INFLUENCE OF OH GROUPS ON THE SPECTRAL CHARACTERISTICS OF Eu^{3+} IONS IN HYBRID ORGANIC-INORGANIC MATERIALS SUNTHESIZED BY SOL-GEL

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OBJECTIVES

Components of High Emission Yield

Rare Earth organic Complexes ($Ln^{3+} = Eu^{3+}, Tb^{3+}$)

High Emission Yield under UV excitation

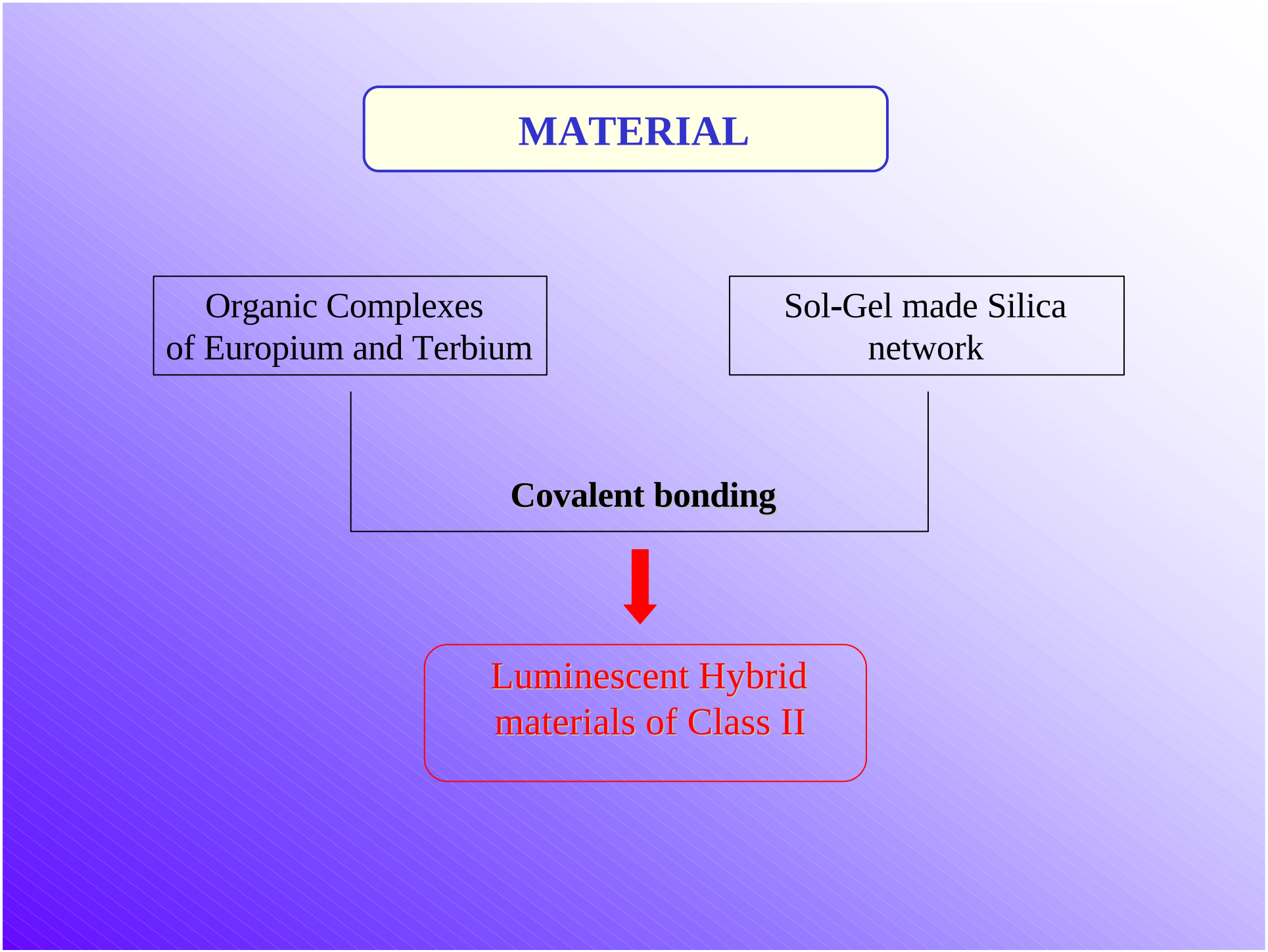
Low Thermal and Mechanical resistance

HYBRID MATERIALS

POWDERS AND FILMS

Applications

- *Lighting*
- *Displays*
- *marking*


MATERIAL
Organic Complexes of Europium and Terbium
Sol-Gel made Silica network
Covalent bonding
Luminescent Hybrid materials of Class II

Organic Complexes of Europium and Terbium

Eu^{3+}, Tb^{3+} ⇨ Narrow emission bands

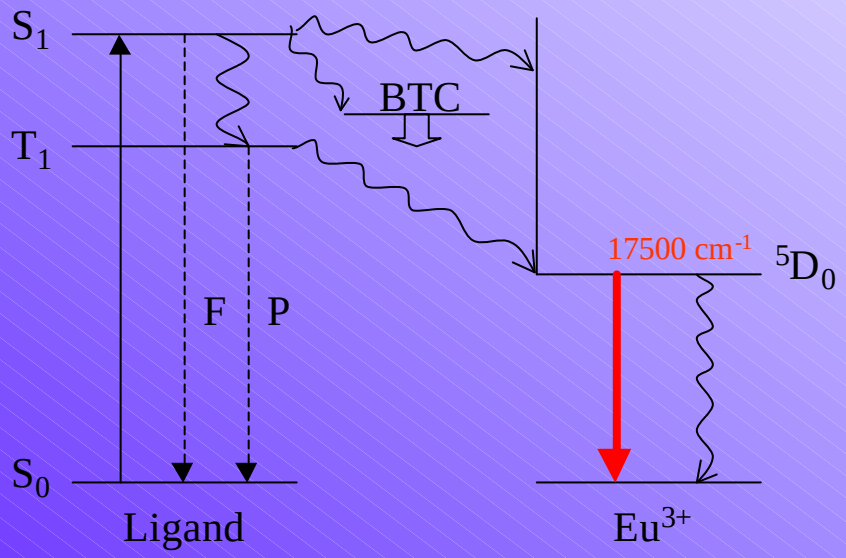
⇨ Long lifetime

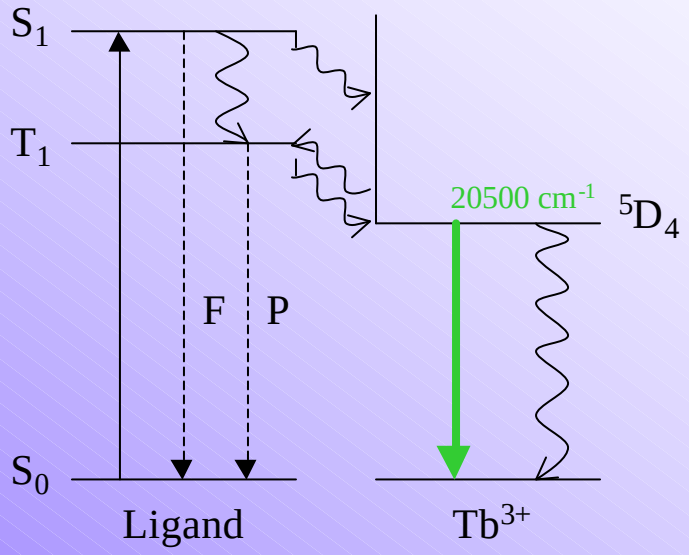
Organic Ligand ⇨ Large absorption bandwidth and high Intensity in the UV-Visible range

