

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



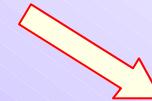
Rare Earth organic
Complexes
(Ln³⁺ = Eu³⁺, Tb³⁺)



*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

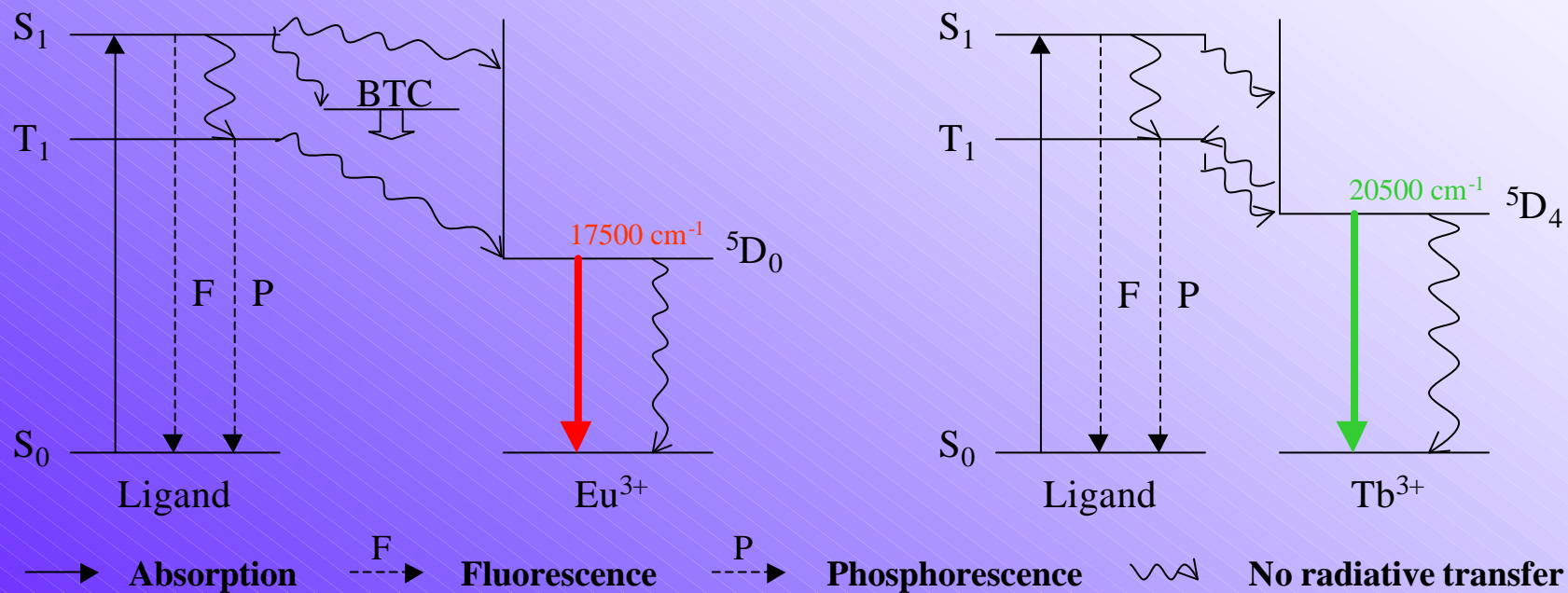


Organic Complexes of Europium and Terbium

Eu³⁺, Tb³⁺ ⇒ 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



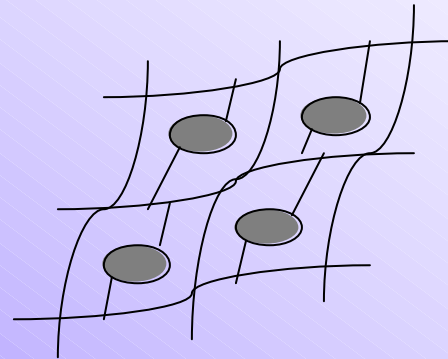
⇒

Emission Yield = Absorption efficiency
 × Transfer energy efficiency Ln³⁺ → 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

