



## Chiral plasmonic effects probed at the single-nanoparticle level

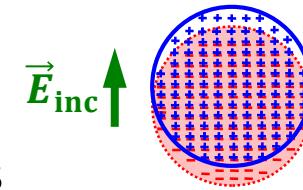
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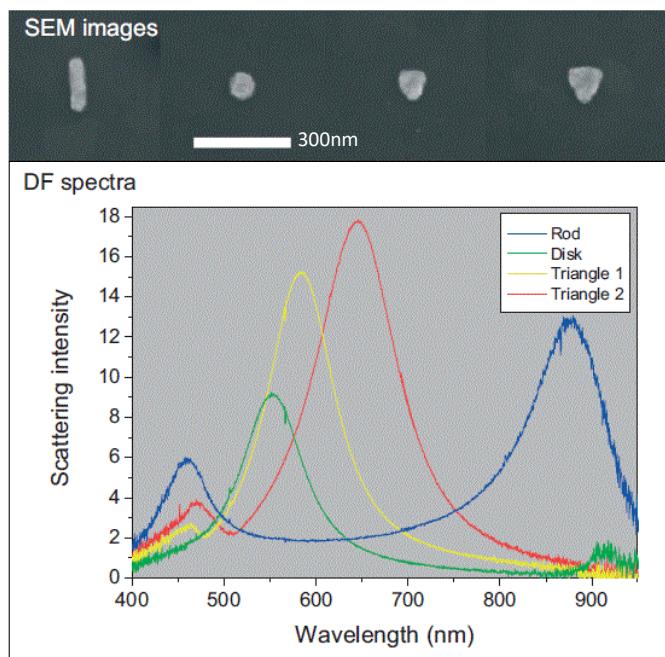
# Localized Surface Plasmon Resonance (LSPR)

- Collective oscillation of the electronic cloud
- Far field observation : extinction / scattering measurements

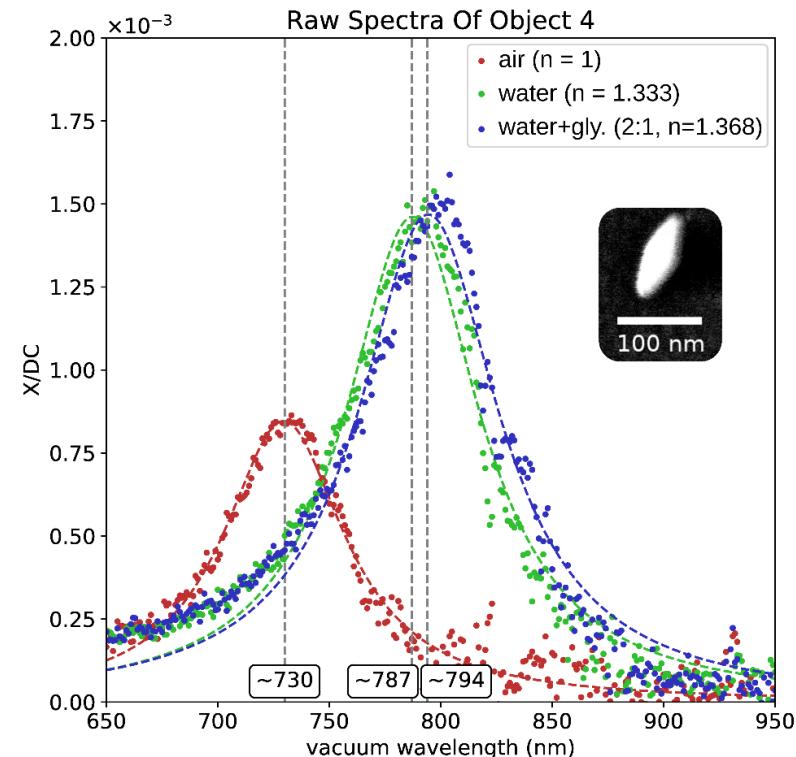


depends on :

- size
- shape
- environment



Murray et al., *Adv. Mat.* (2007), 19, 3771-3782

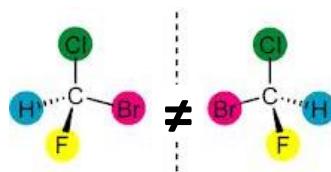


extinction spectra of a gold bipyramid in different medium (air, water and water + glycerol)

Rye et al., *Nanoscale* (2018) 10, 16094-16101

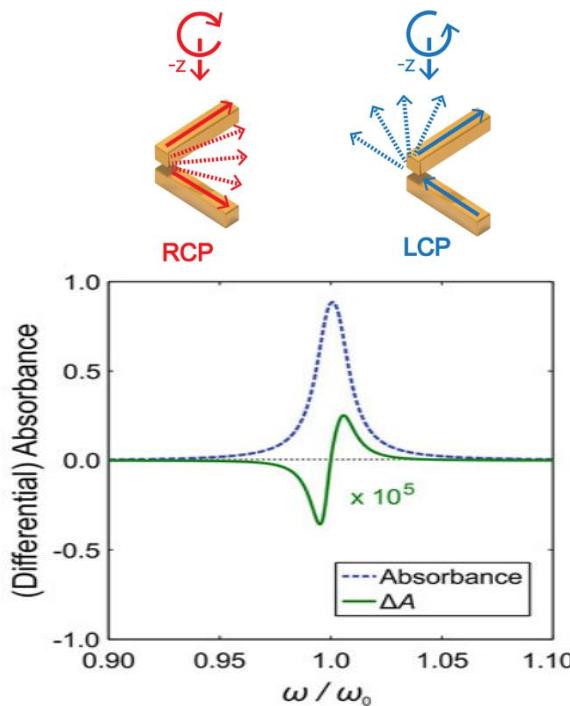
# What happens in the case of a chiral environment or chiral nano-objects ?