⇨ Protected environment

⇨ Energy transfer yield high

TRANSFER ENERGY MECHANISM





Absorption F **Fluorescence** P **Phosphorescence** **No radiative transfer**

Emission Yield = Absorption efficiency

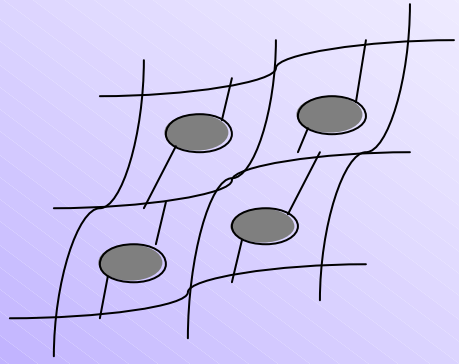
× Transfer energy efficiency $Ln^{3+} \rightarrow$ ligand

× Fluorescence efficiency

Association Mode

CLASS II HYBRIDS

- Strong chemical interactions of covalent or ionic-covalent nature



Inorganic network

Organic component

- Composite at the molecular level

ADVANTAGES

- Increased Chemical Thermal and Mechanical stability
- Organic- Inorganic Interface precisely defined
- Single phase material
- High level doping
- Isolation of active species
- Homogeneous distribution of the emitting centers

OH : INCREASES THE NON RADIATIVE RELAXATION PROCESS

SYNTHESIS

Organic Chromophore

1. Bonding

Functionalized monomer

2. Complexation

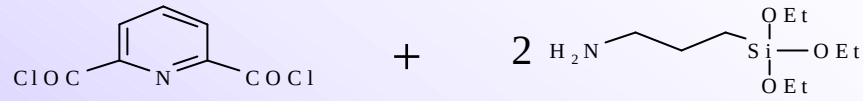
3. Hydrolysis/Condensation

Luminescent Hybrid

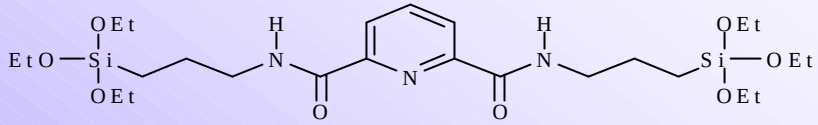
Characterization

- RMN ^{1}H / ^{13}C
- Infra Red
- Mass Spectroscopy
- Molecular Modeling

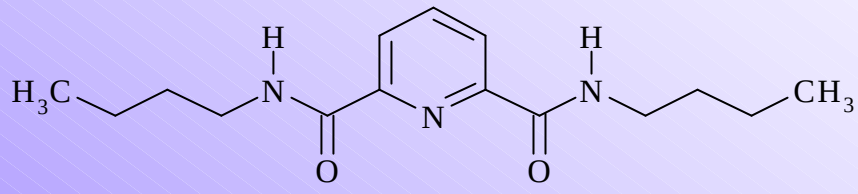
Precursors



Bonding



Monomer M1a

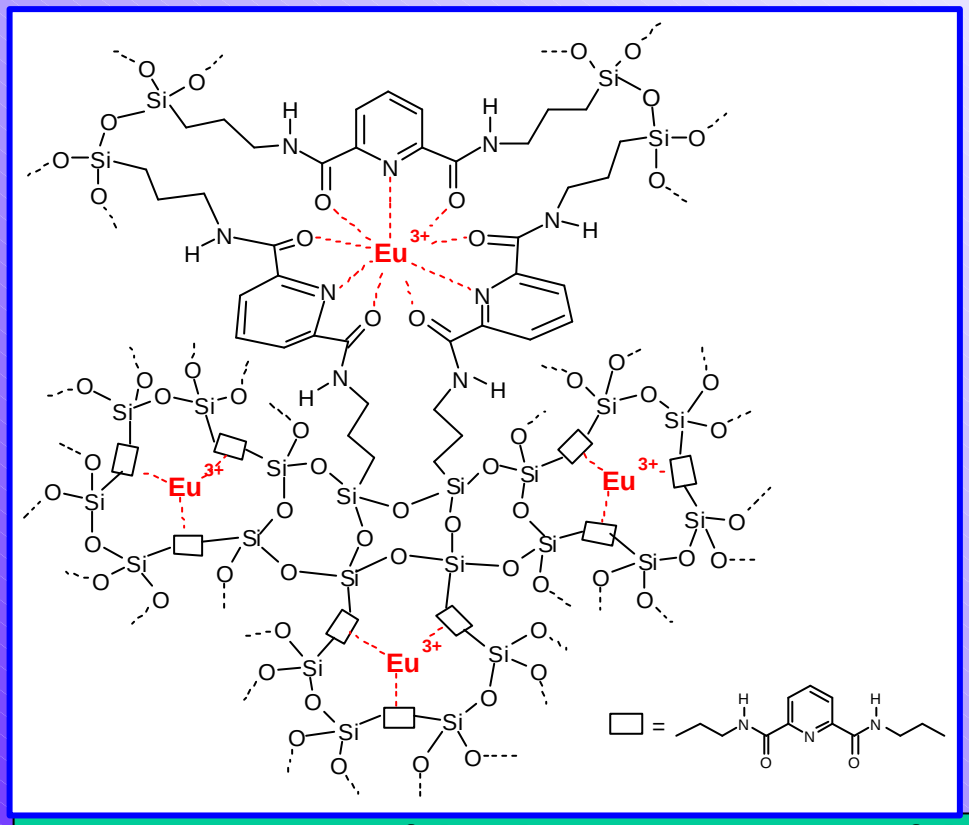


Organic Ligand O1a

Total bonding reaction

Monomer and ligand structure similar

STRUCTURE AND TEXTURE



- Amorphous Materials
- Monolithic Gels

  (Opaque and Transparent)
- Homogeneous texture

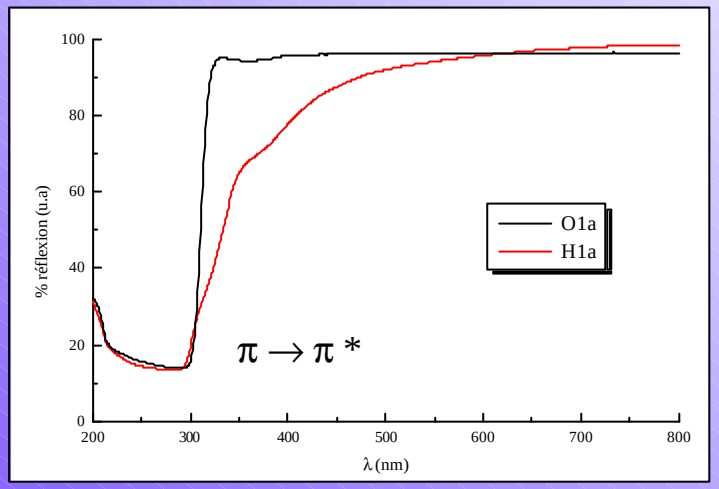
- Conservation of the electronic structure of the luminophore
- Conservation of the coordination mode of Ln^{3+}