Increased Chemical Thermal and Mechanical stability

Organic- Inorganic Interface precisely defined

Single phase material

ADVANTAGES

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



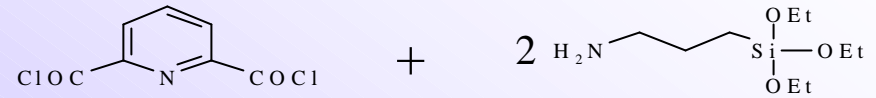
3. Hydrolysis/Condensation

Luminescent Hybrid

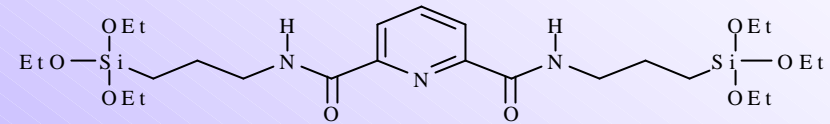
Characterization

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

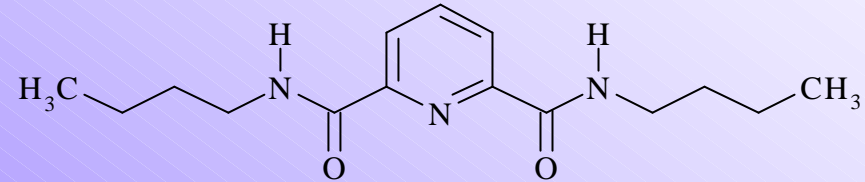
Precursors



Bonding



Monomer M1a



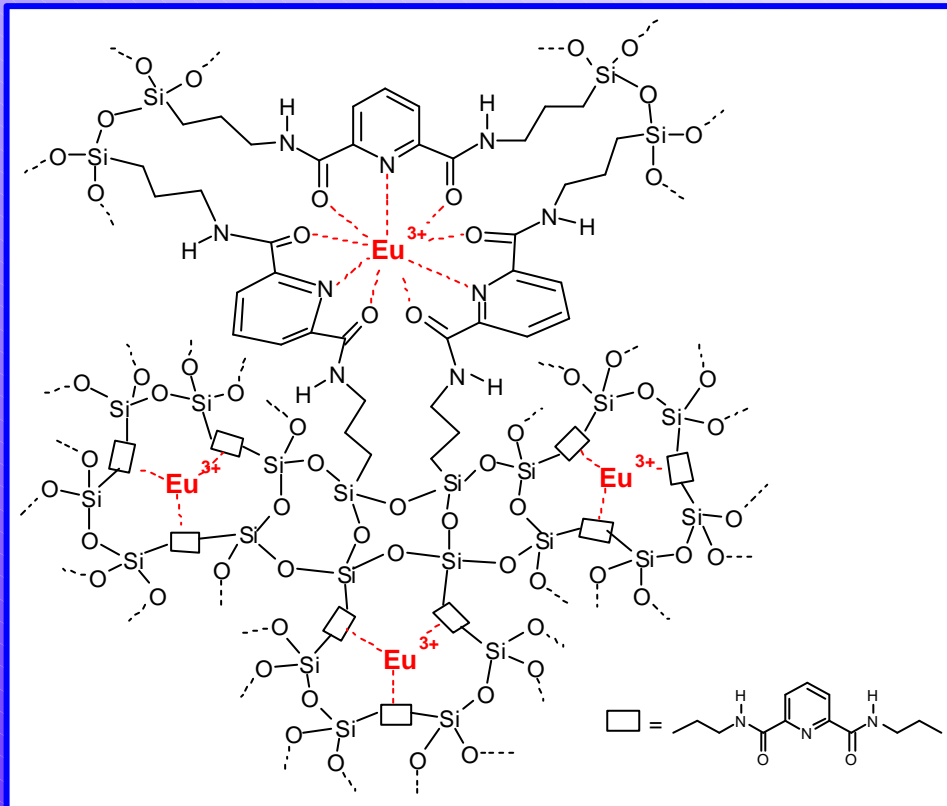
Organic Ligand O1a

Total bonding
reaction



Monomer and ligand
structure similar

STRUCTURE AND TEXTURE

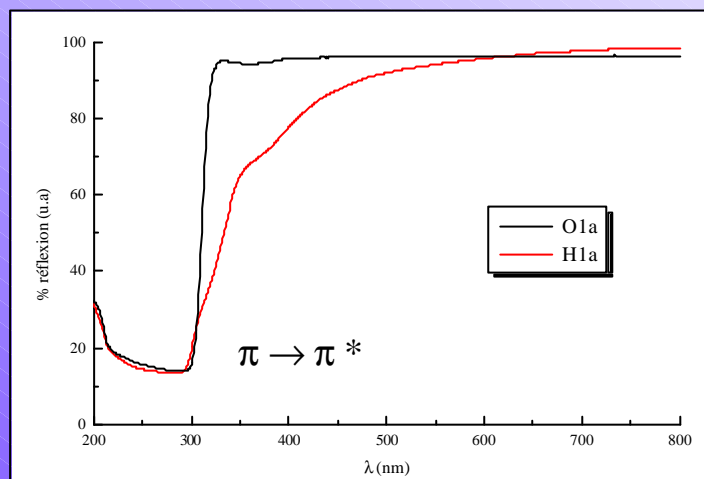


- Amorphous Materials
- Monolithic Gels
(Opaque and Transparent)
- Homogeneous texture

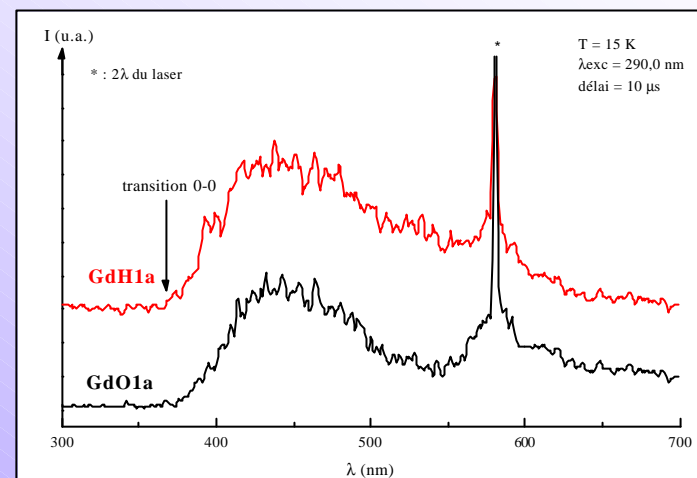
- Conservation of the electronic structure of the luminophore
- Conservation of the coordination mode of Ln^{3+}
 - Double covalent bonding
 - Single phase material with homogeneous distribution of organic and inorganic components

Position of triplet and singlet states

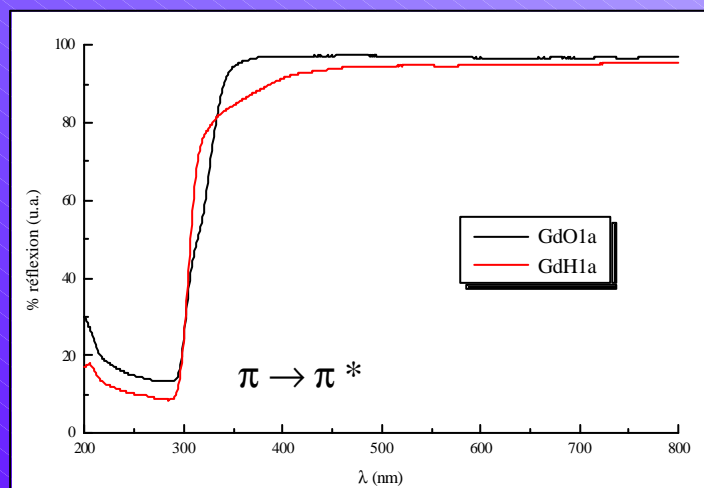
Absorption of gels and free ligands



Phosphorescence Emission



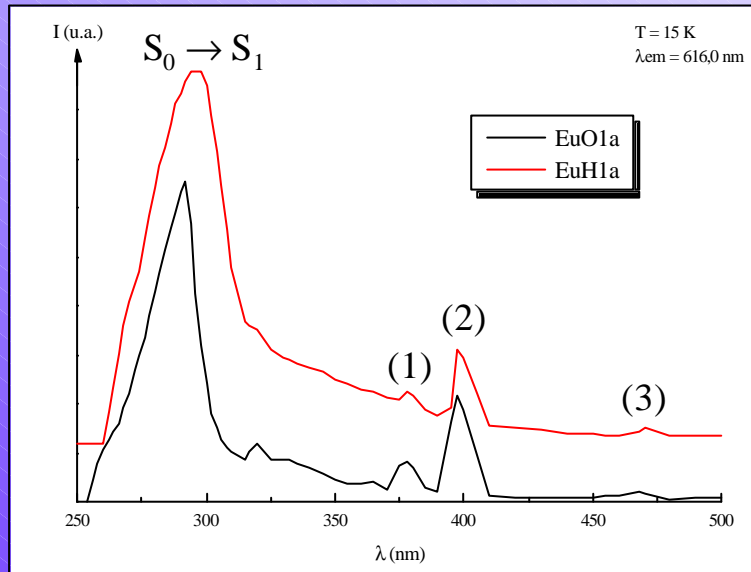
Absorption of hybrids and organic complexes



