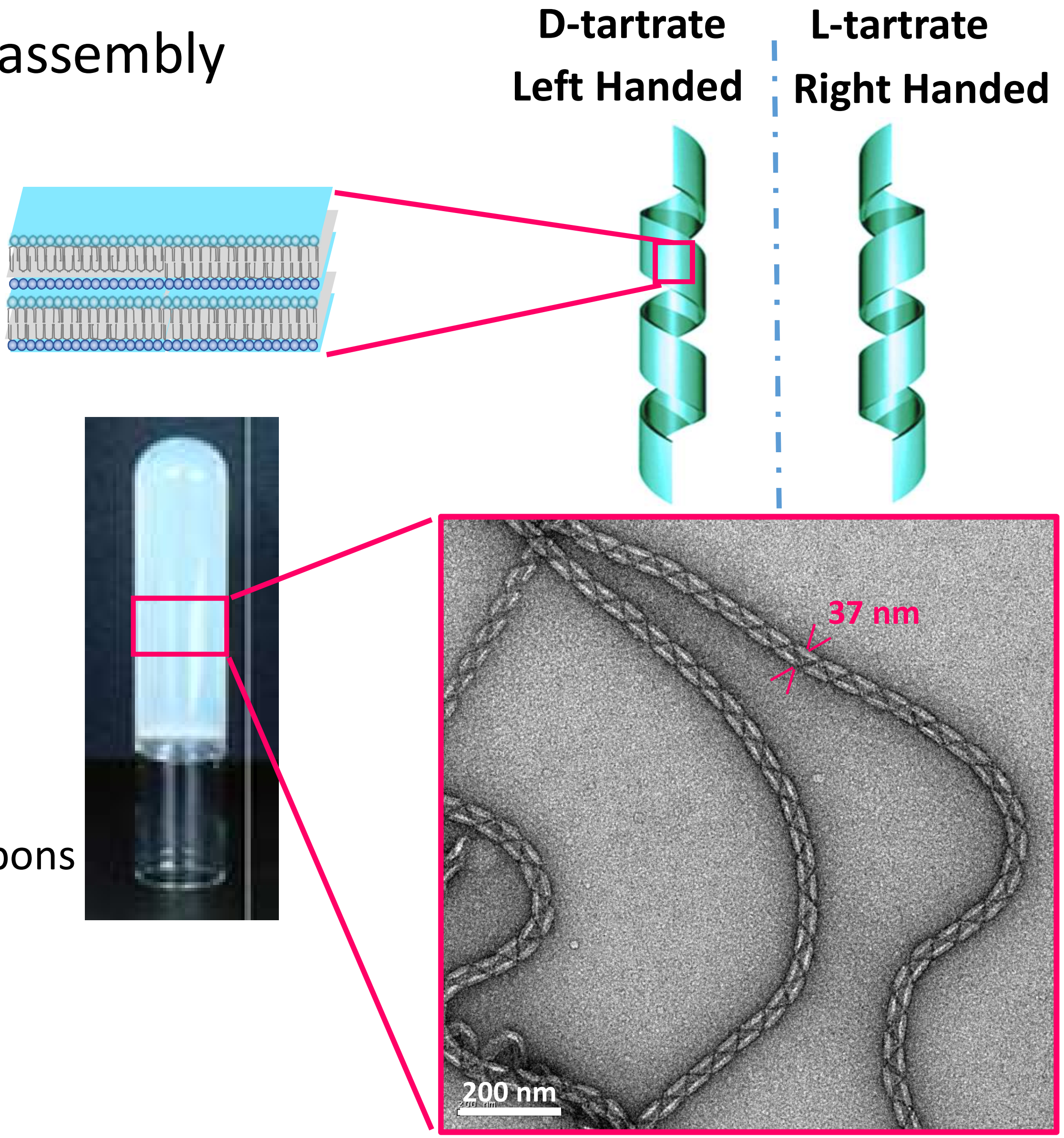
CMA group background: chiral self-assembly

Organic self-assembly

Chiral Counter anion
(L-tartrate)



Gemini 16-2-16



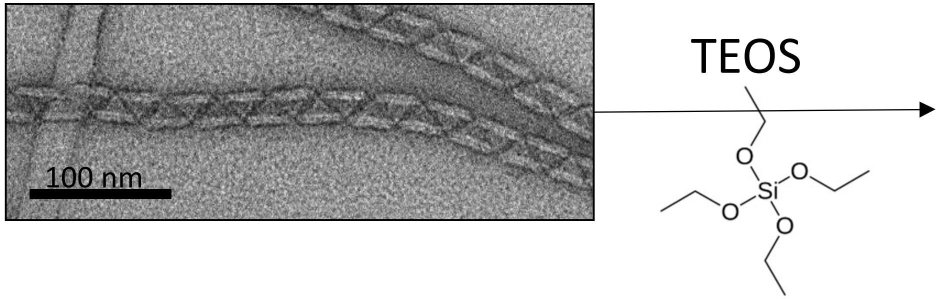
Gel network of helical ribbons
(c = 10 mM in H_2O)