  ❑ Double covalent bonding

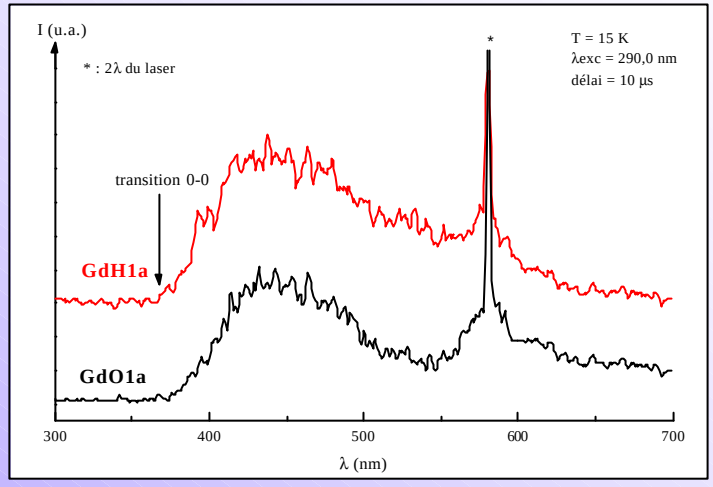
  ❑ Single phase material with homogeneous distribution of organic and inorganic components

Position of triplet and singlet states

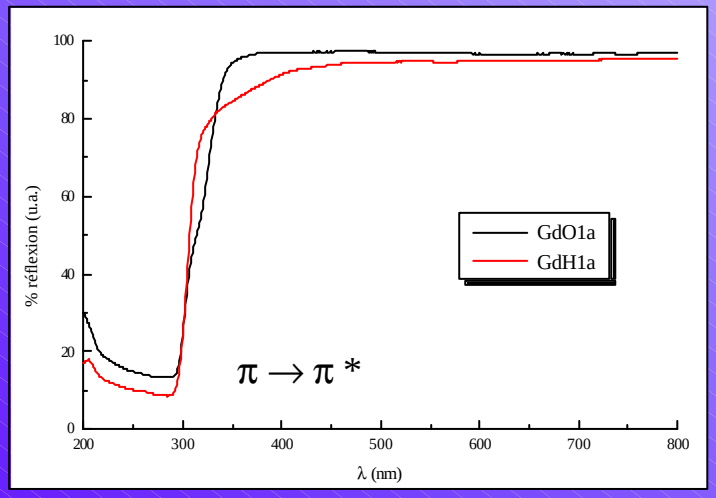
Absorption of gels and free ligands



Phosphorescnce Emission



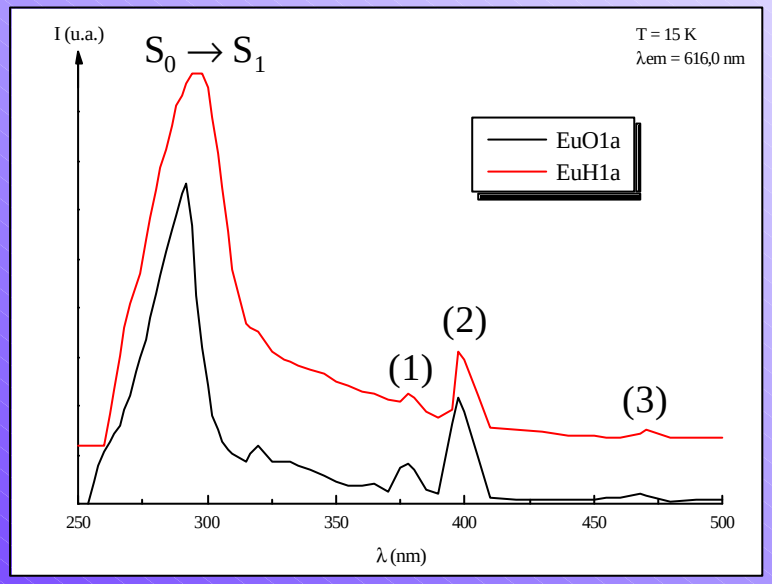
Absorption of hybrids and organic complexes



	organic	**hybrid**
S_1 Free ligand	292 nm (34247 cm^{-1})	294 nm (34014 cm^{-1})
S_1 Gd complex	290 nm (34483 cm^{-1})	288 nm (34722 cm^{-1})
T_1 Gd complex	362 nm (27624 cm^{-1})	369 nm (27100 cm^{-1})

Fluorescence sensitization of Eu^{3+} or Tb^{3+} ions

Excitation spectra of fluorescence $^5D_0$ ® $^7F_2$ de l'ion Eu^{3+}

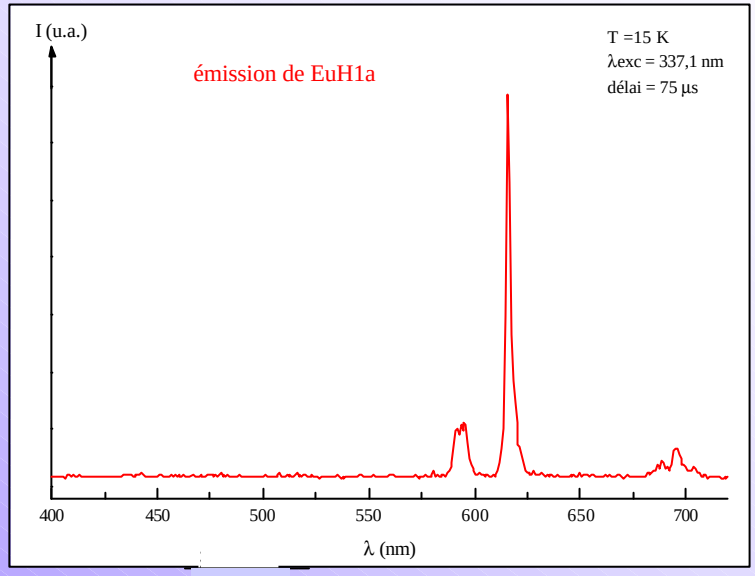


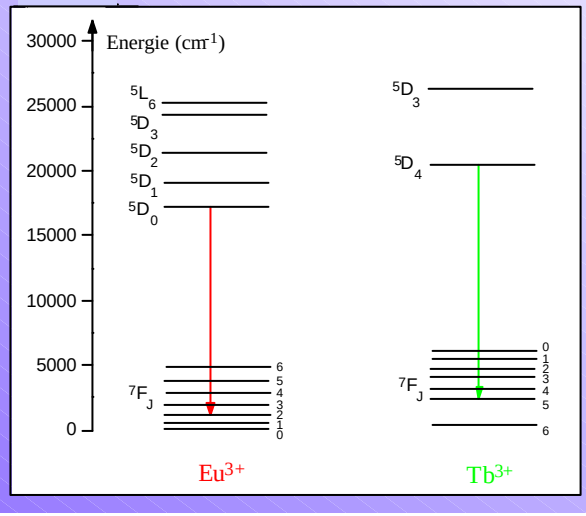
(1) $^7F_0 \rightarrow {}^5D_4$ - (2) $^7F_0 \rightarrow {}^5L_6$ - (3) $^7F_0 \rightarrow {}^5D_2$

