

Design of photonic nanostructures via chirality induction:

A model system towards enantioselective catalysts

Emilie POUGET

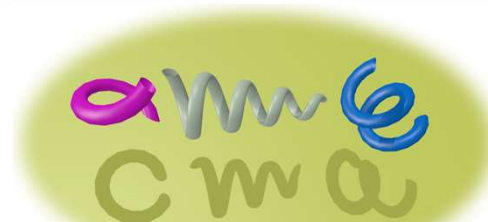
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Institute of Chemistry & Biology of Membranes & Nanoobjects
(UMR5248 CBMN)

CNRS –Bordeaux University - Bordeaux INP

GDR Or-Nano, Strasbourg, October 2023

Institute of Chemistry & Biology of the Membranes & Nanoobjects



Group « Chiral Molecular Assemblies »



Reiko ODA



Sylvain NLATE



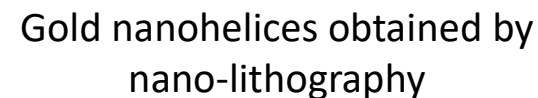
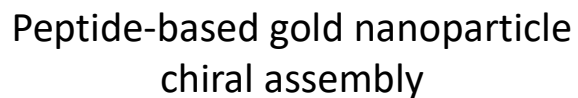
Emilie POUGET



CL: LN LL:



Chiral Nanoassemblies

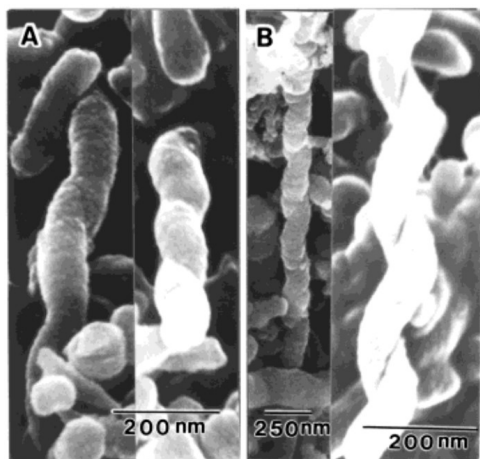
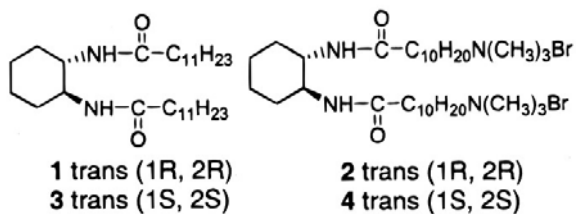


Review: Ma et al., Chem. Rev. 2017, 117, 8041–8093

Chirality at the nanoscale

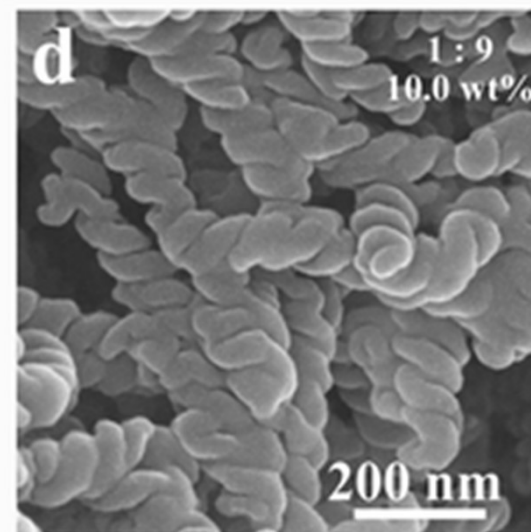
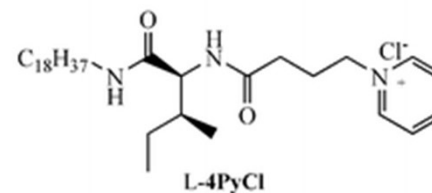
Hybrid helical nanostructures *via* sol-gel transcription

Precursor work: Seiji Shinkai



*Silica transcription of
aminocyclohexane derivatives*

Jung et al., *J. Am. Chem. Soc.* 2000, 122, 5008-5009



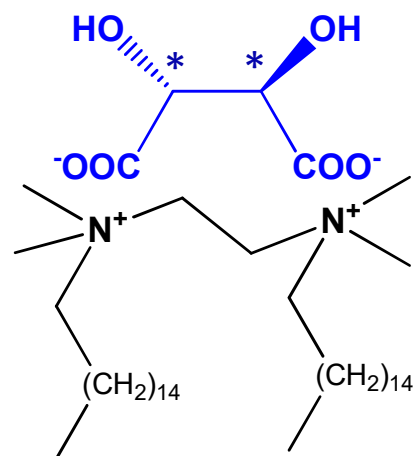
*Silica transcription from chiral
gelator-like cationic surfactant*

Yang et al., *J. Mater. Chem.* 2006, 16, 1644-1650

CMA group background: chiral self-assembly

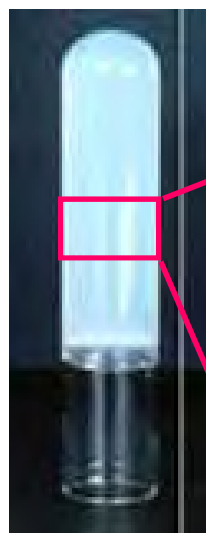
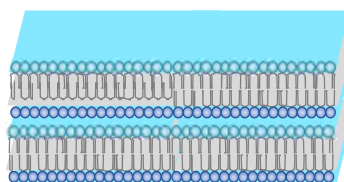
Organic self-assembly

Chiral Counter anion
(L-tartrate)

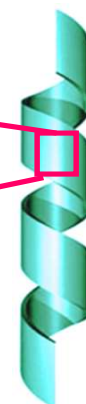


Gemini 16-2-16

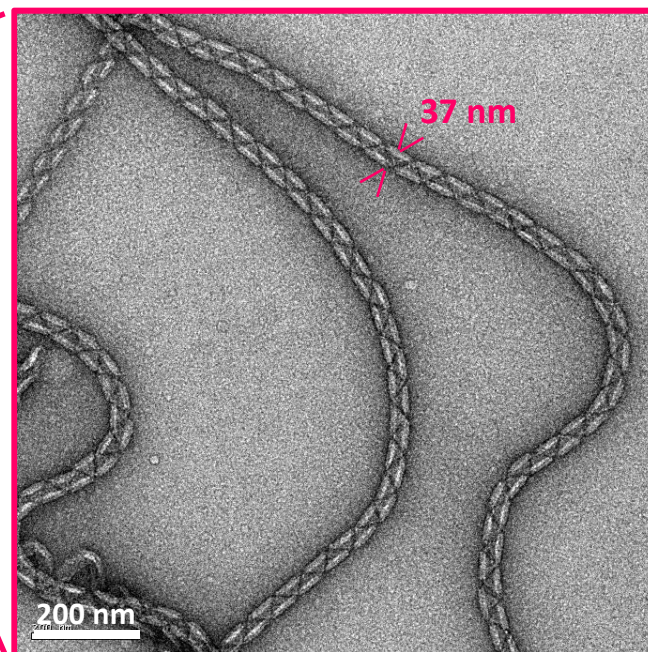
Gel network of helical ribbons
($c = 10 \text{ mM}$ in H_2O)



