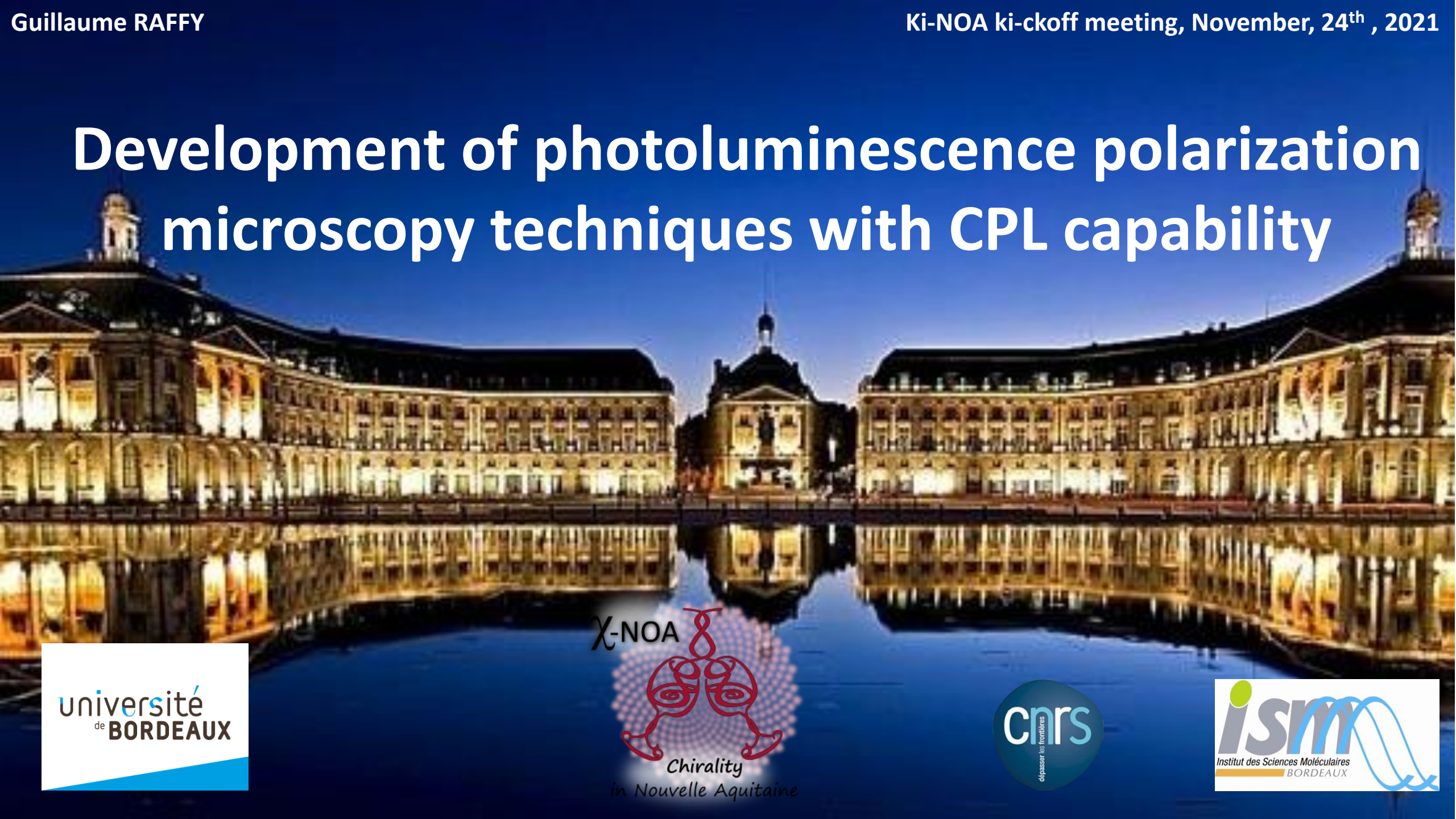
Development of photoluminescence polarization microscopy techniques with CPL capability

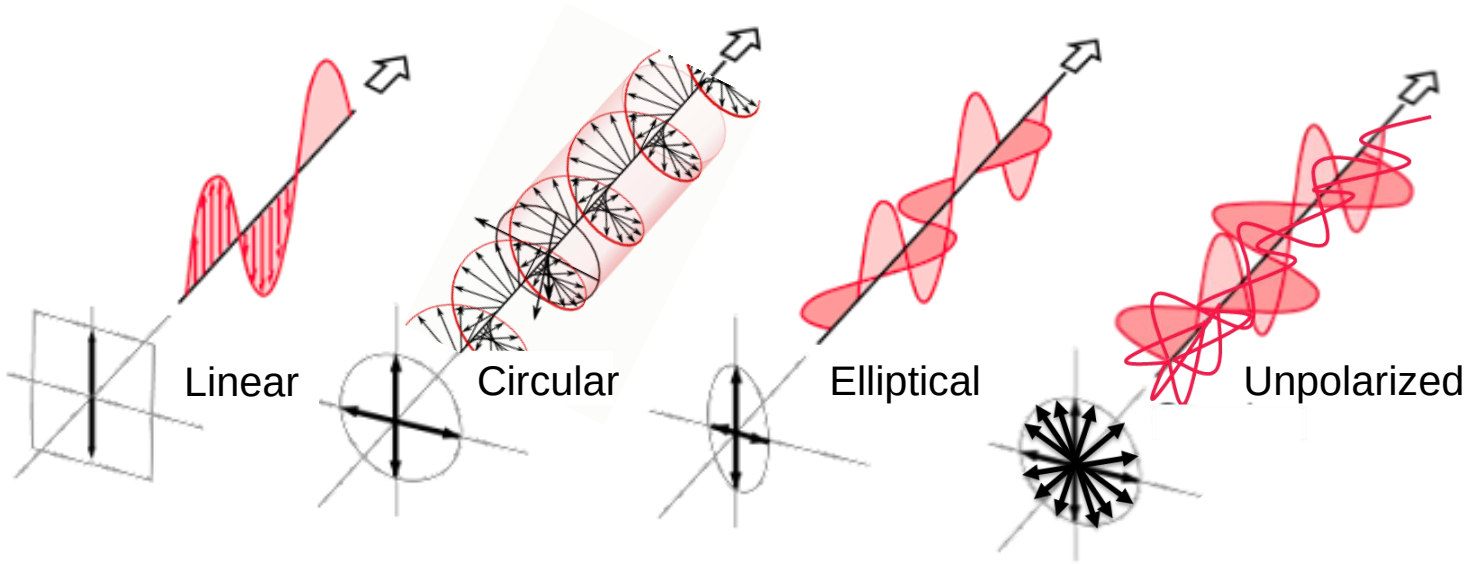


χ-NOA

Chirality in Nouvelle Aquitaine

Information Carried by Polarization

R. Nave, Hyperphysics



Molecular order :