Chirality : geometrical property



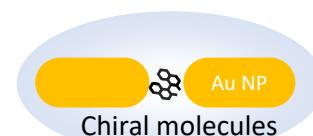
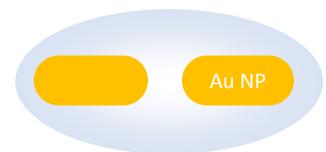
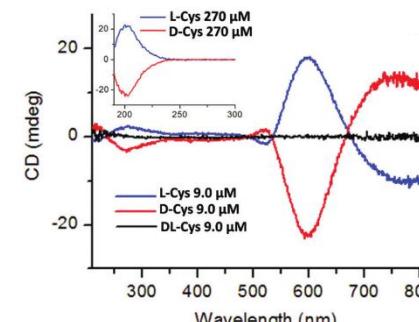
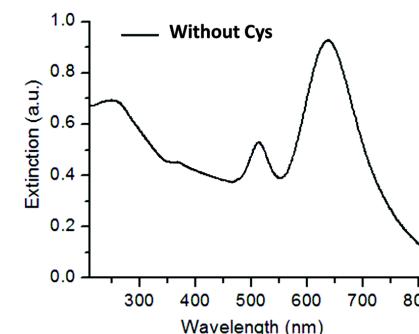
→ Optically : circular dichroism  $CD = \frac{A(\odot) - A(\circ)}{\bar{A}}$

- Geometrically chiral NP



*Chiral Nanophotonics*, Schäferling, Springer, 2017

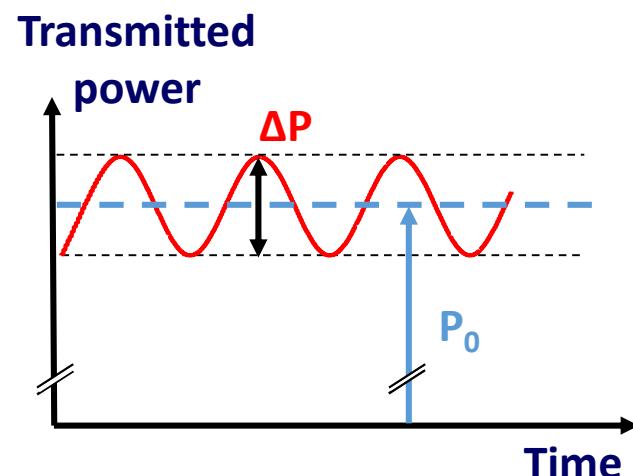
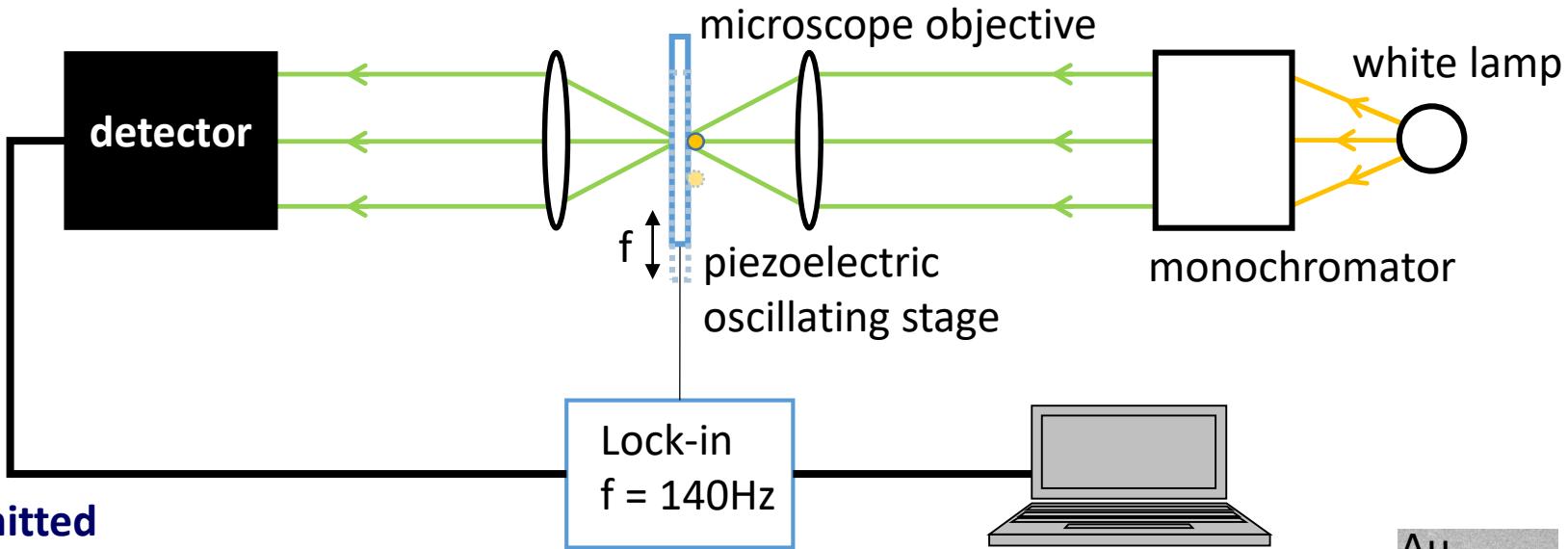
- Chirality transfer