λ_{max} excitation $\Rightarrow$ 292 nm EuO1a

$\Rightarrow$ 294 nm EuH1a

Emission spectrum of Eu^{3+} ion under UV excitation

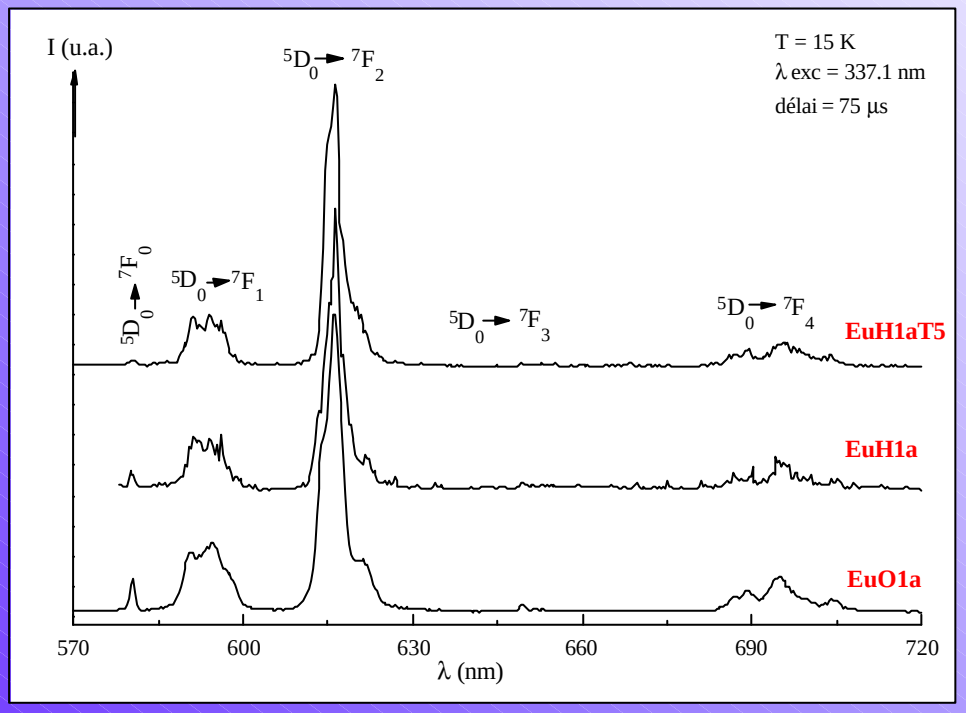




Conservation of the energy transfer mechanism

Emission properties of Eu^{3+}

Emission spectra under UV excitation



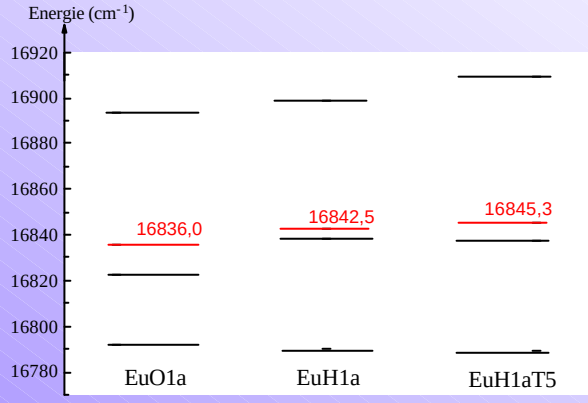
⇨ Amorphous in character

⇨ $^5D_0 \rightarrow {}^7F_2$ (616,0 nm) transition predominates

Infuence of the Sol-Gel matrix

- Shift of $^5D_0$ level towards high energies
  ⇨ $\Delta\nu = 18\ cm^{-1}$

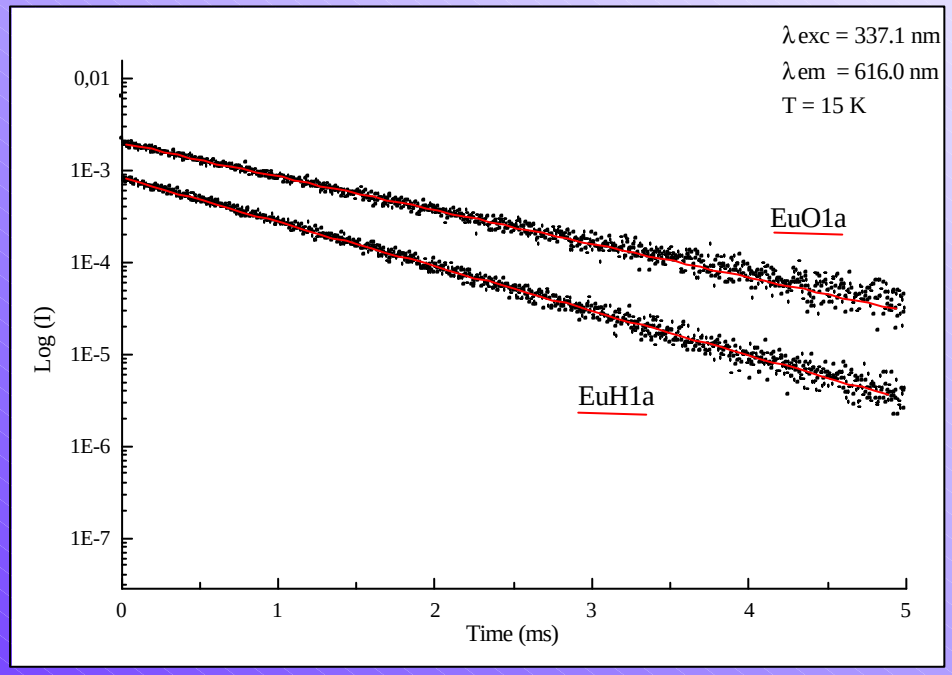
- $^7F_1$ level splitting more important



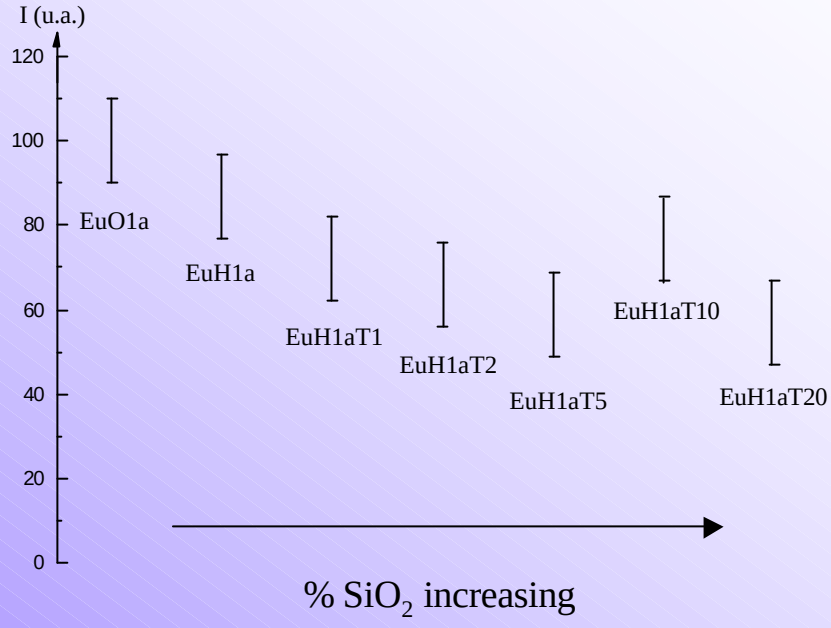
- Enlargement of the transition $^5D_0 \rightarrow {}^7F_2$
  ⇨ $\Delta_{1/2}$ = 76 cm^{-1} → EuO1a
  107 cm^{-1} → EuH1a