	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 $^5\text{D}_0 \text{ @ } ^7\text{F}_2$ de l'ion Eu^{3+}



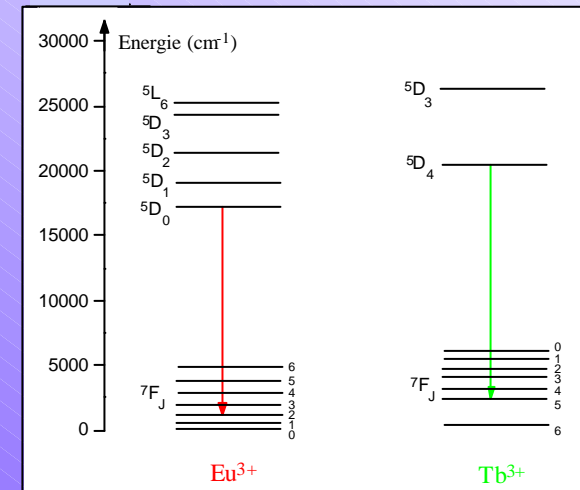
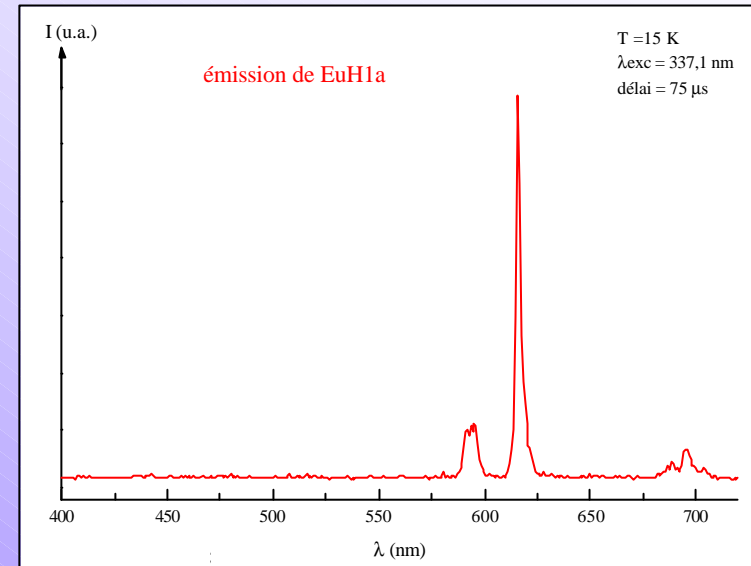
(1) $^7\text{F}_0 \rightarrow ^5\text{D}_4$ - (2) $^7\text{F}_0 \rightarrow ^5\text{L}_6$ - (3) $^7\text{F}_0 \rightarrow ^5\text{D}_2$

λ_{max} excitation \Rightarrow 292 nm EuO1a
 \Rightarrow 294 nm EuH1a



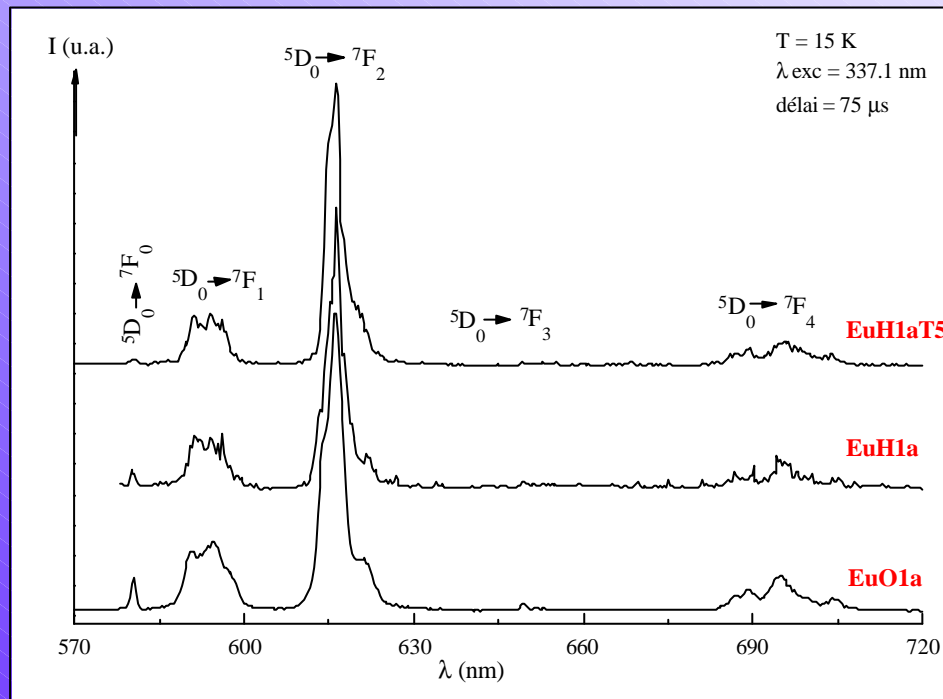
Conservation of the energy transfer mechanism

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



Emission properties of Eu^{3+}

Emission spectra under UV excitation



⇒ Amorphous in character

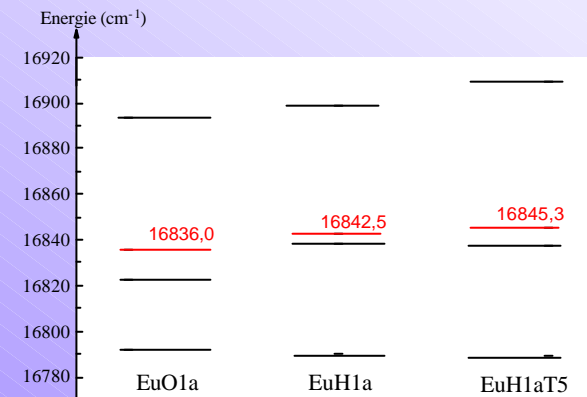
⇒ $5D_0 \rightarrow 7F_2$ (616,0 nm) transition predominates