Orientational information

Chirality information

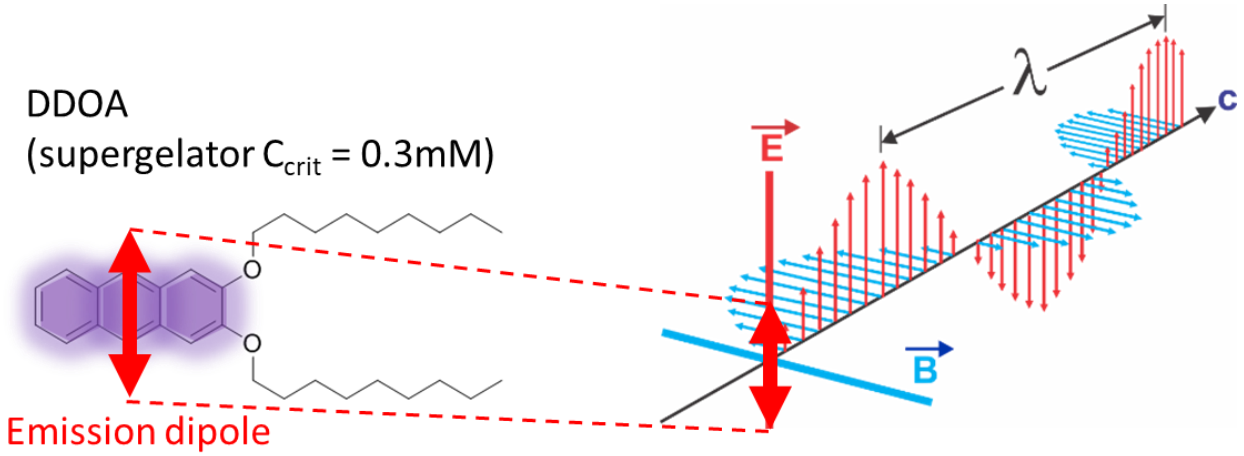
Lots of information

Molecular disorder
or
Information loss (depolarization)
or
Too much information (unresolved)

LPL vs CPL

Non chiral organic compounds

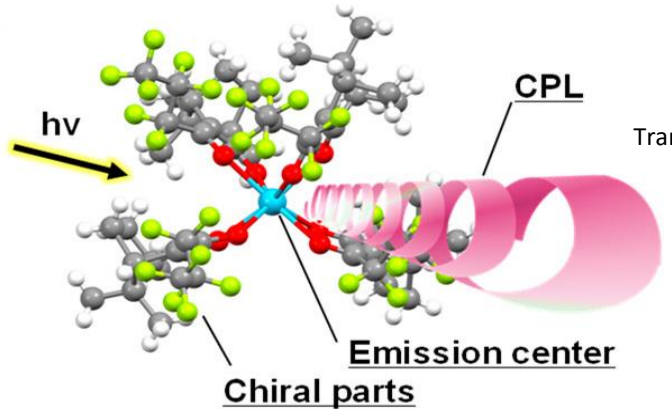
Linear polarization emitters



- Structural information (Molecular order)
- Molecular packing in self –assembly
- Molecular dynamics (anisotropy decay)
- Single molecule/emitter Orientation

Chiral molecule / molecule in chiral environment

Europium complexes : highest molecular CPL emitters



Transition magnetic dipole moment

4f-4f transition

✓ Sharp emission (FWHM < 10 nm)

✓ Effective CPL

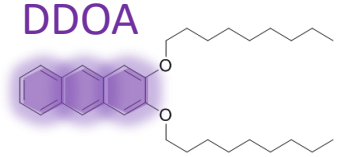
Kitagawa et al., ACS Omega 2020, 5, 8, 3786–3791

- Excited state local chirality
- Chiral induction
  (non chiral chromophores in a chiral nanostructure)

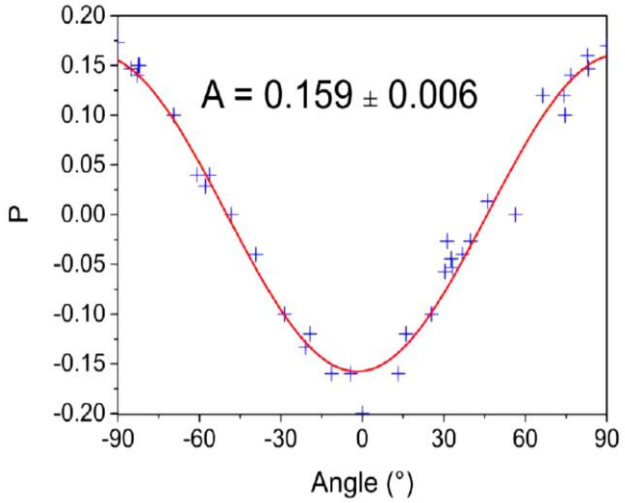
Linear polarization

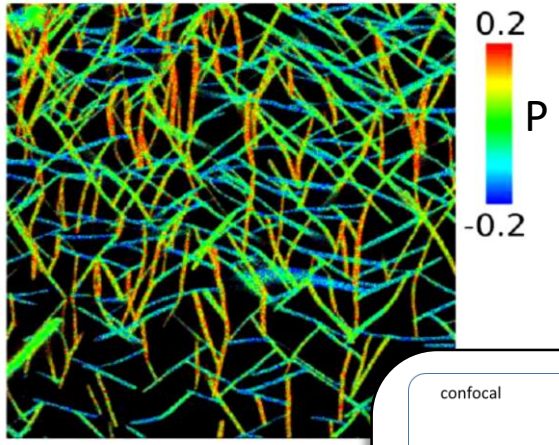
Linear Polarization : Gel fibers vs Crystalline Nano-Ribbons