Lifetime and emission yield

Fluorescence decays



Emission yield



at 15 K

EuO1a ® ***1,22 ms***

EuH1a ® ***1,06 ms***

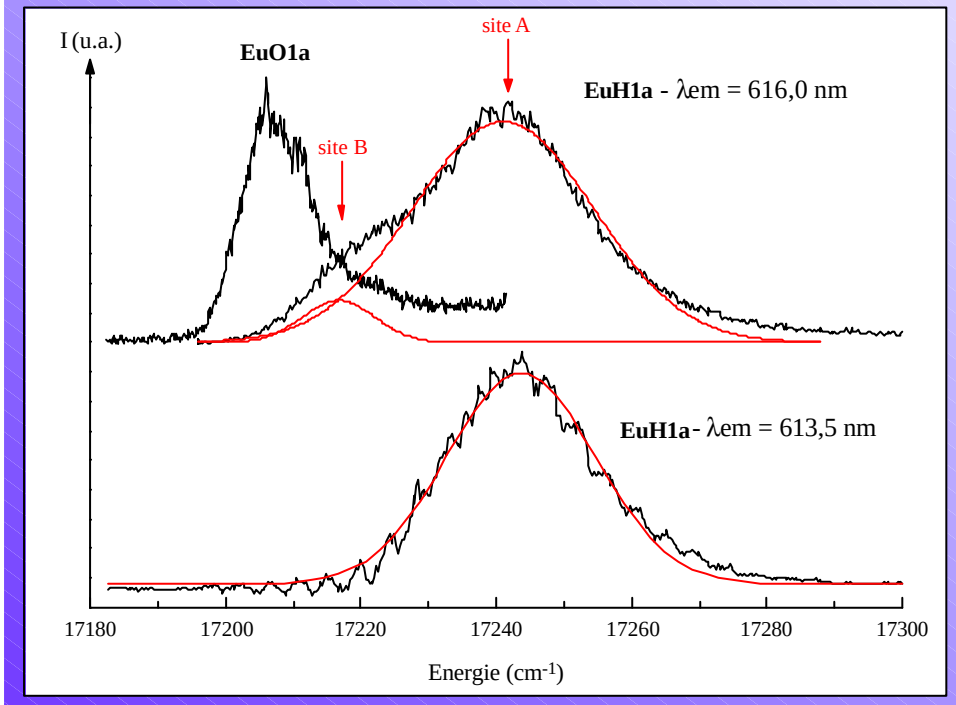
at 300 K

0,85 ms

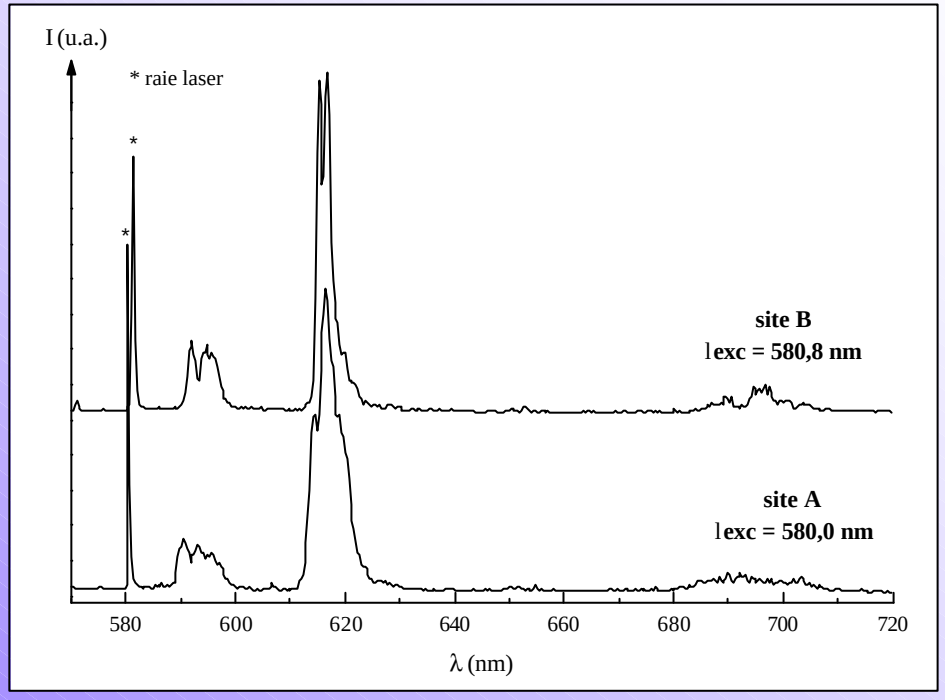
Limited effect of OH groups

Selective Excitation

Excitation spectra $^7F_0$ ® $^5D_0$ of $^5D_0$ ® $^7F_2$ fluorescence at 15 K



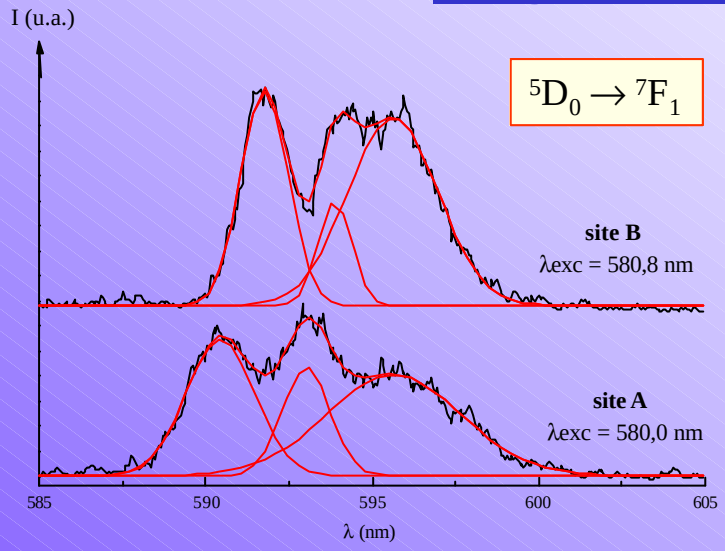
Emission spectra of EuH1a by selective excitation of sites A and B à 15 K



	Energy (cm^{-1})	$D_{1/2}$ (cm^{-1})
EuO1a	**17203**	**12,0**
EuH1a (site A)	**17240**	**21,2**
EuH1a (site B)	**17218**	**12,2**

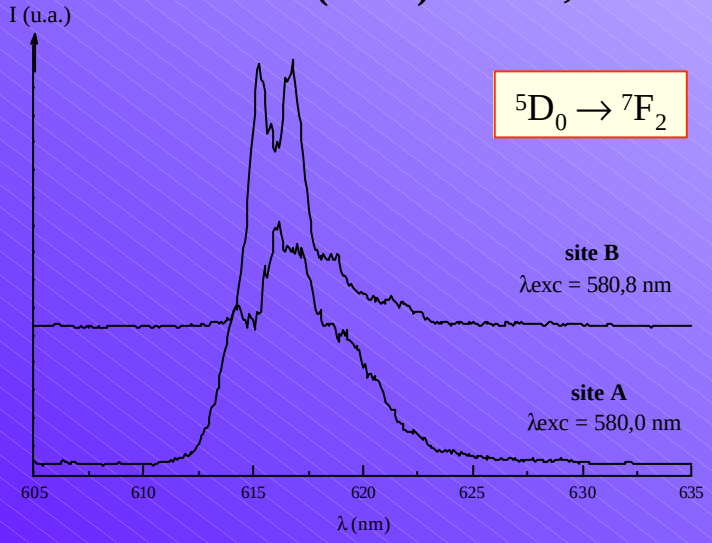
2 Distinct distribution of sites and not connected between them.