Influence of the Sol-Gel matrix

- Shift of $5D_0$ level towards high energies

⇒ $\Delta\nu = 18 \text{ cm}^{-1}$

- $7F_1$ level splitting more important



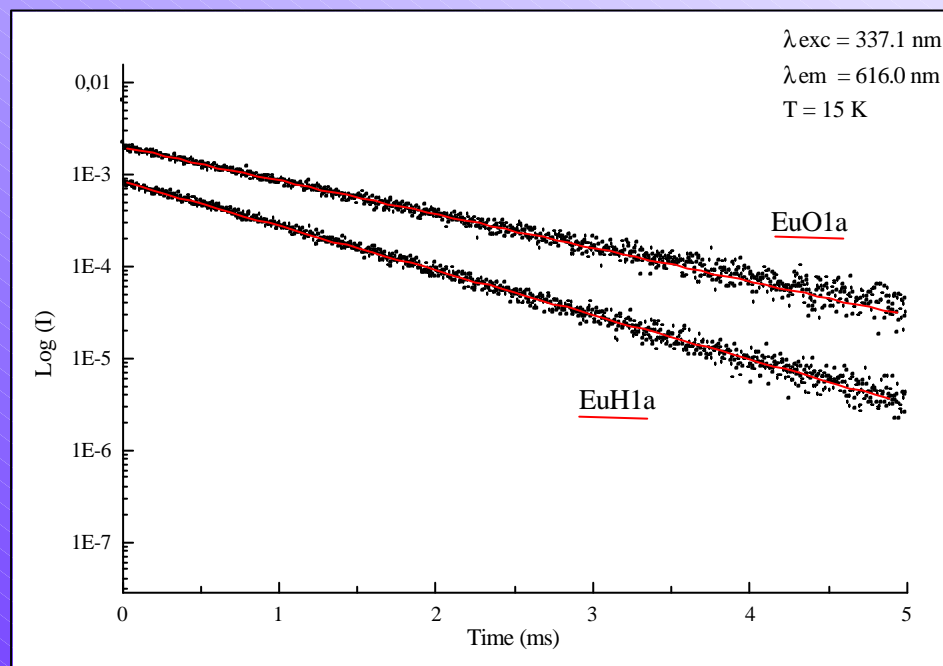
- Enlargement of the transition $5D_0 \rightarrow 7F_2$

⇒ $\Delta_{1/2} = 76 \text{ cm}^{-1} \rightarrow \text{EuO1a}$

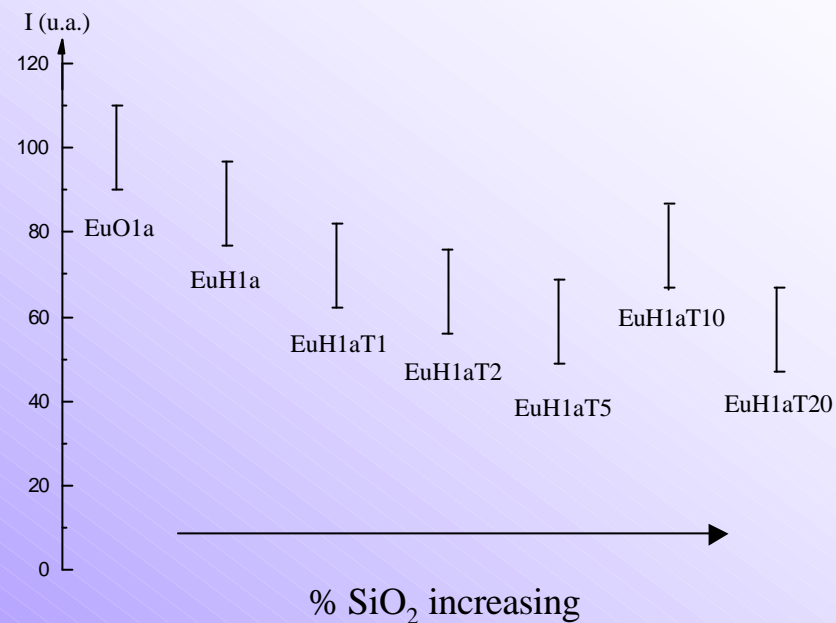
$107 \text{ cm}^{-1} \rightarrow \text{EuH1a}$

