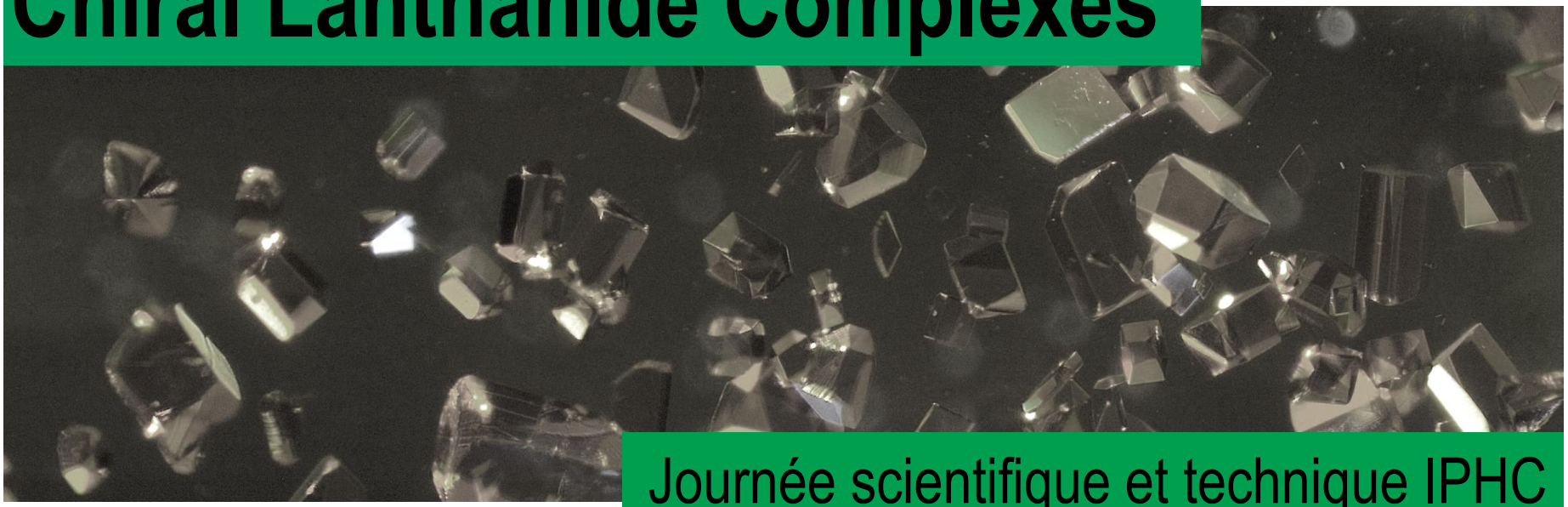
Luminescence of Chiral Lanthanide Complexes

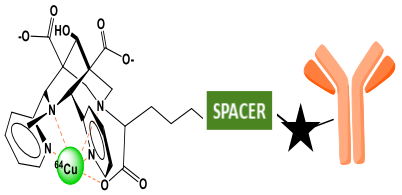


Journée scientifique et technique IPHC

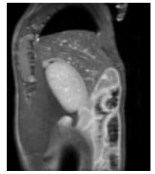
Annika Sickinger
DSA, SynPA team

Synthèse pour l'Analyse (SynPA) Team

Coordination complexes for medical imaging

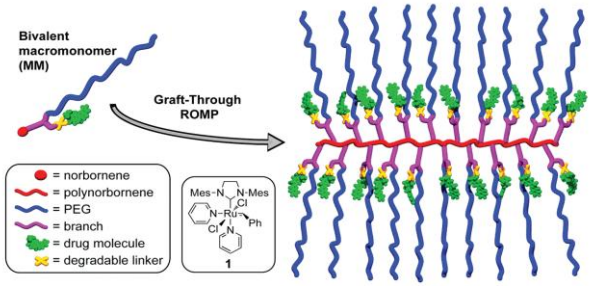


PET radiotracors

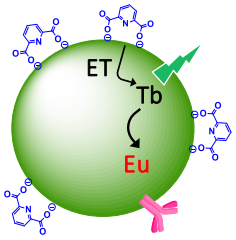


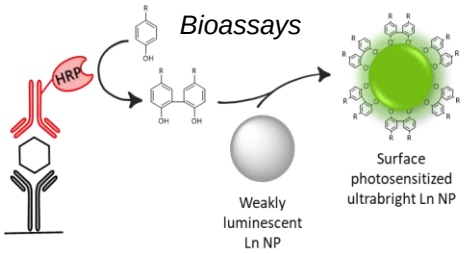
Mn-based MRI contrast agents

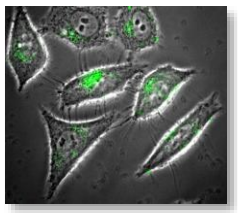
Nanocarriers for drug delivery



Hybrid Lanthanide-Nanoparticles for bioanalytical applications

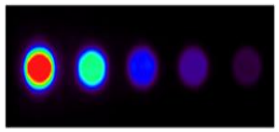




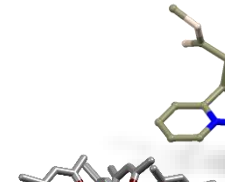


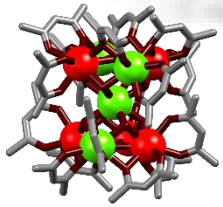
Microscoy

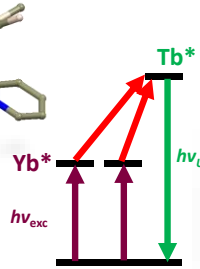
PET and MRI imaging



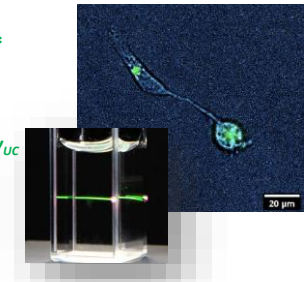
Luminescent lanthanide (Ln) complexes



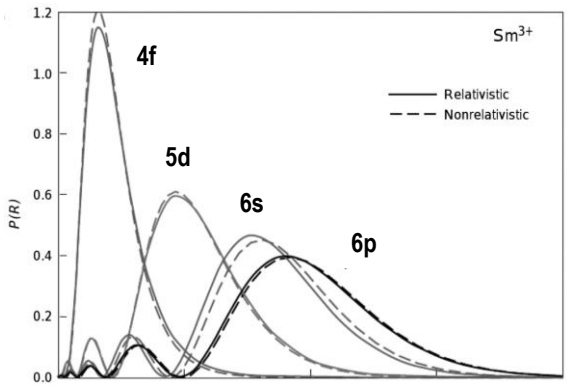




Upconversion



Ln(III) Complexes

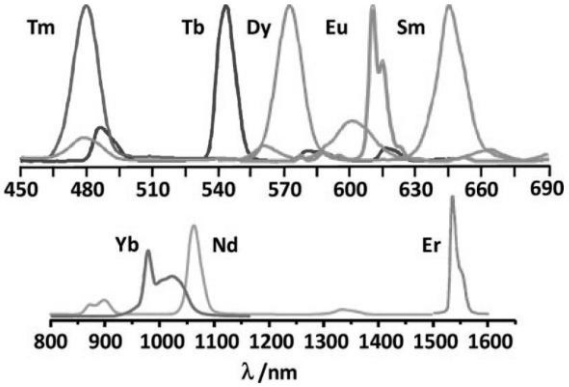


Radial probability distribution

Properties of Ln(III) *f-f* transitions

- Long Excited State Lifetime
- Ladder-like Energy Diagram
- Narrow Emission Lines
- Pronounced MD Nature

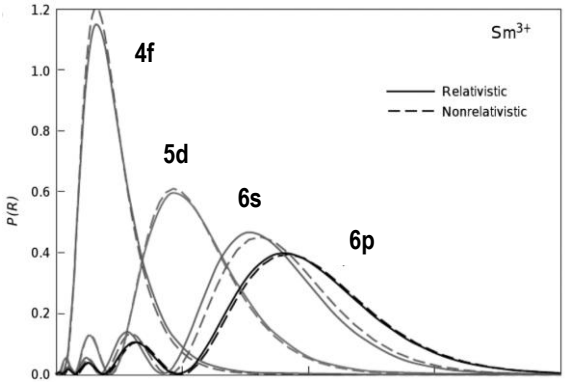
Emission spectra



Lanthanide Complexes

Eur. J. Inorg. Chem. **2005,** 1425. *Chem. Rev.* **2010,** *110,* 2729. *Los Alamos Sci.* **2000,** 26**.** *Eur. J. Inorg. Chem.* **2009,** 4357-4371.