D-tartrate
Left Handed



L-tartrate
Right Handed

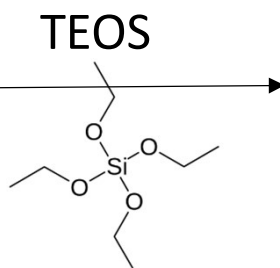


Nature 1999, *JACS* 2007, *JACS* 2002,
J. Phys. Chem. A 2004

The system: silica nanohelices

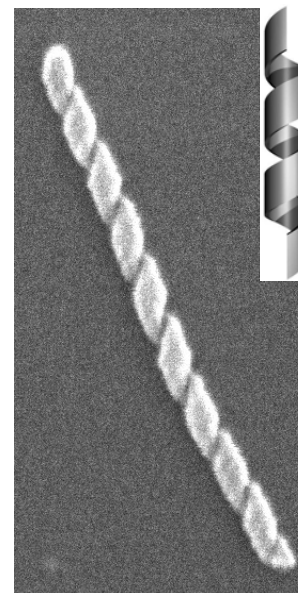
Silica transcription

Organic



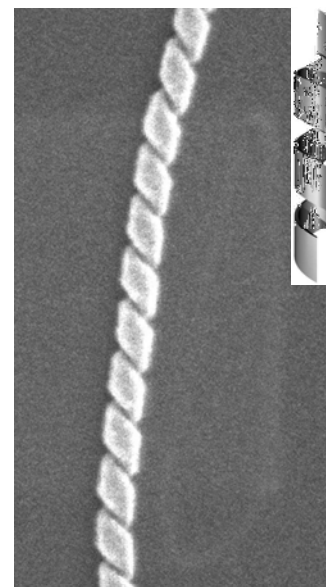
Hybrid organic / silica nanohelices

L-tartrate
Right Handed



L-tartrate

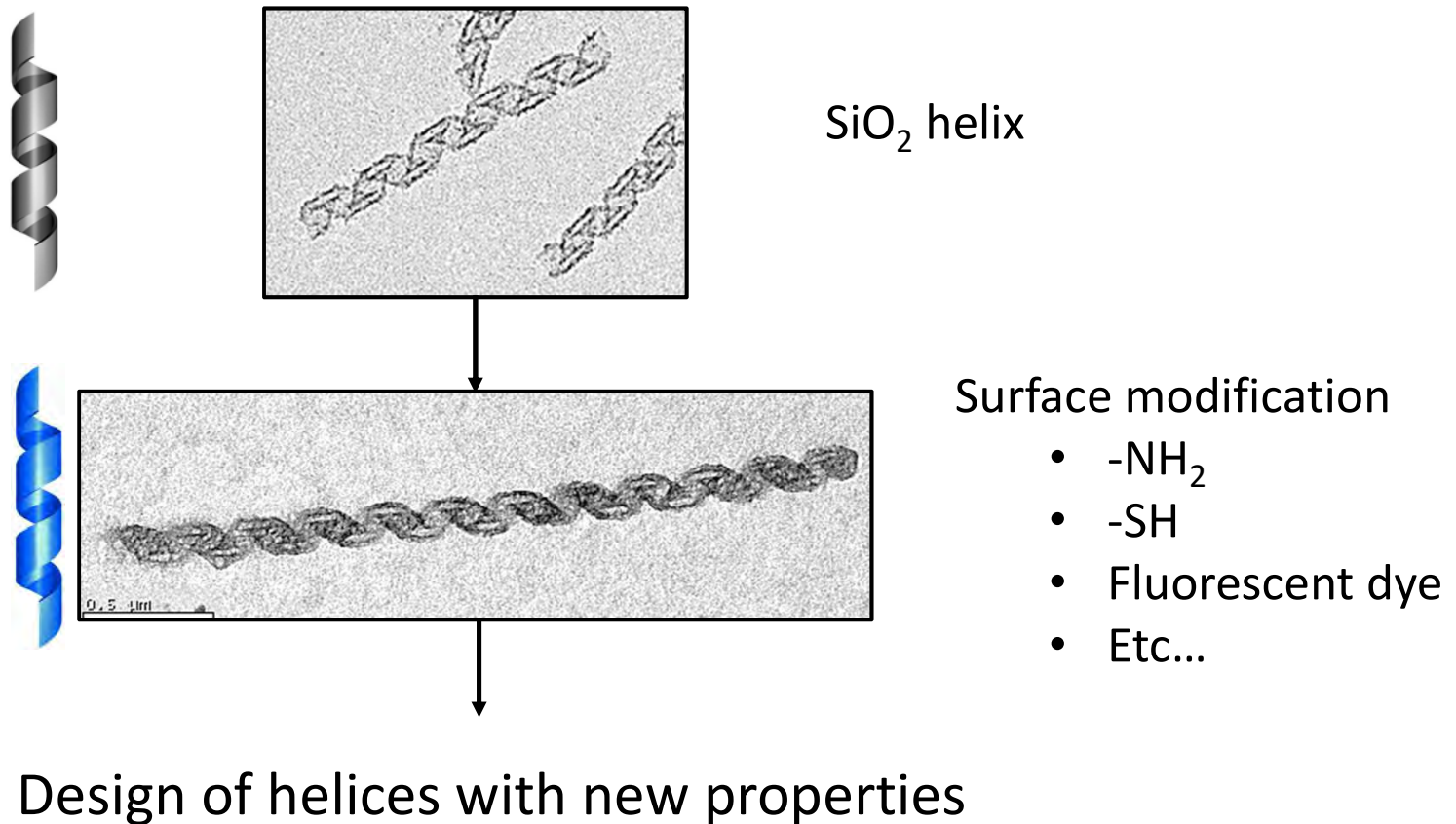
D-tartrate
Left Handed



D-tartrate

Robust system:
solvents, T°, pH, drying

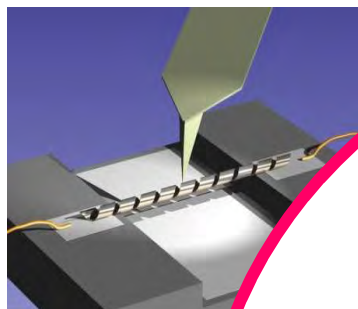
Towards functional materials



Towards functional materials

Secondary mineralization (TiO_2 , ZnO)