Lifetime and emission yield

Fluorescence decays



Emission yield



at 15 K

EuO1a

® 1,22 ms

EuH1a

® 1,06 ms

at 300 K

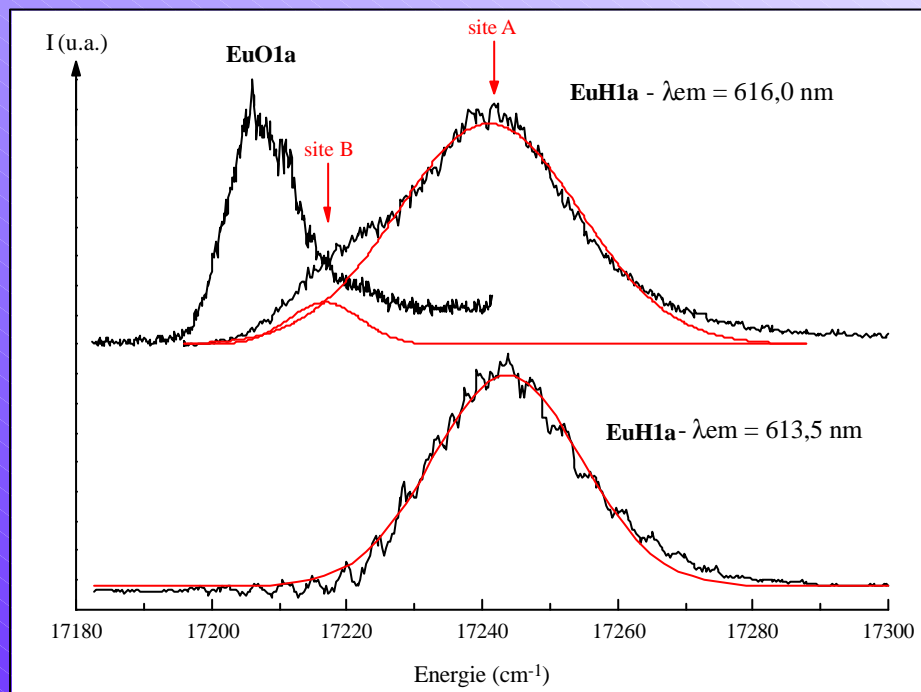
0,85 ms



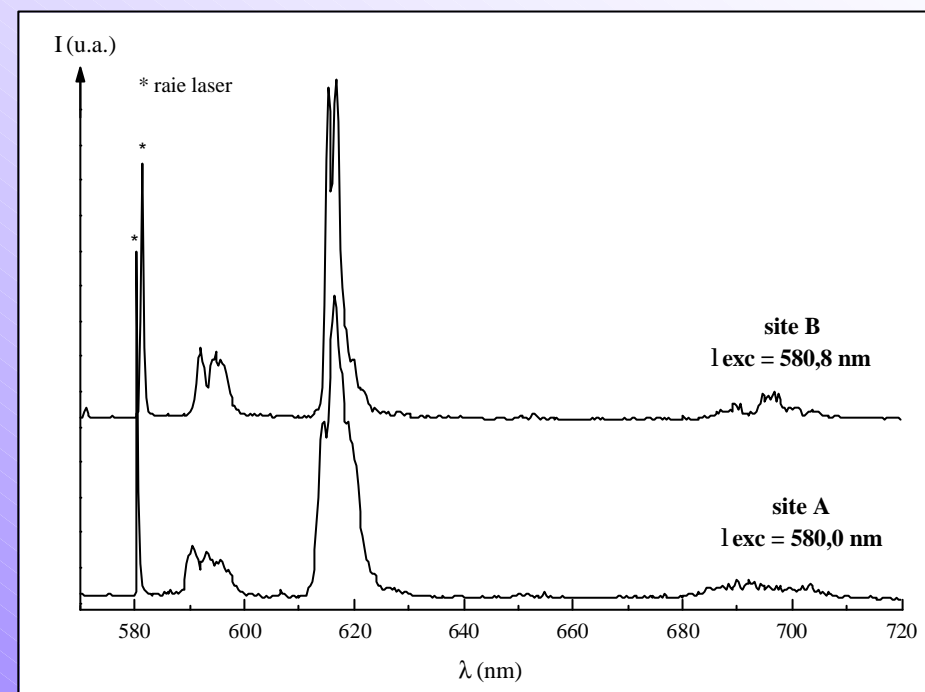
Limited effect of OH groups

Selective Excitation

**Excitation spectra ${}^7F_0 \rightarrow {}^5D_0$ of ${}^5D_0 \rightarrow {}^7F_2$
fluorescence at 15 K**



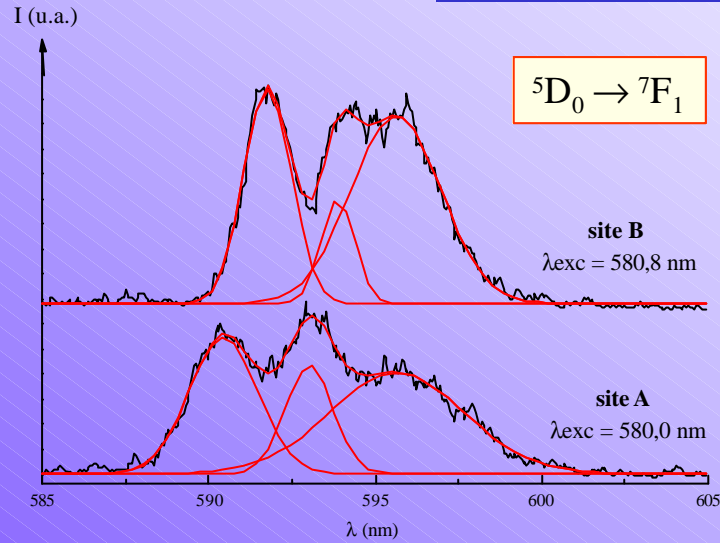
**Emission spectra of EuH1a by selective
excitation of sites A and B à 15 K**



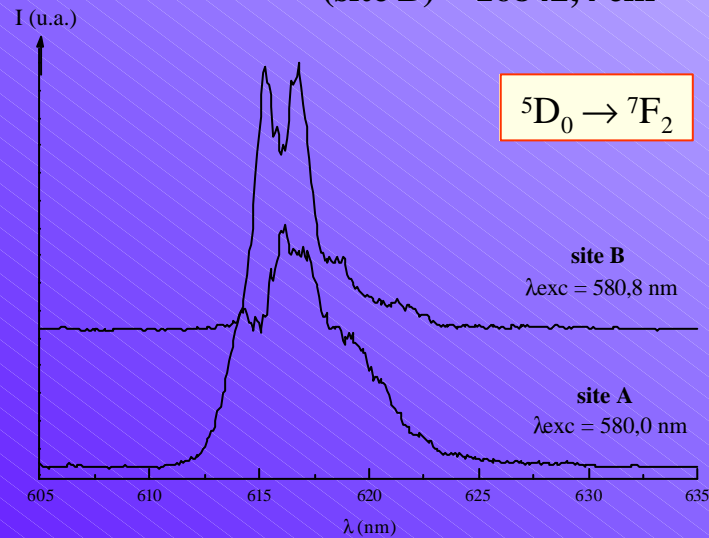
	Energy (cm ⁻¹)	D _{1/2} (cm ⁻¹)
EuO1a	17203	12,0
EuH1a (site A)	17240	21,2
EuH1a (site B)	17218	12,2