Ln(III) Complexes



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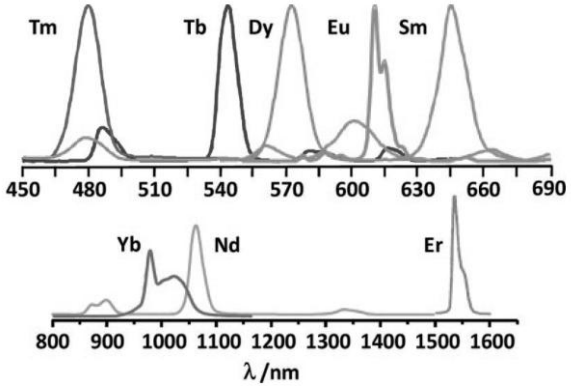
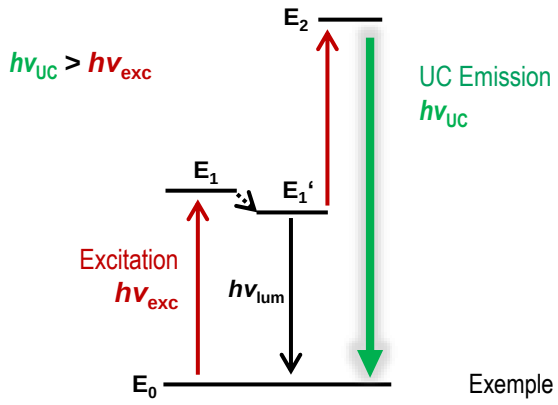


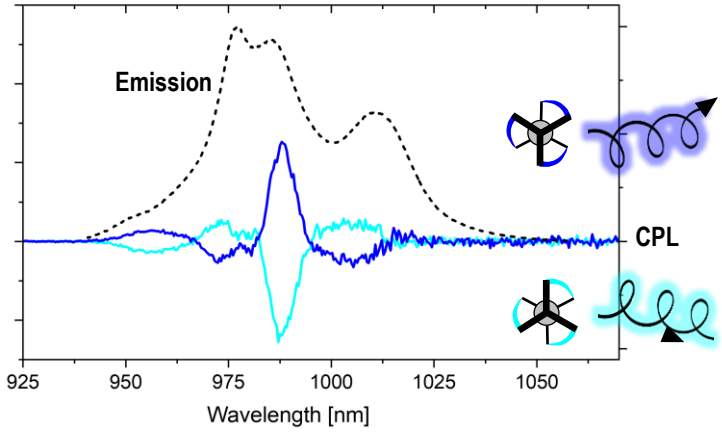
Lanthanide Complexes

Upconversion Emission



Exemple of ESA mechanism.

Circularly Polarized Luminescence



Eur. J. Inorg. Chem. **2005,** 1425. *Chem. Rev.* **2010,** *110,* 2729. *Los Alamos Sci.* **2000,** 26. *Eur. J. Inorg. Chem.* **2009,** 4357-4371.

Circularly Polarized Luminescence (CPL)

→ Ability of chiral systems to rotate the plane of polarized light 

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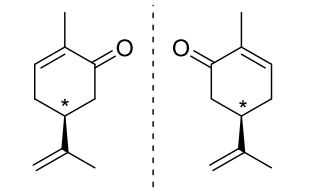
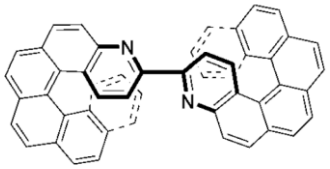
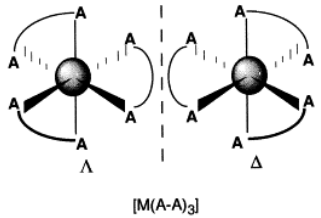
→ Quantification by dimensionless disymmetry factor (max. ± 2)

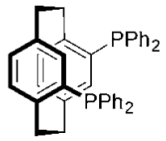
$$g_{lum} = \frac{2(I_L - I_R)}{(I_L + I_R)}$$

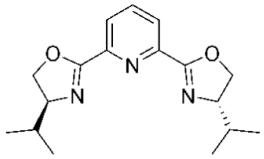


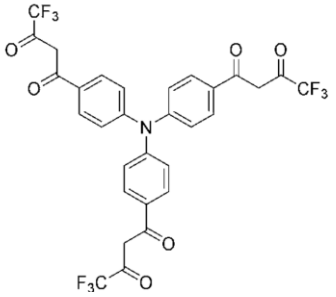


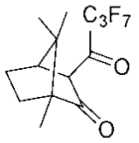


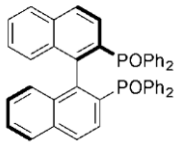
Established ligand systems for chiral complexes:











Nat. Commun. **2023**, *14*, 1065. *Chem. Rev.* **1986**, *86*, 1. *Space Sci. Rev.* **2008**, *135, 187. Front. Chem.* **2020**, *8*, 1-27.

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$$g_{lum} = \frac{2(I_L - I_R)}{(I_L + I_R)}$$

And why Ln^{3+} ??

→ Alternative description of g_{lum} for transition $i \longrightarrow j$

$$g_{lum} = \frac{4\,R_{ij}}{|D_{ij}|}$$

→ CPL amplitude of transition $i \longrightarrow j$ is governed by **rotary strength**

$$R_{ij} = |\mu_{ij}| \cdot |m_{ij}| \cos\theta$$

electric transition dipole moment (ED)

angle between vectors

magnetic transition dipole moment (MD)

→ Normalization by global emission, ruled by overall **transition oscillator strength**

$$D_{ij} = |\mu_{ij}|^2 \cdot |m_{ij}|^2$$

Nat. Commun. **2023**, *14*, 1065. *Chem. Rev.* **1986**, *86*, 1. *Space Sci. Rev.* **2008**, *135, 187. Front. Chem.* **2020**, *8*, 1-27.

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$$g_{lum} = \frac{4\,R_{ij}}{|D_{ij}|} = \frac{4\,|\mu_{ij}|\cdot|m_{ij}|\cos\theta}{|\mu_{ij}|^2 + |m_{ij}|^2}$$

Ideal for high g_{lum}: $|\mu_{ij}| \approx |m_{ij}|$

→ CPL amplitude of transition $i \longrightarrow j$ is governed by **rotary strength** $R_{ij} = |\mu_{ij}|\cdot|m_{ij}|\cos\theta$

→ Normalization by global emission, ruled by overall **transition oscillator strength** $D_{ij} = |\mu_{ij}|^2\cdot|m_{ij}|^2$

mostly: $|\mu_{ij}| >> |m_{ij}|$

Nat. Commun. **2023**, *14*, 1065. *Chem. Rev.* **1986**, *86*, 1. *Space Sci. Rev.* **2008**, *135, 187. Front. Chem.* **2020**, *8*, 1-27.

CPL of Eu^{3+} Complexes

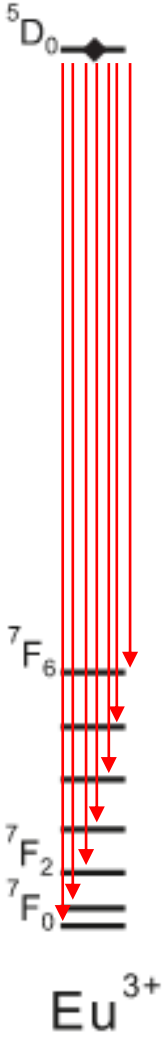
Energy diagram of Ln ions with spectroscopic levels.