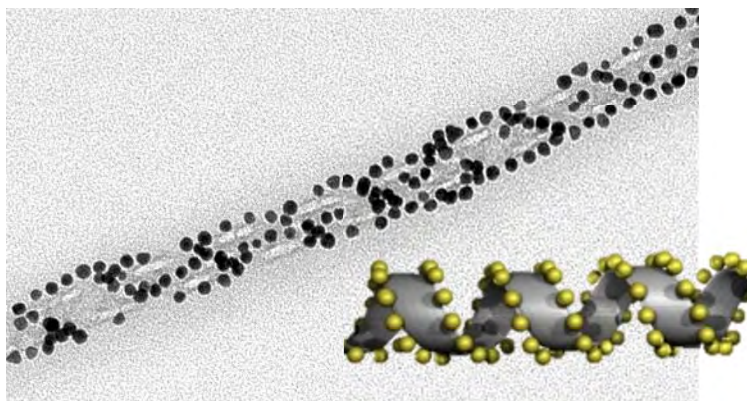
NEMS



M.H. Delville, C.

SiO_2 helix

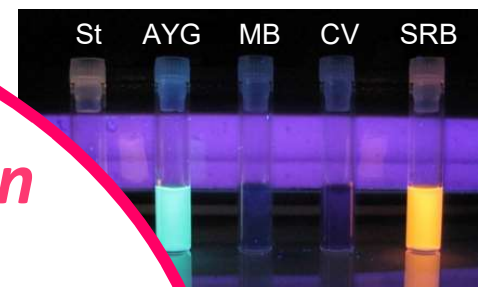
Chiral GNPs organization



Chiral photonics nanodevices

A. Perro

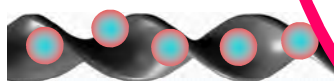
Photochromic chiral devices



Early Polarized
Fluorescent systems

Y. Sagawa (Japan)

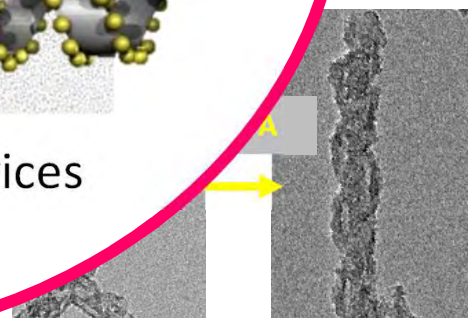
Enantioselective



Heterogen nanocatalysts

S. Nlate, B. Bibal

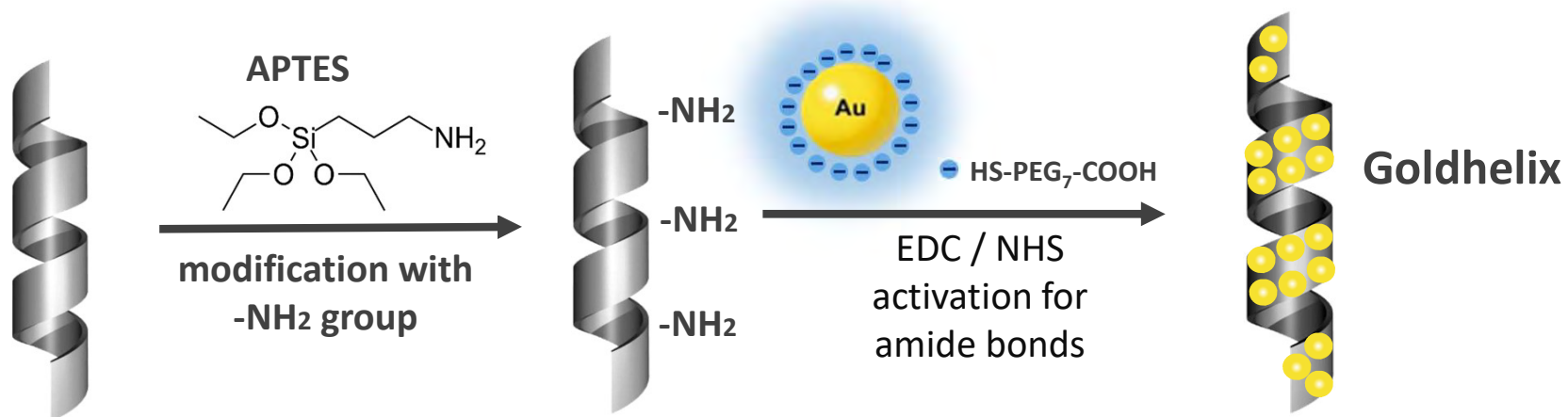
devices



Evidence of MagnetoChiral
Dichroism

E. Hillard
C. Train
G. Rikken

Chiral photonics nanodevices



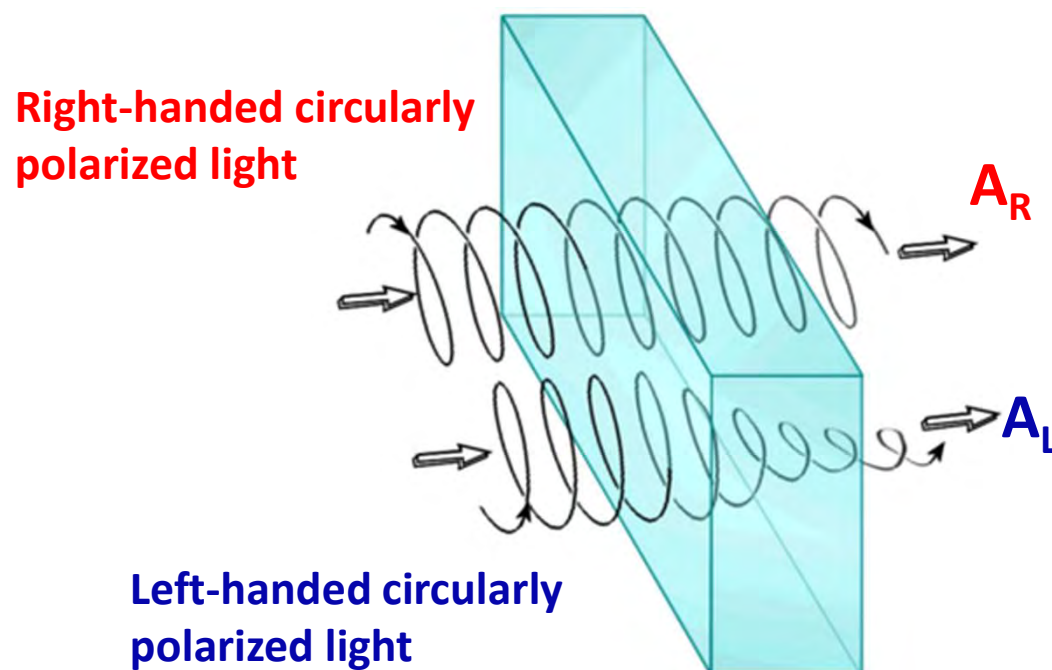
Goldhelices



Chiroptical properties?

