Coordination Chemistry and Reactivity of f Elements

Cours 3 Luminescence of Lanthanides and its Applications

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Learning Outcomes

-Recall basic principles of luminescence

-Understand the causes of fluorescence in lanthanide compounds

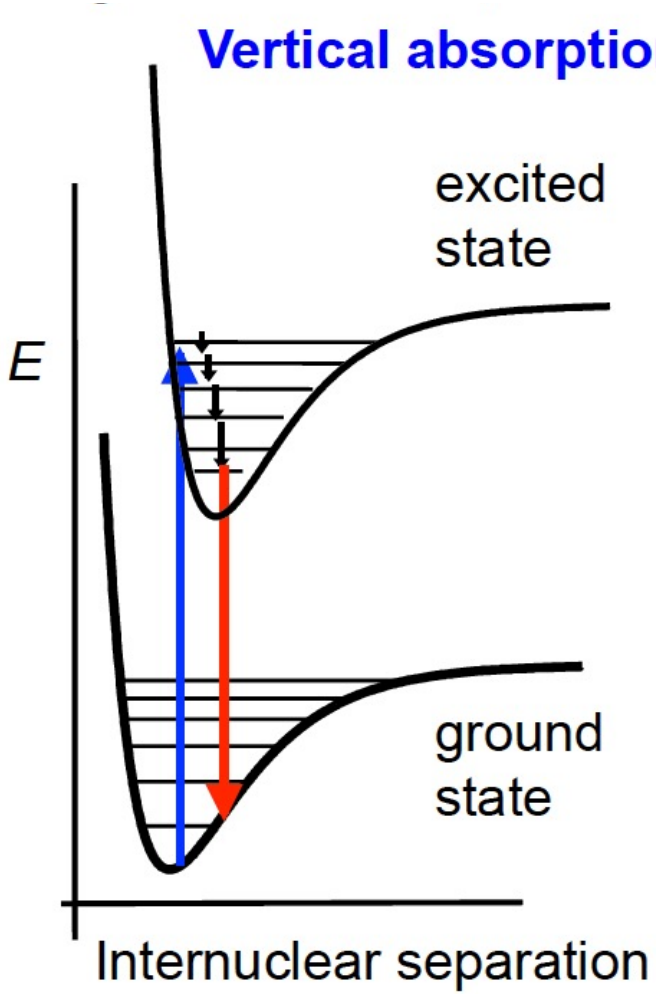
-Recall the antenna effect

-Understand the requirement for application of lanthanide luminescence

-Basis of design of luminescent complexes

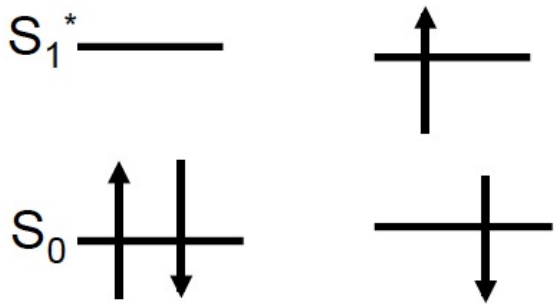
Luminescence

Emission of light after absorption by an organic molecule or a metal complex (electronic transition) that has an accessible lower electronic state



Vibrational relaxation (VR)
Non-radiative de-activation

Vertical emission (radiative decay)
Kasha's rule: emission from lowest vibrational (relaxed) state



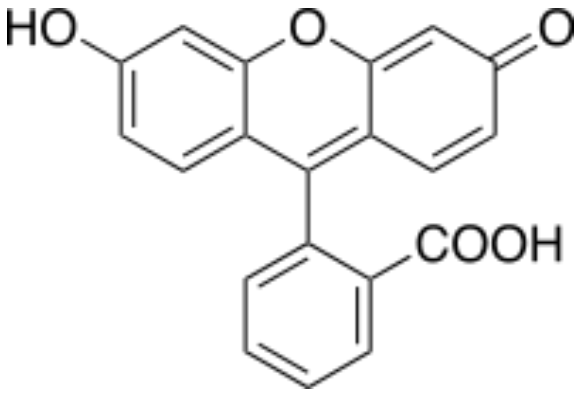
Fluorescence-radiative decay between states of the same multiplicity (2S+1)

Luminescence in Nature

Bioluminescence in the sea

or in the field

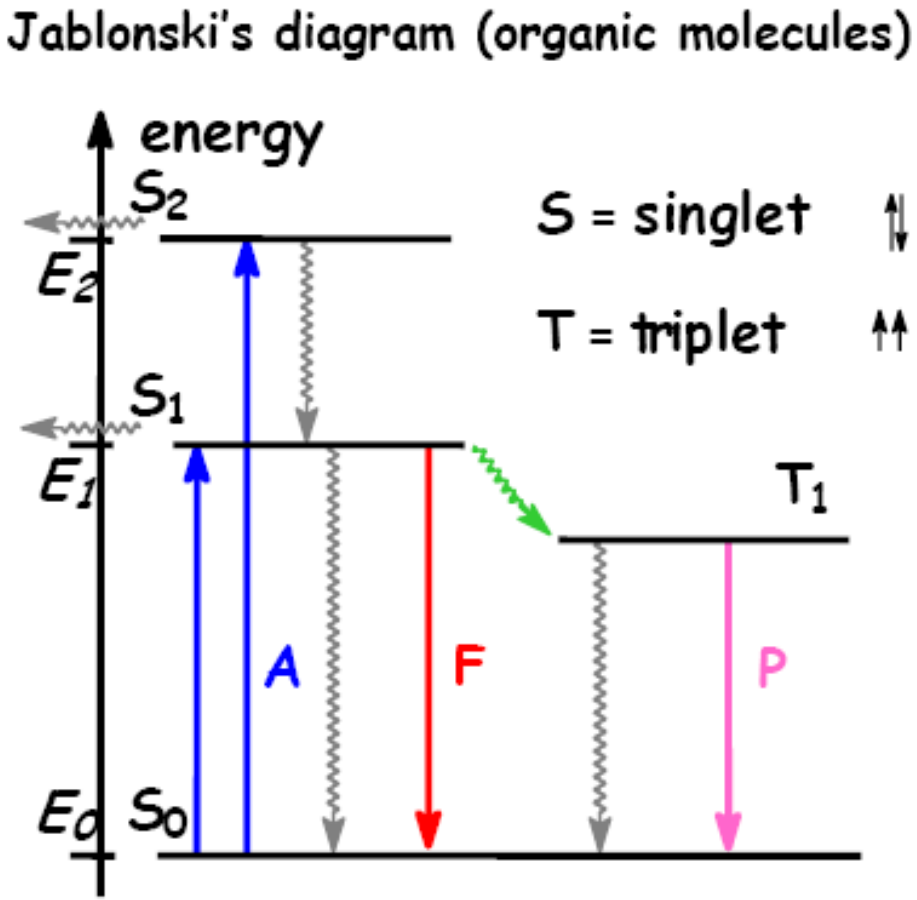
Organic fluorophore: A fluorophore is a chemical compound that can re-emit light upon light excitation. Fluorophores typically contain several combined aromatic groups, or plane or cyclic molecules with several π bonds.



Fluorescein

Short lifetime

Luminescence in Organic Molecules



A = absorption
10^{-16} s

F = fluorescence
10^{-12}–10^{-6} s

P = phosphorescence
10^{-6} – 10s

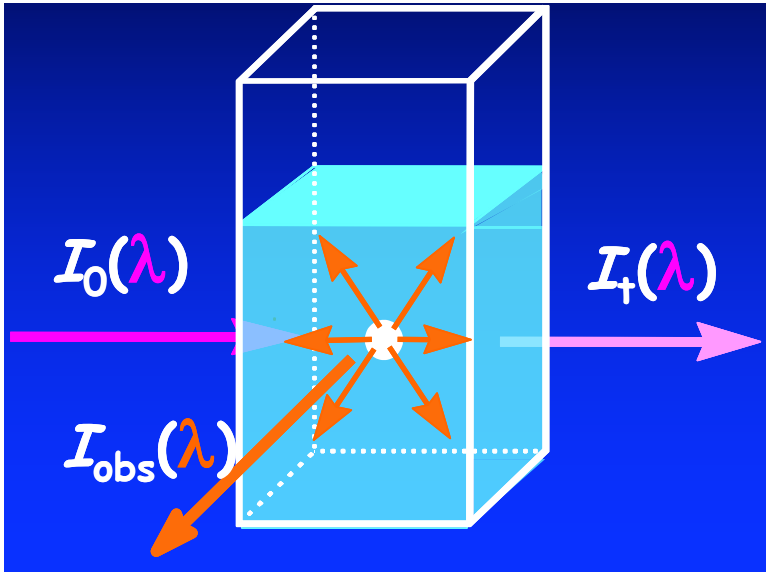
non-radiative de-activation

intersystem crossing

Quantum yield

$$Q = \frac{I_{ém}}{I_{abs}} = \frac{\text{number of emitted photons}}{\text{number of absorbed photons}} = f(T)$$

The quantum yield increases when temperature decreases



$$Q = \frac{I_{em}}{I_0 - I_t}$$

Lifetime

Average time spent in an excited state before radiative decay

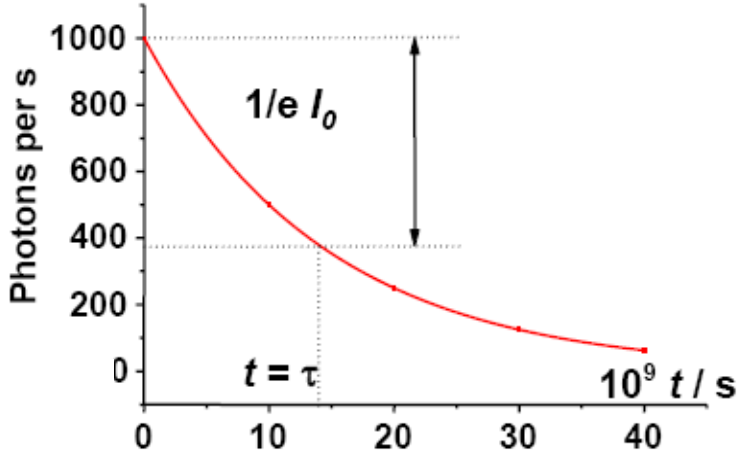
The intensity of emission after a pump pulse decays exponentially