Nature 1999, JACS 2007, JACS 2002,
J. Phys. Chem. A 2004

The system: silica nanohelices

Silica transcription

Organic

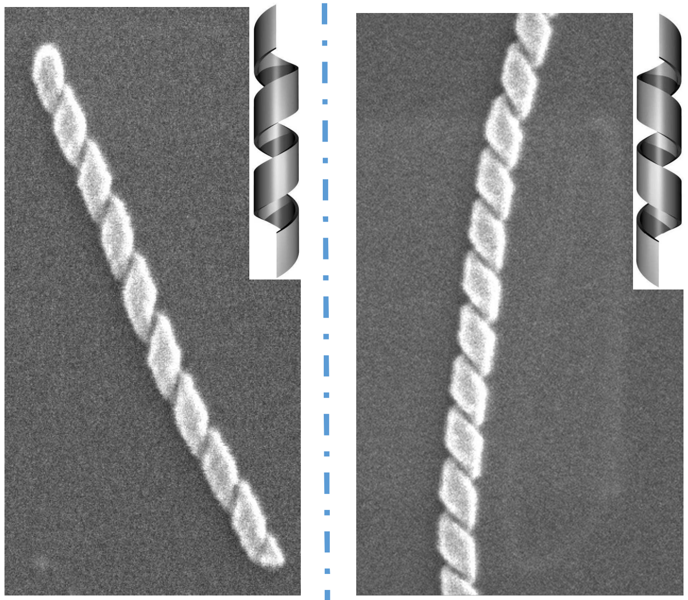


TEOS

<u>Robust system:</u>
solvents, T°, pH, drying

Hybrid organic / silica nanohelices

L-tartrate	**D-tartrate**
Right Handed	**Left Handed**



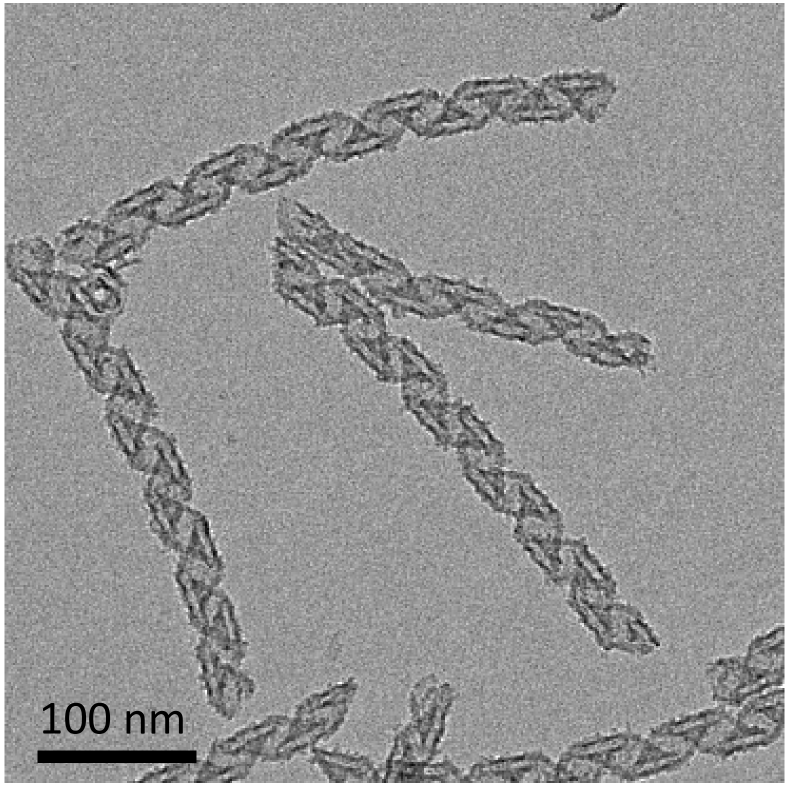
L-tartrate D-tartrate

Delclos T., Nanoletters, 2008

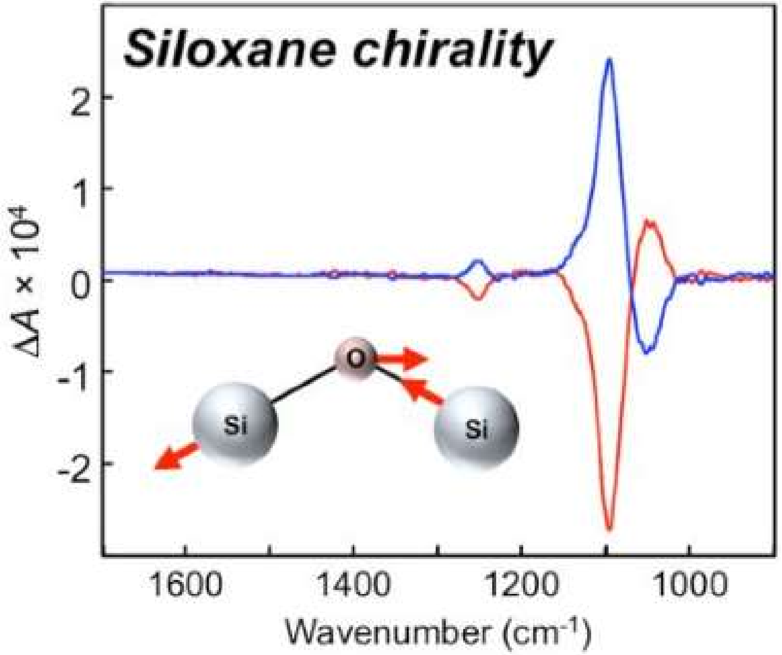
Chiral signal of "amorphous silica"