DDOA

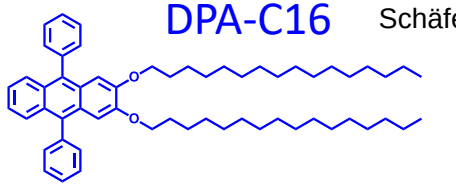


De VET et al., *Small* 2020, 16, 1906723

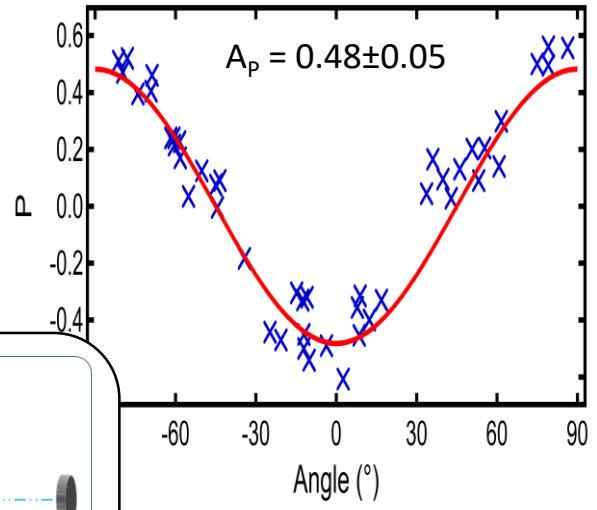


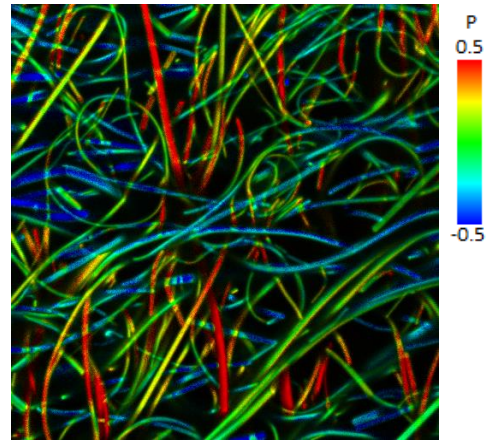


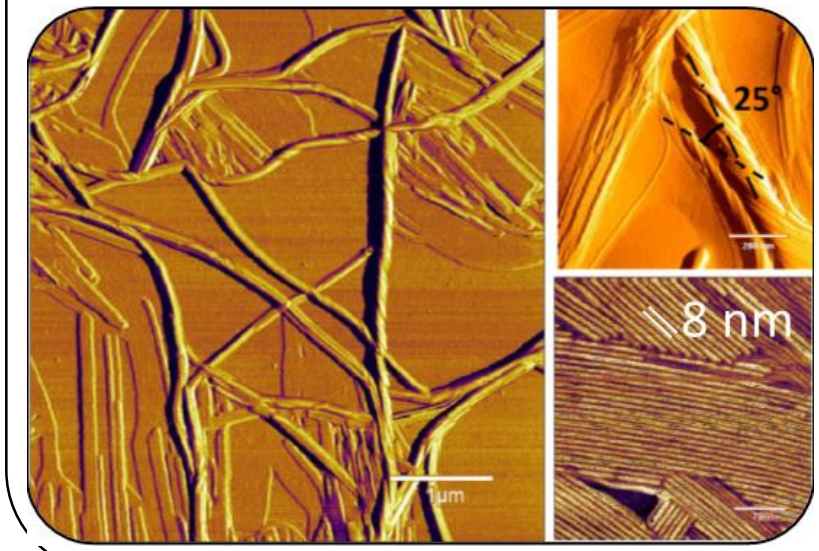
DPA-C16

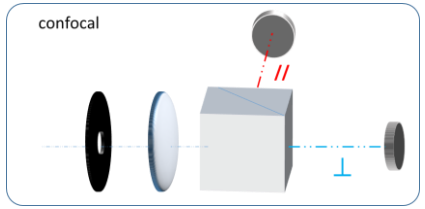


Schäfer et al., *J.Mater.Chem.C*, 2021, **9**, 136-147

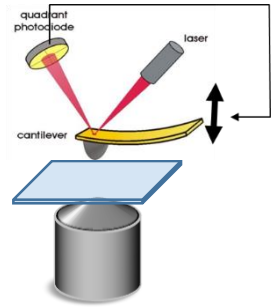


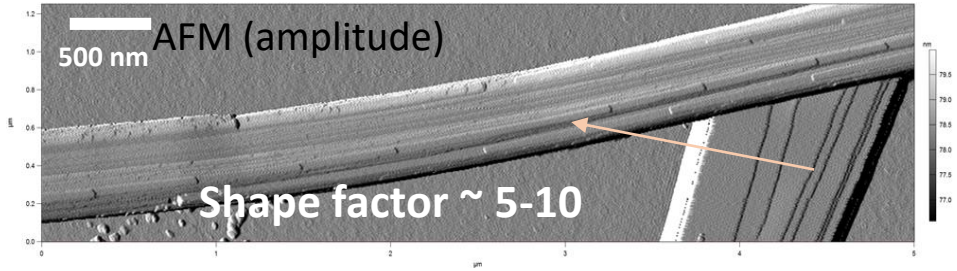


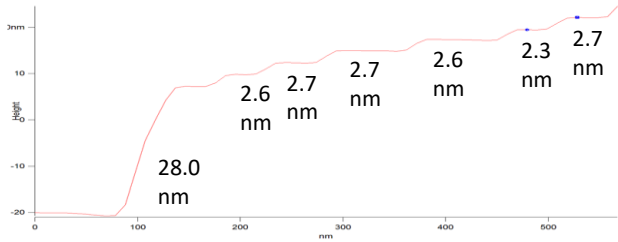




$$P_{emission} = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

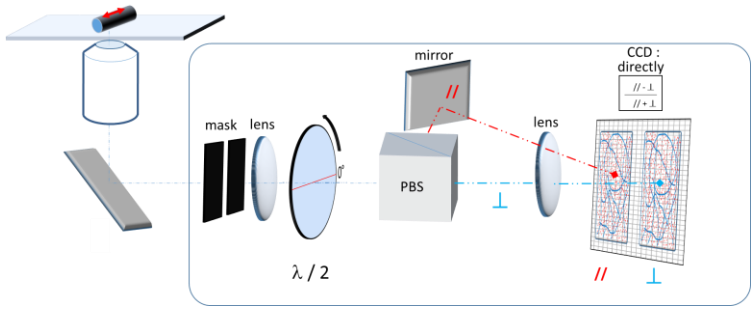


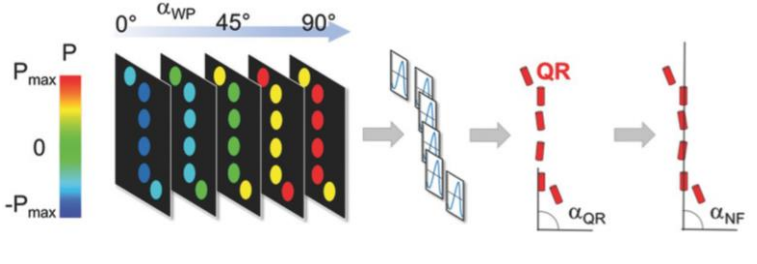


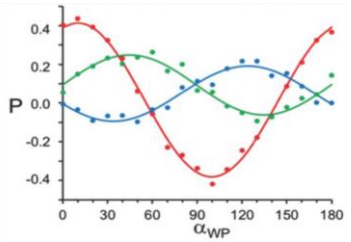


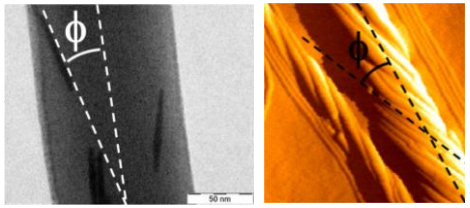
QROM of a hybrid gel (individual QRs on fibers)