If N^* is the number of excited molecules at time t:

$$N^* = N_0^* \cdot e^{-k_r t}$$

$$I(t) = I_{(t=0)} . e^{-\frac{t}{\tau}}$$

$$I(t) = I_{t=0} . e^{-k_r t}$$

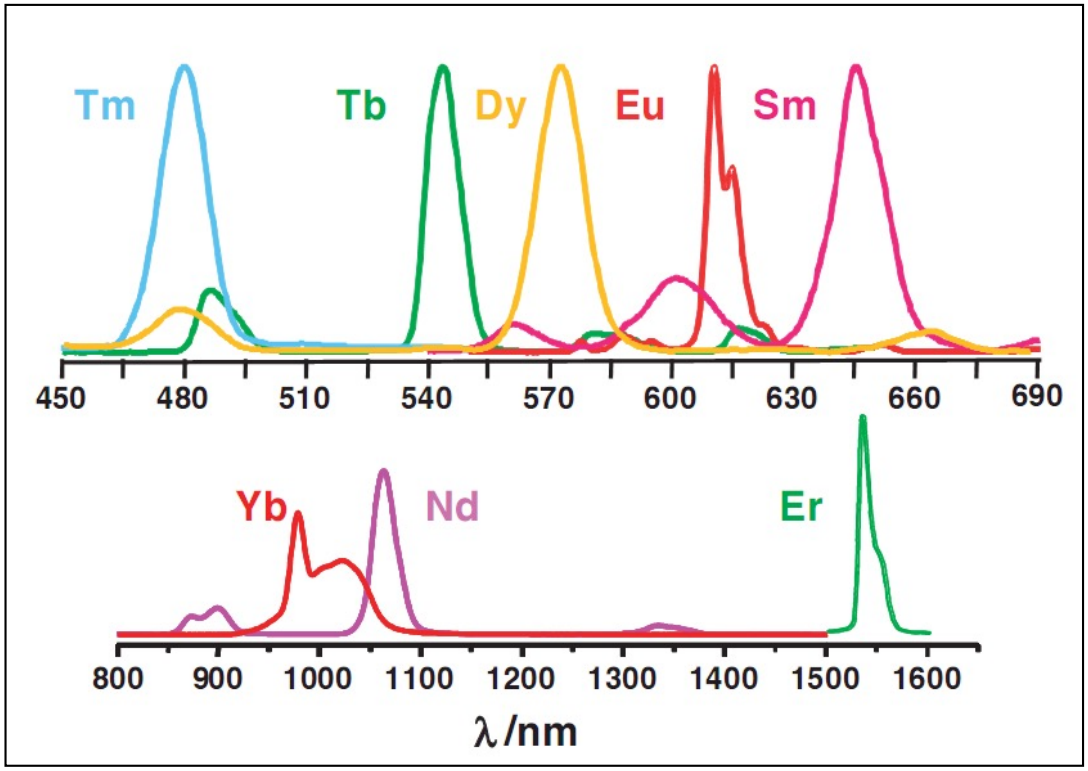


The lifetime of the excited level is given by:

$$\tau = 1/k_{obs} \quad (s)$$

During this time, a fraction 1/e (37%) of the excited molecules has returned to the ground state

Lanthanide(III) Ions Luminescence



Sharp lined Ln(III) emission from UV to NIR

Lanthanide ions exhibit luminescence, emitting radiation from an excited electronic state, the emitted light having sharp lines characteristic of f–f transitions of a Ln^{3+} ion

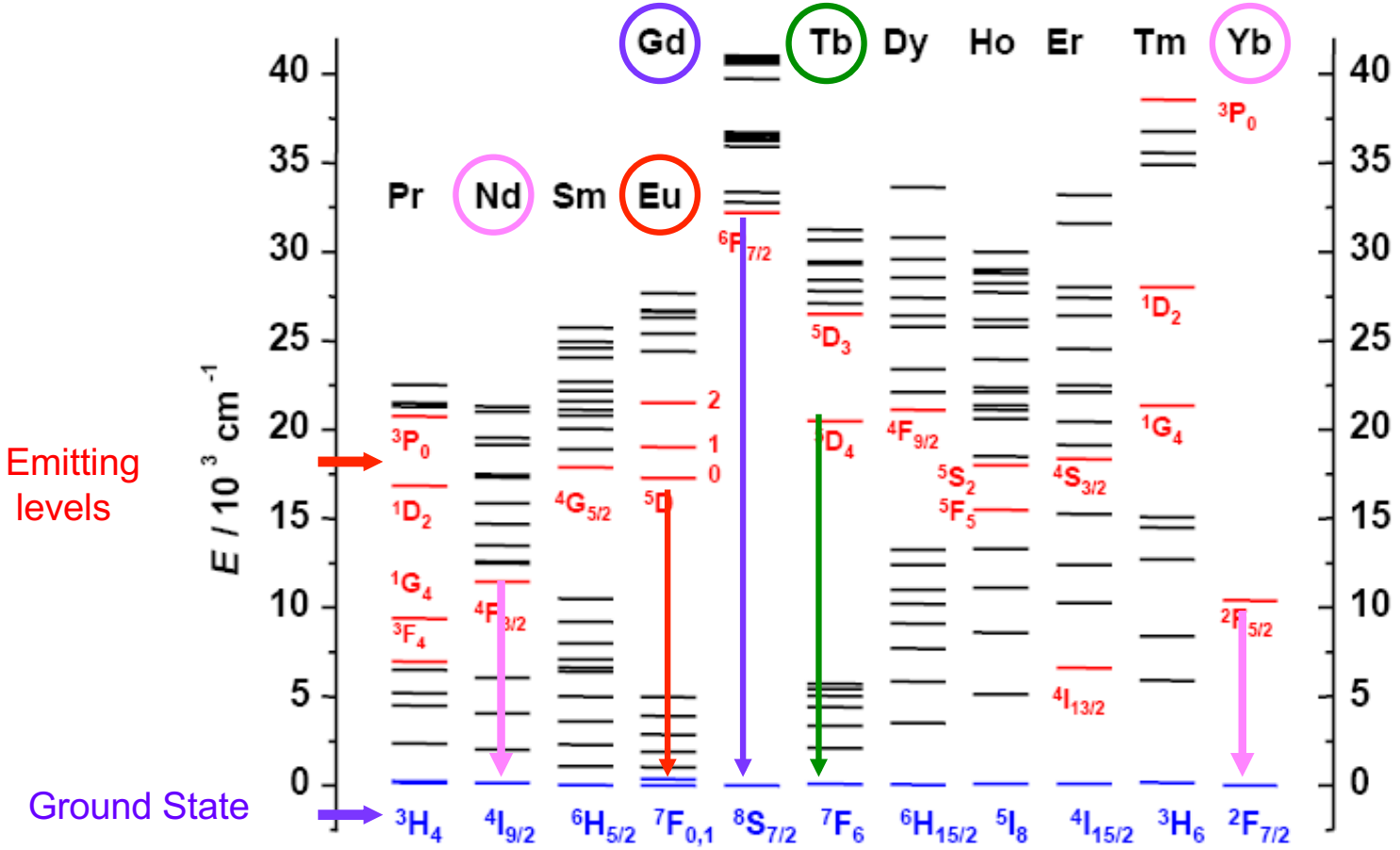
Direct excitation of lanthanide ions is only possible with high energy laser sources due to low absorption coefficient

Ln(III) used as dopants in phosphors (sulfides, fluorides, oxyde phosphate, silicate of non luminescent ions).

Lanthanide Emissive States

- Energy gap :wavelength of emission
- Bigger gap = longer Lifetime

- Non radiative quenching can reduce the lifetime e.g. by vibrations



Eu^{3+}
Emission in the red

Gd^{3+}
Emission in the UV

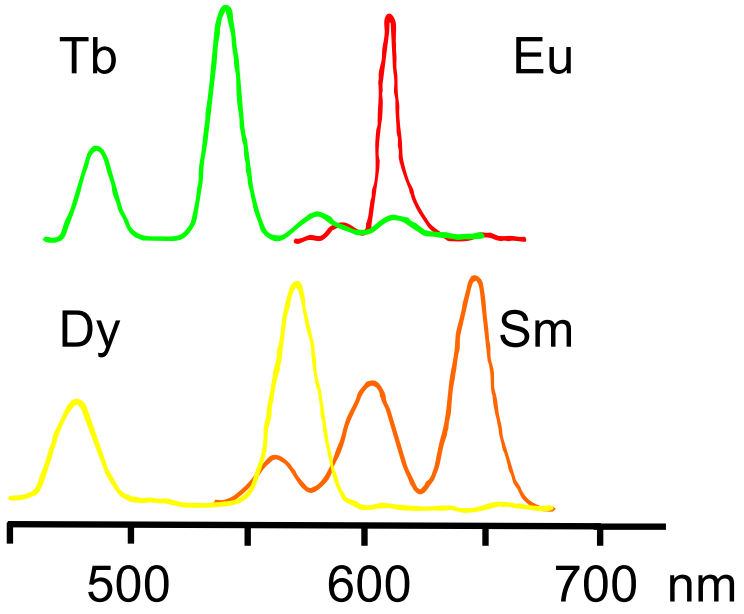
Tb^{3+}
Emission in the green

Nd^{3+}, Yb^{3+}
NIR emission

Lanthanide(III) Ions Luminescence

The smaller the gap between excited and ground state, the larger the contribution of non-radiative de-activation (particularly through vibrations).

Gd^{III} is the best ion, but emits in the UV
Eu^{III}, Tb^{III} have often large intrinsic quantum yields and are used as luminescent probes.



Pr^{III} (1.33 μm), Nd^{III} (1.06 μm), Er^{III} (1.54 μm), and Yb^{III} (0.98 μm) have interesting emission bands in the NIR range, some of them are in the telecommunication window (1 – 1.6 μm)

Lifetimes of Ln^{3+}

- Tb^{3+} and Eu^{3+} millisecond
- Sm^{3+} Dy^{3+} Yb^{3+} Er^{3+} microseconds
- Pr^{3+} Nd^{3+} nanoseconds

Main phosphors used in lighting

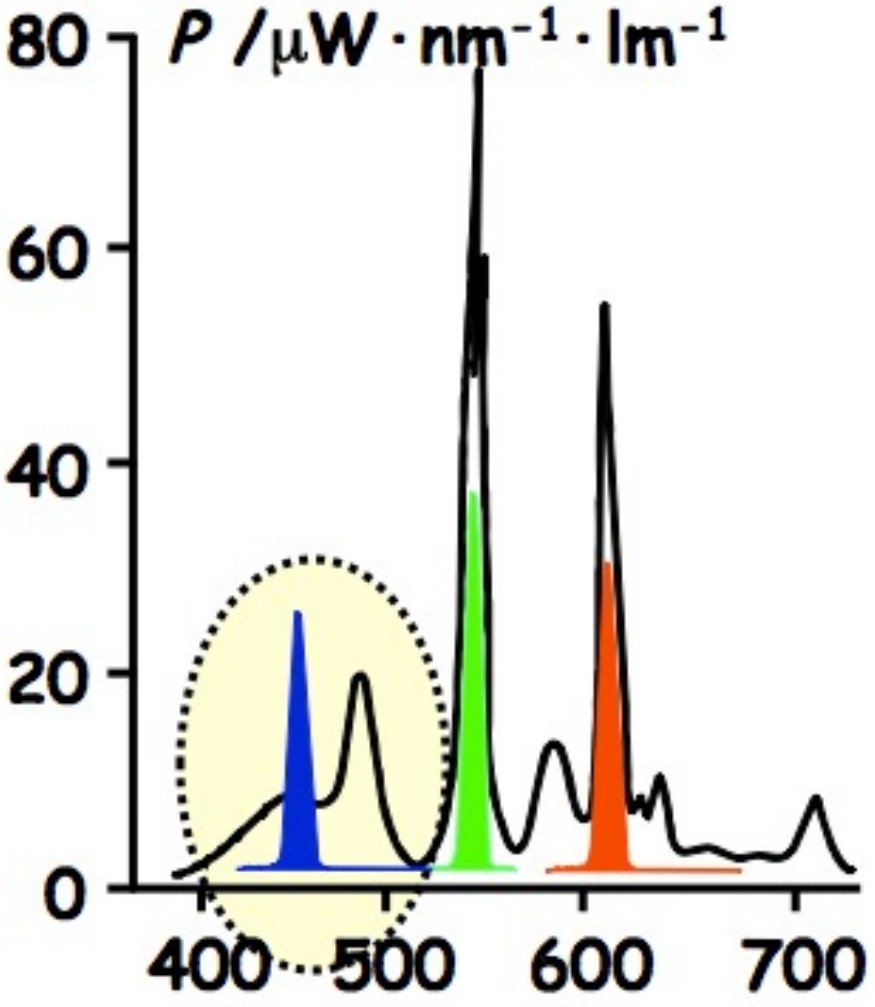
Year	Phosphor		
1960	$Ca_5(PO_4)_3Cl:Sb^{3+},Mn^{2+}$ (white)		
1974	$BaMg_2Al_{16}O_{27}:Eu^{2+}$	$CeMgAl_{10}O_{19}:Tb^{3+}$	$Y_2O_3:Eu^{3+}$
1990	$BaMgAl_{10}O_{17}:Eu^{2+}$ $(Sr,Ca)_5(PO_4)_3Cl:Eu^{2+}$	$(La,Ce)PO_4:Tb^{3+}$ $CeMgAl_{10}O_{19}:Tb^{3+}$ $(Gd,Ce)MgB_5O_{10}:Tb^{3+}$	$Y_2O_3:Eu^{3+}$
2005	$BaMgAl_{10}O_{17}:Eu^{2+}$	$(La,Ce)PO_4:Tb^{3+}$	$Y_2O_3:Eu^{3+}$