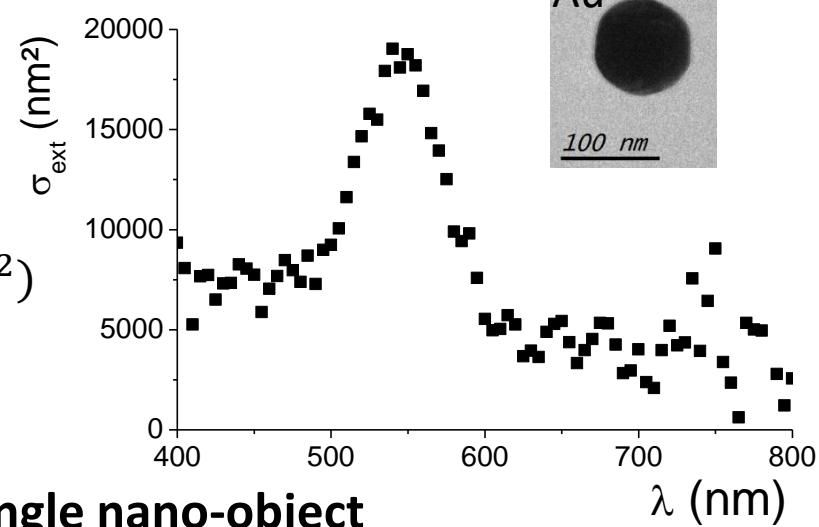
Zhai et al., *Nanoscale* (2015) 7, 10690-10698

# Spatial Modulation Spectroscopy

a transmission spectrophotometer for individual nanoparticles



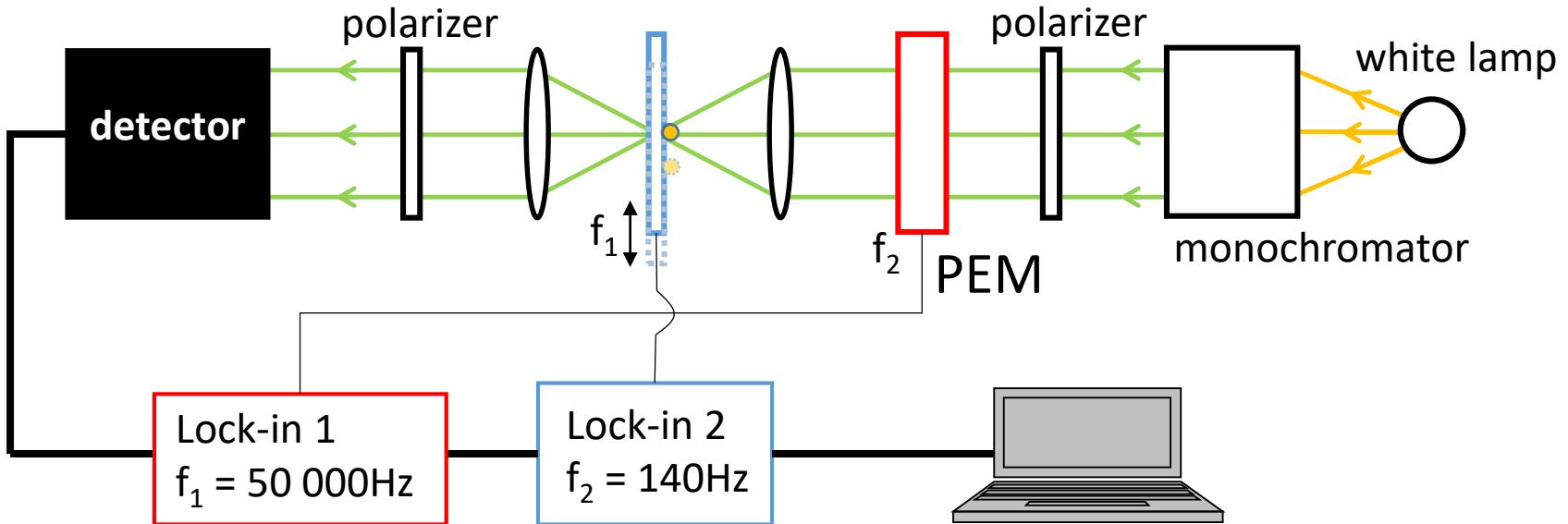
$$\left( \frac{\Delta P}{P_0} \right)_f \rightarrow \sigma_{ext} (nm^2)$$