Eu^{3+}: $^5D_0 \rightarrow {}^7F_J$

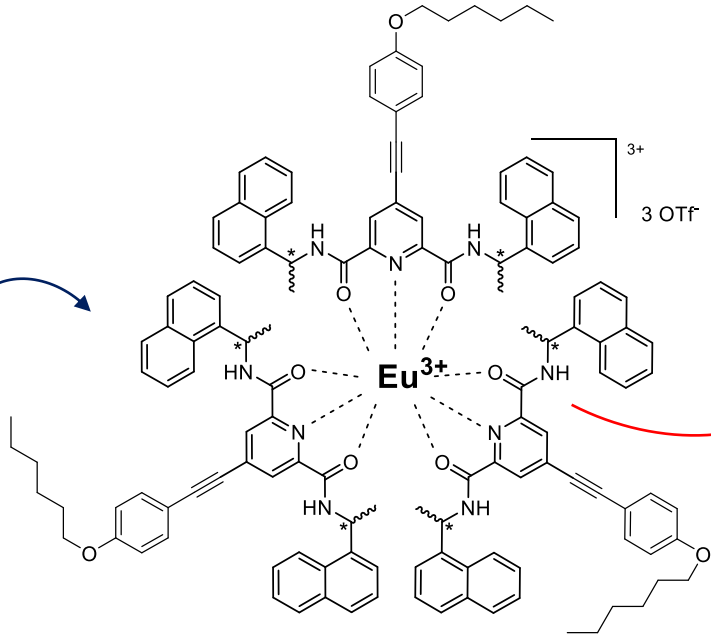
Methods Appl. Fluoresc. **2014**, *2*, 012001. *Front. Chem.* **2020**, *8*, 1-27.

CPL of Eu^{3+} Complexes

Eu^{3+}: $^5D_0 \rightarrow {}^7F_J$ (J =0-6)

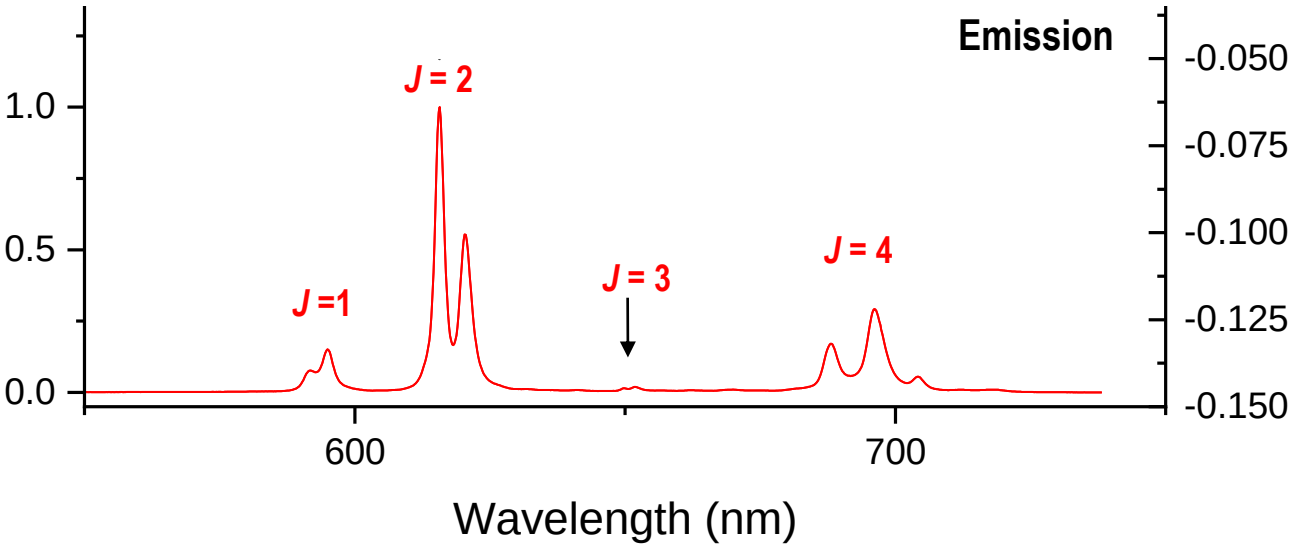


Excitation of Antenna, Sensitization of Ln(III)



Ln(III) emission

9-Coordinate dipicolinate complexes



Inorg. Chem. Front., **2021**, *8*, 914.

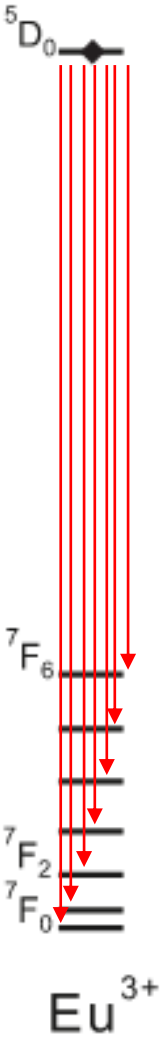
CPL of Eu^{3+} Complexes

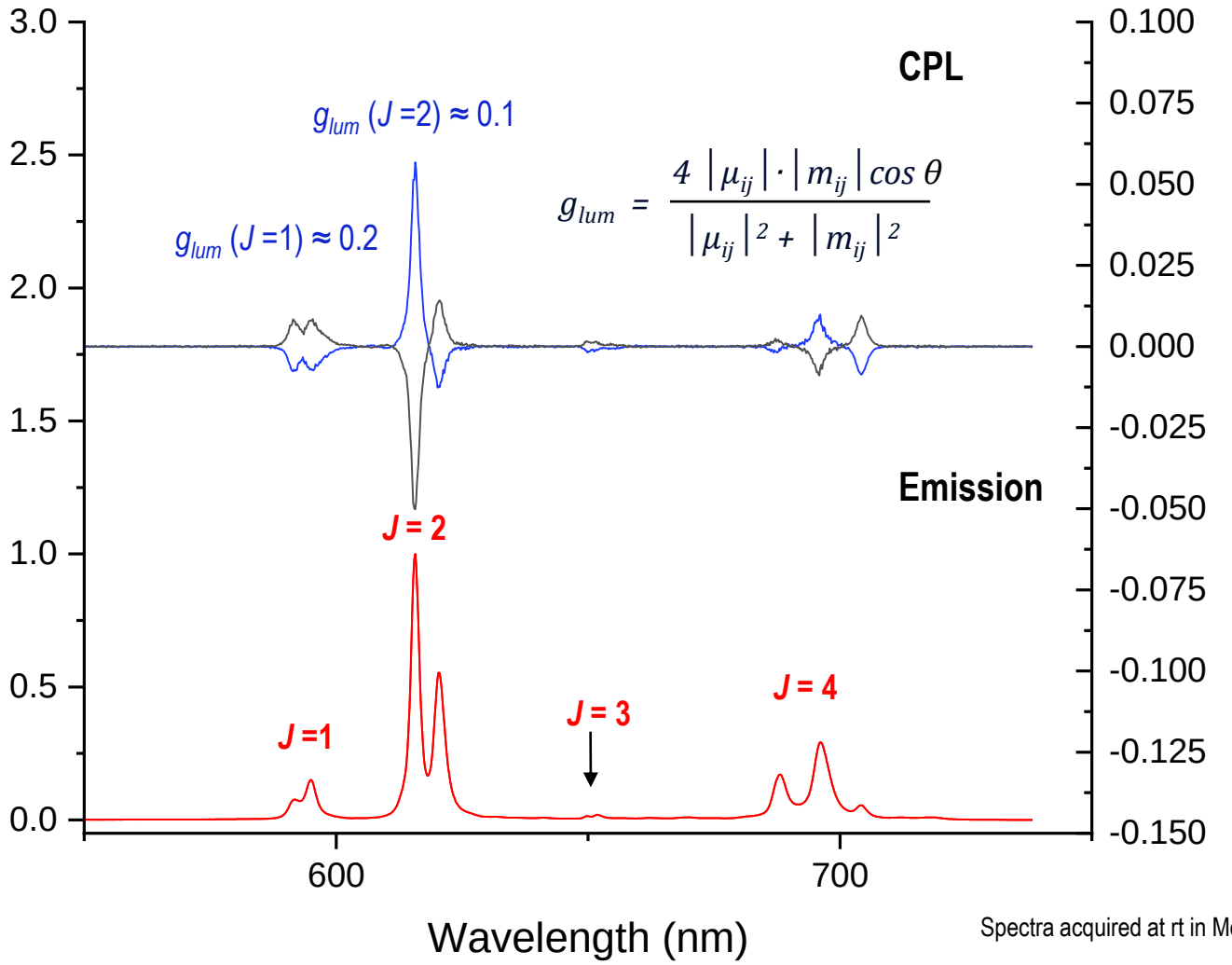
Eu^{3+}: $^5D_0 \rightarrow {}^7F_J$ (J =0-6)