Spectral Distribution of a Fluorescent Light

$BaMg_2Al_{16}O_{27}:Eu^{II}$

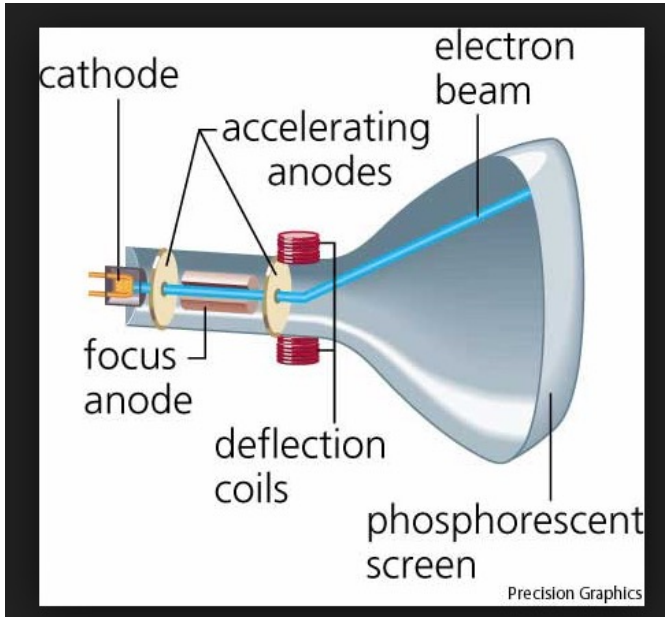
$CeMgAl_{11}O_{19}:Tb^{III}$

$Y_2O_3:Eu^{III}$



Phosphors used in cathodic tubes

Flourescence			Wavelength Peak(s) nm	Composition	Application
Amber				$InBO_3$:Tb+$InBO_3$:Eu,	
Blue			450	ZnS:Ag	
Green			545	Y_2O_2S:Tb	Display tubes
Green			545	Y_2SiO_5:Tb	Projection tubes
Green			520	$Y_3(Al,Ga)_5O_{12}$:Ce	Beam index tubes
White				(Zn,Cd)S:Cu,Cl+(Zn,Cd)S:Ag,Cl	
White				$InBO_3$:Tb+$InBO_3$:Eu+ZnS:Ag	
Yellow			588	$InBO_3$:Eu	
Yellow-Green			550	$InBO_3$:Tb	
Yellow-Green			544	$Y_3(Al,Ga)_5O_{12}$:Tb	Projection tubes
Green			535		General purpose oscillos



Antenna Effect

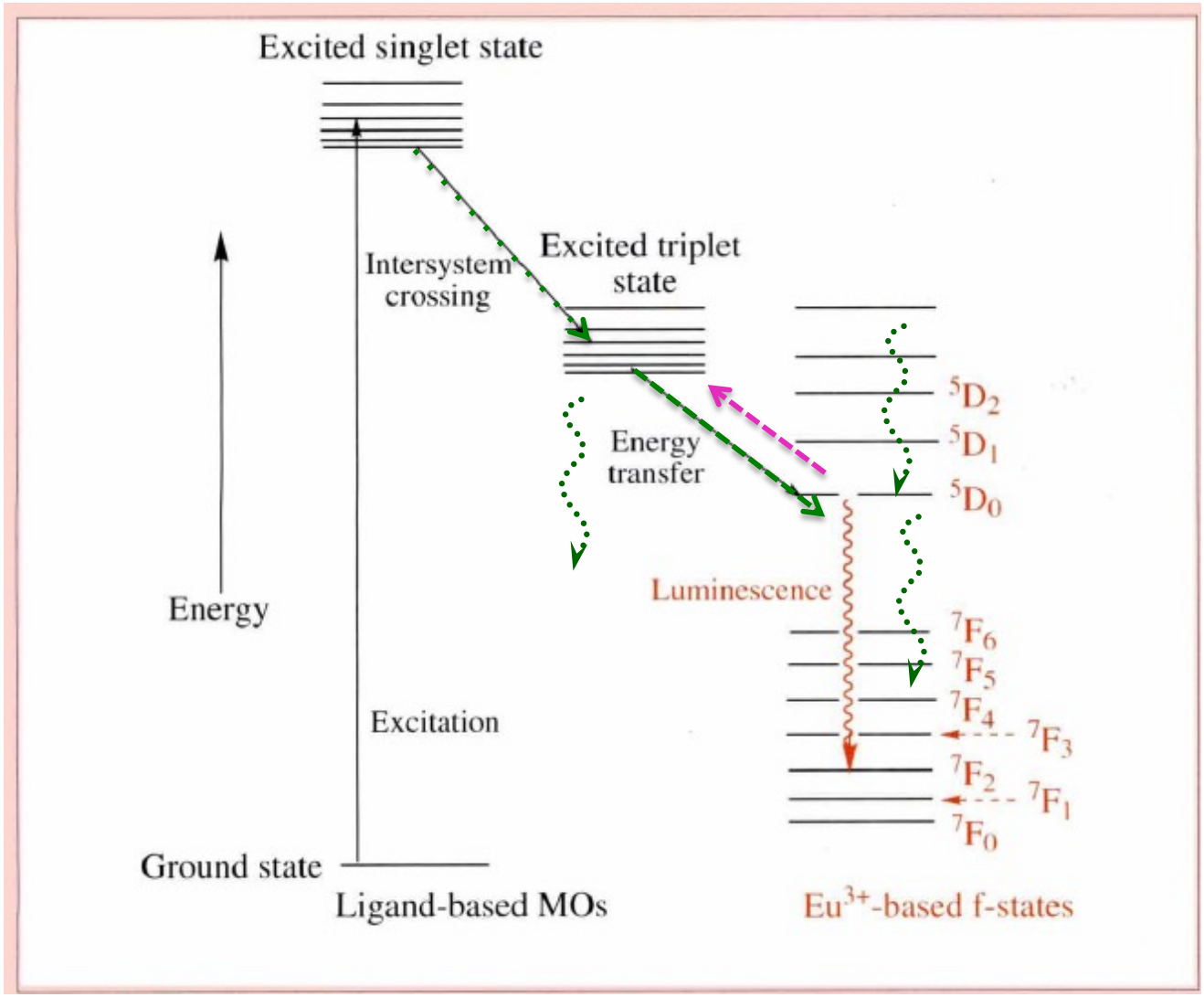
Indirect excitation, called sensitisation is achieved through lattice or attached ligands

light harvesting | Energy transfer | light emission

The excited states of Ln^{III} ions are usually long-lived with lifetimes in the range μs to ms, so that the ligand triplet state plays a major role in the energy transfer process.

☹ Water molecules or solvent molecules desactivate the luminescence

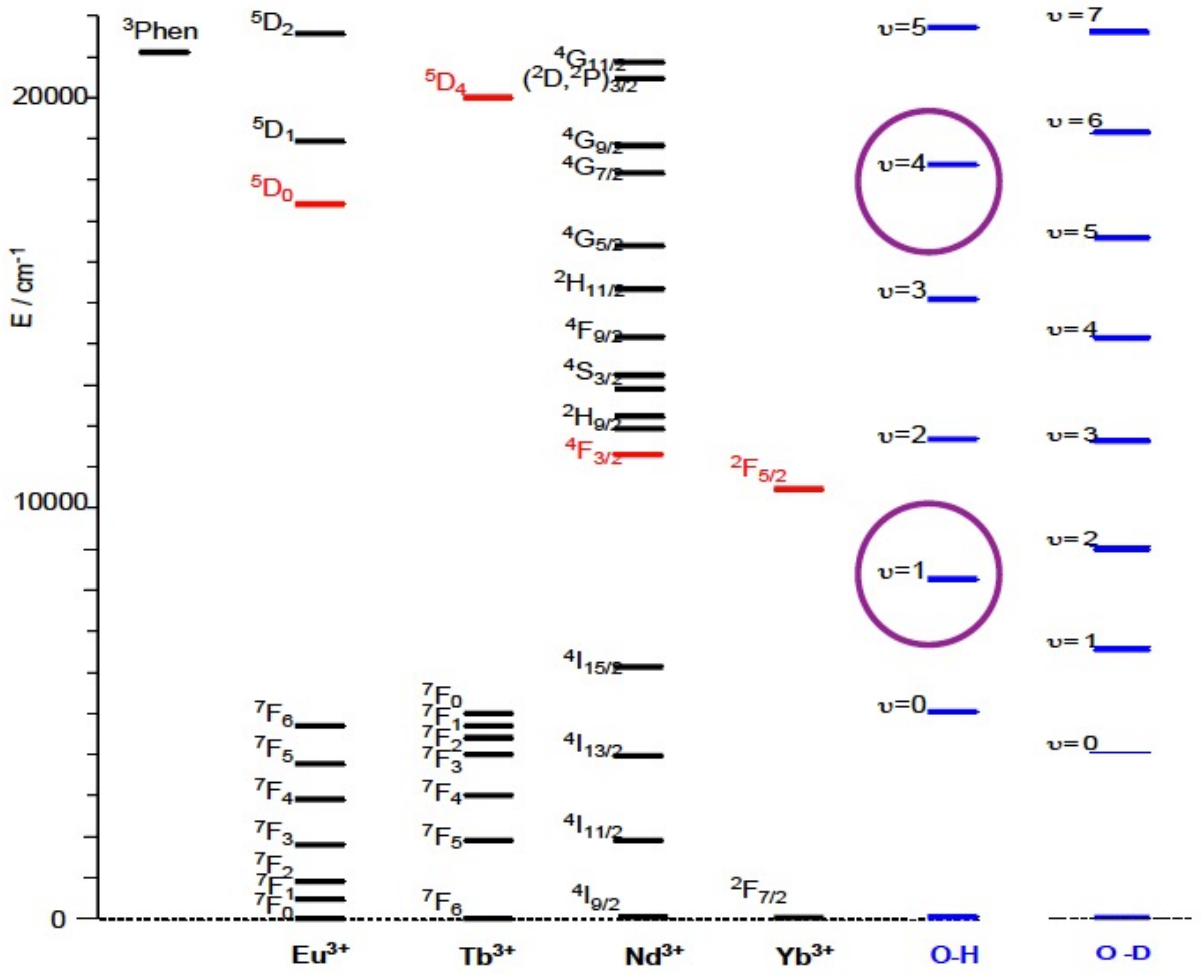
Indirect excitation with a ligand with strong absorption coefficient



Non-radiative emission

The most likely acceptor levels for Eu^{3+} and Tb^{3+} are 17 200 and 20 400 cm^{-1} respectively, so the triplet level in the acceptor ligand needs to be above 22 000 cm^{-1}, otherwise competing thermally activated back-energy-transfer occurs.