Coll. Thierry Buffeteau, ISM

Vibrational Circular Dichroism

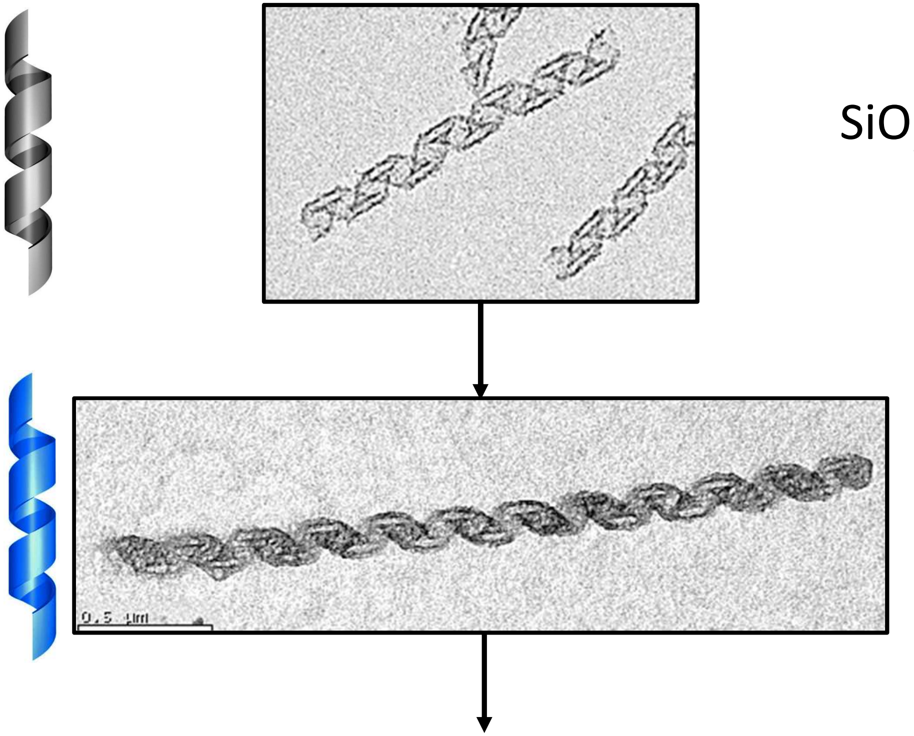


Okazaki et al., NanoLetters 2016



Si-O-Si asymetric stretching vibration

Towards functional materials



SiO$_2$ helix

Surface modification

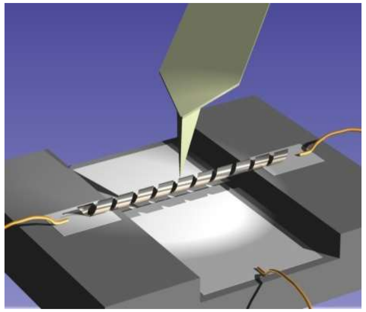
- -NH$_2$
- -SH
- Fluorescent dye
- Etc…

Design of helices with new properties

Towards functional materials

Secondary mineralization (TiO_2, ZnO)

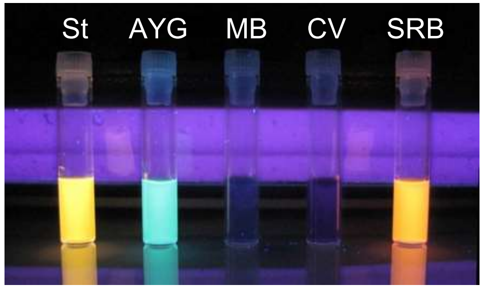
NEMS



M.H. Delville, C. Bergaud

SiO_2 helix

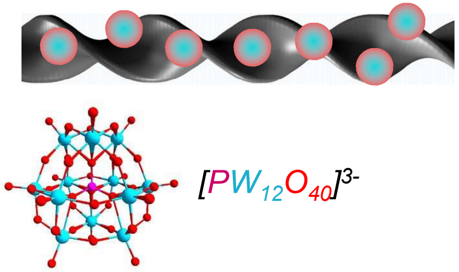
Photochromic chiral devices



Circularly Polarized
Photoluminescent systems

Pr. Ihara, Pr. Sagawa (Japan)

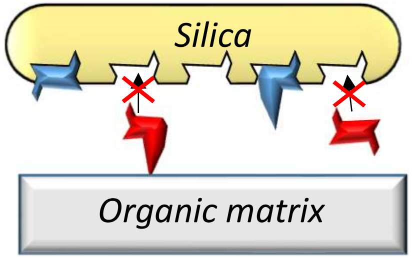
Enantioselective catalysis



Heterogen nanocatalysts

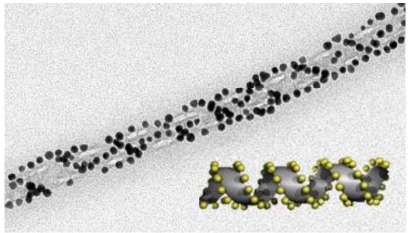
S. Nlate, B. Bibal

Enantio-separation



A. Perro

Chiral GNPs organization



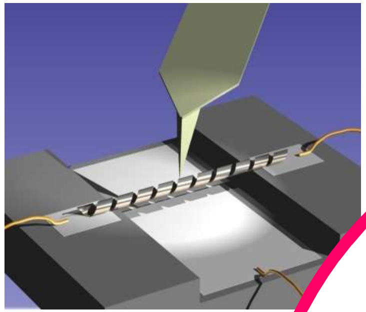
Y. Battié
M. Pauly
V. Ponsinet
P. Barois