***f-f* transitions**

ED transitions forbidden by Laporte's rule → low $|\mu_{ij}|$

MD transitions allowed for ΔJ= 0, +/-1 (except 0-0)



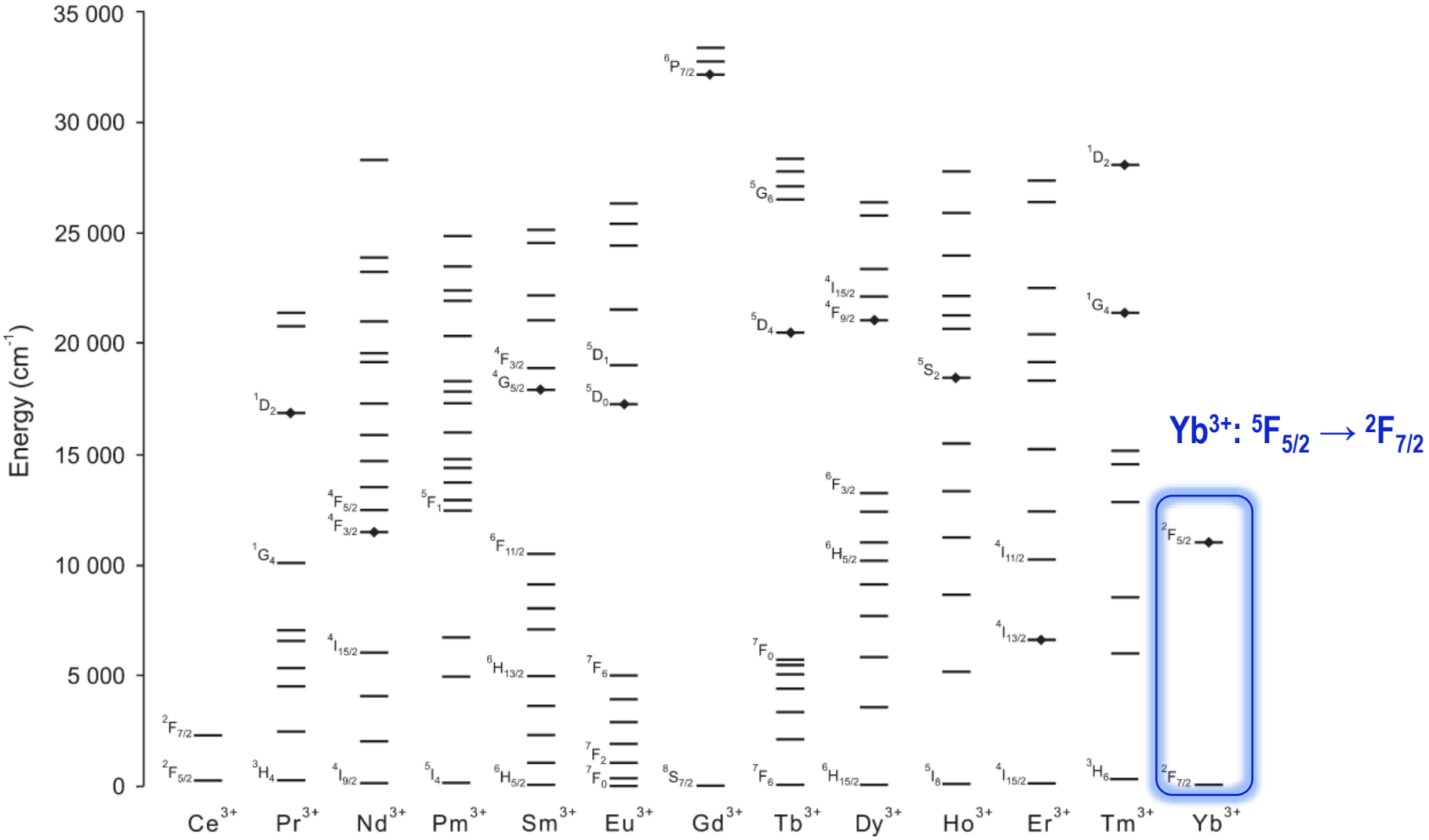


Spectra acquired at rt in MeOH.

Inorg. Chem. Front., **2021**, *8*, 914.

CPL of Yb^{3+} Complexes

Energy diagram of Ln ions with spectroscopic levels.



Yb^{3+}: $^5F_{5/2} \rightarrow {}^2F_{7/2}$

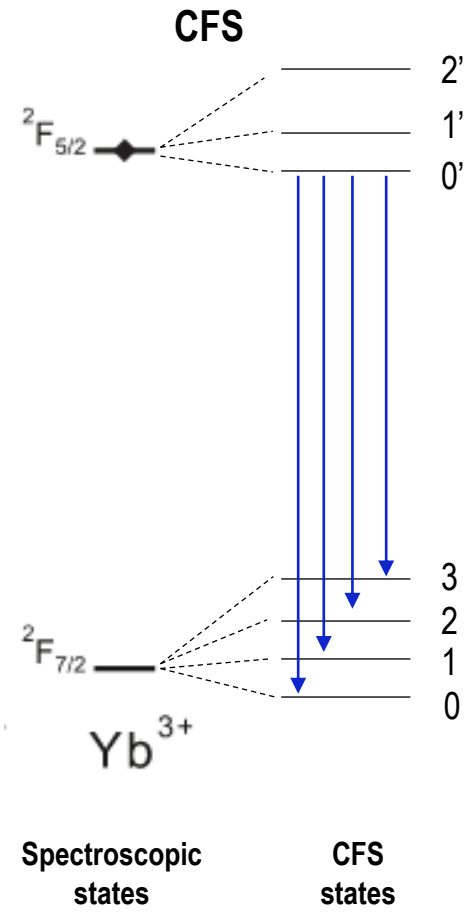
Methods Appl. Fluoresc. **2014**, *2*, 012001. *Front. Chem.* **2020**, *8*, 1-27.

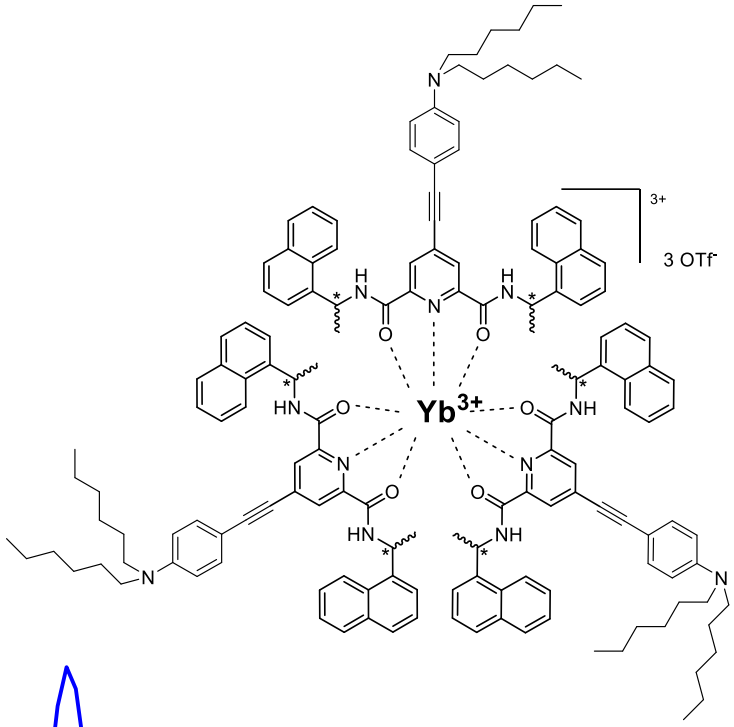
CPL of Yb^{3+} Complexes

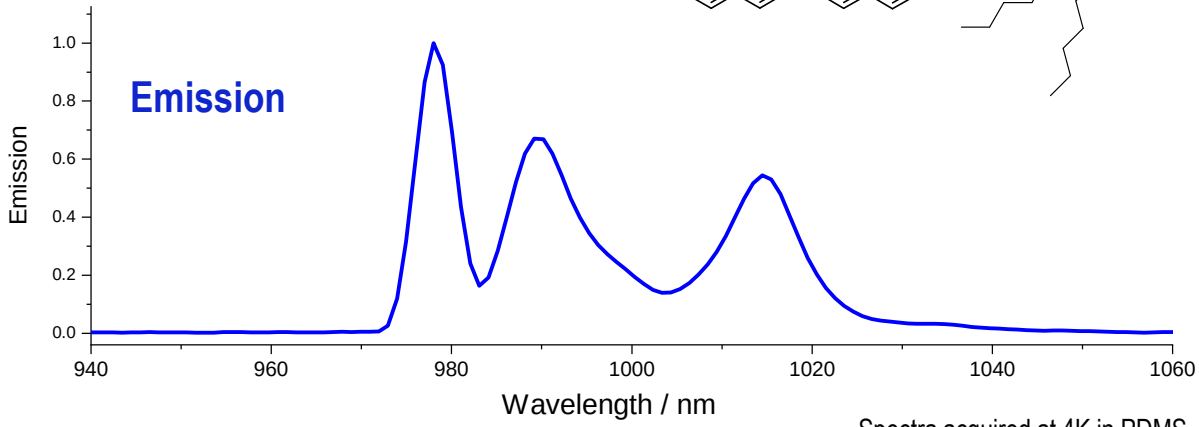
Crystal field splitting

In ligand field, spherical symmetry of electronic structure and genereracy of spectroscopic levels is lifted (m_j sub-levels)