Luminescence quenching by OH, N-H, C-H



- Ln excited states are quenched by: O-H, N-H and C-H vibrations
- Limited quenching by O-D oscillators:- (Hooke's law)

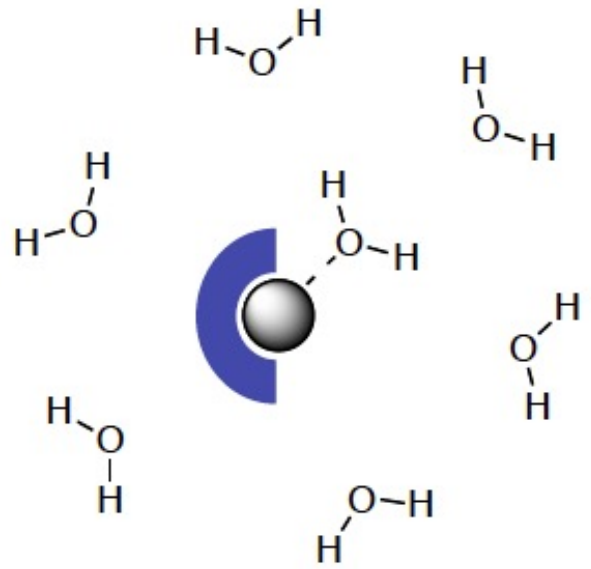
Number of Coordinated Water Molecules (q)

- Lanthanide coordination compounds are labile:

$$[Ln(H_2O)_9]^{3+} + H_2O \rightleftharpoons [Ln(H_2O)_8(H_2O)]^{3+} + H_2O$$

- Use quenching of O-H vs. O-D oscillators to determine **q**

Horrocks Equation: $q = A(k_{H2O} - k_{D2O} - B)$



k = rate constant of decay = $1/\tau$

A, B = proportionality constants

A corrects for inner sphere quenching

B corrects for outer sphere quenching

A and B values have been determined for Eu^{3+}, Tb^{3+}, Yb^{3+} (Nd^{3+} and Sm^{3+})

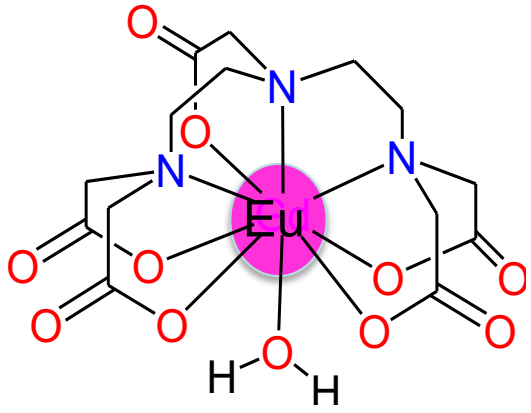
W. D. Horrocks, Jr. and D. R. Sudnick, *J. Am. Chem. Soc.*, 1979, **101**, 334-340.

Number of Coordinated Water Molecules (q)

Q. For the Eu^{3+} complex determine q:

τ_{H2O} = 0.63 milliseconds (ms)

τ_{D2O} = 2.60 milliseconds



$q = A(k_{H2O} - K_{D2O} - a)$

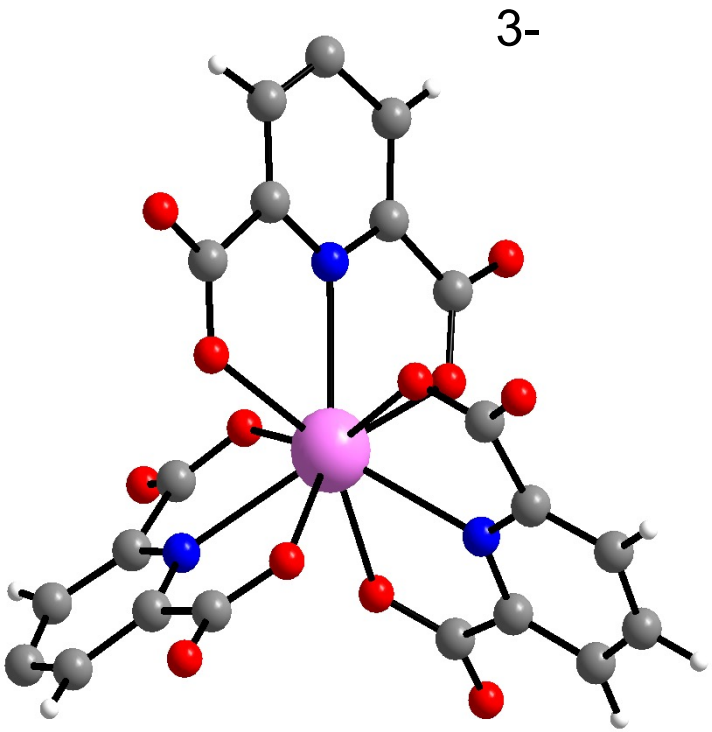
A= 1.11 ms

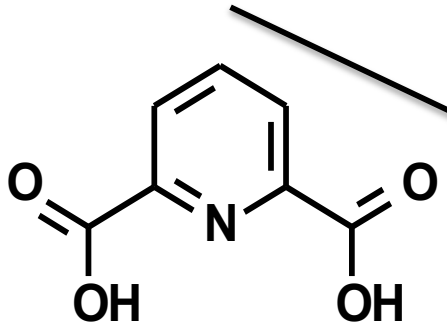
a= 0.32 ms^{-1}

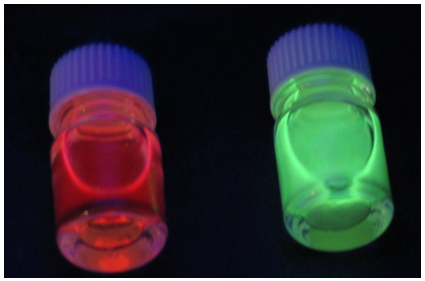
q= 1.11((1/0.63-1/2.60)-0.32) = 1.05

1.05 water molecules bind the europium cation

Europium(III): tris(dipicolinate)







Eu(III) Tb(III)

LogK_i = 8.7, 8.1, and 5.6 (i = 1-3)

$\tau(^5D_0)$ = 1.54 and 1.67 ms

The terbium complex emits in the green

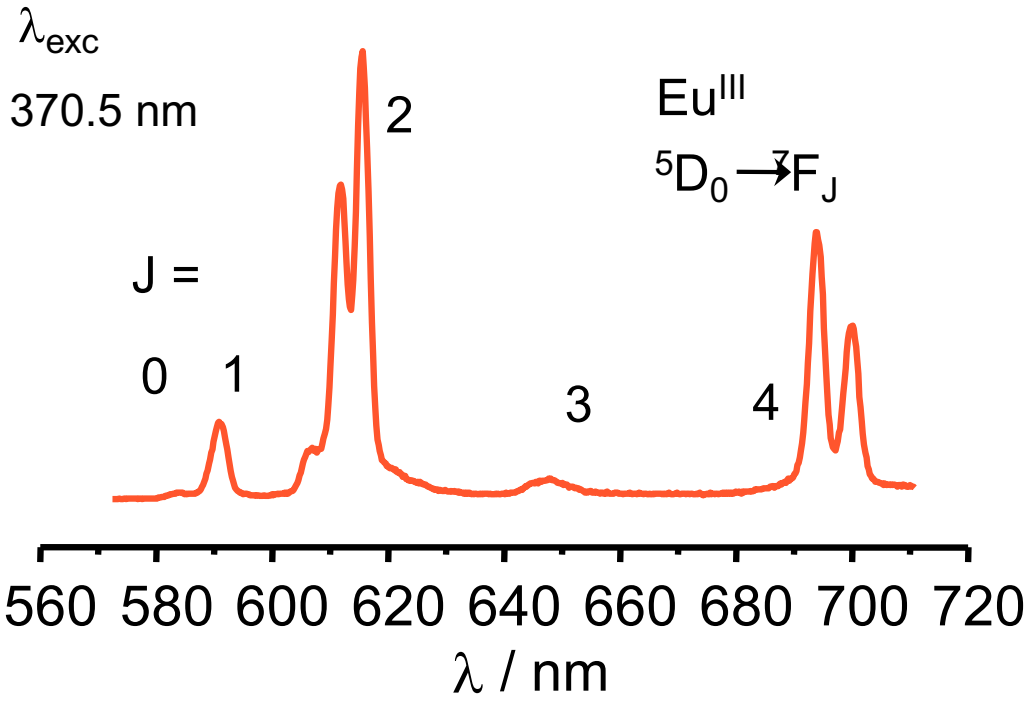
The europium complex emits in the red

- Q_{Eu} = 13.5%

$[Tb(dpa)_3]^{3-}$ Q_{Tb} = 26.5%

Security inks

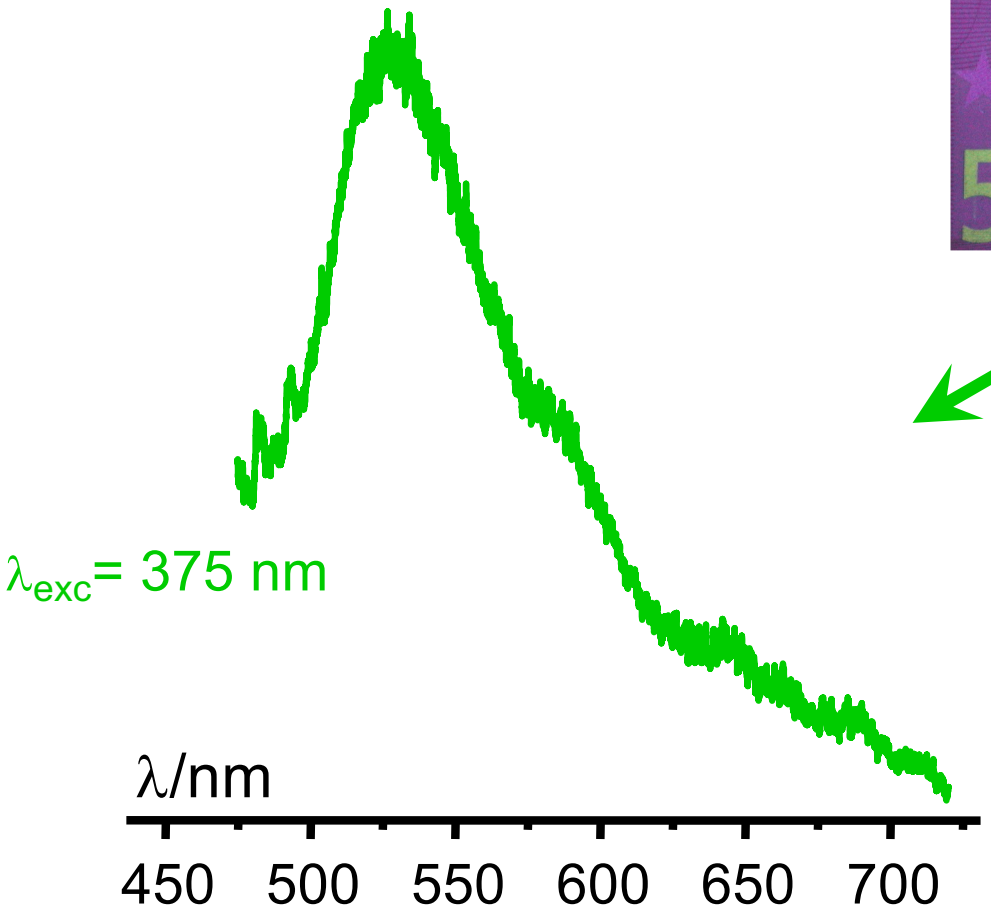
The euro is protected by the luminescence from europium: red from Eu^{III}