Chiral photonics
nanodevices

Towards functional materials

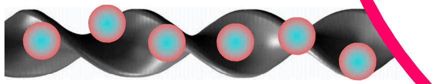
Secondary mineralization (TiO_2, ZnO)

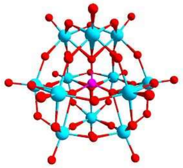
NEMS



M.H. Delville, C. Be

Enantioselective ca





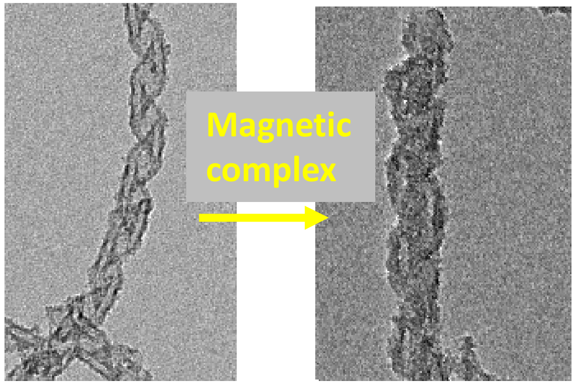
$[PW_{12}O_{40}]^{3-}$

Heterogen nanocatalysts

S. Nlate, B. Bibal

SiO_2 helix

Chiral magnetic devices

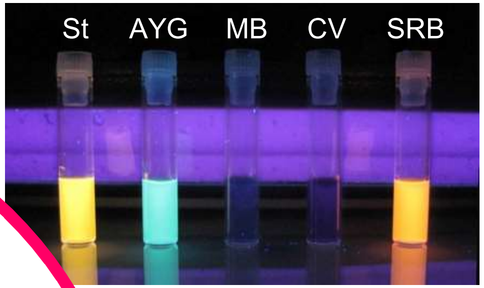


Evidence of MagnetoChiral Dichroism

Org

A. Perro

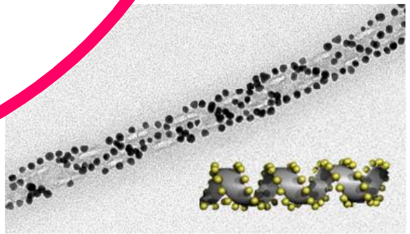
Photochromic chiral devices



Circularly Polarized
oluminescent systems

ra, Pr. Sagawa (Japan)

GNPs organization



Chiral photonics nanodevices

Y. Battié
M. Pauly
V. Ponsinet
P. Barois

Magnetic nanohelices for magnetochiral dichroism (MChD)

In the MaChiNaCo project, new nanocomposites showing induced magnetochiral dichroism, based on magnetic objects organized on silica nanohelices, are designed, synthesized and characterized.

ANR PCR MaChiNaCo.

Start January 2020

Elizabeth A. Hillard

Synthesis of coordination complexes

Patrick Rosa (research staff)
Lucas Robin (IE)

Benoit Pichon

Synthesis and functionalization of magnetic nanoparticles

Corinne Bouillet (research staff)

Emilie Pouget

Synthesis and characterzation of chiral nanocomposites

Reiko Oda (research staff)
Sylvain Nlate (research staff)
Gautier Duroux (PhD)

Geert Rikken

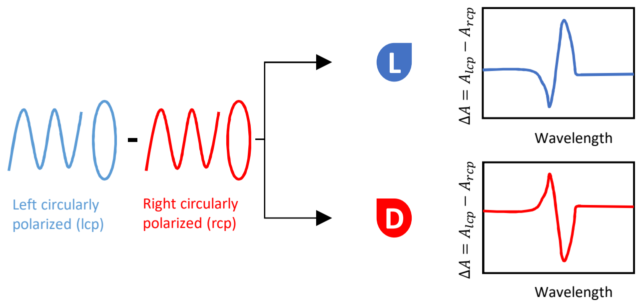
Optical experiments

Cyrille Train (research staff)
Ivan Breslavetz (research staff)
Ghanadie Novitchi (research staff)
Matteo Azori (research staff)

Magnetic nanohelices for magnetochiral dichroism (MChD)

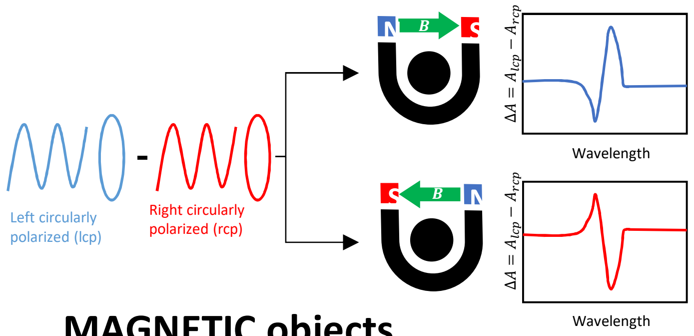
MChD = Cross effect between the natural Circular Dichroism (chiral molecules) and the Magnetic Circular Dichroism (answer to a magnetic field due to Zeeman effect)

CD = differential absorption of
the LCP and RCP.