Origin of the 2 distribution of sites



$^5D_0 \rightarrow {}^7F_1$

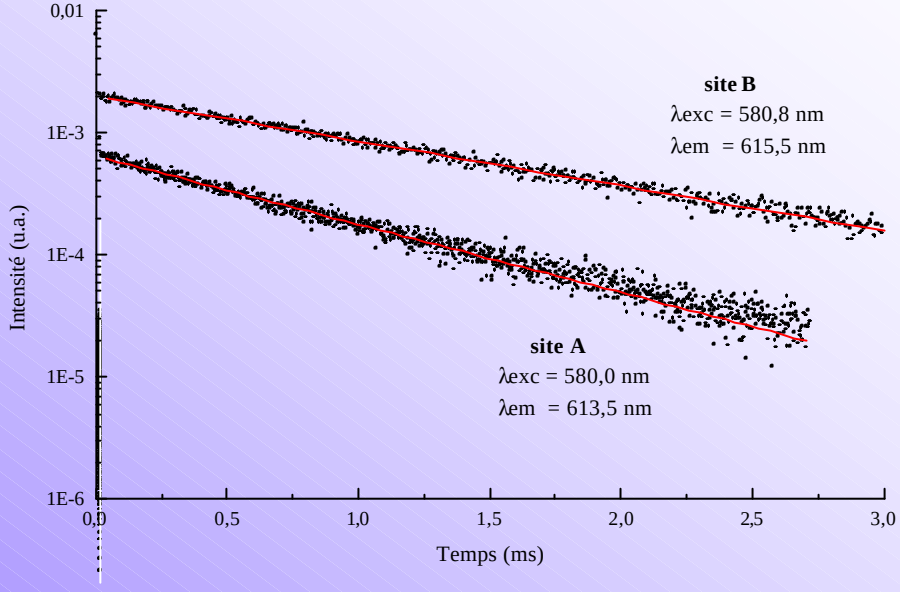
barycentre $^7F_1$ (site A) = 16863,2 cm^{-1}
(site B) = 16842,4 cm^{-1}



$^5D_0 \rightarrow {}^7F_2$

$D_{1/2}$ (site A) = 150 cm^{-1}
(site B) = 107 cm^{-1}

Lifetime



t (site A) = 0,90 ms
(site B) = 1,18 ms

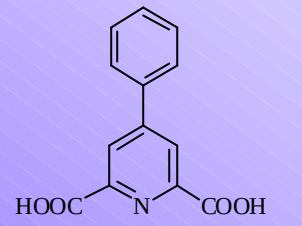
Site A Þ with OH
Site B Þ without OH

UV EXCITATION Þ SITE B

CHROMOPHORE MODIFICATION

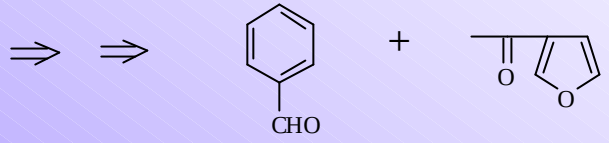
⇨ **Absorption cross section**

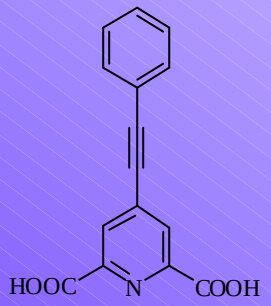
⇨ **Energetic position of the triplet state**



2,6-dicarboxy-4-phényl-pyridine

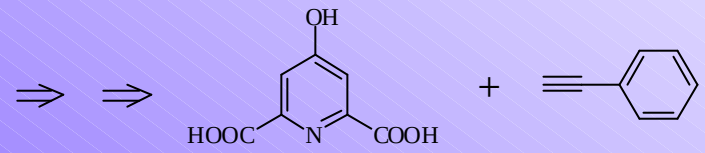
acide **2**

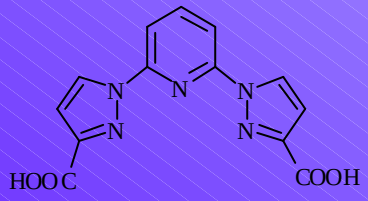




2,6-dicarboxy-4-phényléthynyl-pyridine

acide **3**



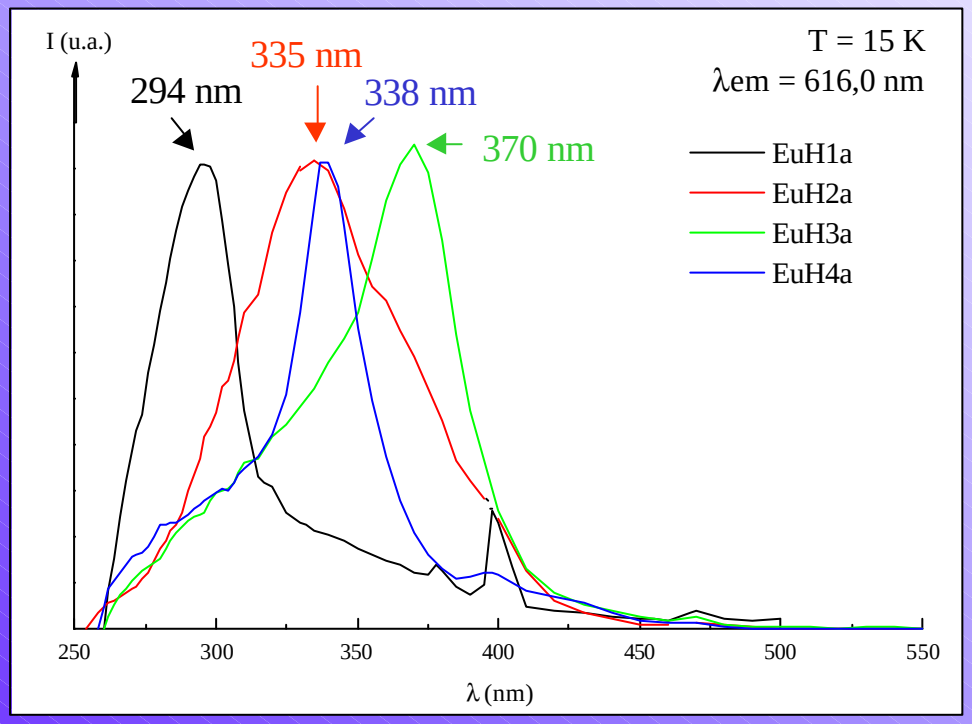


2,6-di(3'-carboxypyrazolyl)-pyridine

acide **4**

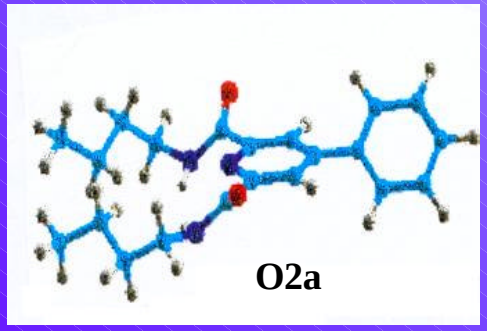
Chromophore energy levels

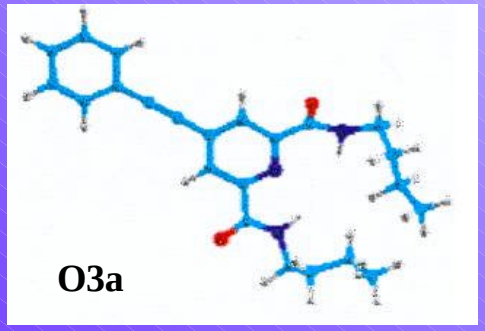
Excitation spectra of fluorescence $^5D_0$ ® $^7F_2$ (Eu^{3+})