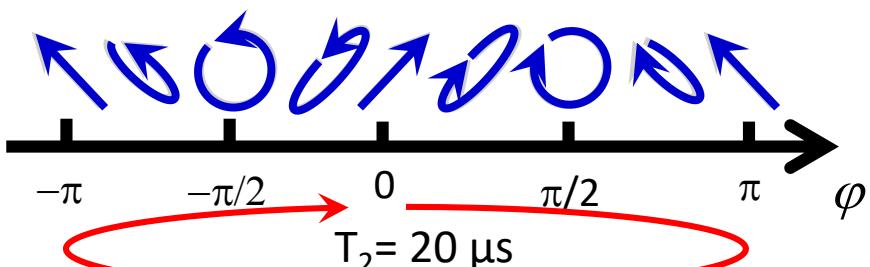
→ extinction of a single nano-object

Billaud et al., J. Phys. Chem. C, (2008), 112, 978  
Billaud et al., Rev Sci. Instrum. (2010), 81, 043101

# SMS set-up with polarization control: double modulation

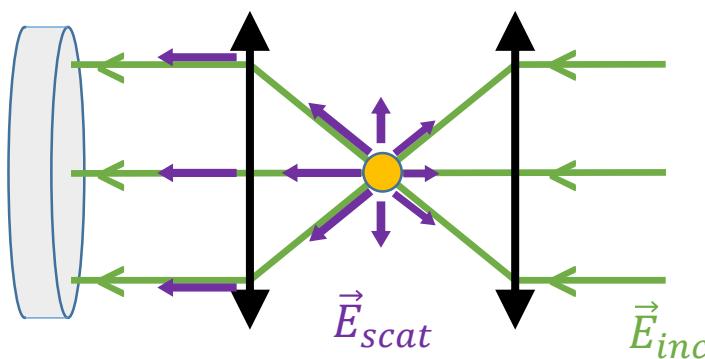


Photoelastic modulator (PEM) : periodic modulation of the light polarization



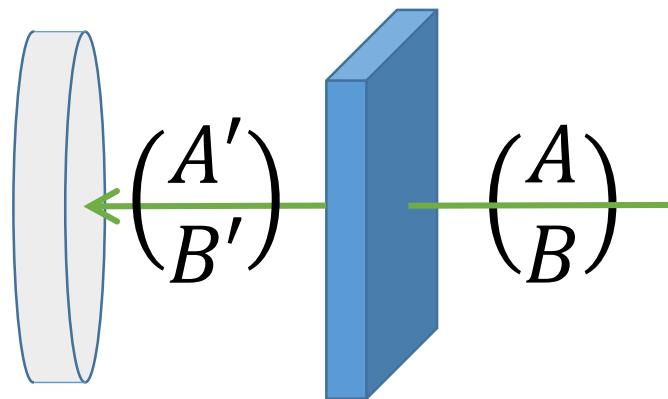
→ Extinction's polarization dependency

# From optical theorem to Jones formalism



$$\begin{aligned}\vec{E}_{coll} &= \vec{E}_{inc} + \vec{E}_{scat} \\ &= \vec{E}_{inc} + \bar{\chi} \vec{E}_{inc}\end{aligned}$$

$$\vec{E}_{coll} = \mathbf{M} \vec{E}_{inc}$$



$$\begin{matrix} (A') \\ (B') \end{matrix} = \mathbf{M} \quad \begin{matrix} (A) \\ (B) \end{matrix}$$

$$\vec{E}_{coll} = \mathbf{M} \vec{E}_{inc}$$

Anisotropic object:

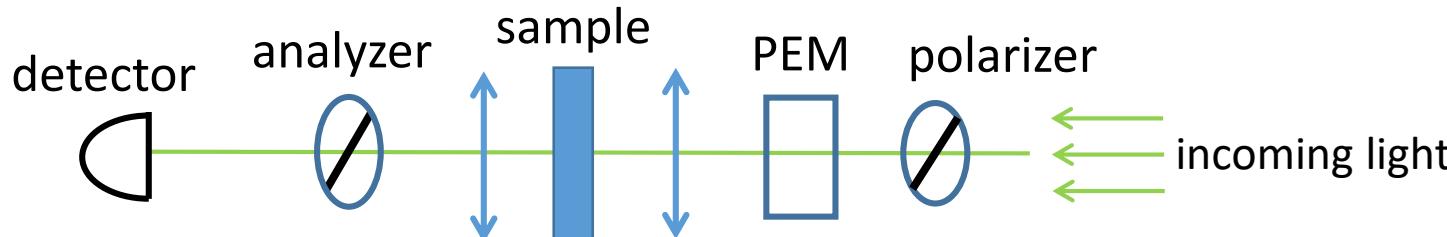
$$\mathbf{M} = \begin{pmatrix} A_1 & 0 \\ 0 & A_2 \end{pmatrix} \theta$$

$$A_i = A_0 \begin{cases} e^{-\alpha_i/2} & \text{light extinction} \\ e^{-ik_i/2} & \text{phase} \end{cases}$$