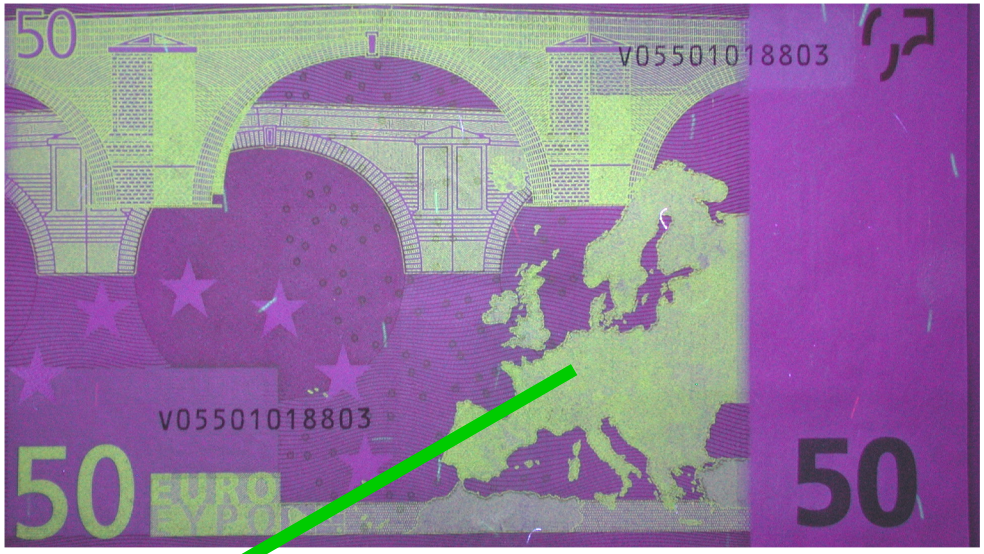


UV

Security inks

Possibly Eu^{II} ?





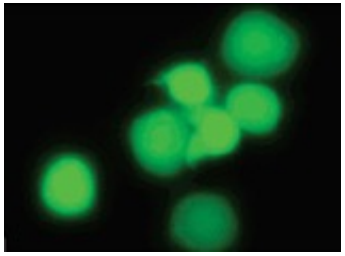
UV

Luminescent BioProbes

63 **Eu**

65 **Tb**

Visible



Cellular imaging,
Bio-essays

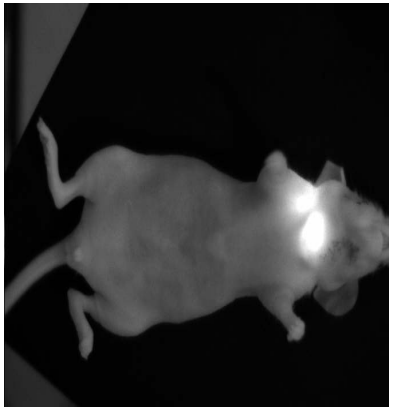
60 **Nd**

68 **Er**

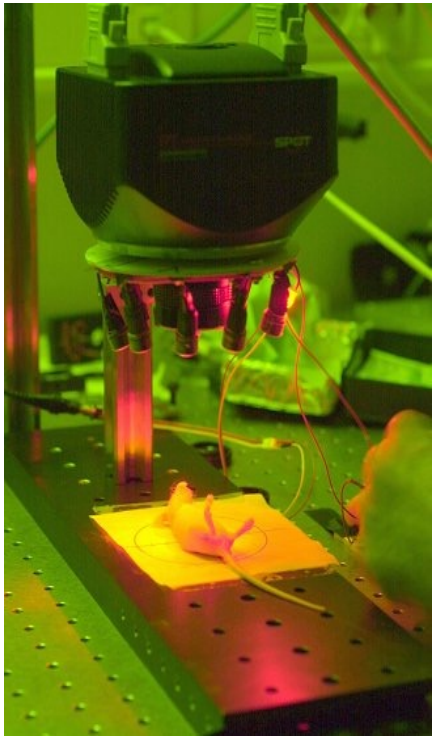
70 **Yb**

Near-IR

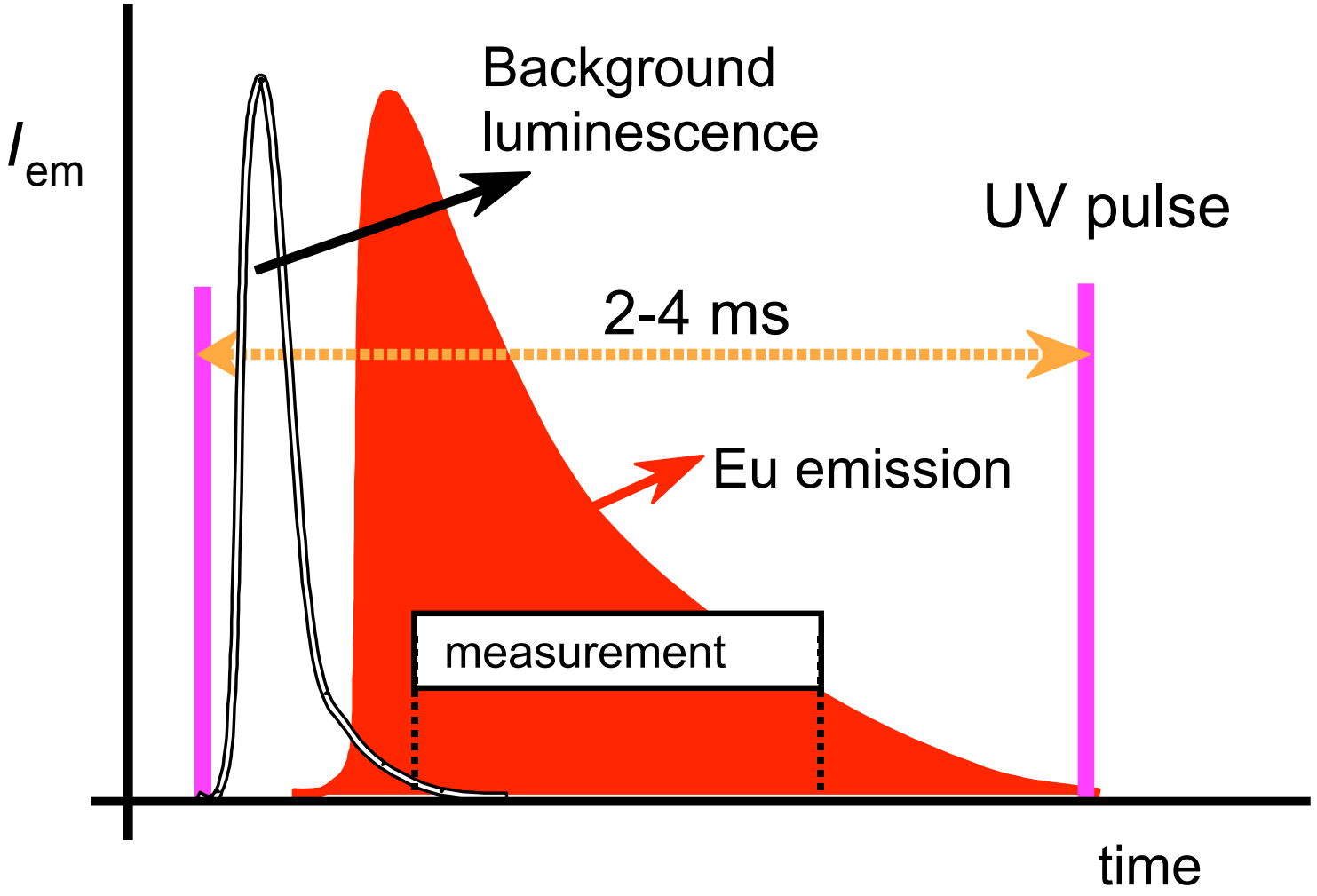
High sensitivity
Low penetration



In vivo imaging
Main application in open surgery



Time-resolved luminescence : an essential tool



Tracing biomolecular interactions

Molecular interactions between biomolecules are key mechanisms in living cells.

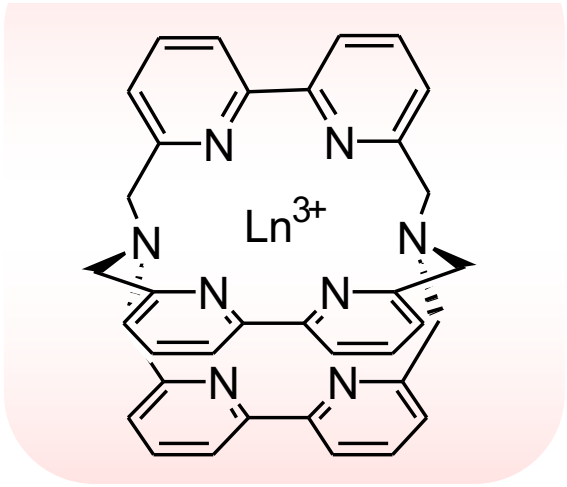
Moreover, high throughput screening strategies are being developed in which pharmaceutical industry is testing as many compounds as possible (from combinatorial chemistry) on molecular targets.

Henceforth the need for developing adequate analytical techniques able to work in the microliter range.

Homogeneous immunoassays based on Ln^{III} luminescence are ideal in this respect.