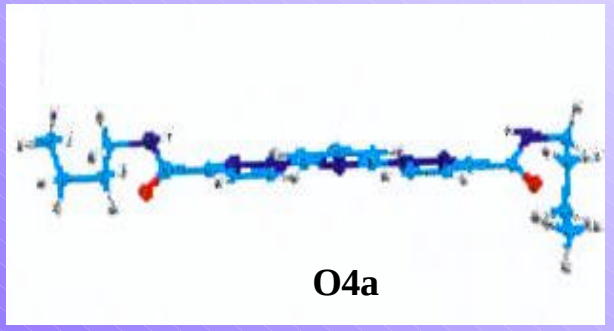


S_1 et T_1 levels position measured on Gd hybrid complexes

	S_1	T_1
GdH1a	34722 cm^{-1}	27100 cm^{-1}
	(288 nm)	(369 nm)
GdH2a	30303 cm^{-1}	23041 cm^{-1}
	(330 nm)	(434 nm)
GdH3a	27933 cm^{-1}	21505 cm^{-1}
	(358 nm)	(465 nm)
GdH4a	29762 cm^{-1}	25252 cm^{-1}
	(336 nm)	(396 nm)

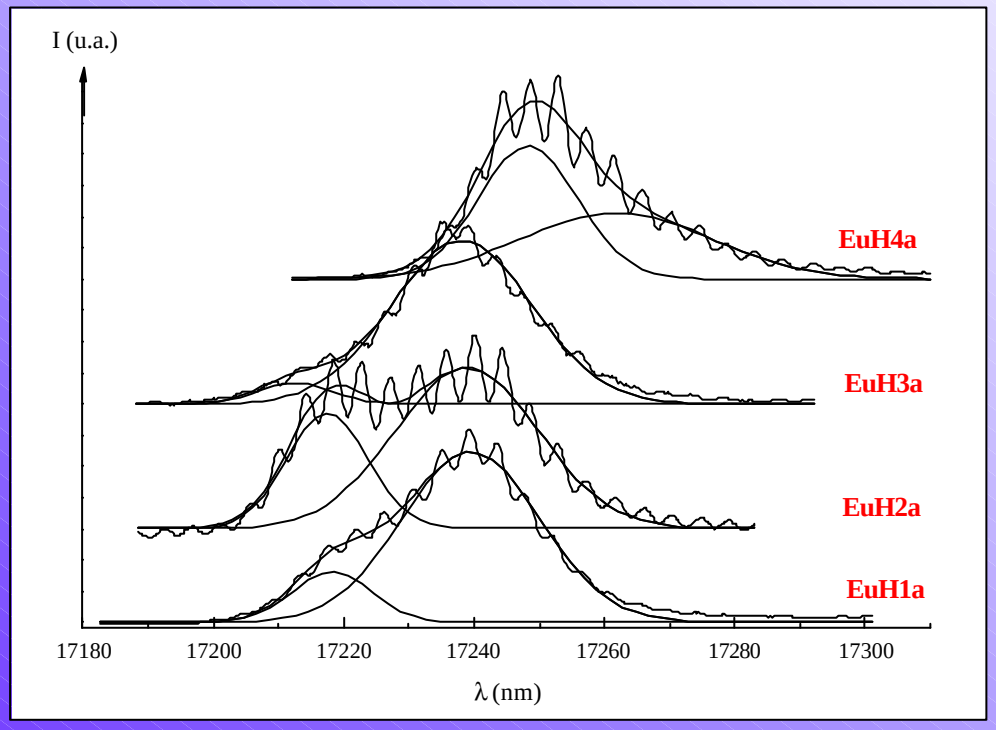






OH coupling effects

Excitation spectra of $^7F_0$ ® $^5D_0$ (l em = 616,0 nm, T = 15 K)



	Site A		Site B	
	energy (cm^{-1})	$\Delta_{1/2}$ (cm^{-1})	energy (cm^{-1})	$\Delta_{1/2}$ (cm^{-1})
EuH1a	17240	21,2	17218	12,2
EuH2a	17238	21,6	17212	11,1
EuH3a	17239	22,1	17218	12,4
EuH4a	17262	24,3	17248	13,5

$^5D_0$ levels lifetime

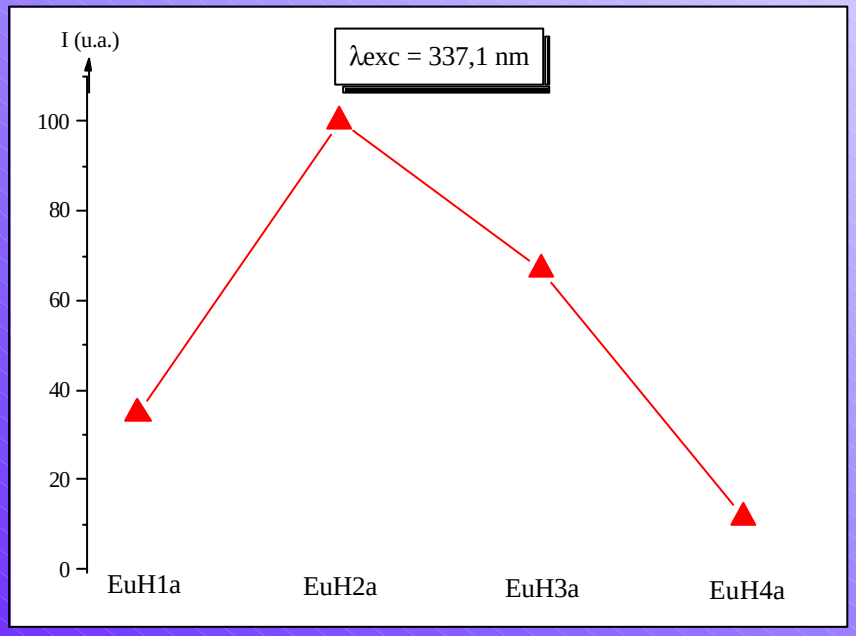
(λexc = 337,1 nm - T = 15 K)