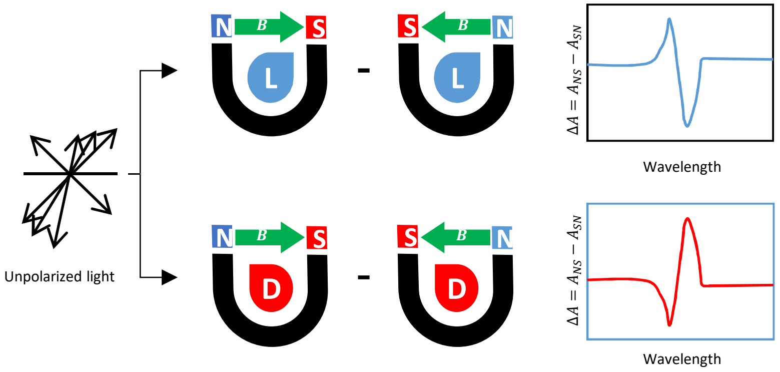
CHIRAL objects

Magnetic CD = differential absorption of the
LCP and RCP regarding the direction of B.



MAGNETIC objects

MChD = differential absorption of the
non-polarized light depending of B

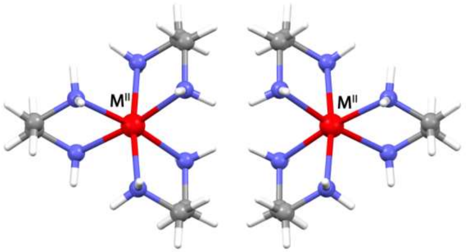


**CHIRAL and
MAGNETIC
objects**

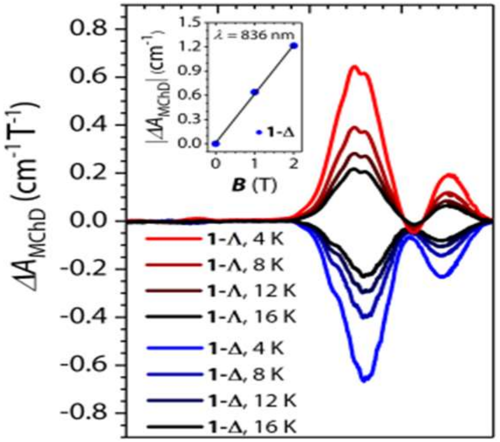
Magnetic nanohelices for magnetochiral dichroism (MChD)

MChD on magnetic and chiral crystals

E. Hillard
P. Rosa

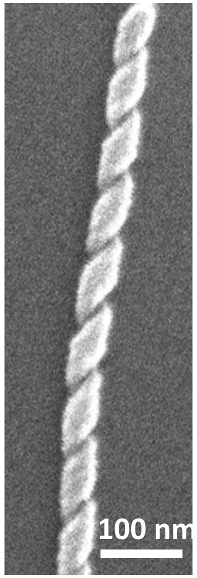


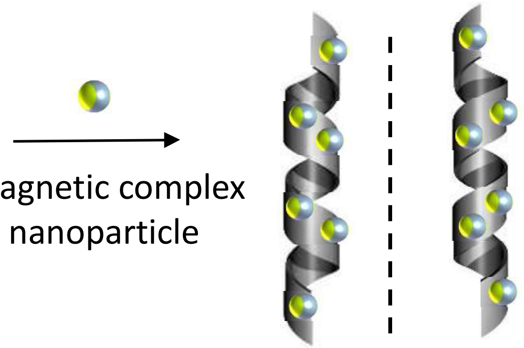
tris(1,2-diaminoethane)nickel(II)



Atzori et al., Sci. Adv., 2021

Our strategy:





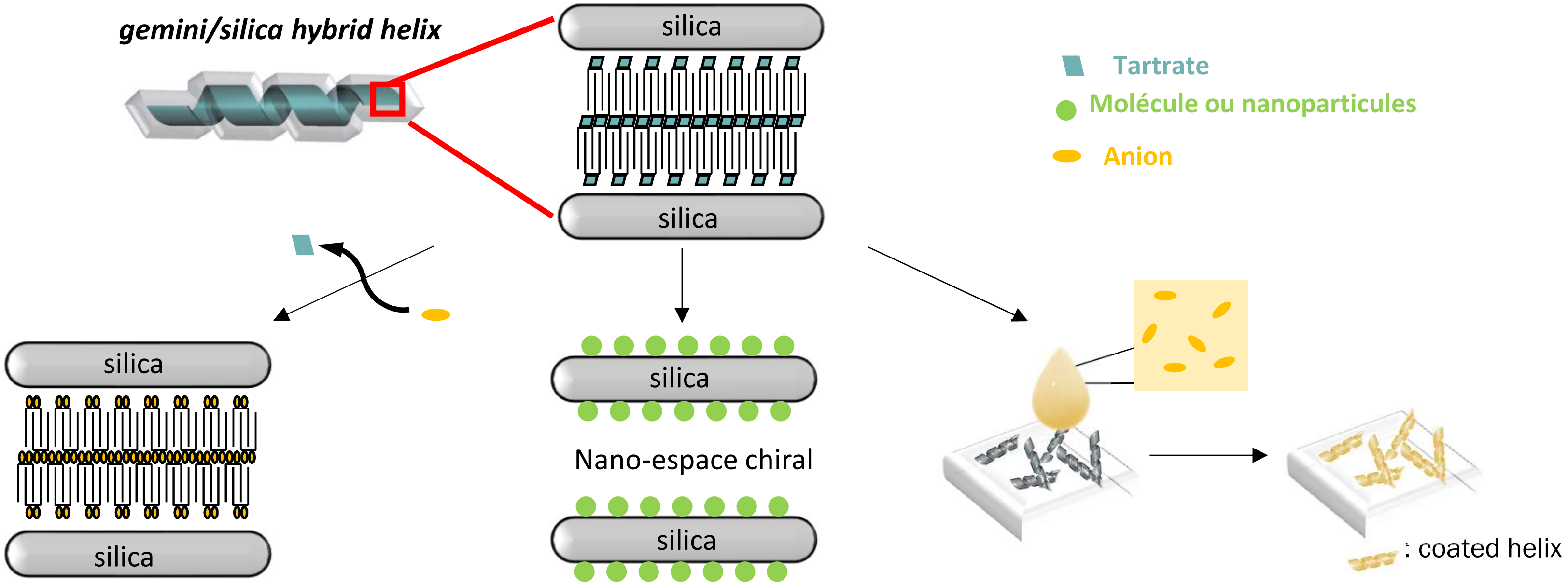
Magnetic complex
or nanoparticle

**Manetochiral
dichroism?**

Use the silica nanohelices to induce chirality on simple magnetic molecules and particles

Magnetic nanohelices for magnetochiral dichroism (MChD)

Different induction strategies



Strategy 1
Ion exchange of the gemini counter-ion

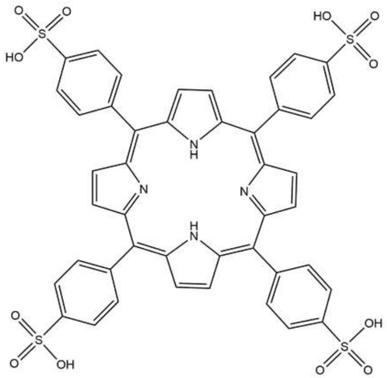
Strategy 2
Grafting on the silica surface

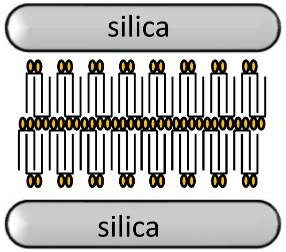
Strategy 3
Dropcast

Magnetic nanohelices for magnetochiral dichroism (MChD)

Example of preliminary results with a porphyrin

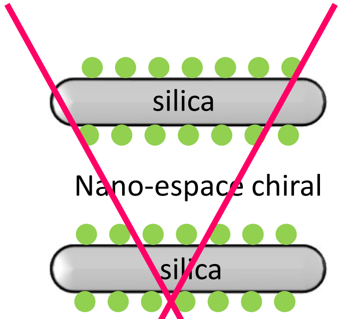
TPPS





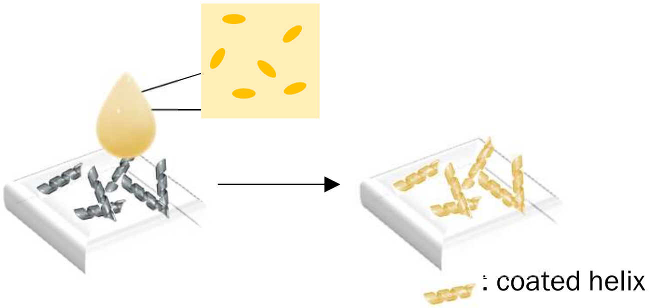
Strategy 1

Ion exchange of the gemini counter-ion



~~***Strategy 2***~~

~~*Grafting on the silica surface*~~



Strategy 3

Dropcast

No chirality induction

Magnetic nanohelices for magnetochiral dichroism (MChD)