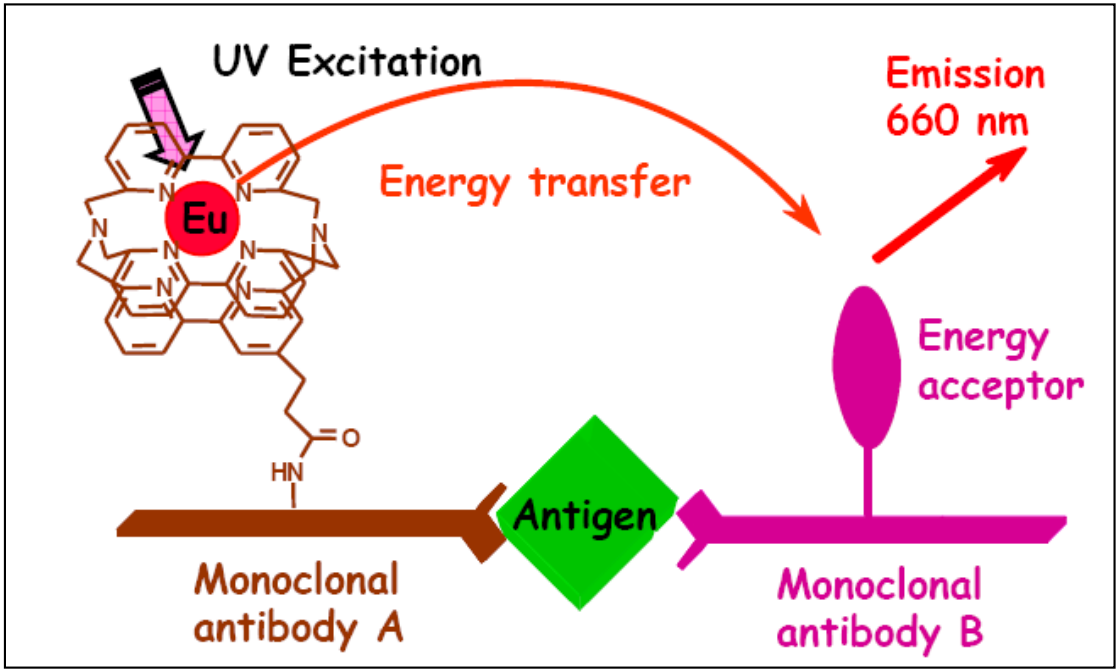
Technically a luminescence resonance energy transfer (LRET) is used.

Commercial Luminescent Ln(III) complexes



- ☞ Emission in visible light
- ☞ Low quantum yields

FRET : Foster Resonance Energy Transfer



q = 2

Φ(Eu) = 2%

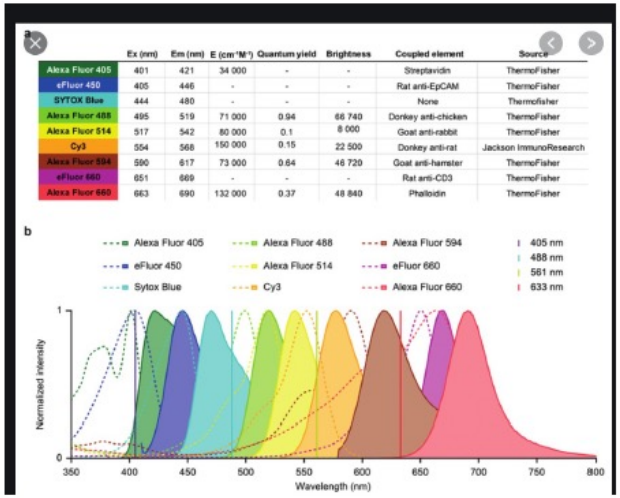
Φ(Tb) = 3%

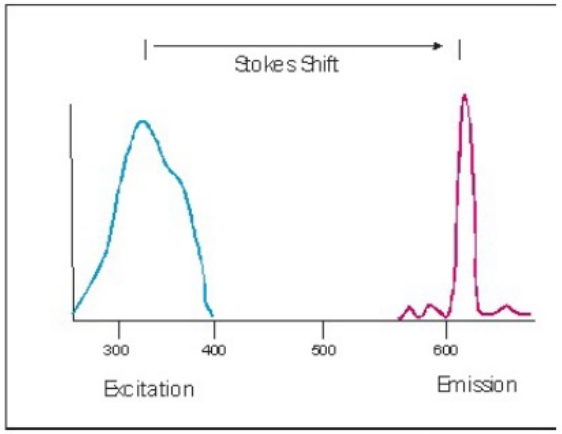
The large Lns Stokes' shift (difference between excitation and emission wavelengths) and the narrow emission peaks contribute to increasing signal-to-noise ratio.

Lehn J.-M. et al, *Angew. Chem. Int. Ed.,* 26, 1266 (1987)

Advantages of Ln(III) complexes

Large Stokes Shifts : can be up to several hundreds of nm
In organic reagents they are commonly 30 nm



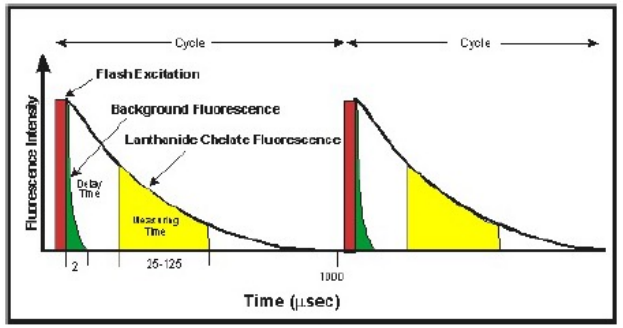


Europium

Long lifetimes: Time resolved luminescence

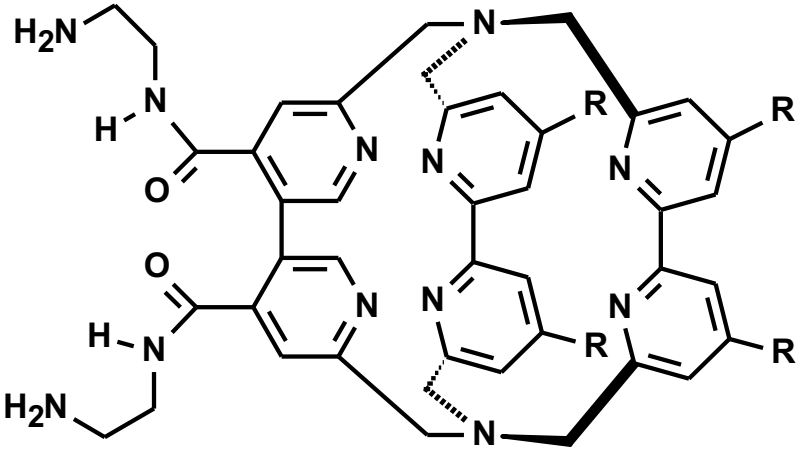
High intrinsic QY Q^{Ln}_{Ln} but overall ligand sensitised luminescence depends on the transfer $Q^{Ln}_{L} = \eta_{sens} Q^{Ln}_{Ln}$

Q^{Ln}_{Ln} can be very high in rigid inorganic solids



Stable complexes for bioanalytical applications

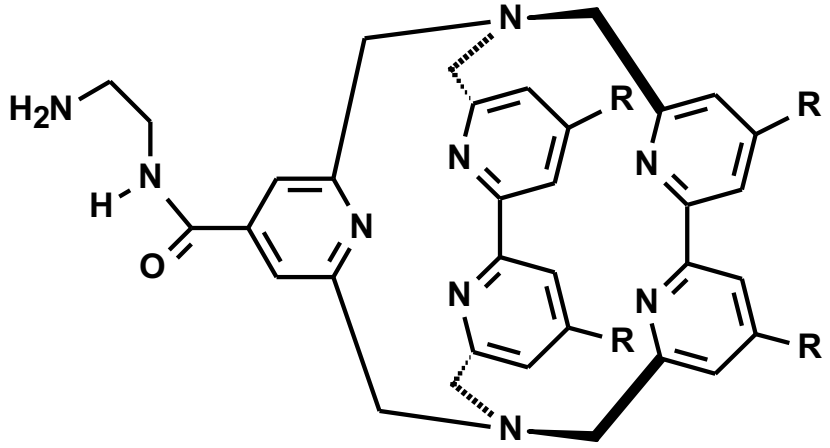
- Commercial kit Delfia for immunoassays with (bpy.bpy.bpy) cryptate as stain



Low quantum yield =0.02%
(3 water molecules bound to Ln^{3+}) and PET Photo Electron Transfer) processes

It is possible to increase to 10% by adding F^- that binds strongly Ln

PET process (leading to the reduction into Eu^{II}) can be minimized by decreasing the cavity size, since the ionic radius of Eu^{II} is larger (1.30 Å) compared to Eu^{III} (1.12 Å, CN = 9).



Designing Highly luminescent Ln(III) Probes

- Highly stable complexes
- The ligand should be polydentate and prevent coordination of water molecules that desactivate luminescence

-The ligand should incorporate a chromophore for antenna effect

-The largest values of quantum yields occur when the triplet state energy is close to the energy of one of the higher excited states of the metal ion; if the energy of the feeding state becomes closer to the energy of the emitting state, back transfer operates. For Eu^{III} and Tb^{III}, a ‘‘safe’’ energy difference minimizing this process is around 2500–3500 cm^{-1} and this probably applies to the other LnIII ions too.

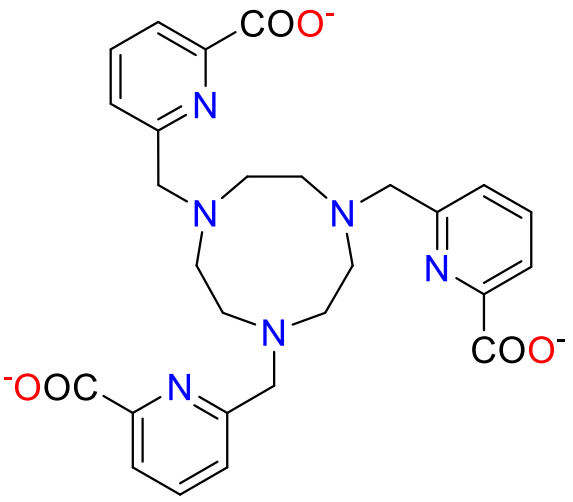
- Back transfer can result in reduction of Eu^{III} to Eu^{II}

-For some ligands the luminescence of the terbium complexes is quenched by oxygen and this can be used in determining the oxygen concentration in biological media

- The ligand architecture is important in the presence of the same chromophore

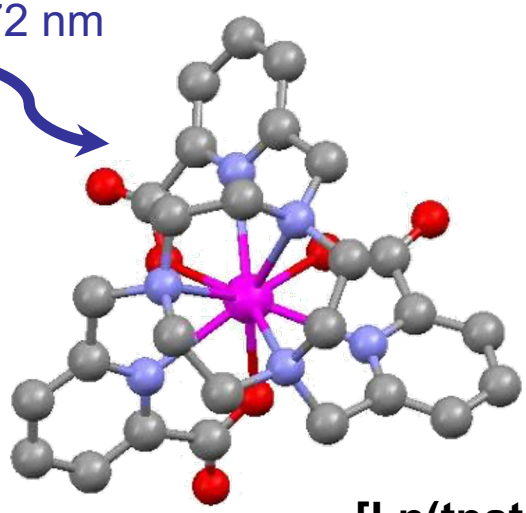
Chem. Soc. Rev., 2010, 39, 189–227

Highly luminescent Ln(III) complexes

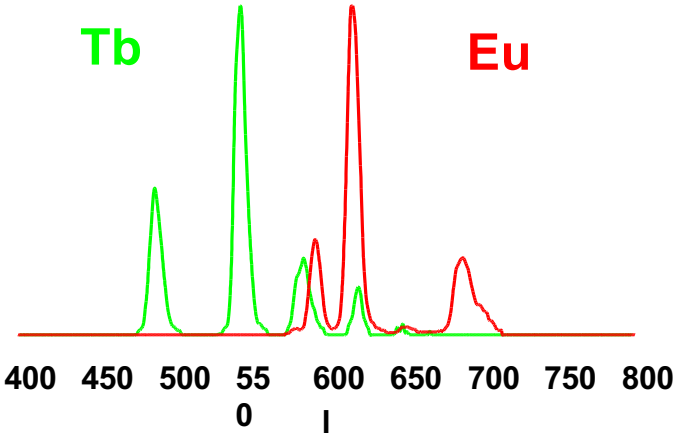


Mazzanti

272 nm



[Ln(tpatcn)]