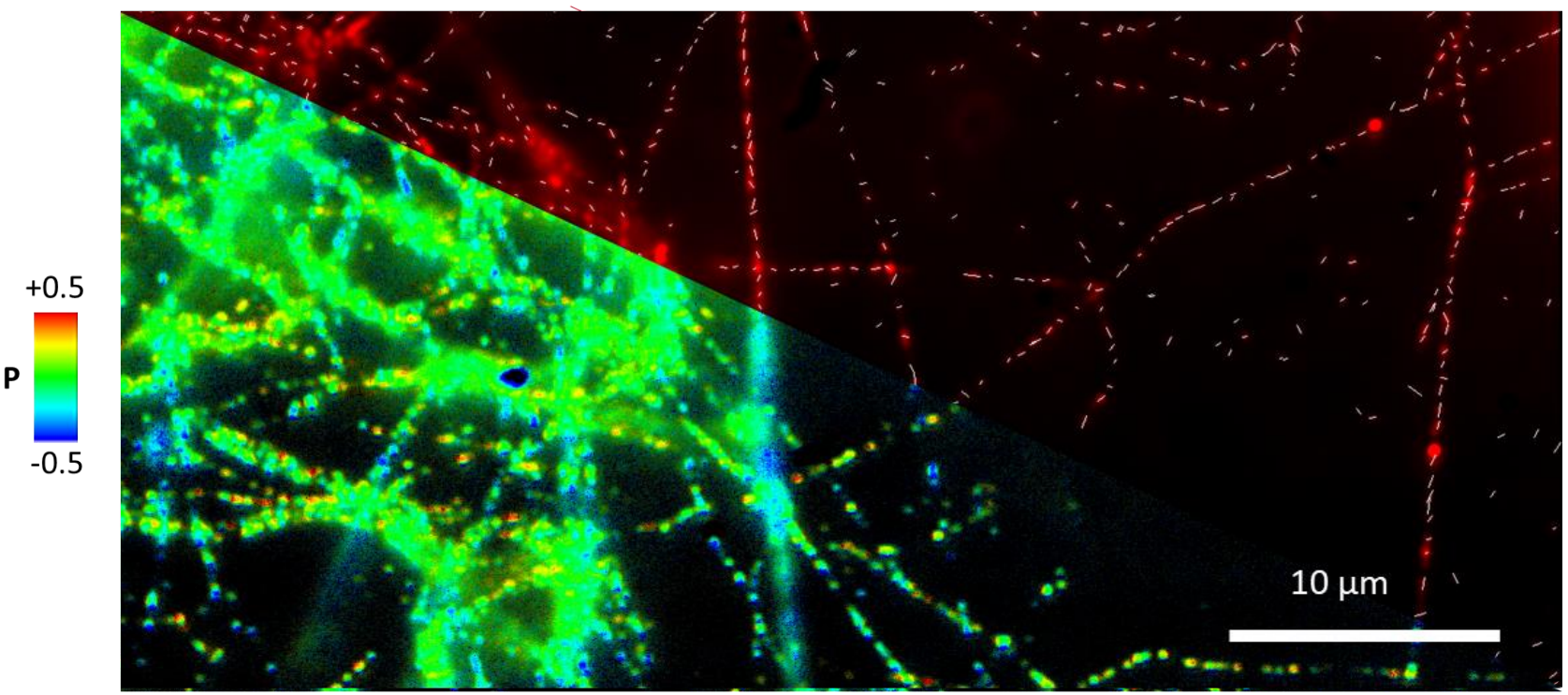
Small **2018**, 1802311

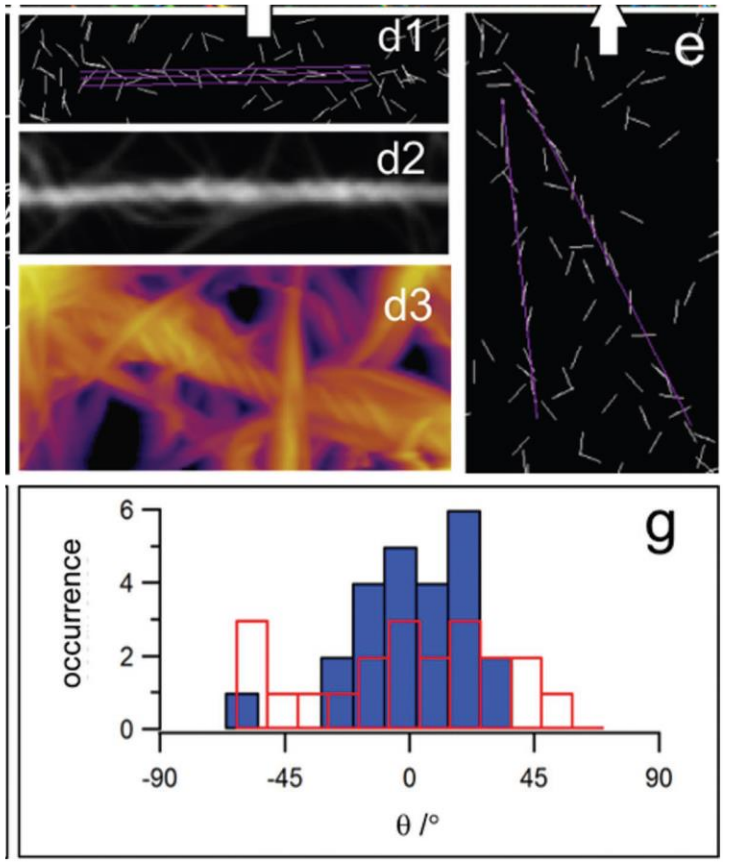






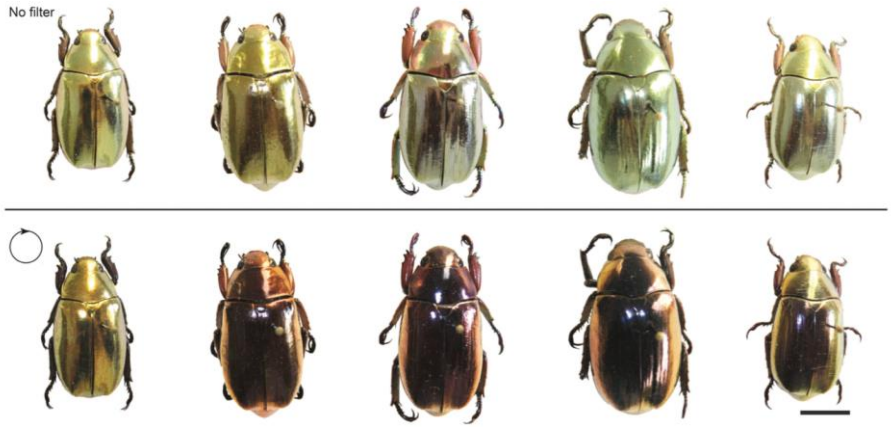


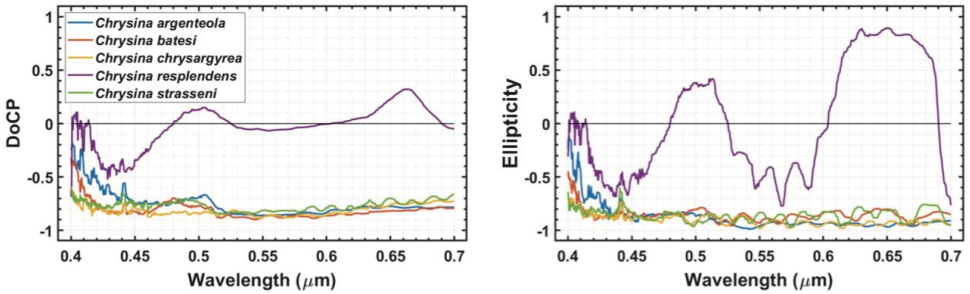




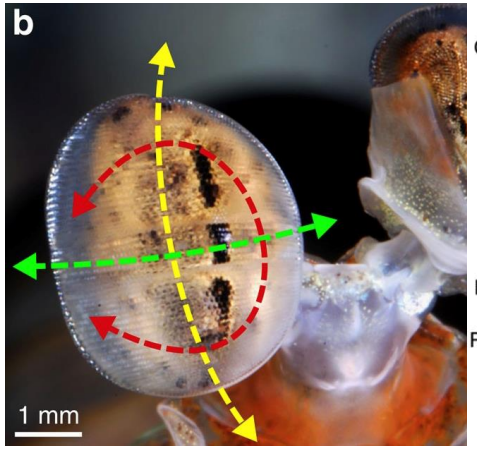
Circular Polarization

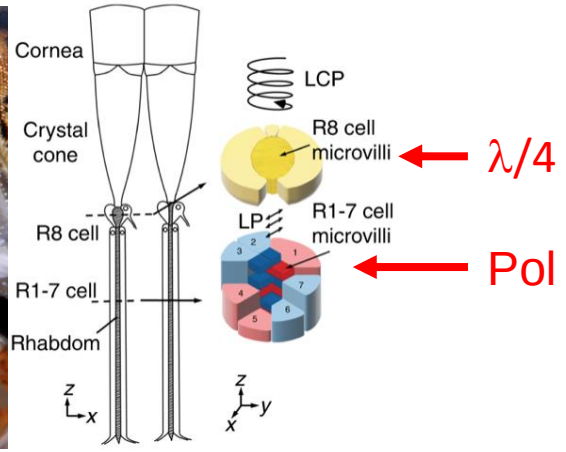
Circular Polarization in Nature





Appl. Opt., 59, F85 (2020)





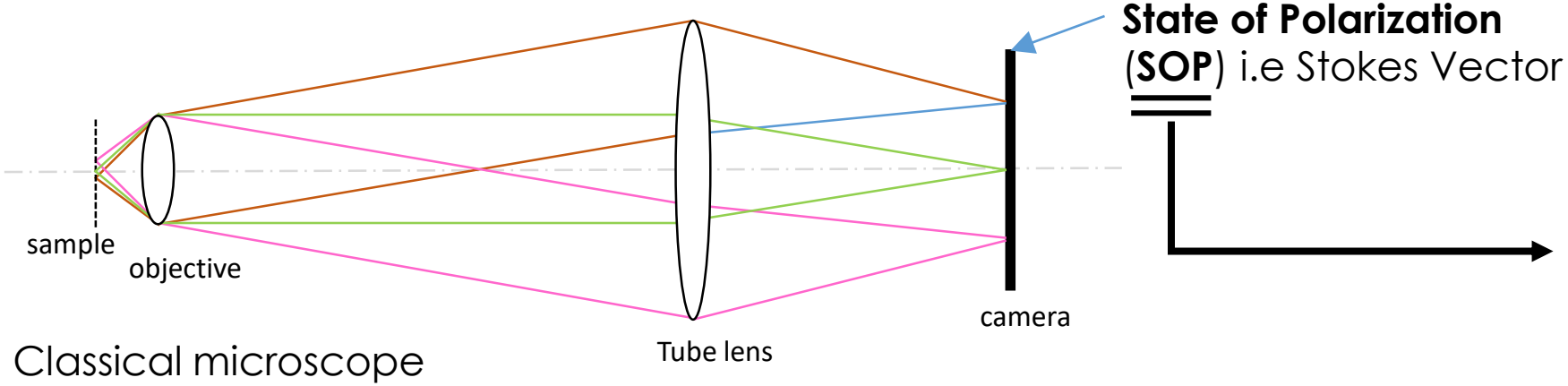
Daly et al., Nat Commun **7,** 12140 (2016)

Basiri et al., *Light: Science & Applications* **8**:78 (2019)

Challenges in CPL Microscopy

- Typical glum is small (0.001) for common organic chromophores
- High NA objectives collect longitudinal electric field (E_z) component
- Sensitive to small optical aberrations and residual birefringence in optics
- Correction matrices will be wavelength- and position- dependent
- Strong **L**inear**PL** can be misinterpreted as **C**ircular**PL** :