**2 Distinct distribution of sites
and not connected between them.**

Origin of the 2 distribution of sites

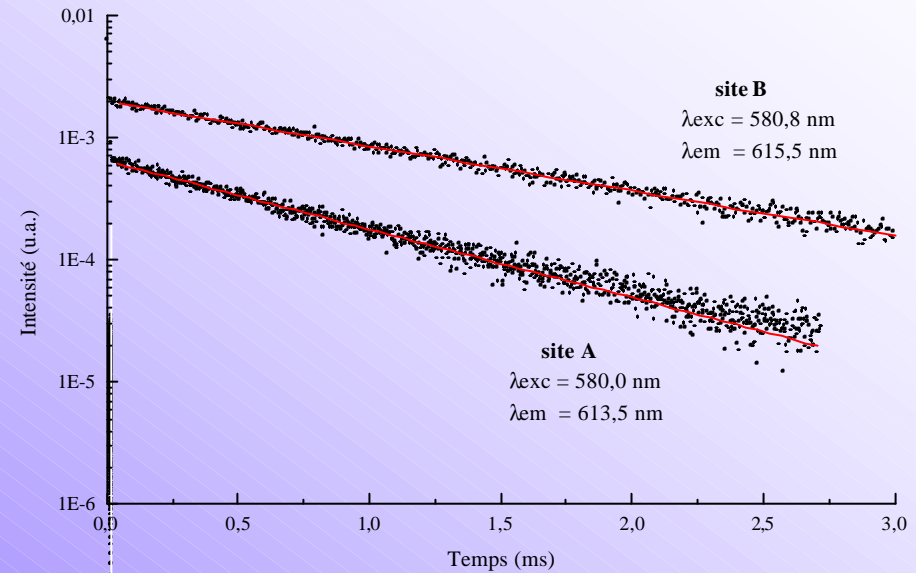


barycentre 7F_1 (site A) = $16863,2 \text{ cm}^{-1}$
(site B) = $16842,4 \text{ cm}^{-1}$



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

Lifetime



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

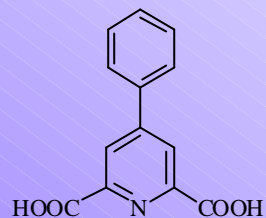
Site A \bar{P} with OH
Site B \bar{P} without OH

UV EXCITATION \bar{P} SITE B

CHROMOPHORE MODIFICATION

⇒ Absorption cross section

⇒ Energetic position of the triplet state

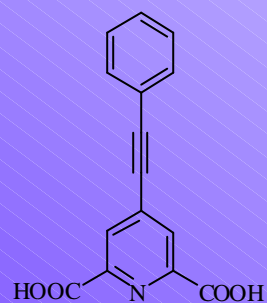


2,6-dicarboxy-4-phényl-pyridine

acide 2

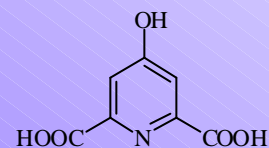


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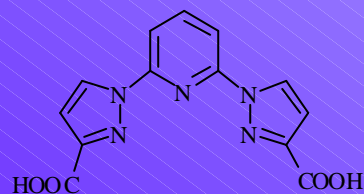
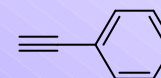


2,6-dicarboxy-4-phényléthynyl-pyridine

acide 3

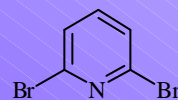


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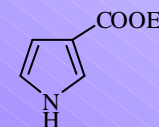


2,6-di(3'-carboxypyrazolyl)-pyridine

acide 4

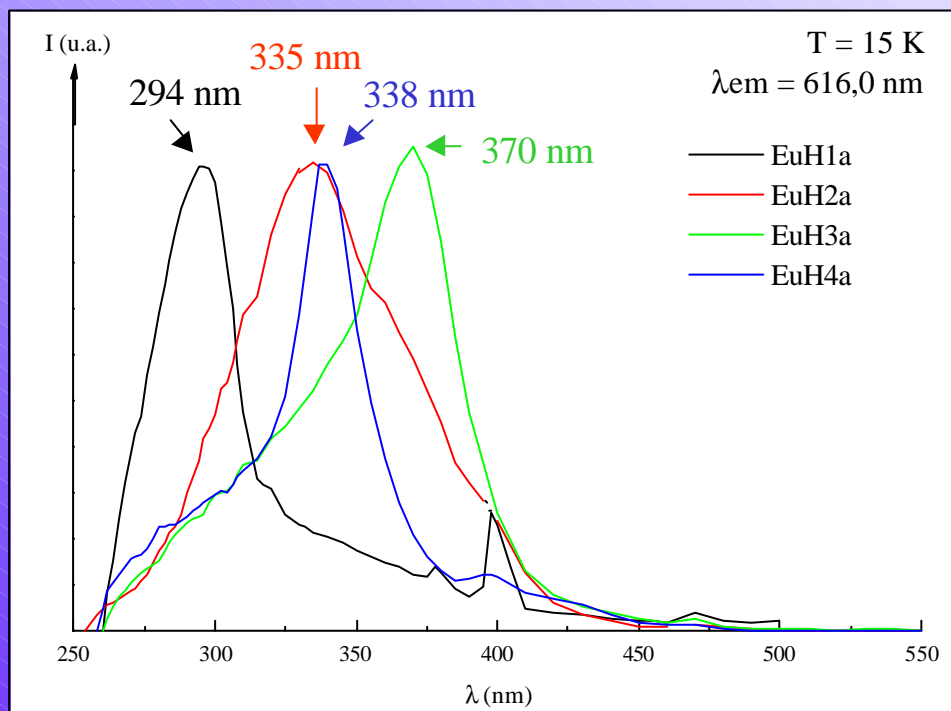


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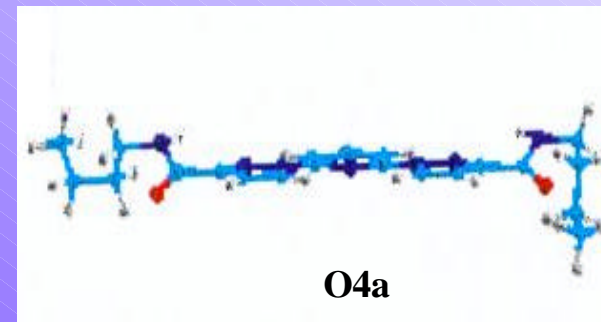
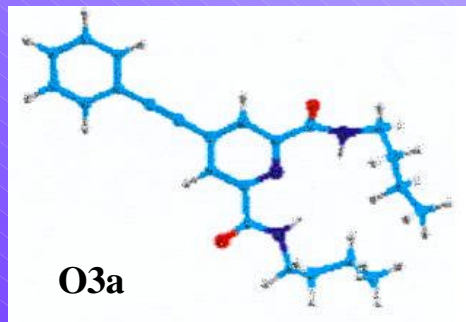
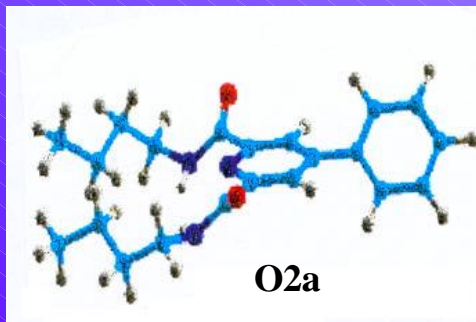
Chromophore energy levels