Circular Dichroism (CD)

- Chiroptical absorption of polarized light



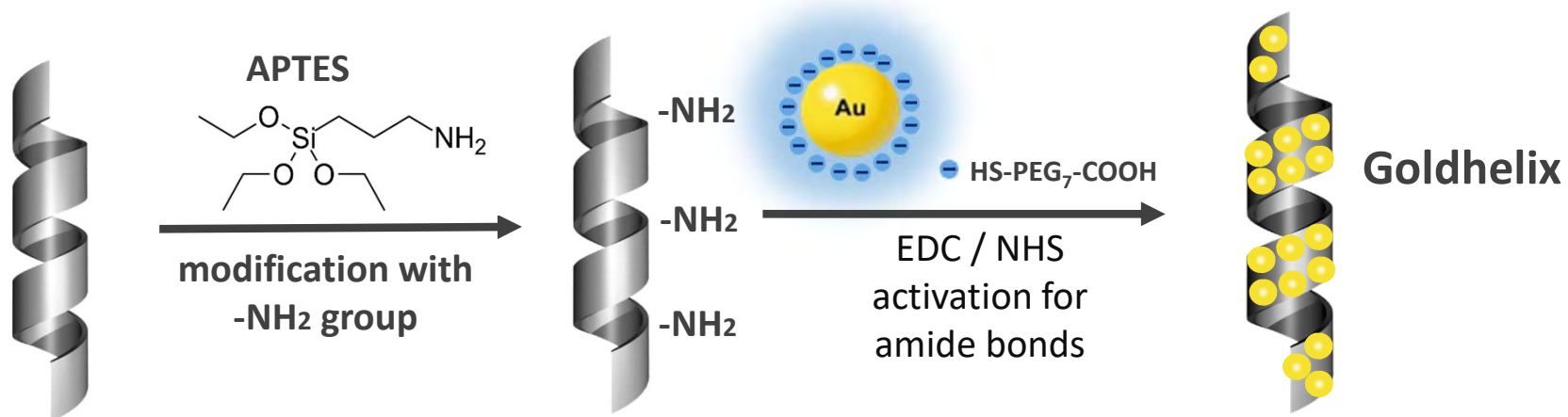
For chiral samples:

$$\Delta A = A_L - A_R \neq 0$$

$$C_L \neq C_R$$

$$g_{abs} = \frac{\Delta A_{CD}}{A} \approx \frac{\theta_{abs}[mdeg]}{32982 * A}$$

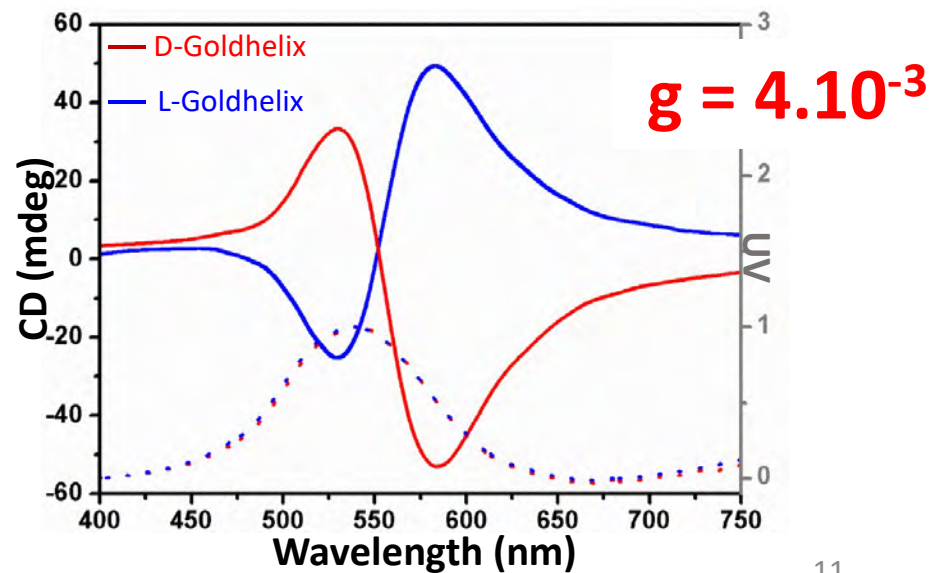
Chiral photonics nanodevices



Goldhelices



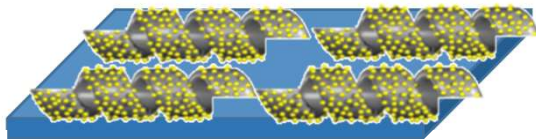
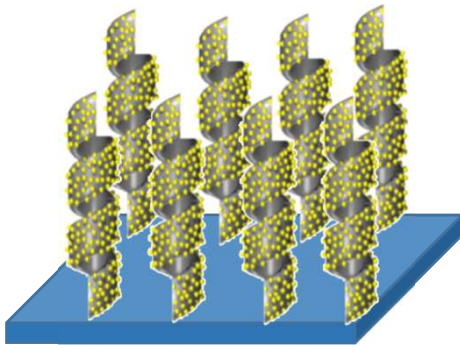
CD signal at the plasmon wavelength



Applications?

What can we do with these Goldhelices?

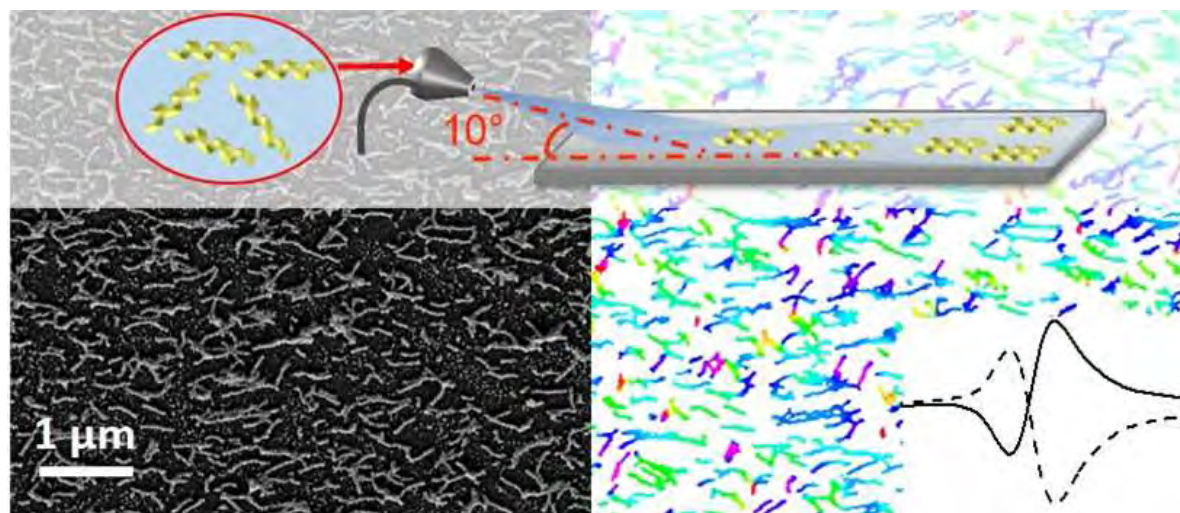
2D and 3D organization
towards macroscopic devices