# Measurement

$$M = \begin{pmatrix} A_1 & 0 \\ 0 & A_2 \end{pmatrix} \theta$$

$$A_i = A_0 \boxed{e^{-\alpha_i/2}} \boxed{e^{-ik_i/2}}$$



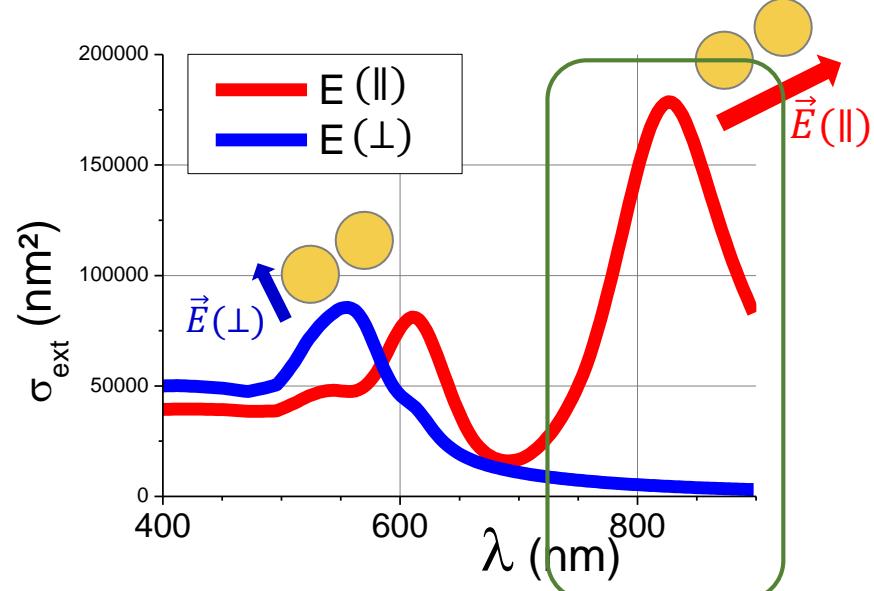
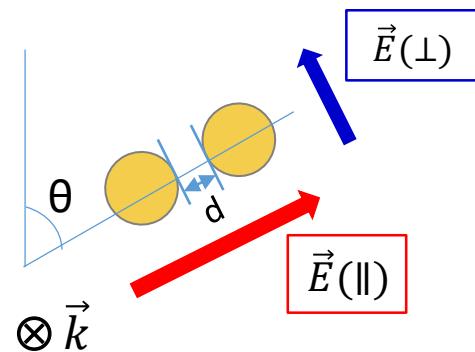
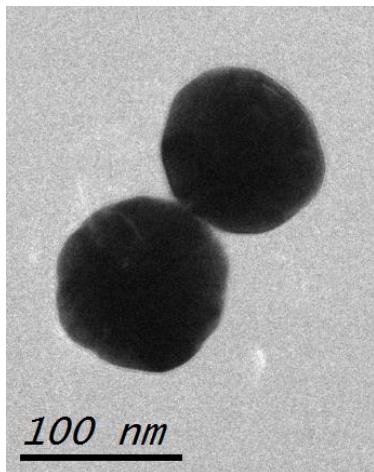
$$\vec{E}_{coll} = (A) (M) (PEM) (P) \vec{E}_{inc}$$

$$\rightarrow I = \|\vec{E}_{coll}\|^2$$

the collected intensity depends on the nano-object anisotropy parameters

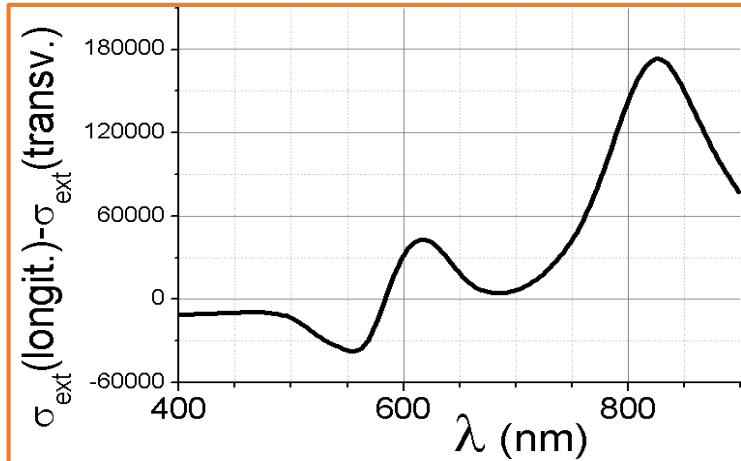
- $\theta$  : orientation of the eigenvector basis
- **Dichroism** :  $\Delta\alpha = \alpha_1 - \alpha_2$
- **Birefringence** :  $\Delta k = k_1 - k_2$