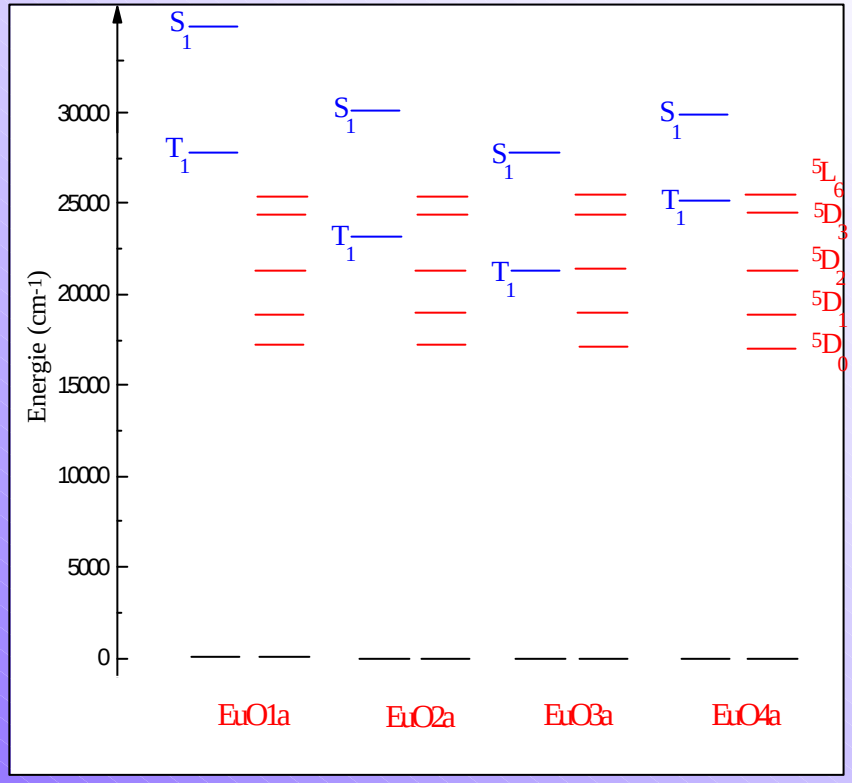
⇨ *Europium Complexes*

	organic	hybrid
EuO(H)1a	1,22 ms	1,06 ms
EuO(H)2a	0,88 ms	0,68 ms
EuO(H)3a	0,75 ms	0,69 ms
EuO(H)4a	1,15 ms	0,64 ms

Photoluminescence Yield

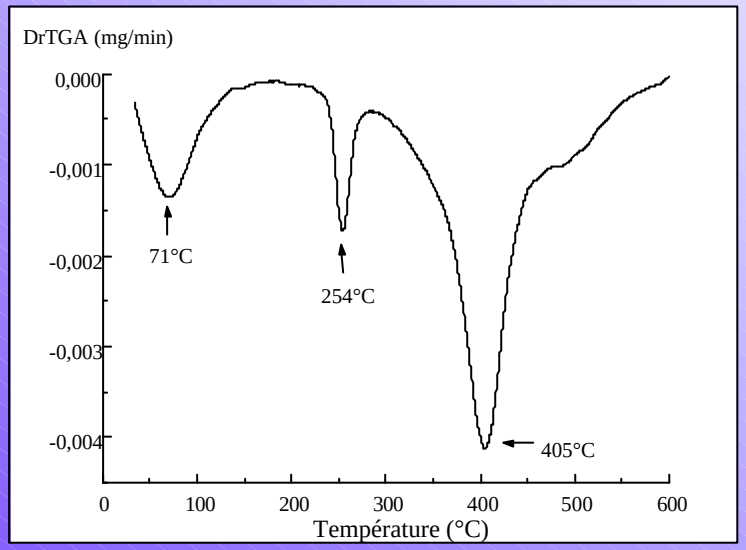
Europium Complexes

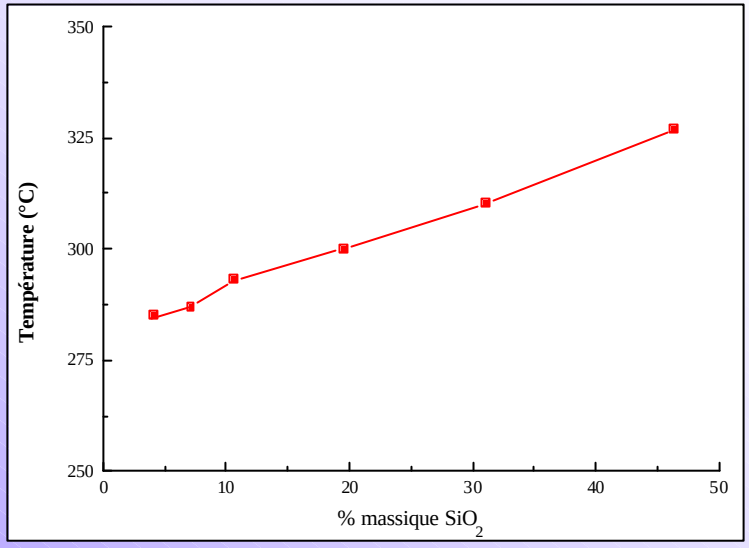


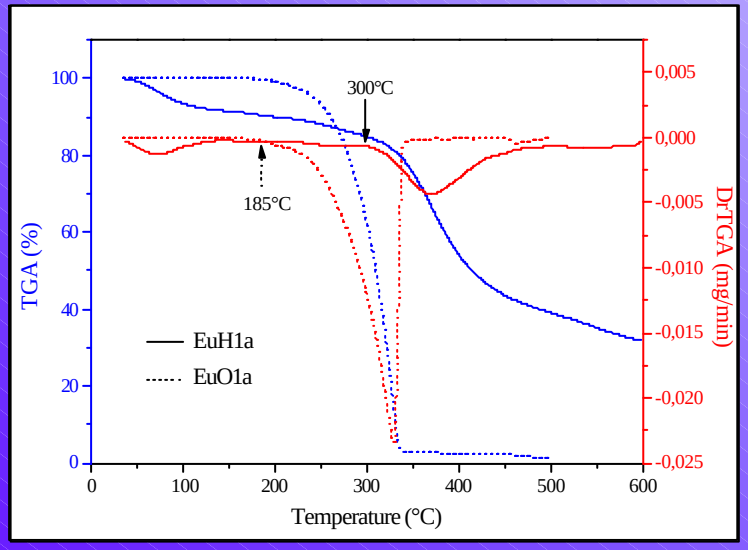


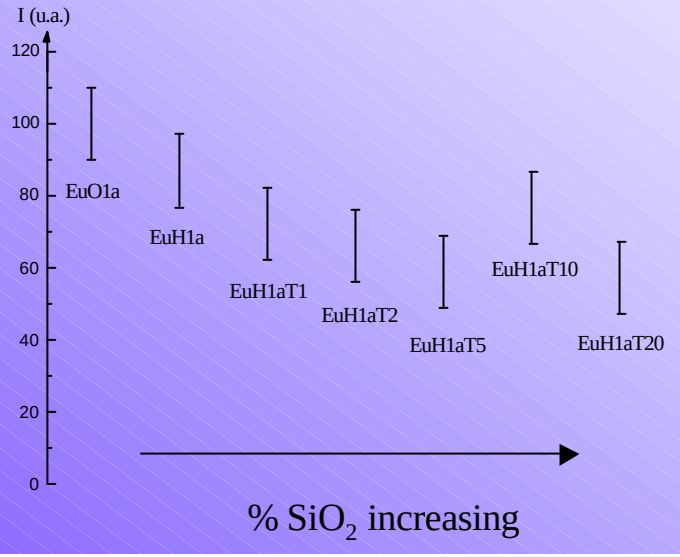
TGA-DTA ANALYSIS

Thermal stability gain from 115°C to 150°C









SUMMARY

- Organic-Inorganic Luminescent Hybrids
  - → Sol-Gel Synthesis
  - → Covalent bonding
- Emission Properties
  - → Sol-Gel matrix effects (OH, NH)
  - → UV sensitization mechanisms
- Potential Applications
  - → Luminescence Yield preserved
  - → Thermal resistance improved