Tune the optical properties

Macroscopic devices

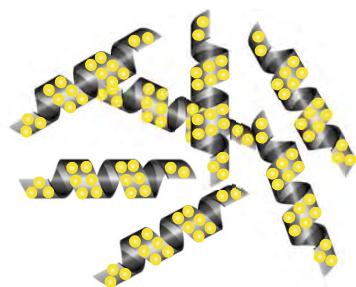
2D orientation by Grazing Incidence Spraying



Coll. Matthias Pauly, ICS

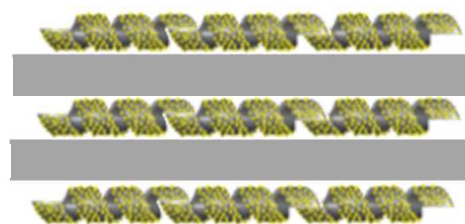
Coll. Yann Battié, LCPA2MC

Non-oriented



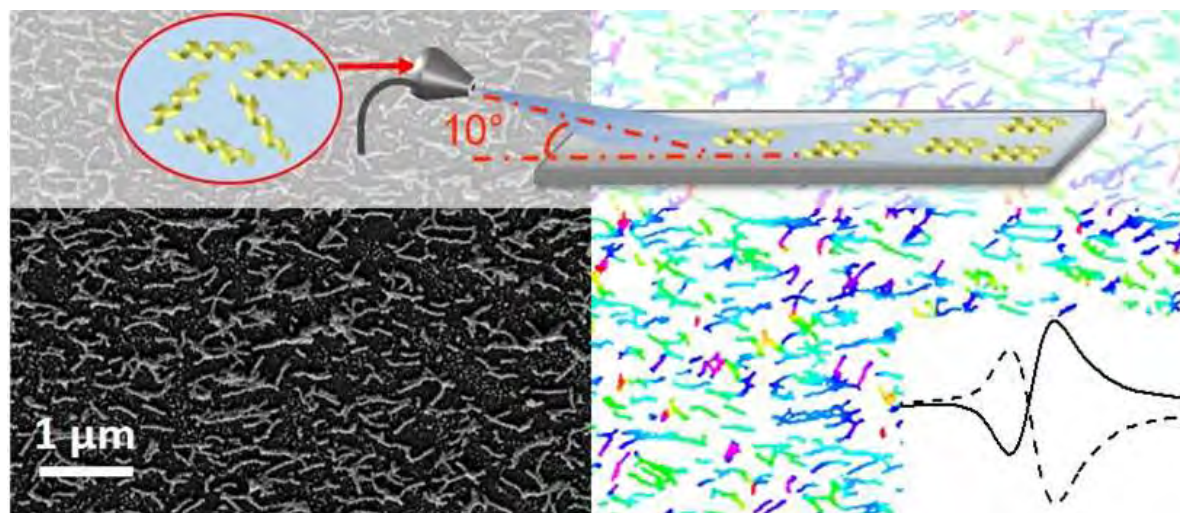
VS

Oriented



Macroscopic devices

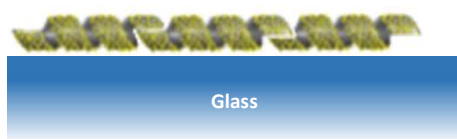
2D orientation by Grazing Incidence Spraying



Coll. Matthias Pauly, ICS

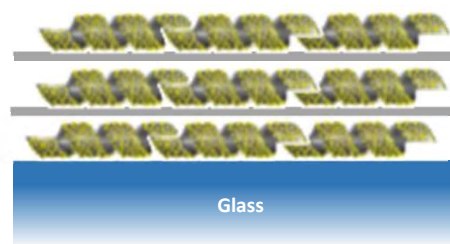
Coll. Yann Battié, LCPA2MC

Monolayer



VS

Multilayers

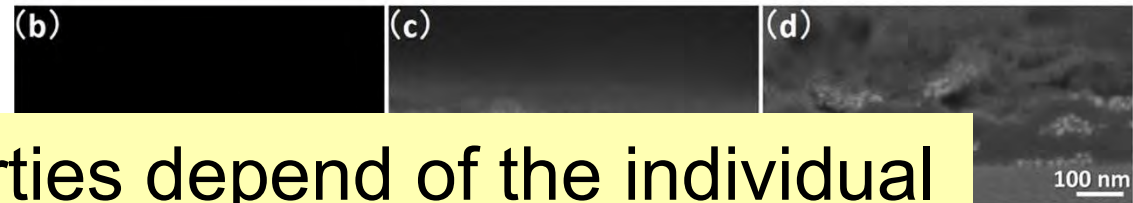
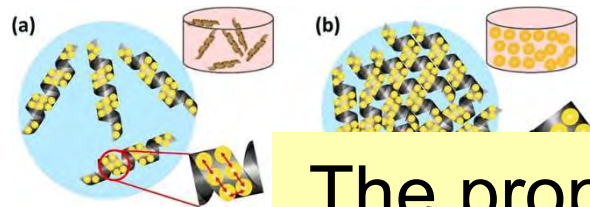
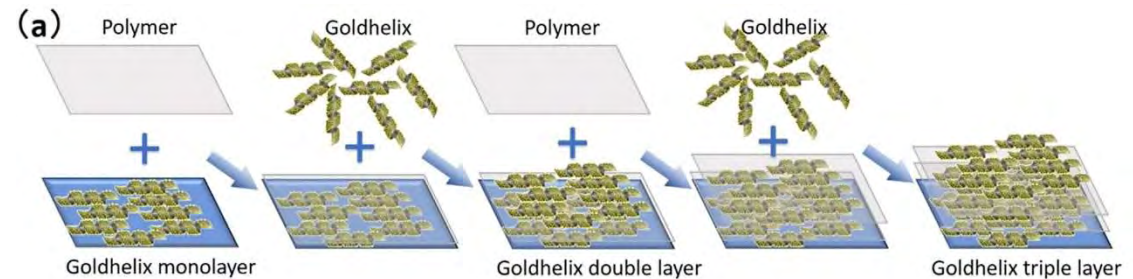