*several measurements for different orientations of the analyzer*

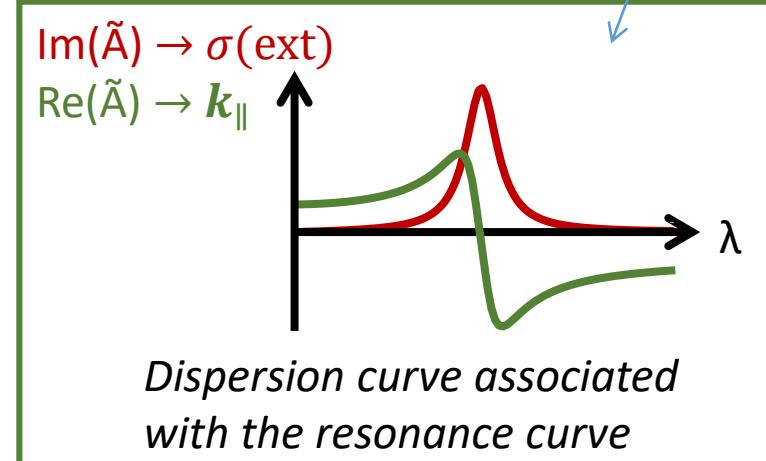


## expectations

- $\Delta\alpha = \alpha_{||} - \alpha_{\perp}$  : linear dichroism

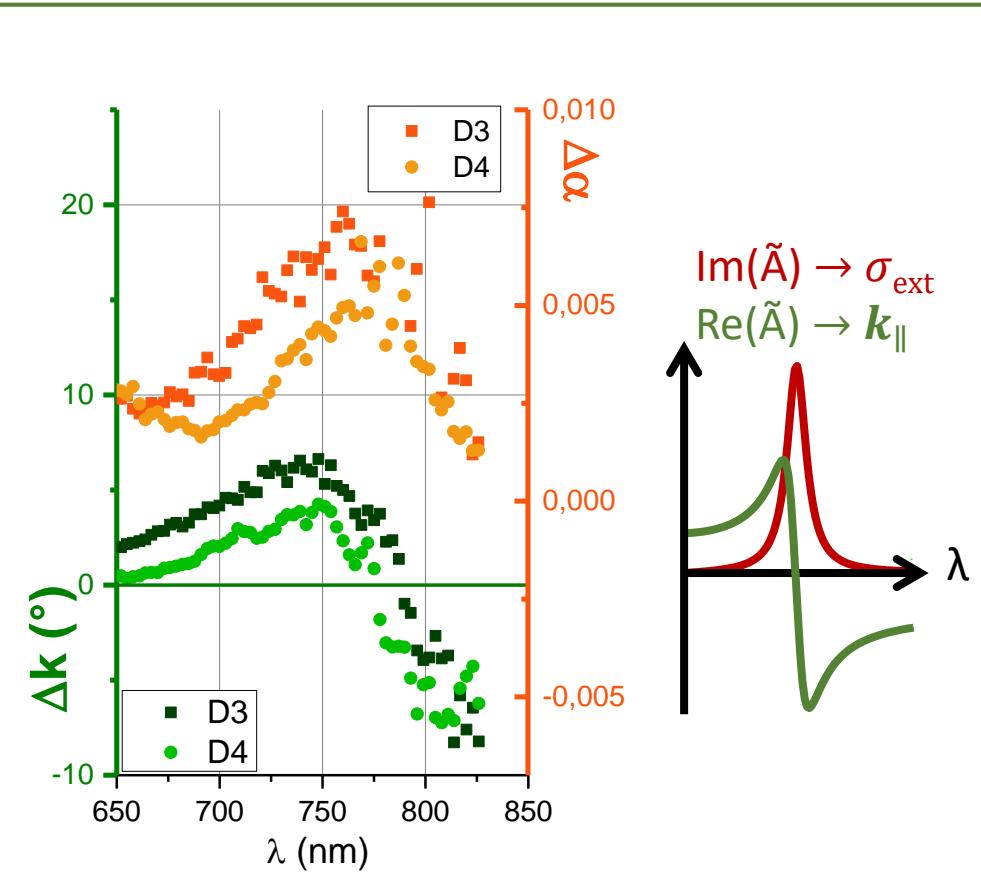
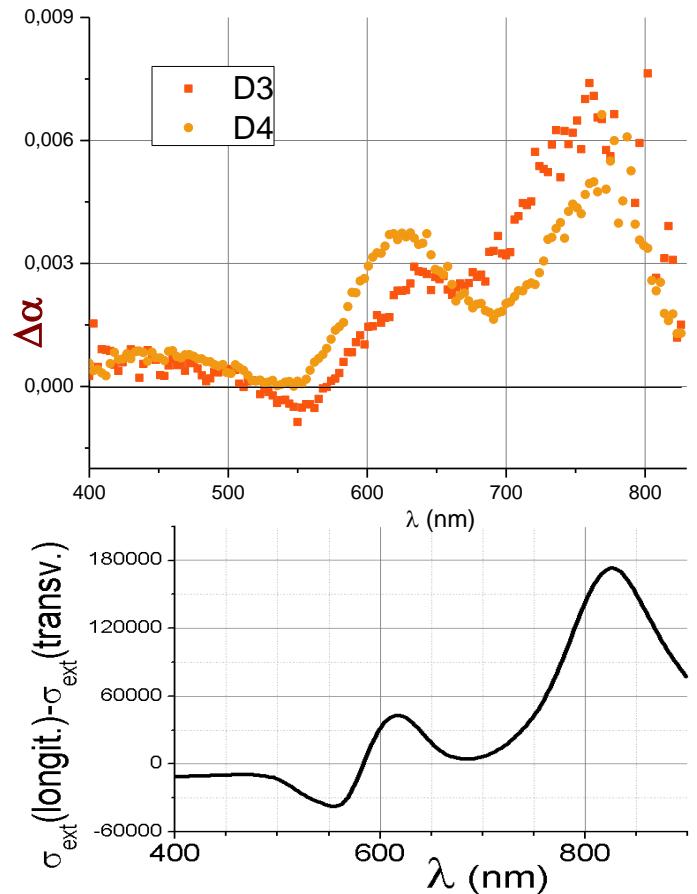
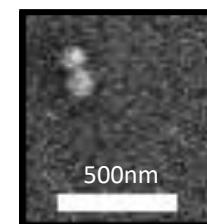
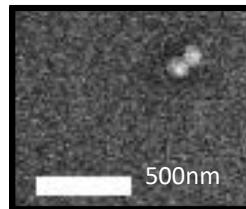