CPL microscope–➔ Complete Polarimetry* microscope

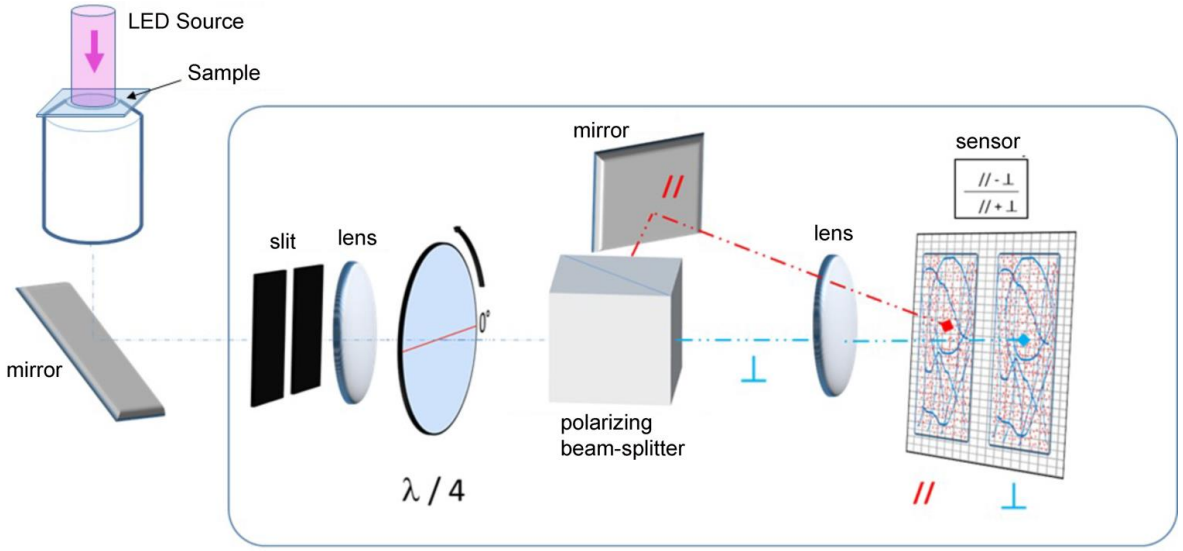


*Measuring here the **State of Polarization** (**SOP**) i.e Stokes Vector

Derivable values from SV :

DOP : *degree of polarization*
DOLP : *degree of linear polarization*
DOCP : *degree of circular polarization*
Azimuth : *orientation of linear component*
Ellipticity : *ratio of major/minor axes of ellipse*
g_{lum} : *dissymmetry factor of CPL*

Stokes Vector polarimetry

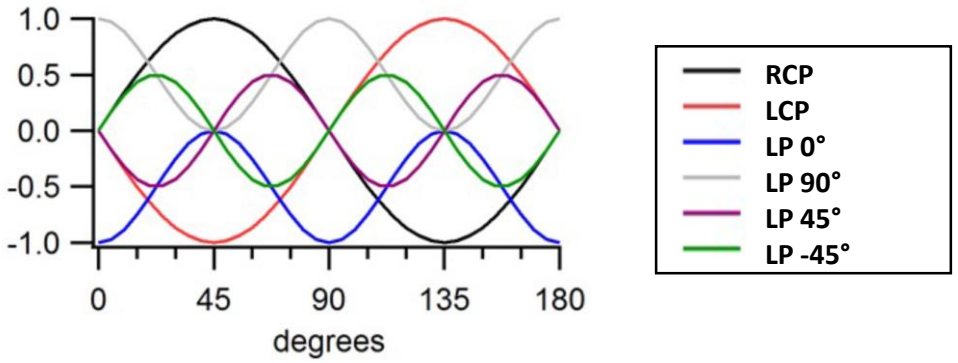


Complete Stokes vector

$$\begin{pmatrix} s_0 \\ s_1 \\ s_2 \\ s_3 \end{pmatrix} = \begin{pmatrix} I_{total} \\ I_H - I_V \\ I_{45°} - I_{135°} \\ I_{left} - I_{right} \end{pmatrix}$$

CPL only

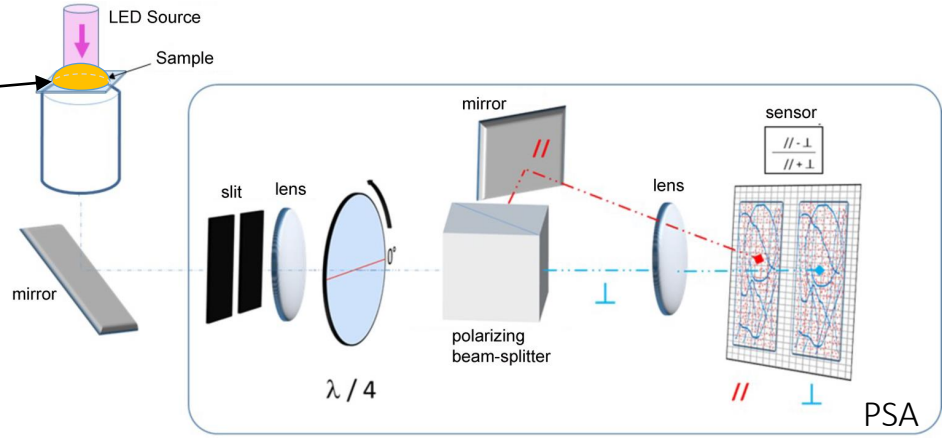
$$g_{lum} = 2 \cdot \frac{I_{left} - I_{right}}{I_{left} + I_{right}} = 2\frac{s_3}{s_0}$$



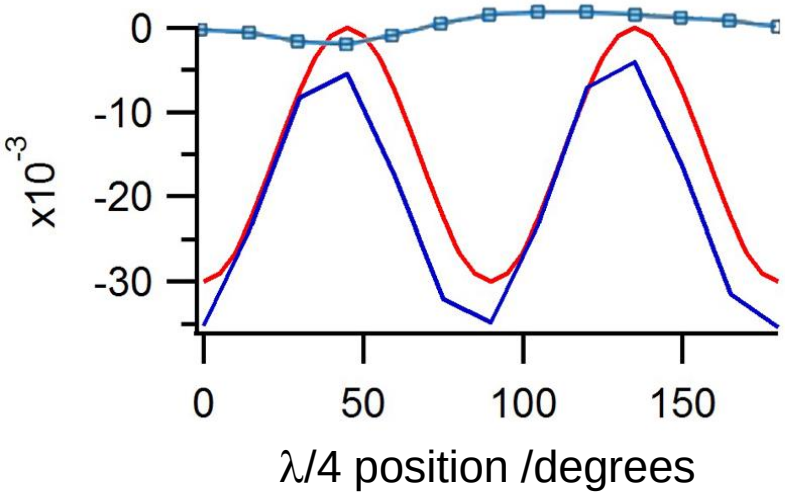
Polarimetry on reference samples

1st Control experiment : **Unpolarized reference sample**:

Unpolarized emission:
Non-chiral chromophore in solution under unpolarized excitation