Yb^{3+}: $^5F_{5/2} \rightarrow {}^2F_{7/2}$







Spectra acquired at 4K in PDMS.

Phys. Chem. Chem. Phys. **2024**, *26*, 15776–15783.

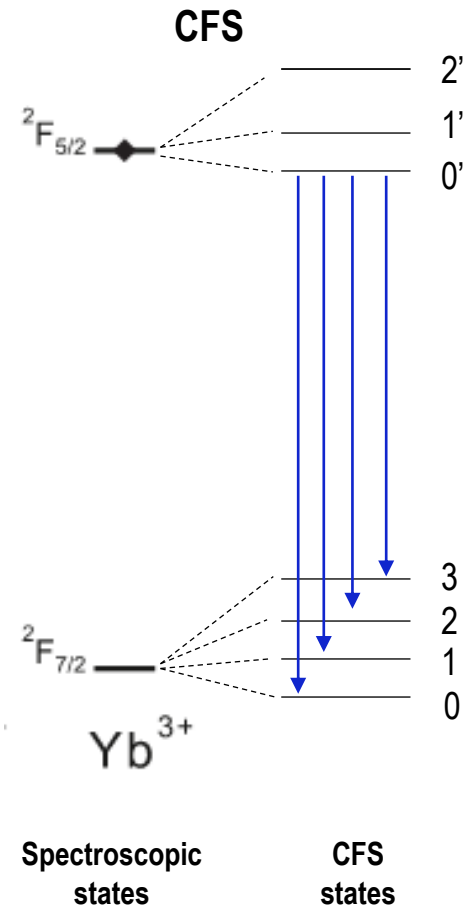
CPL of Yb^{3+} Complexes

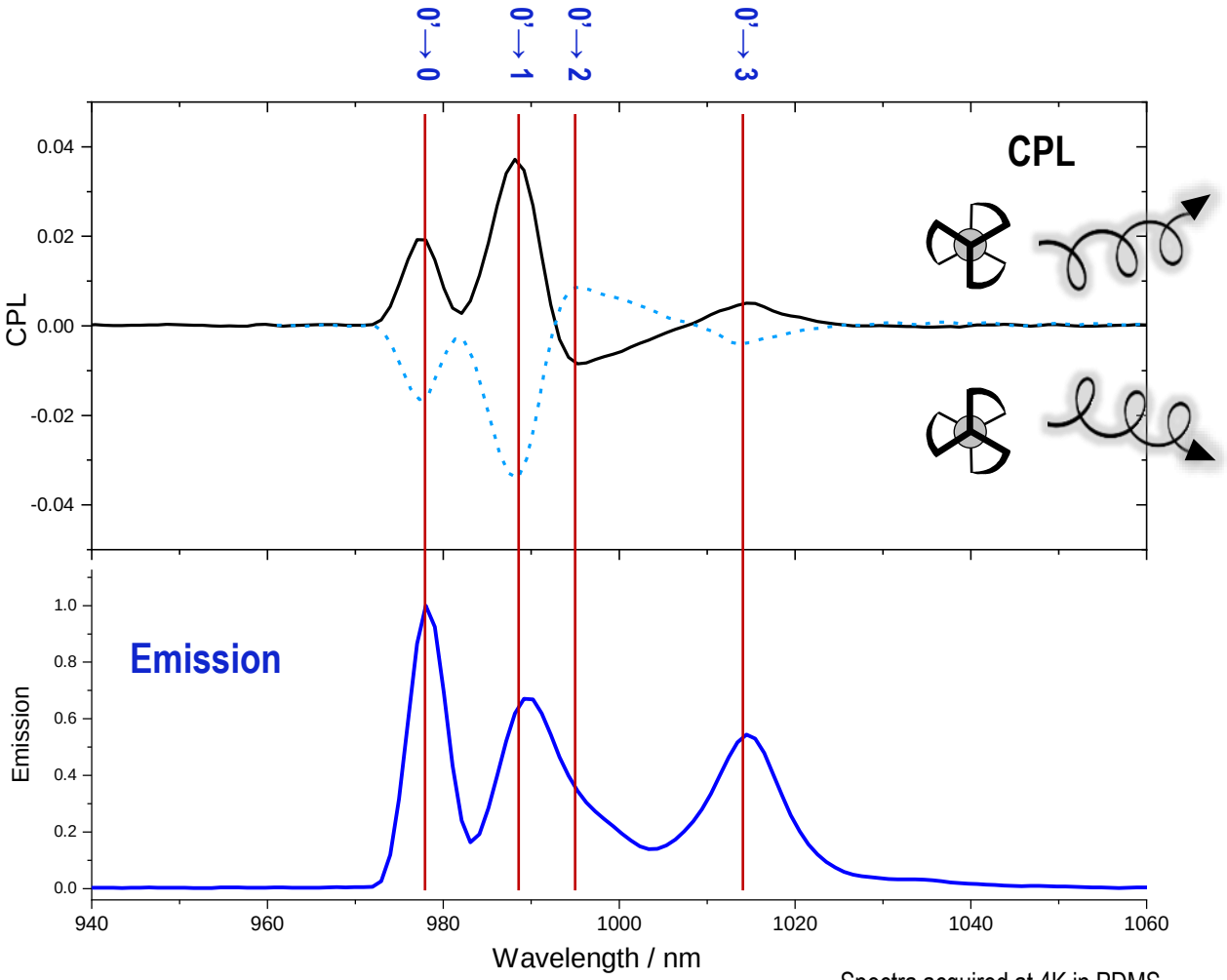
→ Mirror-type spectra for two enantiomers

→ Improved discrimination of individual transitions

→ Each CFS transition has its own CPL response (intensity + sign)

Yb^{3+}: $^5F_{5/2} \rightarrow {}^2F_{7/2}$





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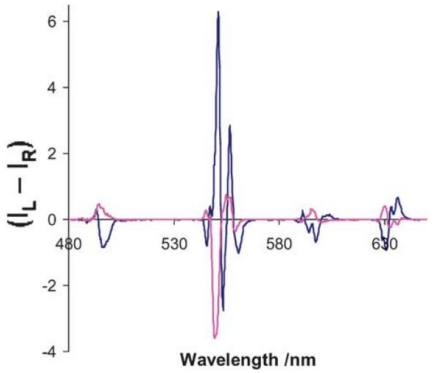
Phys. Chem. Chem. Phys. **2024**, *26*, 15776–15783.

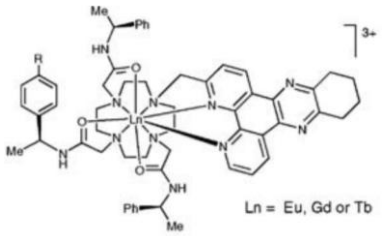
Fundamental insight in Lanthanide photophysics

Applications

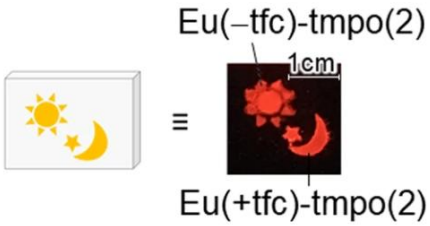
- Anti-counterfeit devices / security inks
- Display technologies
- Molecular / Biological sensing

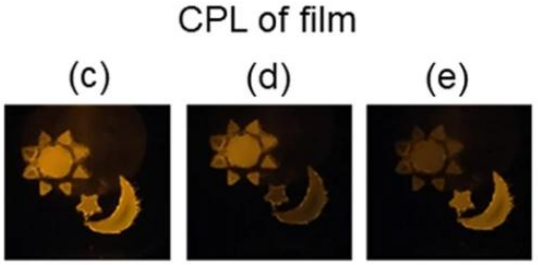
  (induction/change of CPL in presence of chiral peptides)





Chem. Commun., **2008**, 4261-4263.