- $\Delta k = k_{||} - k_{\perp}$  : phase modification



# Linear anisotropy

$\Delta\alpha$  &  $\Delta k$



information about the phase from the intensity

- good agreement with theoretical predictions
- validation of the double modulation technique

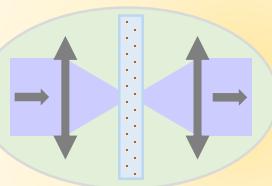
Linear anisotropy

Chiral assembly

Individual chiral object

## CHIRALITY

### Chiral molecules in polymers



Detection of  
CD up to  $10^{-4}$

### Chiral nanostructures

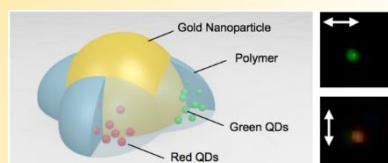


assembly

single



### Coupling chiral molecules + plasmonic NP



Zhou et al., *Nano Lett.* (2015),  
15, 11, 7458-7466

Collab. L2n



## Chiral objects : Gammadiions



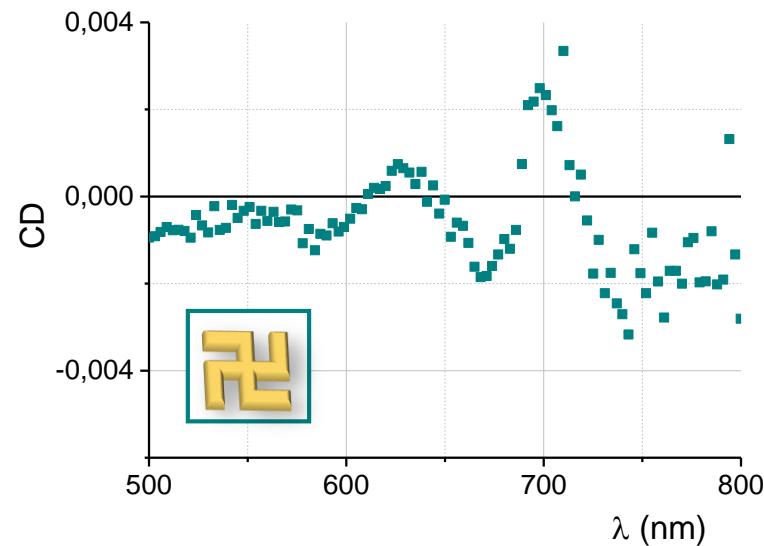
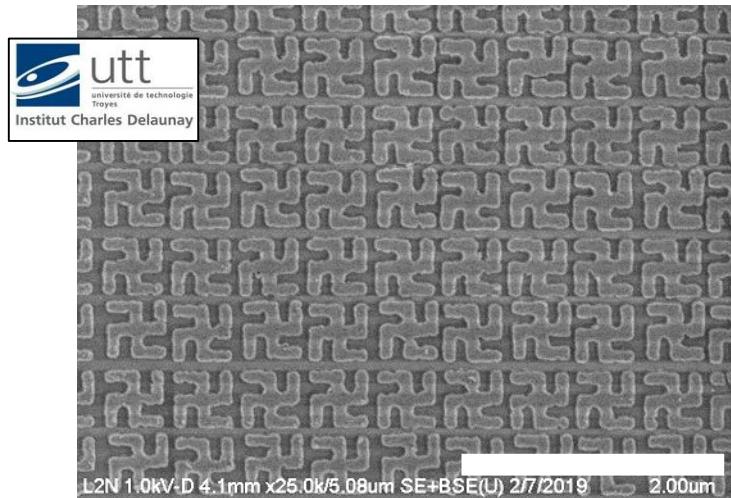
Kuwata-Gonokami et al., *PRL* (2005), 95, 227401