Raw data modulation



If aluminum mirror is used

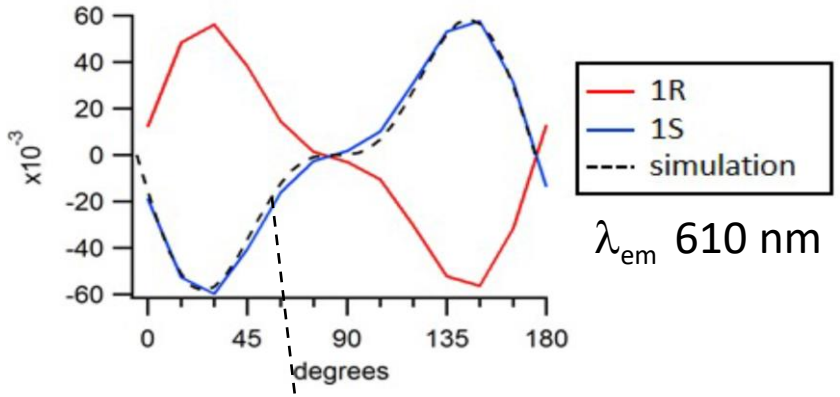
If dichroic mirror is used

Simulation with :

- **DOLP = 0.03**
- Orientation = 0°

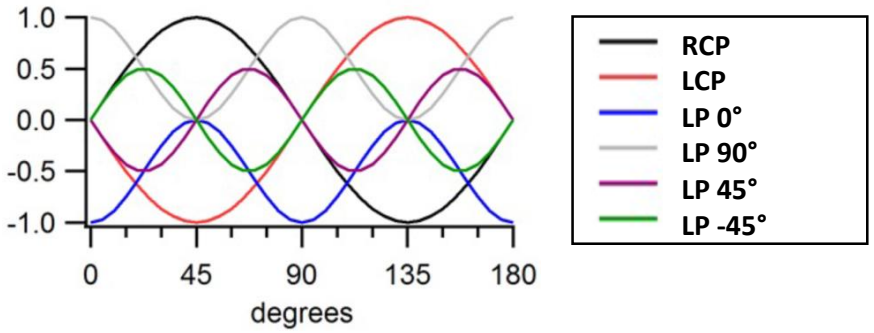
Polarimetry on reference samples

2nd Control experiment : **High CPL reference sample**:

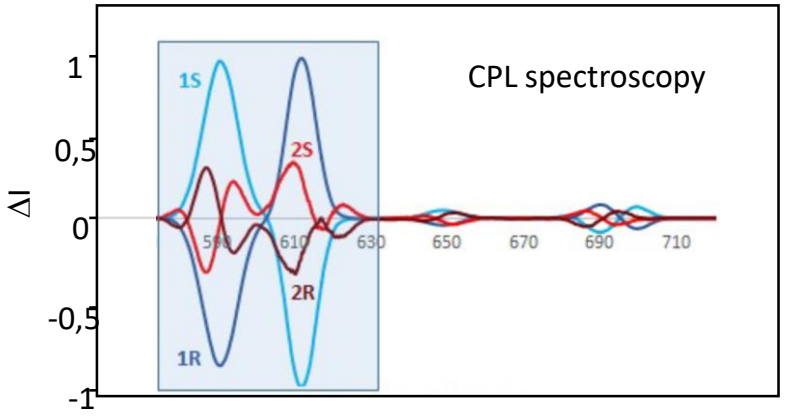


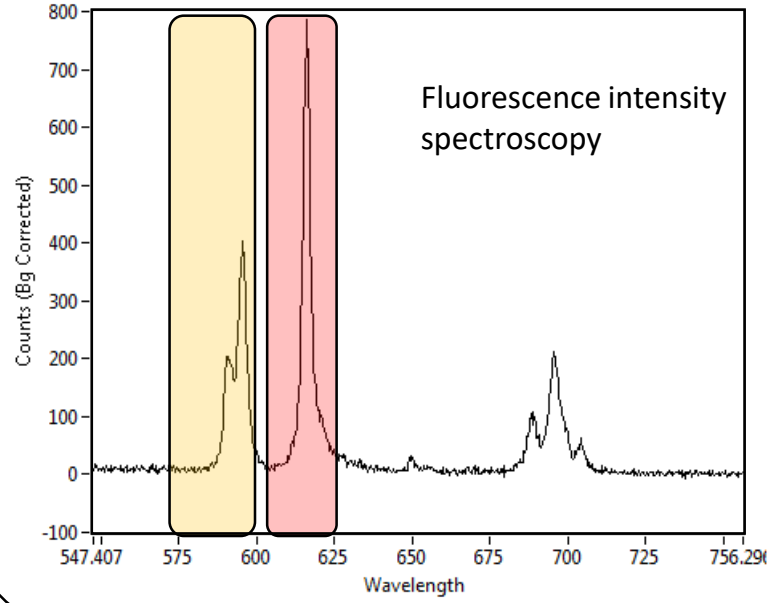
λ_{em} 610 nm

$$\begin{pmatrix} s_0 \\ s_1 \\ s_2 \\ s_3 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0.045 \\ 0.045 \end{pmatrix} \rightarrow \text{LPL} \quad \rightarrow \text{CPL}$$