Commun. Chem., **2020**, *3*, 119.

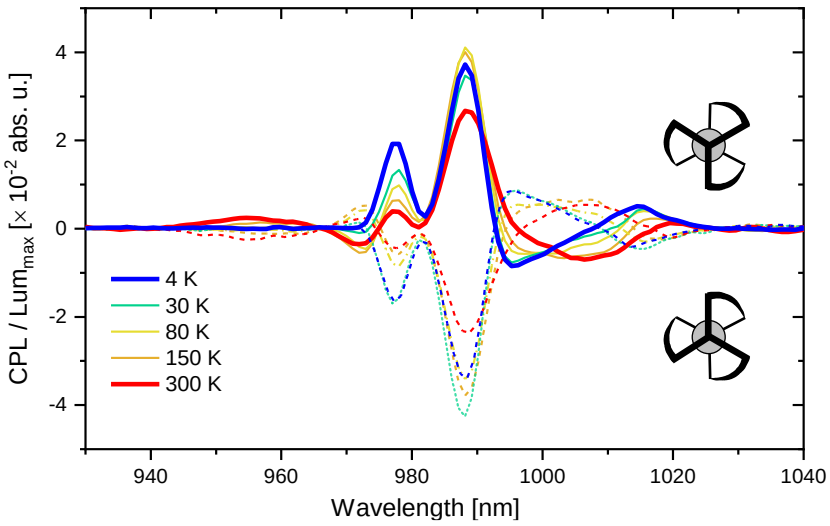
!

CPL response (and g_{lum}) is not constant for one emission band/wavelength

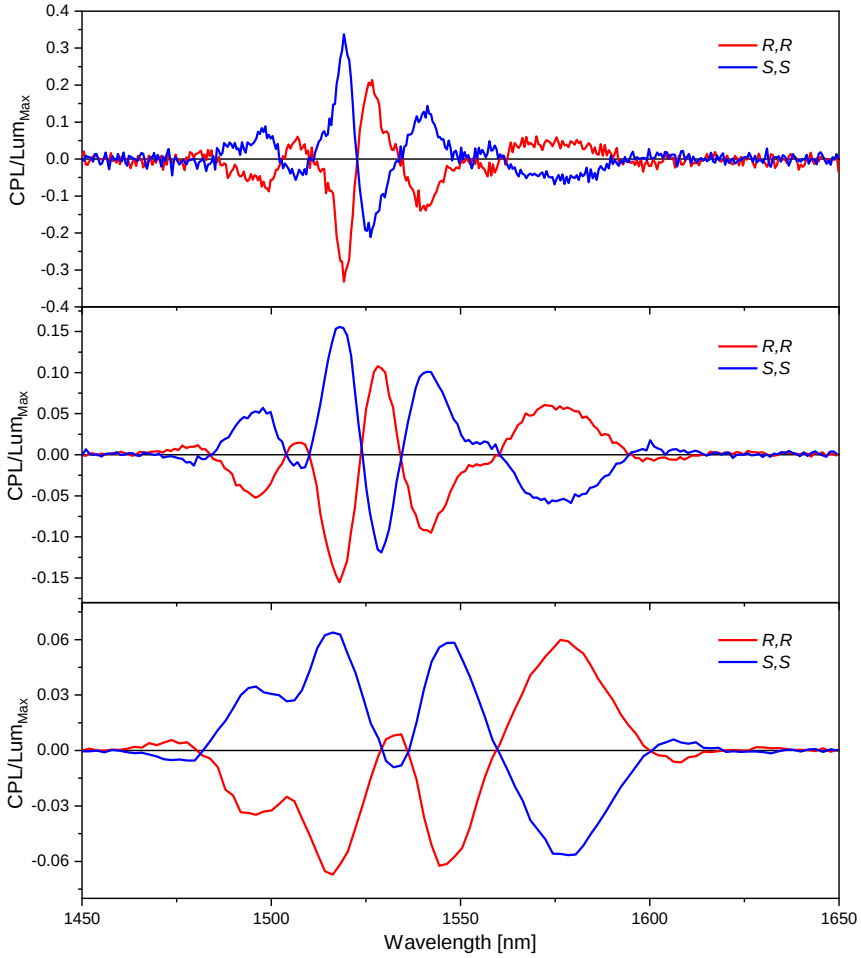
Lanthanide-CPL

Fundamental insight in Lanthanide photophysics

Yb^{3+}-CPL at variable temperature



Er^{3+}-CPL at variable bandwidth



CPL activity / g_{lum} values vary with :

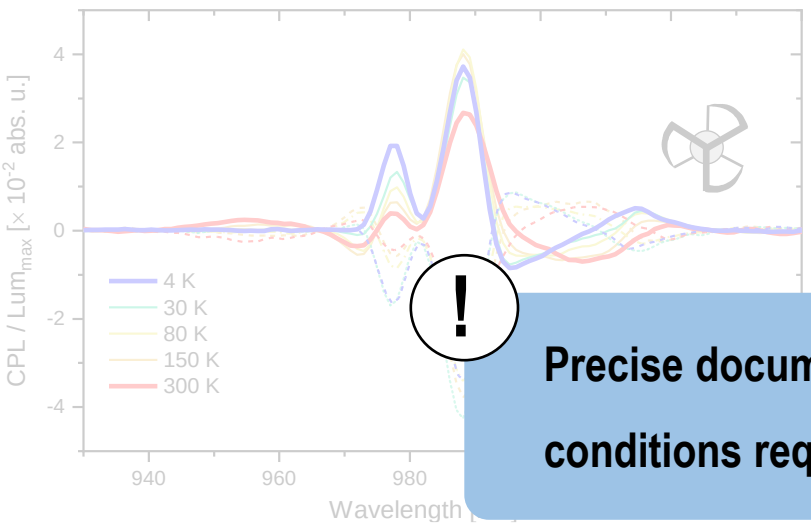
- Wavelength
- Temperature (population of hot bands !)
- Experimental bandwidth

Phys. Chem. Chem. Phys. **2024**, *26*, 15776–15783. *J. Mater. Chem. C*, **2024**, *12*, 4253-4260.