Hendry et al., *Nature Nanotech.* (2010), 5, 11, 783

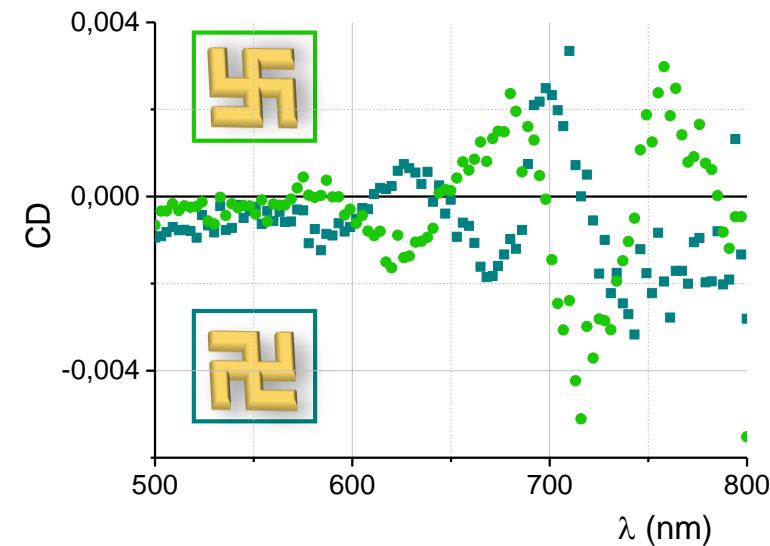
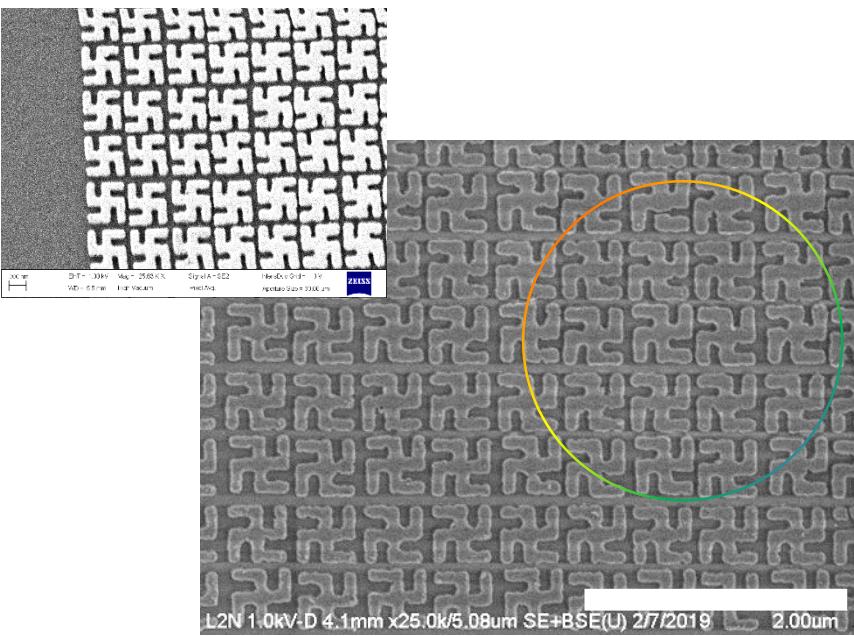
Arteaga et al., *OE* (2016), 24, 3, 2242

Garcia-Guirado et al., *Nano Lett.* (2018), 18, 6279-6285

Lithographied lattice of gold gammadiions

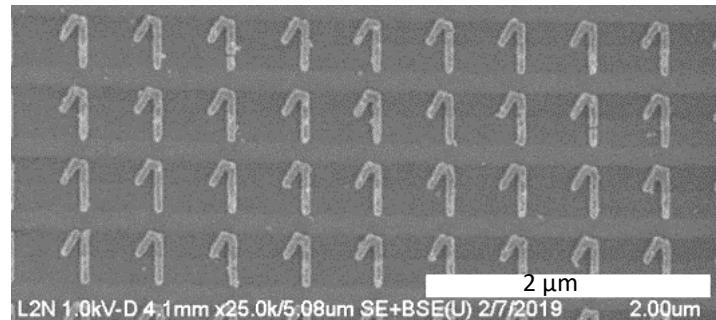
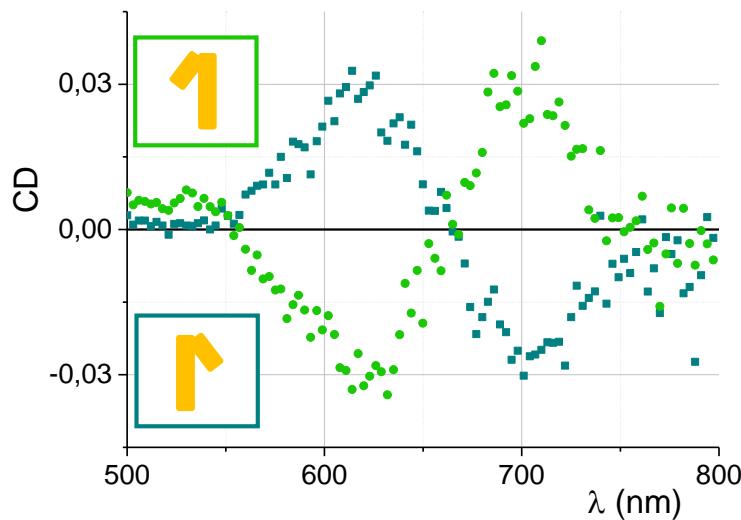


## Chiral objects : Gammadiions



- Good mirroring of the structures
- CD of a few gammadiions

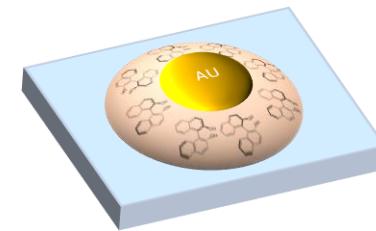
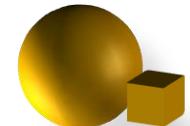
## Chiral objects : « One »



- CD spectrum of a few structures
- Mirroring effects observed
- Further investigations required to interpret the spectra

# Conclusion & perspectives

- Demonstration of a new technique to probe individual anisotropic NPs
  - Chiro plasmonic lattices and finite element method simulations
- Circular dichroism of various single nano-objects
  - Investigation of the coupling between a single NP and chiral molecules



## Team « Clusters & Nanostructures »

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M.-A. Lebeault (co-supervisor)  
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J. Lermé          M. Broyer  
S. Hermelin      M. Hillenkamp



C. Moulin



**Thank you for  
your attention !**