Macroscopic devices

2D orientation by Grazing Incidence Spraying

Coll. Matthias Pauly, ICS

Coll. Yann Battié, LCPA2MC



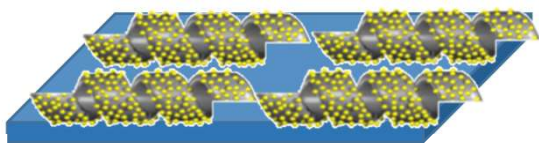
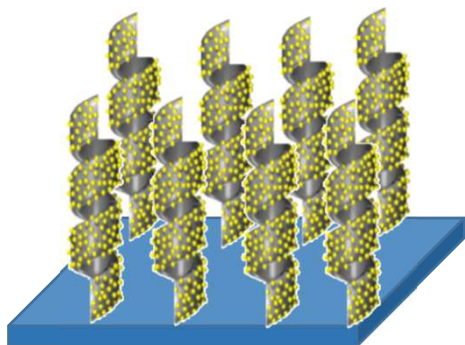
The properties depend of the individual objects AND their assembly

objects AND their assembly								
Sample	Bulk	Monolayer	Multilayers		Monolayer	Multilayers (3 layers)		
			Gap			Gap		
			0 nm	56 nm		1 nm	13 nm	33 nm
LD	0	0	0	0	0.038	0.051	0.035	0.045
g-factor (.10-3)	4.4	4.3	0	3.7	4.3	1.3	1.8	4.4

Applications?

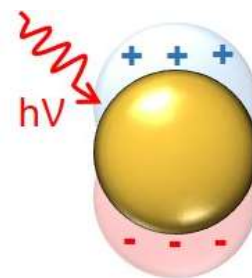
What can we do with these Goldhelices?

2D and 3D organization
towards macroscopic devices



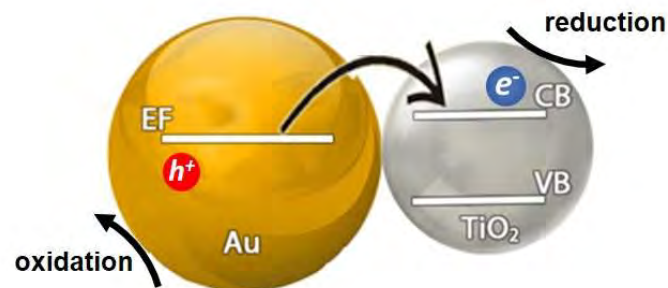
Tune the optical properties

A step towards enantioselective
photocatalysis?



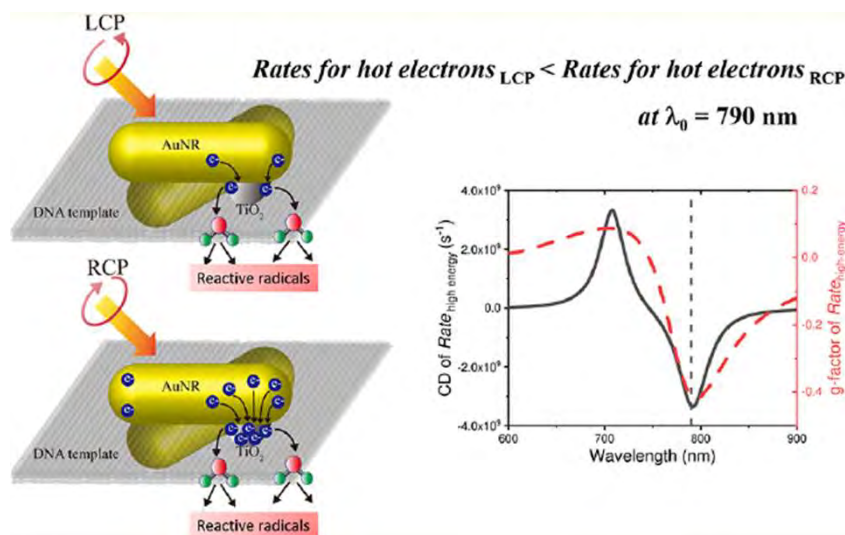
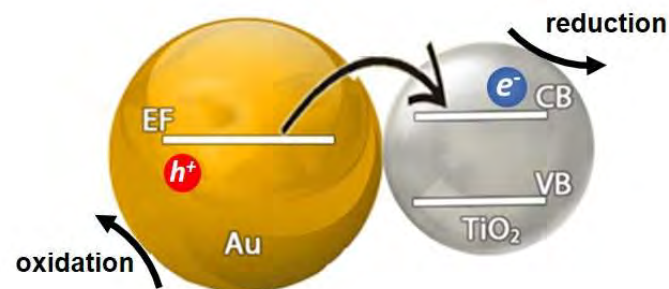
Using the chirality of this plasmon in photocatalysis?

A preliminary result with hot charge carriers



A step towards enantioselective photocatalysis?

Hot charge carriers can be created when a **high-energy photon of electromagnetic radiation (such as light) strikes a metal**. The energy from the photon can be transferred to an electron, exciting the electron out of the valence band, and forming an electron-hole pair.



NANO LETTERS

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Letter
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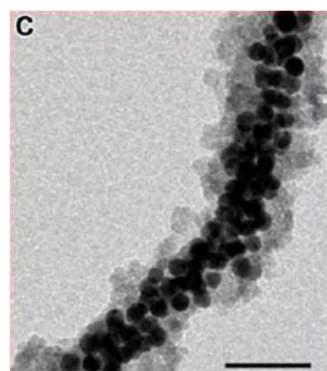
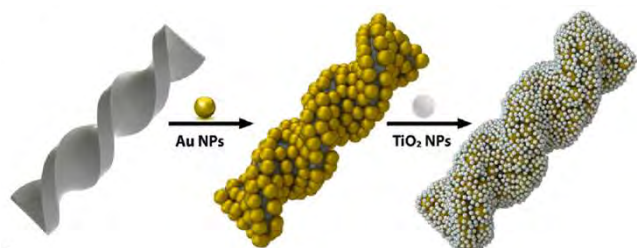
Chiral Plasmonic Nanocrystals for Generation of Hot Electrons: Toward Polarization-Sensitive Photochemistry

Tianji Liu,^{†,‡,§} Lucas V. Besteiro,^{†,§,¶} Tim Liedl,^{||} Miguel A. Correa-Duarte,[⊥] Zhiming Wang,^{*,†} and Alexander O. Govorov^{*,†,§}

A step towards enantioselective photocatalysis?