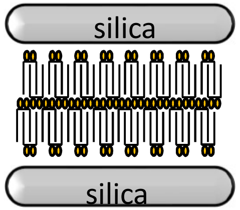
UV-vis

B = 0

B = 1T

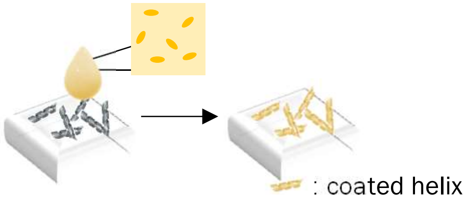
Strategy 1

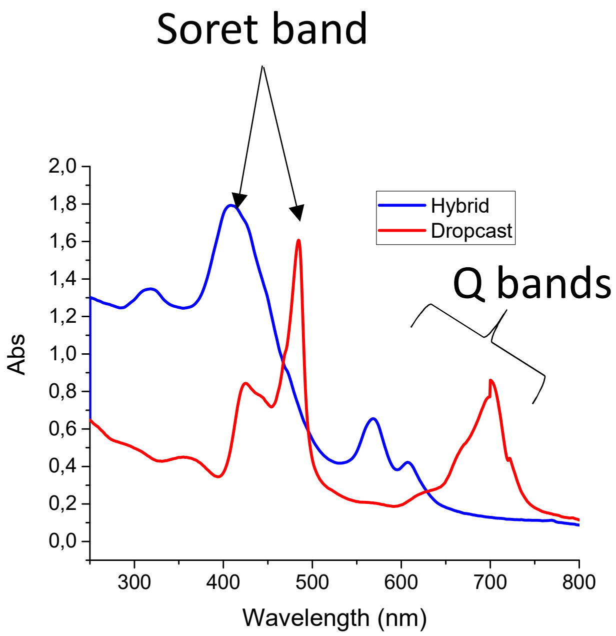
Ion exchange of the gemini counter-ion



Strategy 3

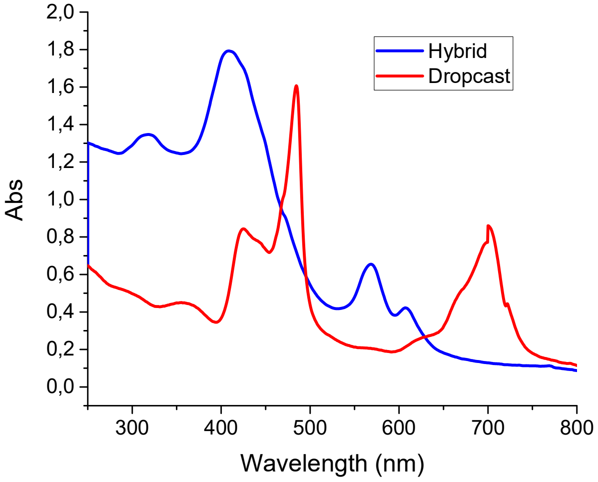
Dropcast





Soret band

Q bands



Aggregation of the porphyrins when dropcasted

Magnetic nanohelices for magnetochiral dichroism (MChD)