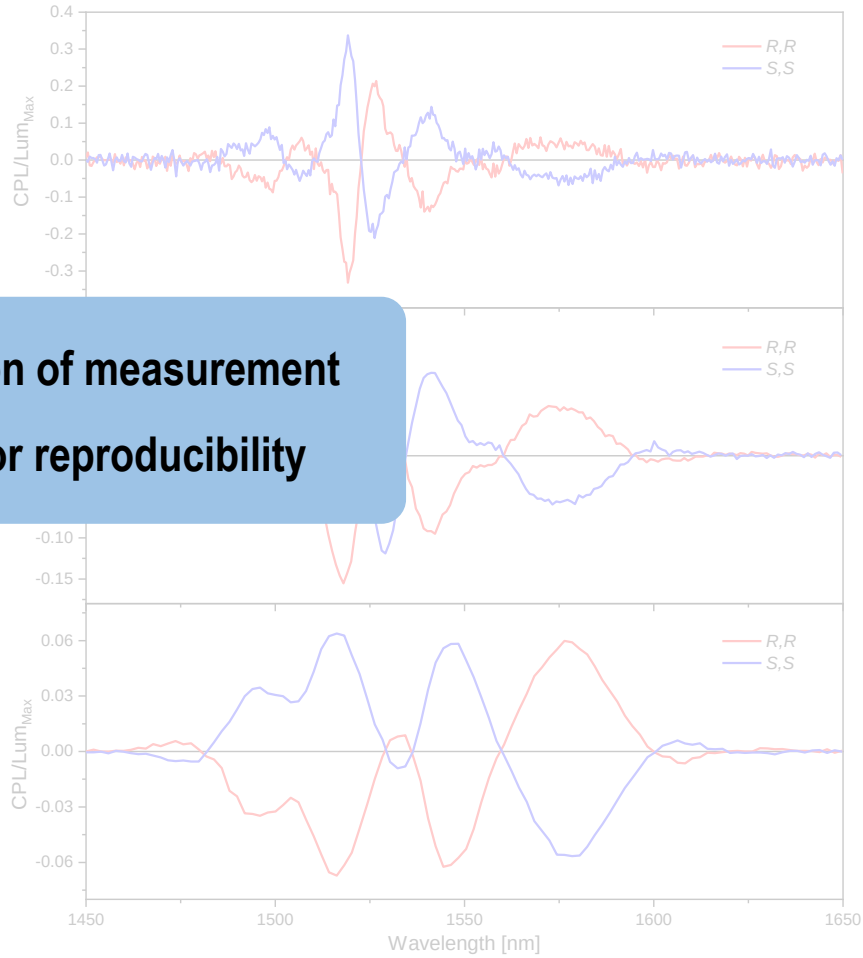
Lanthanide-CPL

Fundamental insight in Lanthanide photophysics

Yb^{3+}-CPL at variable temperature



Er^{3+}-CPL at variable bandwidth



Precise documentation of measurement conditions required for reproducibility

CPL activity / g_{lum} values vary with :

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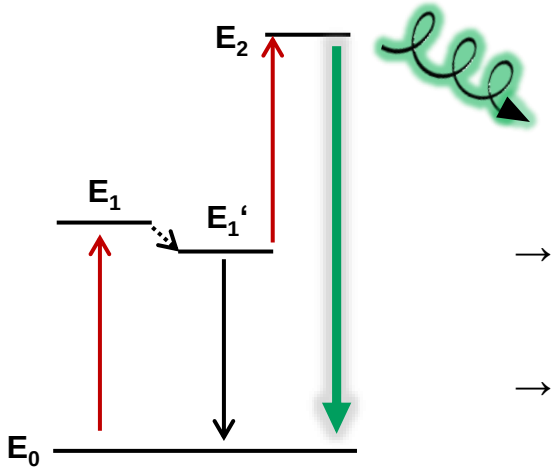
- Temperature (population of hot bands !)
- Experimental bandwidth

Phys. Chem. Chem. Phys. **2024**, *26*, 15776–15783. *J. Mater. Chem. C*, **2024**, *12*, 4253-4260.

Envisaged Project

Combination of **Upconversion Emission (UC)** and **Circularly Polarized Luminescence (CPL)** in one molecular complex



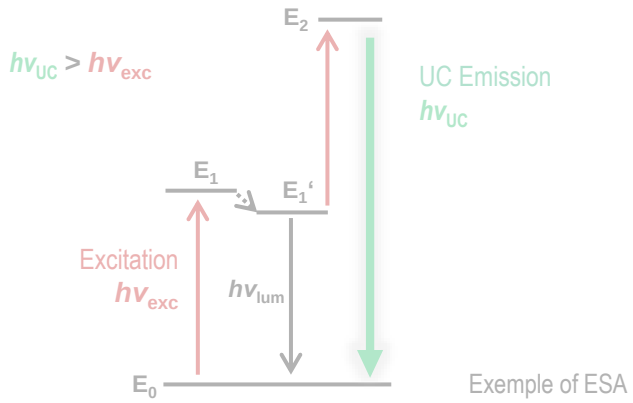
Insight into chiral activity of higher excited states

→ Fundamental knowledge in Ln^{3+} photophysics

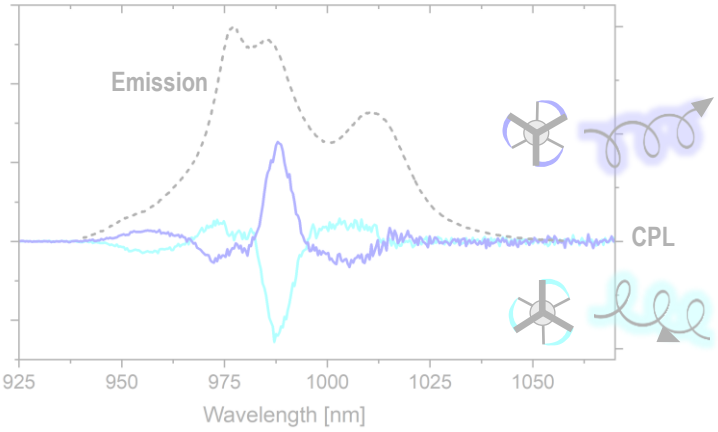
→ Novel materials with unprecedented properties

Lanthanide Complexes

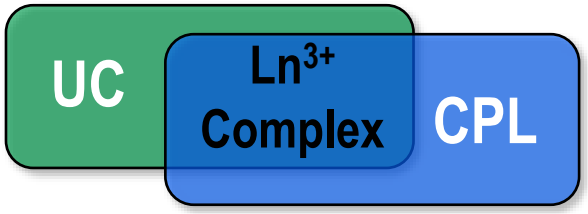
Upconversion Emission

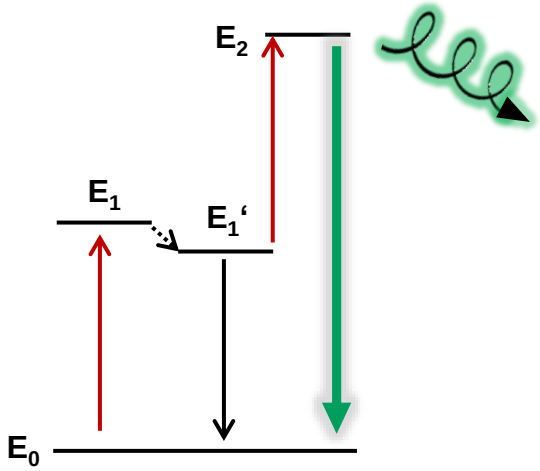


Circularly Polarized Luminescence



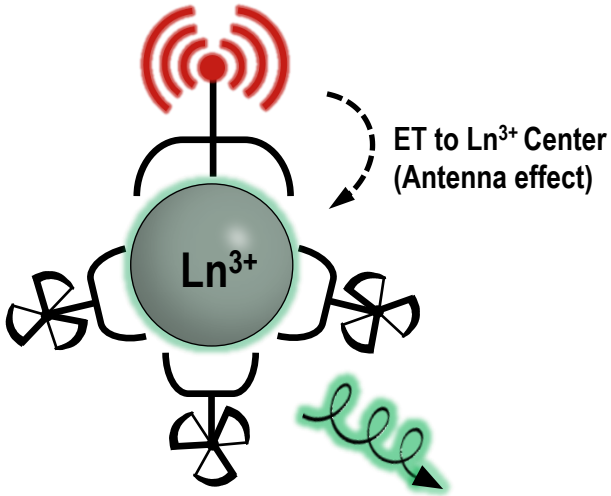
Envisaged Project





Insight into chiral activity of higher excited states

Excitation of chromophore

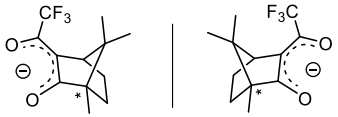


Emission of UC- CPL

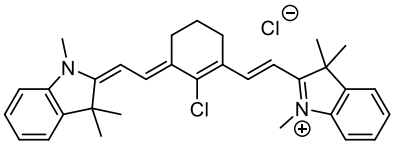
$Ln^{3+} = Er^{3+}$

Requirements on Complex Design

i) Induction of chirality



ii) Efficient sensitization
(antenna with high absorption cross-section)



iii) Maximum decrease of non-emissive deactivation pathways *(CN = 9, deuteration,…)*