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



S_1 et T_1 levels position measured on Gd hybrid complexes

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

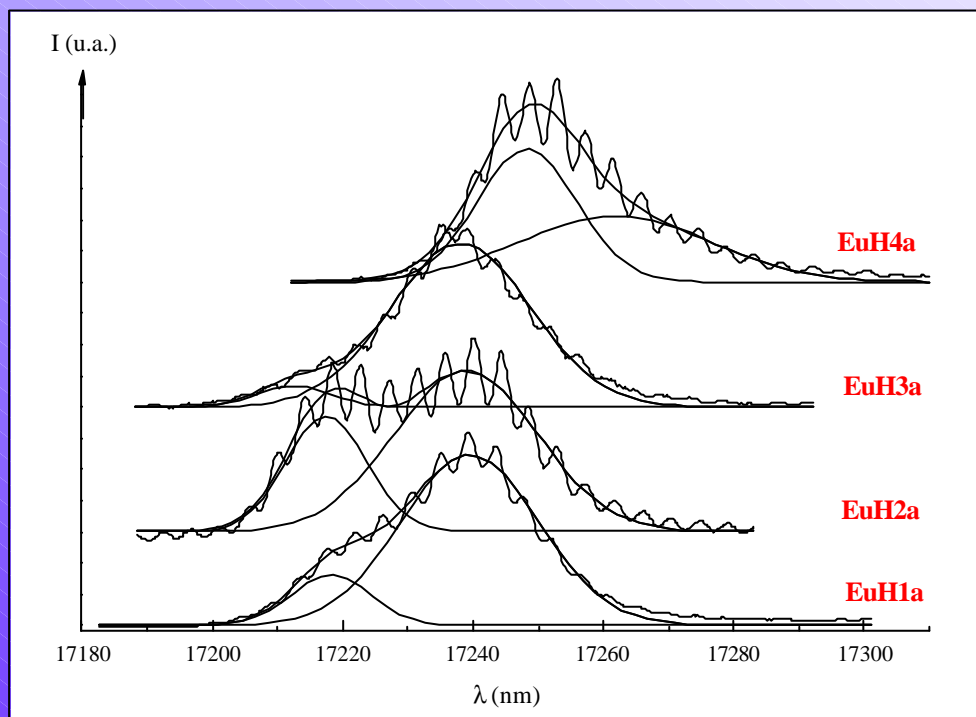


OH coupling effects

Excitation spectra of ${}^7F_0 \text{ @ } {}^5D_0$ (l em = 616,0 nm, T = 15 K)

5D_0 levels lifetime

($\lambda_{exc} = 337,1 \text{ nm} - T = 15 \text{ K}$)



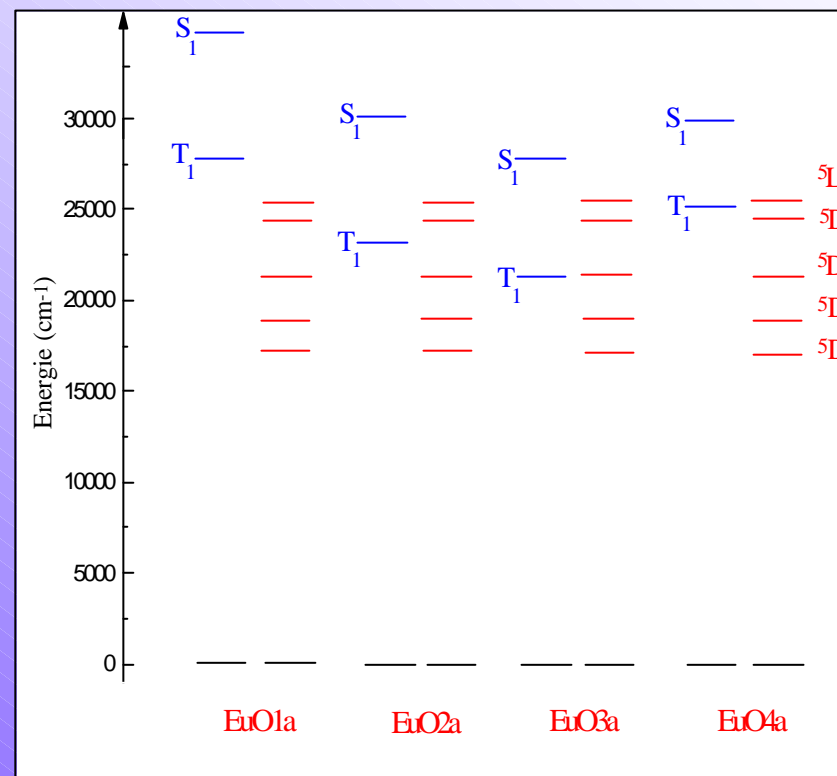
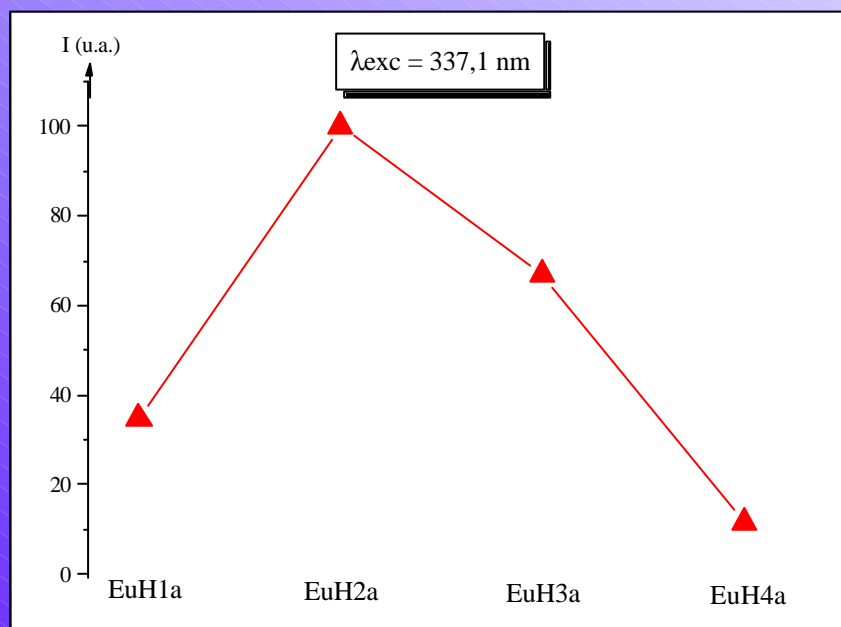
⇒ *Europium Complexes*