The Goldhelices: a model system

Coll.: - Miguel Comesana-Hermo (ITODYS, Paris)
- Miguel Correa-Duarte (Vigo Univ.)
- Alexander Govorov (Ohio Univ.)



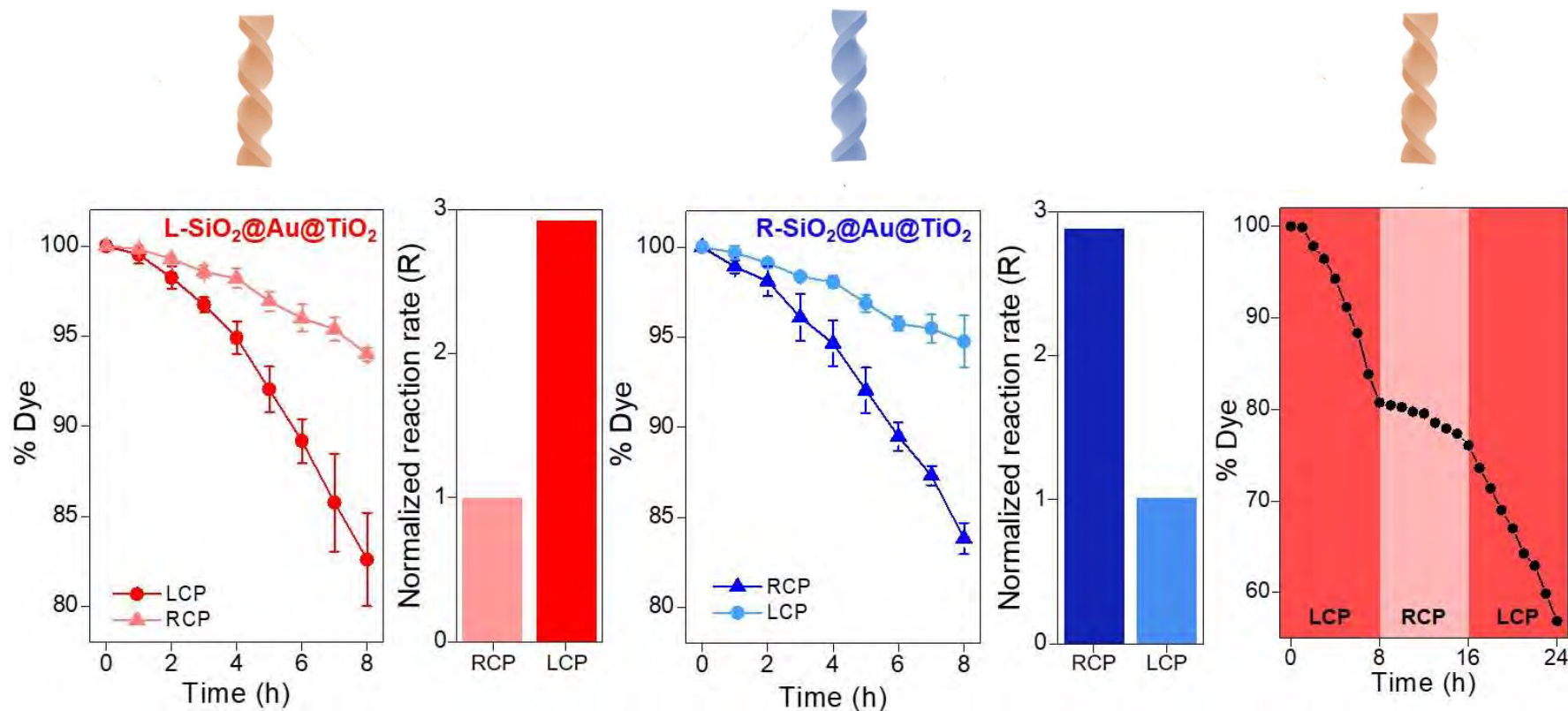
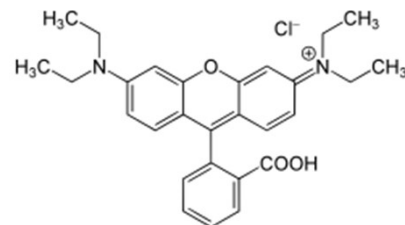
Goldhelix ($d_{\text{GNP}} = 11 \text{ nm}$) + TiO_2 NPs $d=5 \text{ nm}$.
Electrostatic deposition via LBL.

The photo-transformation of rhodamine B (RhB) has been chosen as model photocatalytic reaction in order to demonstrate the asymmetric response of the hot carriers with respect to the helicity of the circularly polarized light (CPL).



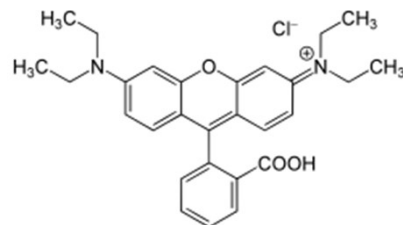
A step towards enantioselective photocatalysis?

Selective degradation of RhB

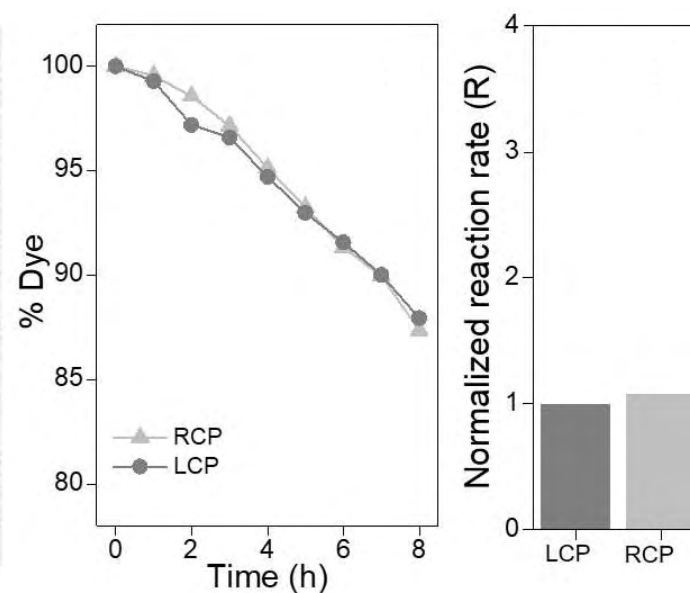
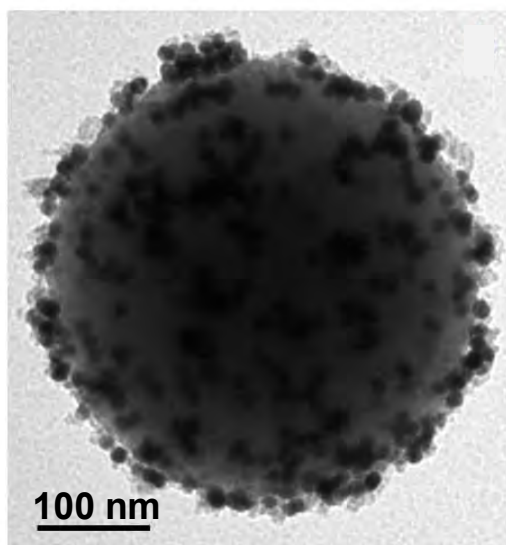
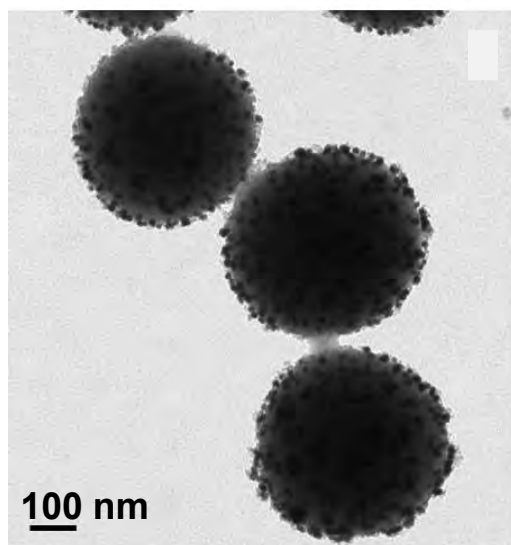