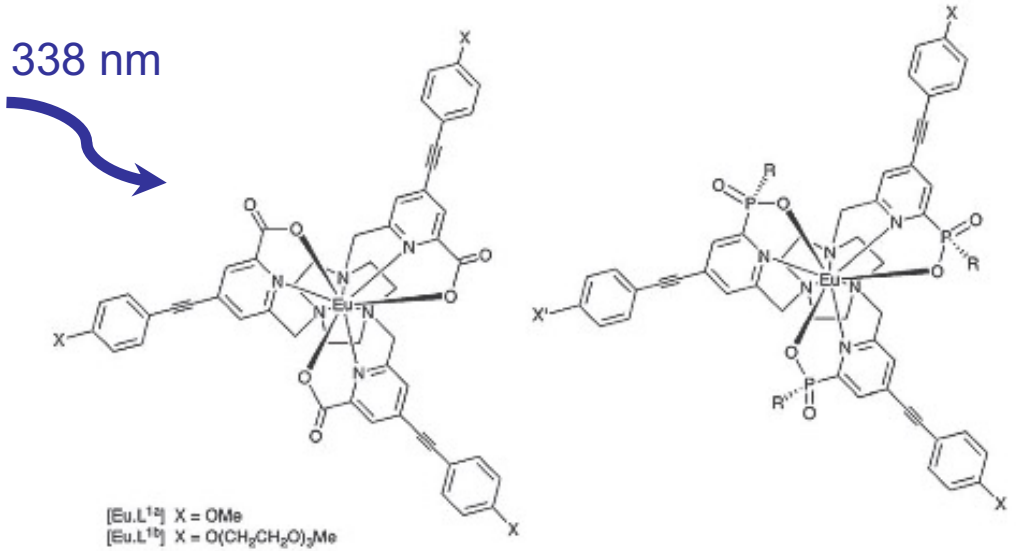


Φ(Tb) = 60 %

Φ(Eu) = 9 %

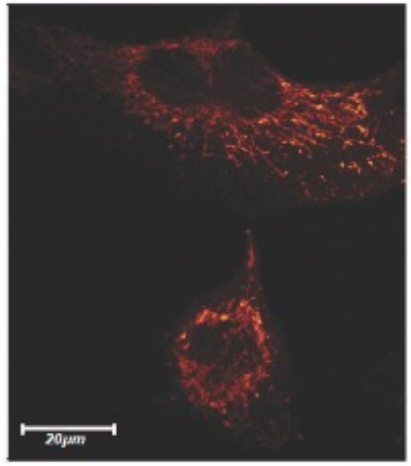
Good water stability
No bound water molecules

338 nm

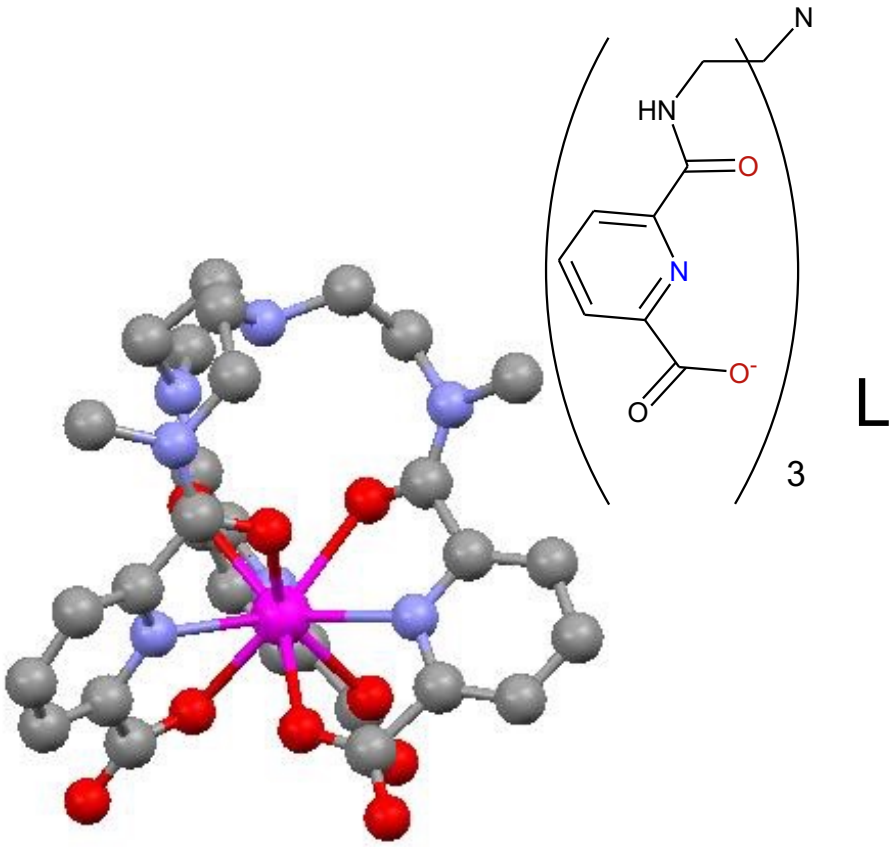


Parker

Φ(Eu) = 48-54 %



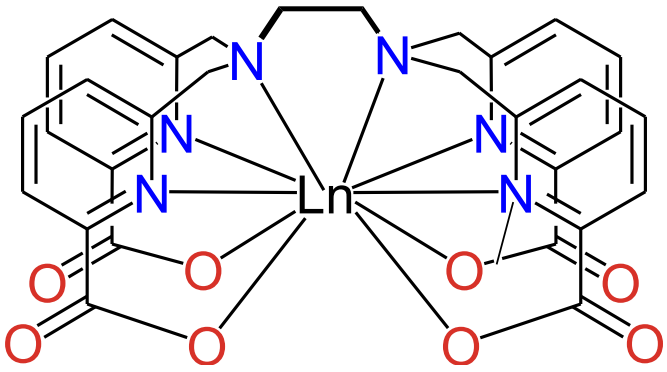
Important Effect of the Ligand Architecture



$[Eu(L)_3]$ $Q_{Eu} = 0.18\ \%$

$[Tb(L)_3]$ $Q_{Tb} = 0.9\ \%$

C. Piguet et al.,*Inorg. Chem*. 2003



Q(Tb) = 45%

Q(Eu) = 7%

$\tau_{H2O}(Tb)=3.0$ ms

$\tau_{H2O}(Eu) = 1.7$ ms

(logβEuL = 15.3(3))

Ca(II) (logβCaL = 8.5 (5)

Mazzanti et al., *Angew. Chem. 2005*

Luminescent chemical sensors

The specific spectroscopic properties of Ln^{III} ions make them ideal luminescent probes:

- easily recognizable line-like spectra
- long lifetimes of excited states
- large Stokes' shift upon ligand excitation

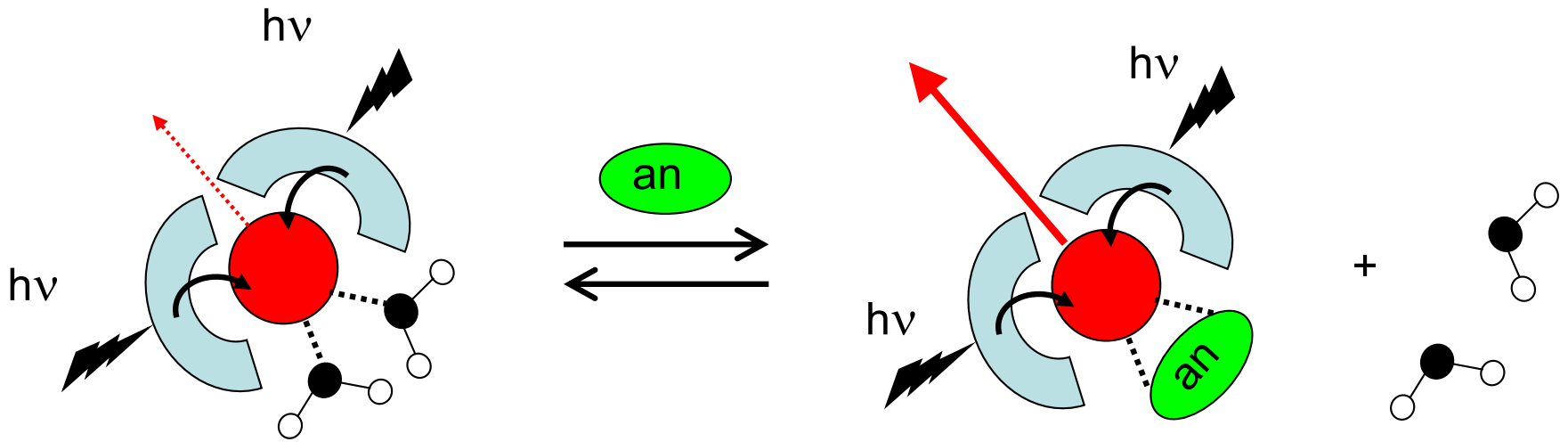
Time-resolved luminescence allows high signal-to-noise ratios, henceforth high sensitivity

Lanthanide-containing luminescent probes can be used as:

- structural probe (site symmetry)
- analytical probes (mainly for bio-analyses)
- imaging probe for medical diagnosis (tumor imaging)

Luminescent Lanthanide Probes

a) Direct binding of the analyte modifies the Ln^{III} inner-sphere coordination



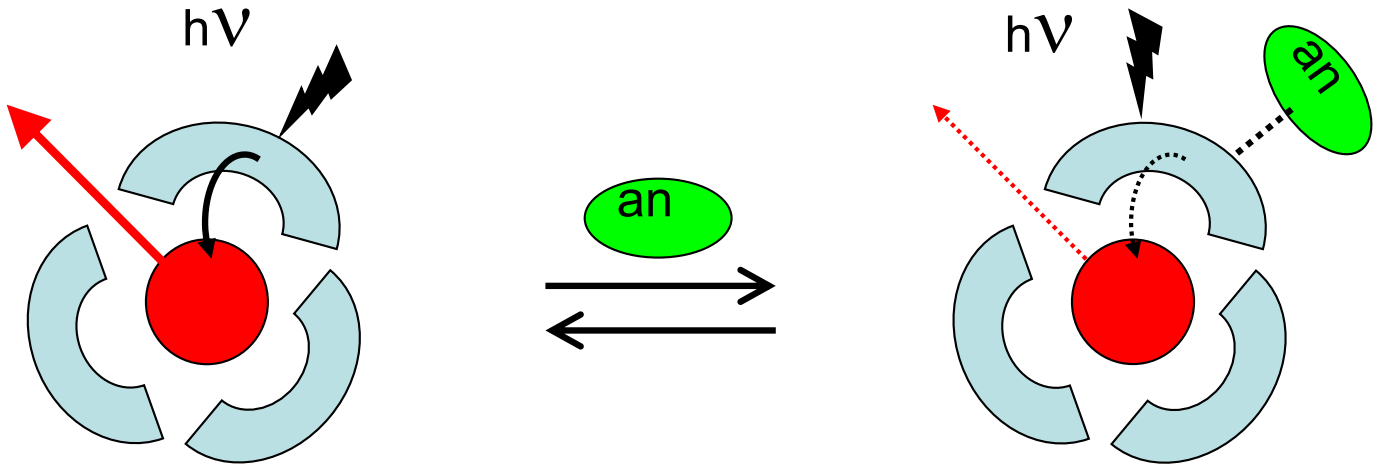
Here, water molecules are expelled, increasing luminescence emission