	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

	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

Photoluminescence Yield

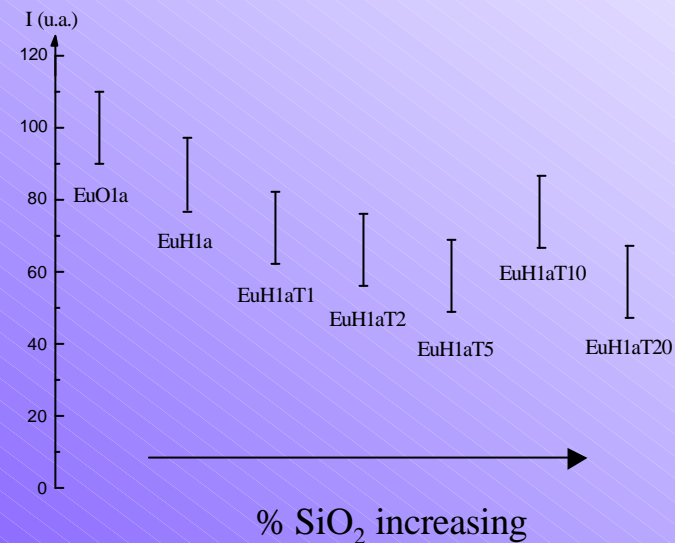
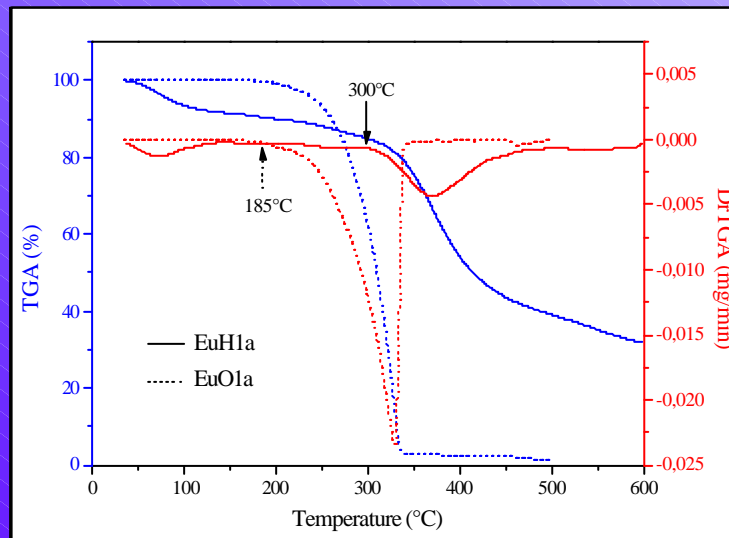
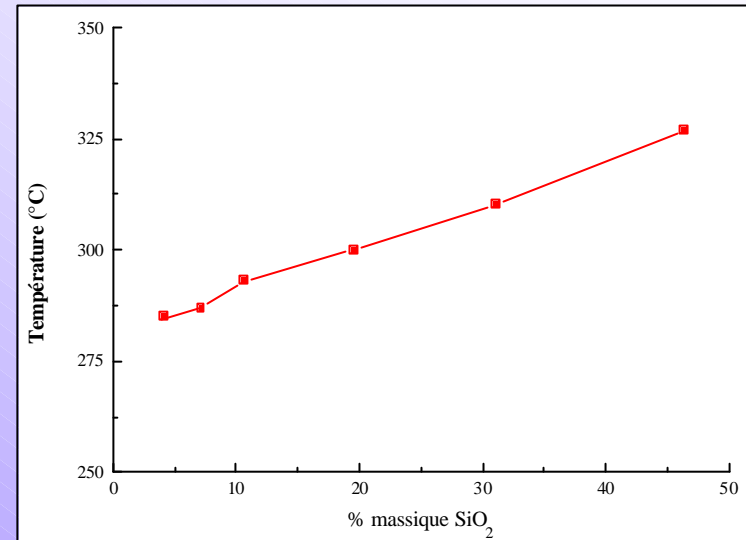
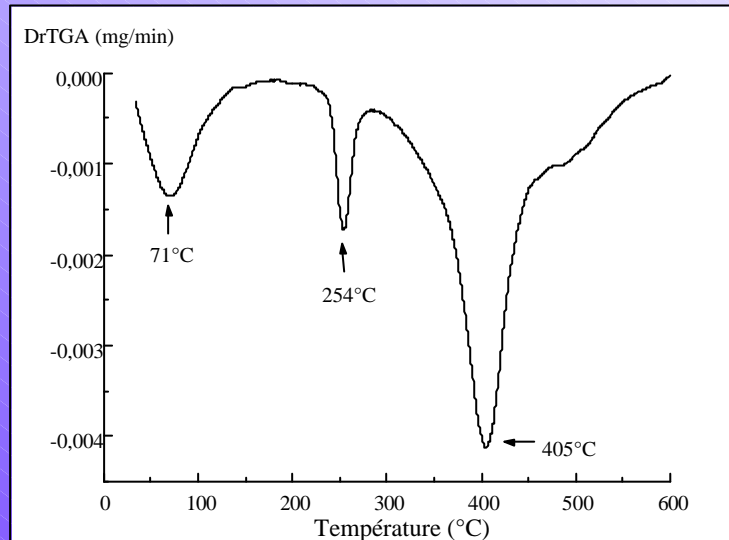
Europium Complexes



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