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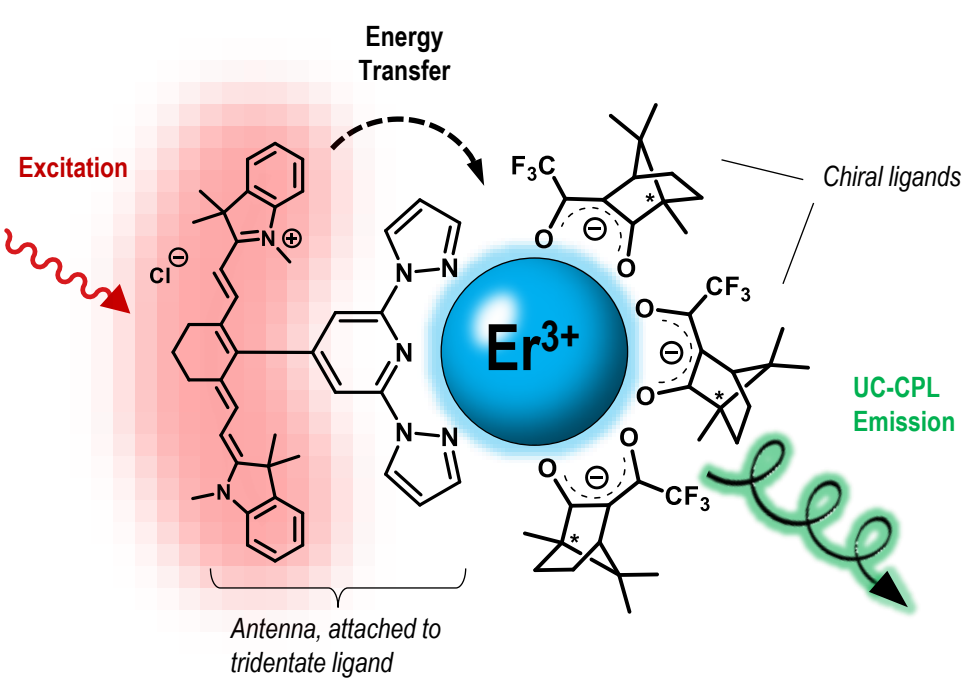
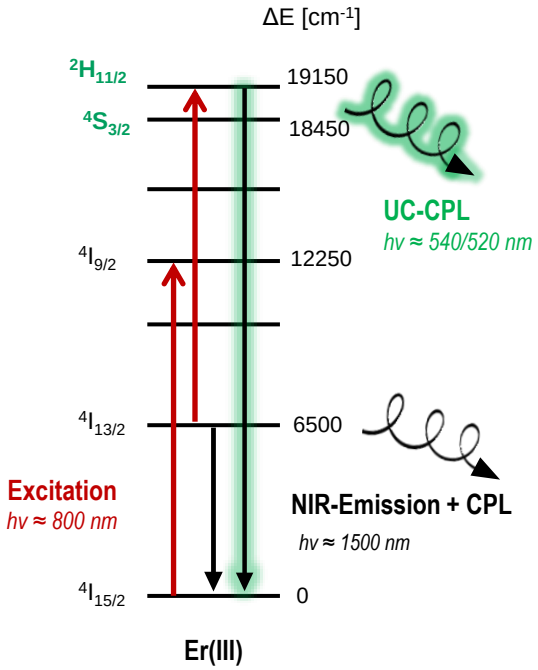
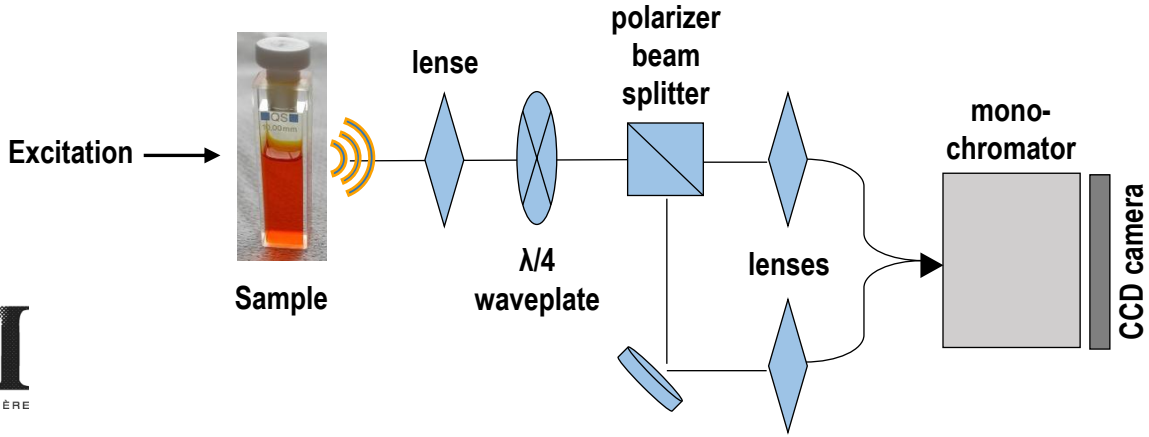
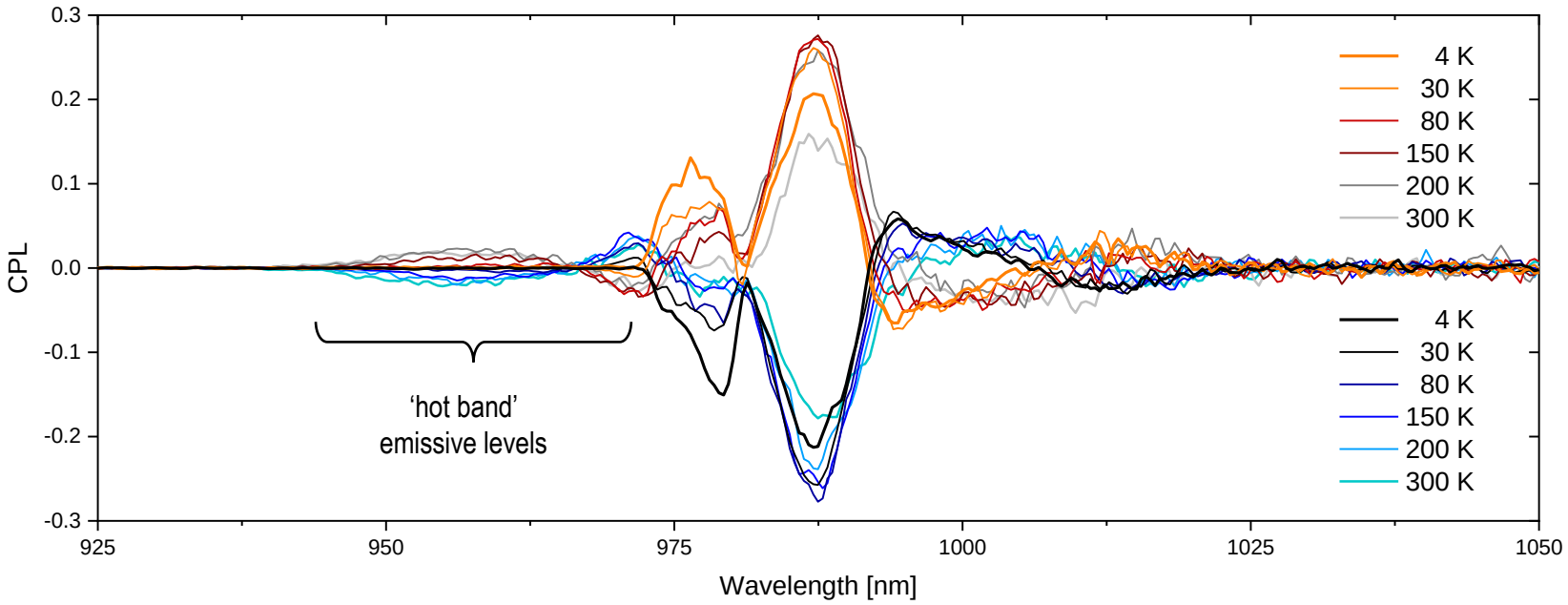

Energy
Transfer
Excitation
Chiral ligands
Er3+
UC-CPL
Emission
Antenna, attached to
tridentate ligand


ΔE [cm-1]
2H11/2
4S3/2
4I9/2
4I13/2
4I15/2
19150
18450
12250
6500
0
UC-CPL
hν ≈ 540/520 nm
Excitation
hν ≈ 800 nm
NIR-Emission + CPL
hν ≈ 1500 nm
Er(III)

CPL setup


Excitation
Sample
lense
λ/4
waveplate
polarizer
beam
splitter
lenses
mono-
chromator
CCD camera


CPL
Wavelength [nm]
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
925
950
975
1000
1025
1050
'hot band'
emissive levels
4 K
30 K
80 K
150 K
200 K
300 K
4 K
30 K
80 K
150 K
200 K
300 K