A step towards enantioselective photocatalysis?

Selective degradation of RhB

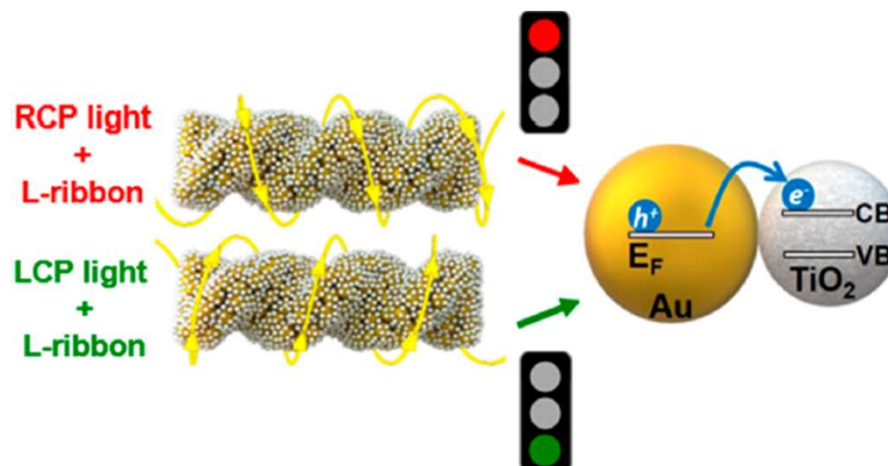


Comparison with a non-chiral sample



Can we go further with these Goldhelices?

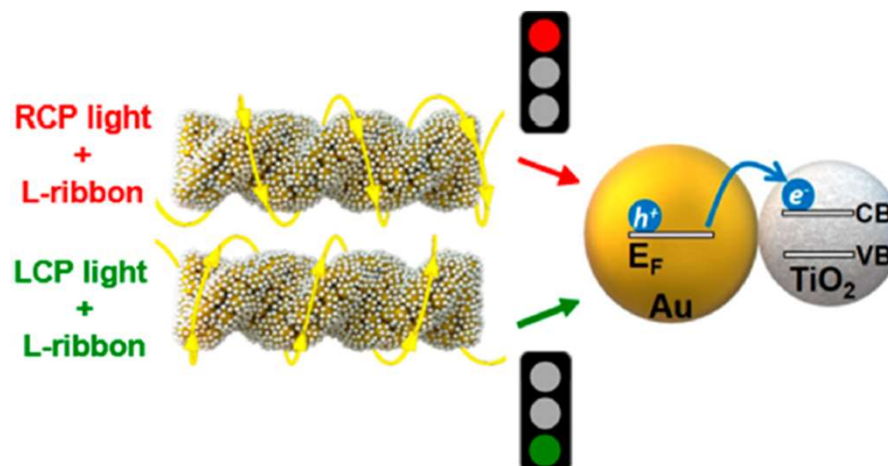
Asymmetric response of the hot carriers with respect to the helicity of CPL



NEXT STEP? Asymmetric photocatalysis?

Can we go further with these Goldhelices?

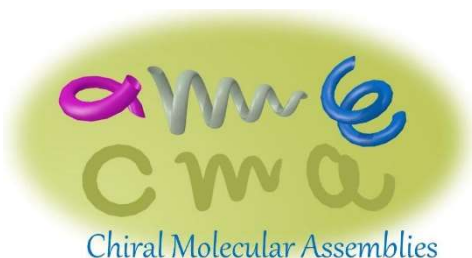
Asymmetric response of the hot carriers with respect to the helicity of CPL



Chiral plasmonic for photocatalysis

starting in November

*Miguel Comesana Herno (ITODYS), Matthias Pauly (ICS),
Emilie Pouget (CBMN) and Lucas Besteiro (Vigo Univ., Spain)*



Acknowledgment



This project has received funding from Amadeus Labex (University of Bordeaux) and CSC (China)

CMA's group

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Sylvain Nlate

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Jie Gao (Goldhelices)
Charlène Brissaud (silver)
Lucas Robin (Goldhelices)
Jiaji Cheng
Rumi Tamoto
Guillaume Le Saux
Alicia Delavier
Grégoire Piet

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GIS: M. Pauly (ICS, Strasbourg)
MMP: Y. Battié (LCPA2MC, Metz)
Tomo: O. Ersen (IPCMS, Strasbourg)
Hot e⁻: Miguel Comesana-Hermo (ITODYS, Paris), Miguel Correa-Duarte (Vigo Univ.), Alexander Govorov (Ohio Univ.)

Platforms: IECB Biophysico-chimie structurale (TEM), IECB Chirality (CD), Ellipsometry core facility of LCP-A2MC (MMP), Electron Microscopy Platform of ICS (SEM), Electron Microscopy Platform of IPCMS (tomo)





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**BIOMEDICAL
ASPECTS OF
COLLOIDS AND
VECTORIZATION**



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MICELLES AND
INTERFACIAL
PHENOMENA**



**COLLOIDAL
PARTICLES AND
SELF-ASSEMBLY**



**FOOD COLLOIDS
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APPLICATIONS**



**POLYMER
SOLUTIONS, GELS
AND PHASE
BEHAVIOUR AND
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**SURFACE FORCES,
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