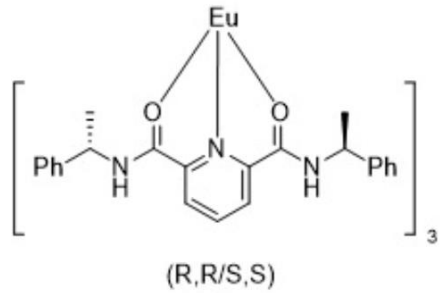


N,N'-bis(1- phenylethyl)-2,6-pyridinedicarboxamide





glum ~0.2

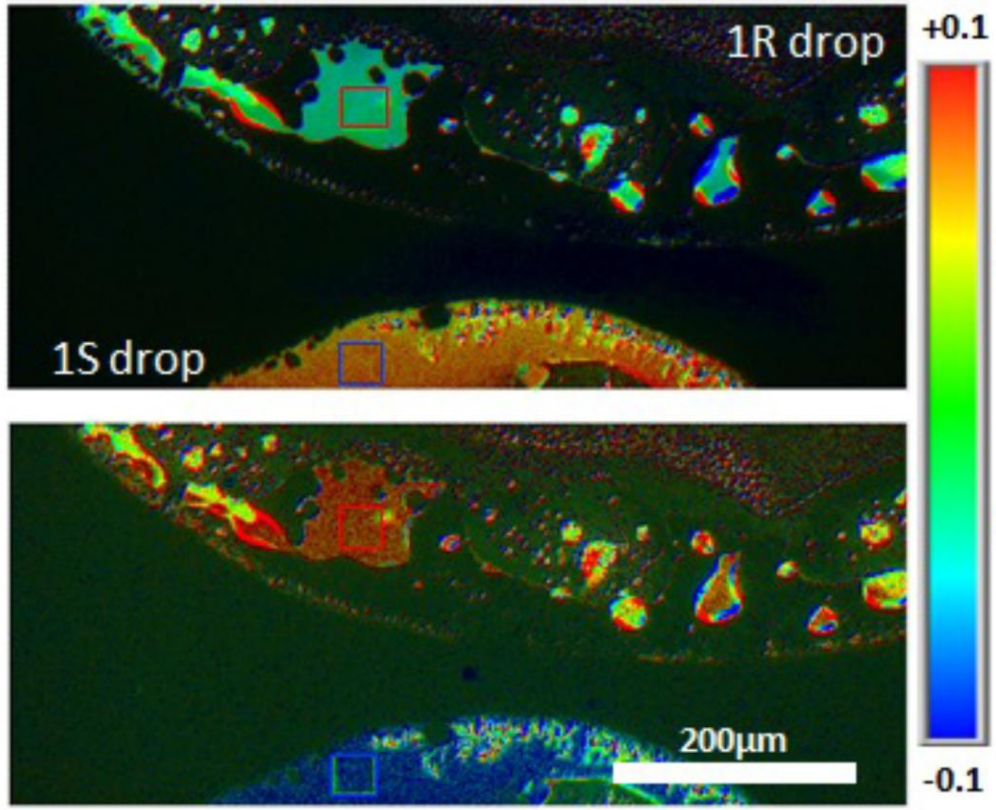


(R,R/S,S)

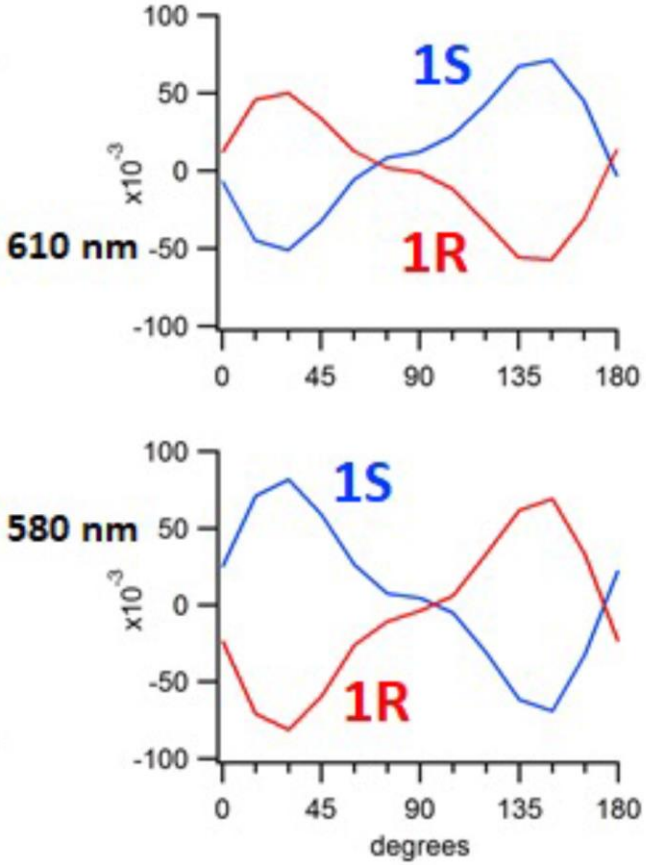
Chem. Commun., 2007, 3676–3678

Preliminary Results

Dissymmetry factor map (g_{lum}) Low NA 10x



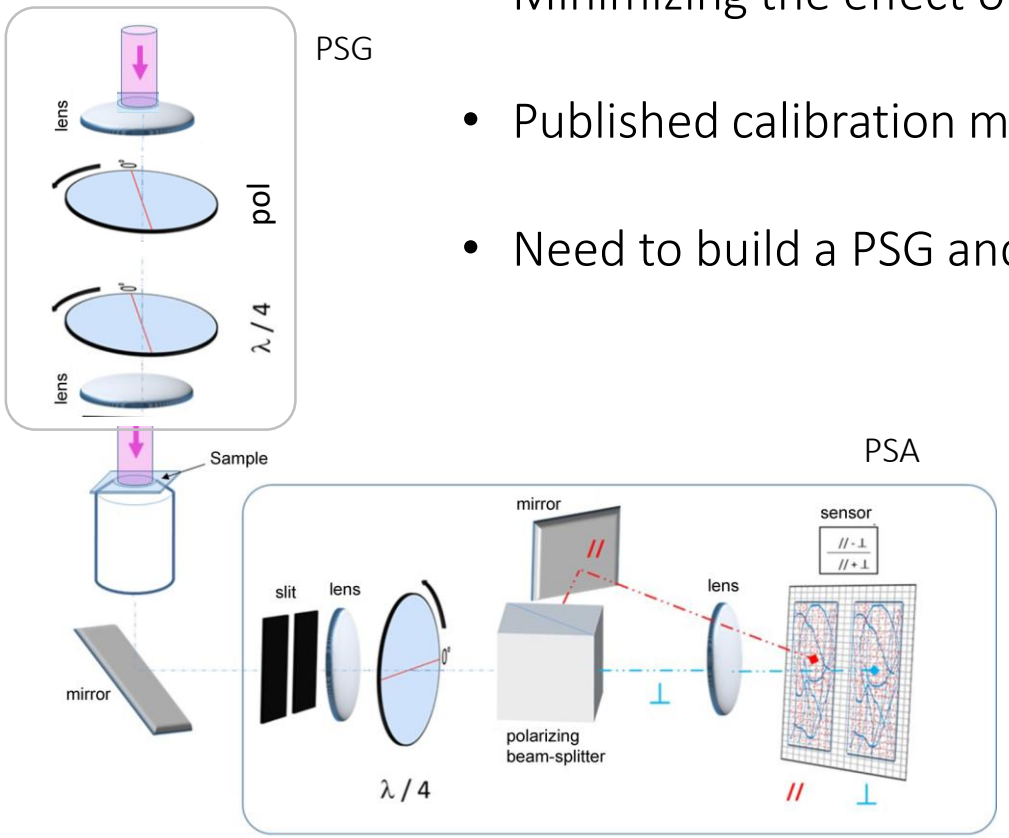
Raw measurements (iv-ih/iv+ih)



Data are mirror images both between enantiomers and between spectral bands of opposite chirality

perspectives

- Full Müller matrix calibration necessary to reach g_{lum} ~10^{-3}
- Minimizing the effect of optics on polarization (dichroic)
- Published calibration methods exist (Eigenvalue Calibration Method)
- Need to build a PSG and adapt the ECM method



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FEDER