CD

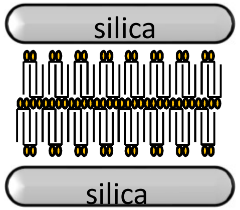
B = 0

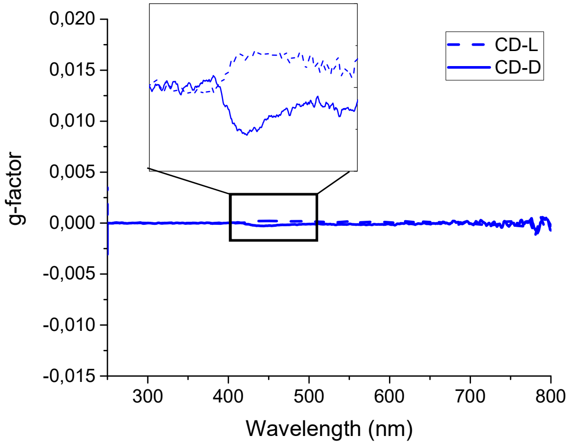
MCD

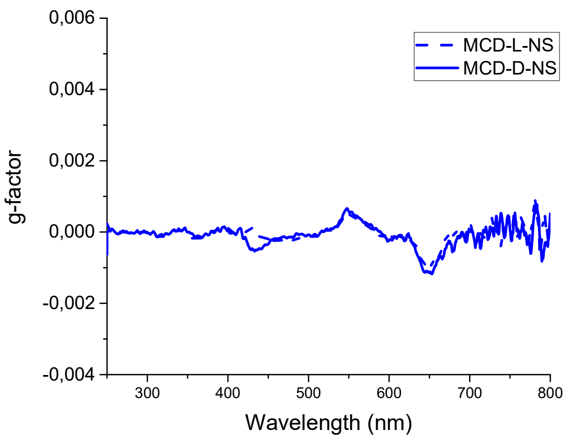
B = 1T

Strategy 1

Ion exchange of the gemini counter-ion

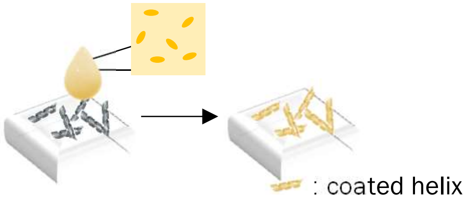


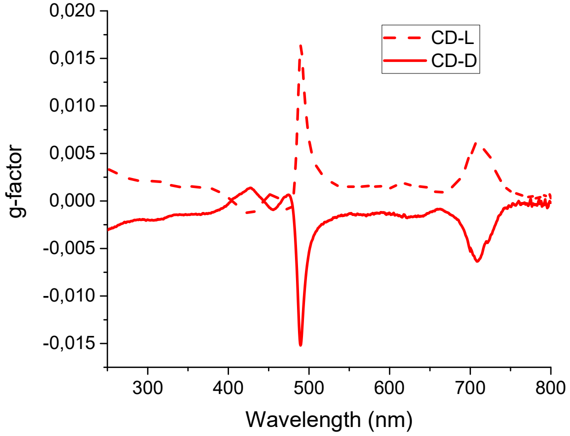


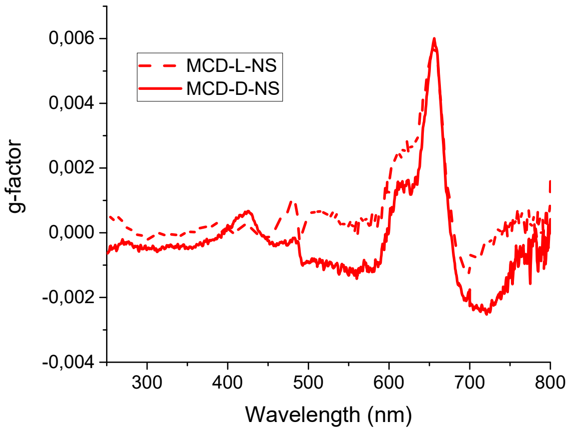


Strategy 3

Dropcast



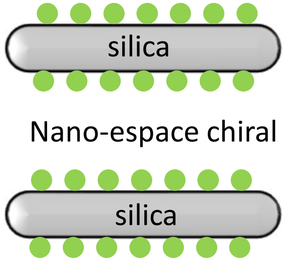


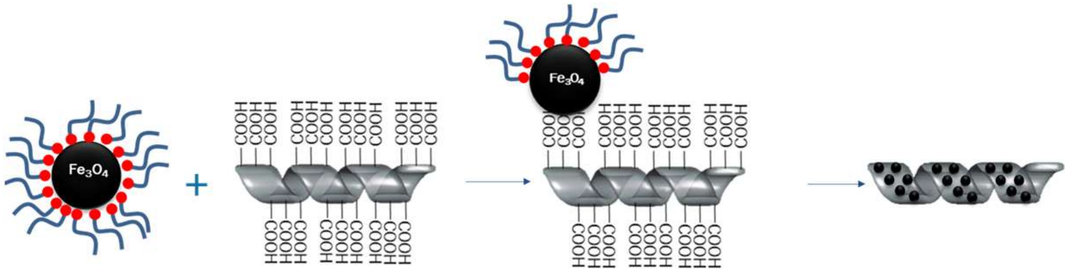


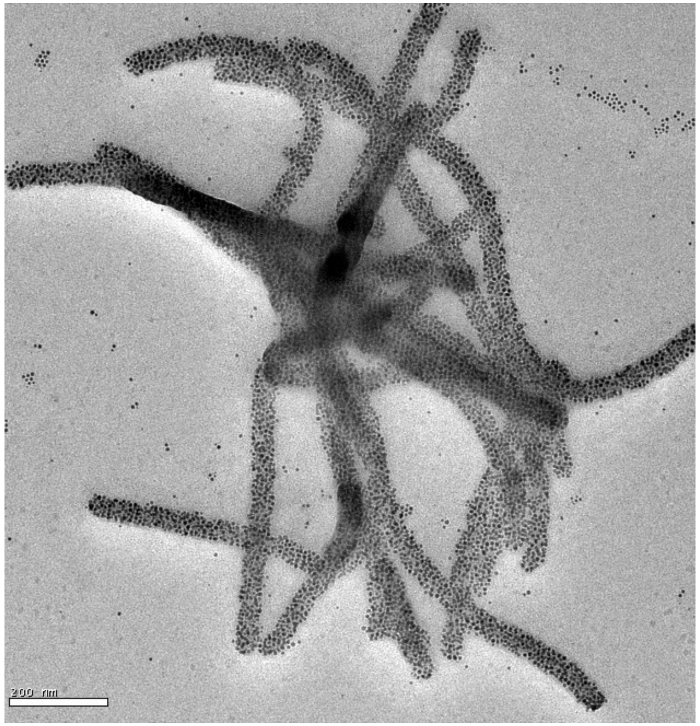
Magnetic nanohelices for magnetochiral dichroism (MChD)

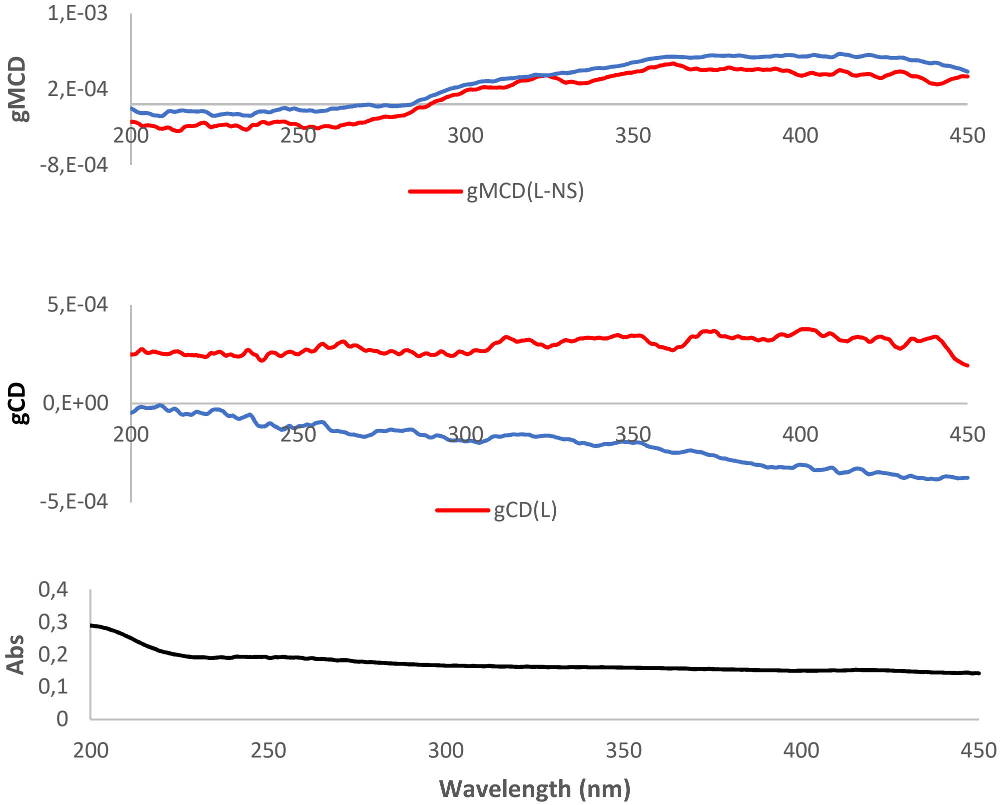
Strategy 2

Grafting on the silica surface









A lot of questions to answer…..

- MChD signal?
- Influence of the grafting method on the induced CD and why?
- Why MCD is principaly on the Q-bands?
- Influence of a metalic center?
- Why we don't have chirality induction with the magnetite NPs?
- ….

To be continued….