Chem. Soc. Rev. 2005, *34*, 1048

Luminescent Lanthanide Probes

b) Binding of the analyte to a ligand modifies its energy- transfer properties

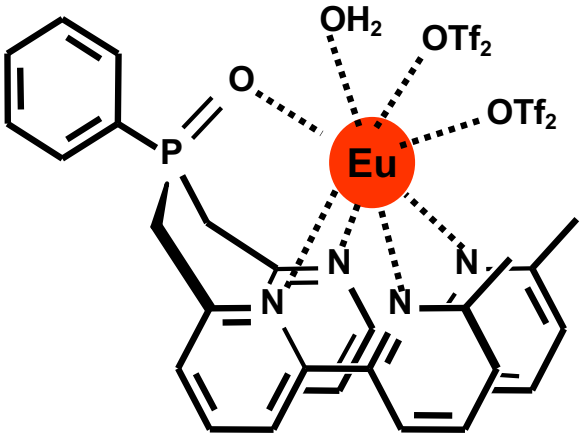
or c) initiate an energy transfer process to the metal ion



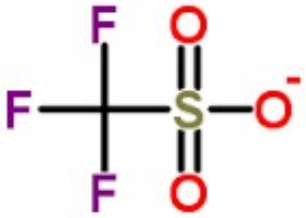
Here, binding of the analyte results in a quenching of the metal-centered luminescence.
Alternatively, luminescence can be activated by such a binding.

Energy transfer may occur trough Foster mechanism (dipole-dipole (coulombic) coupling or *virtual photon*) that is distance dependent
Dexter energy transfer (electron transfer) is usually associated with quenching

Modification of inner coordination sphere: anion analysis



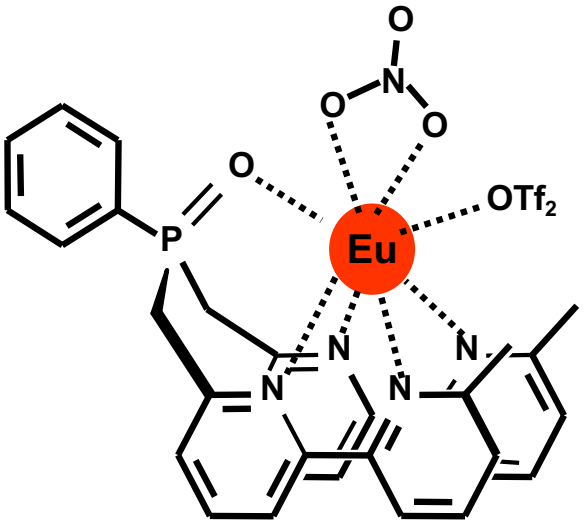
OTf = $CF_3SO_3^-$



In acetonitrile:

Q **= 2.6 %**

t = 0.86 ms



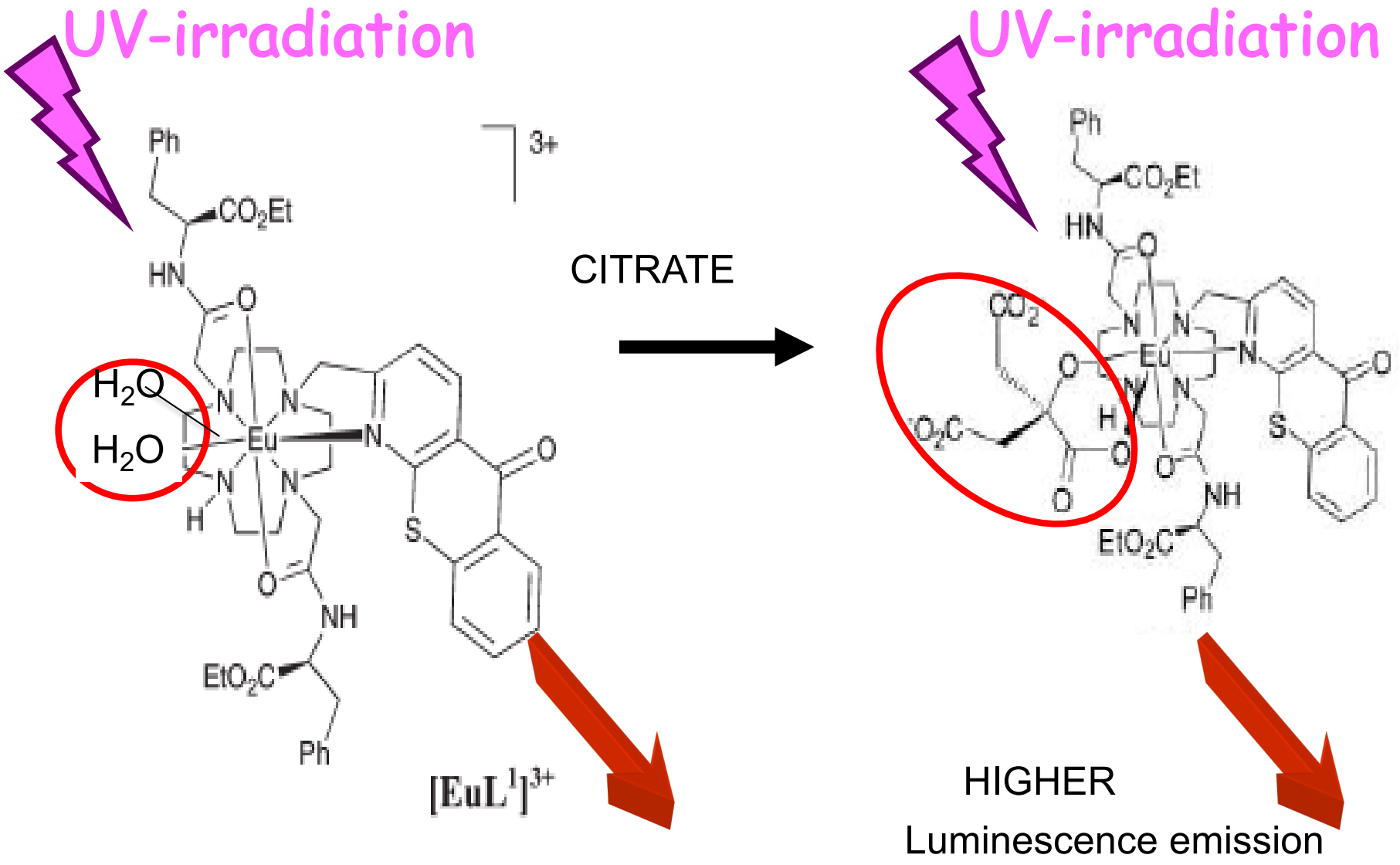
Q **= 30 %**

t = 1.45 ms

$K_{assoc} = 10^6$

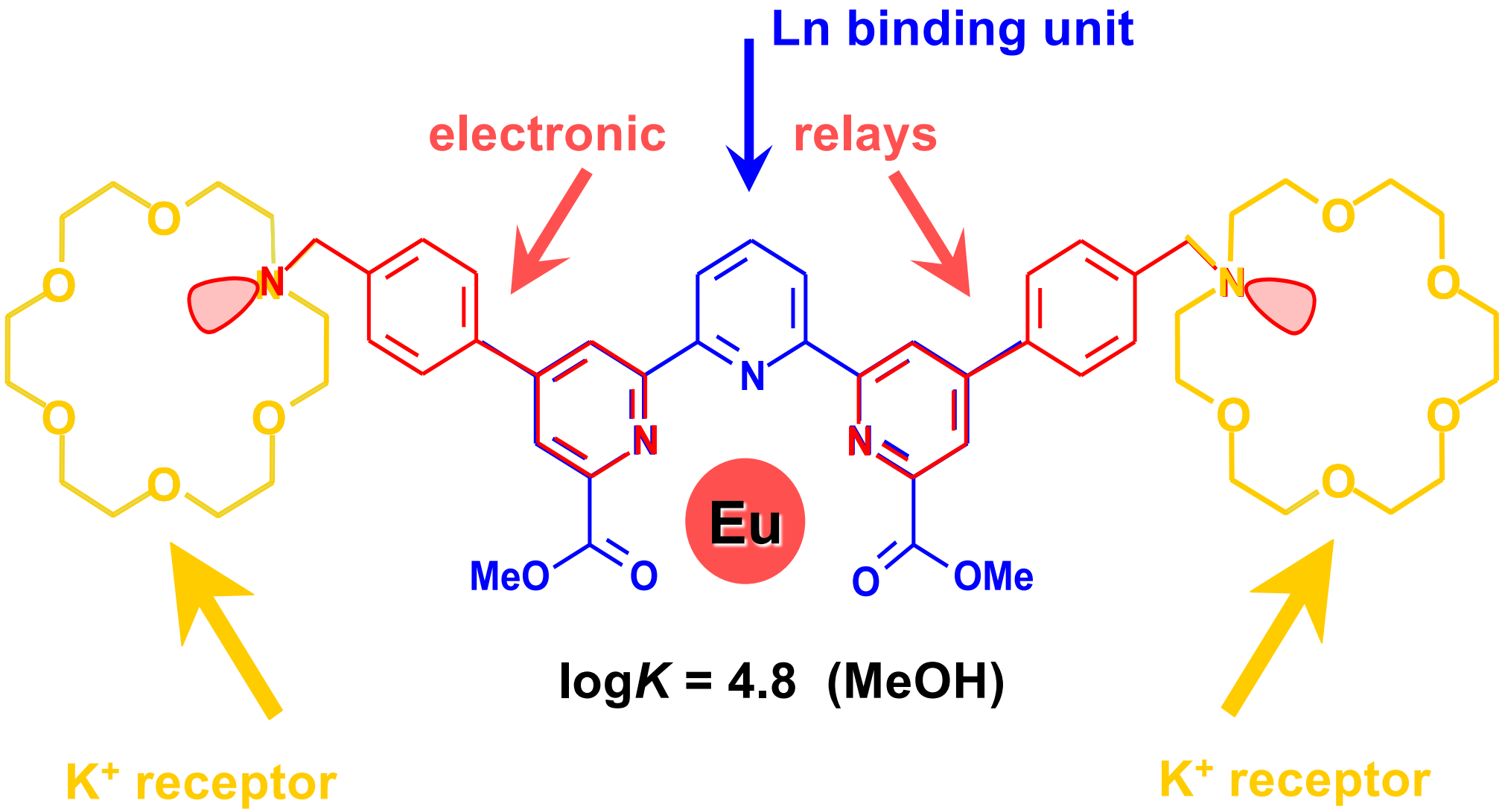
J. Am. Chem. Soc. **2002**, *124*, 7779

Citrate Detection: in vivo Marker in Prostate Cancer



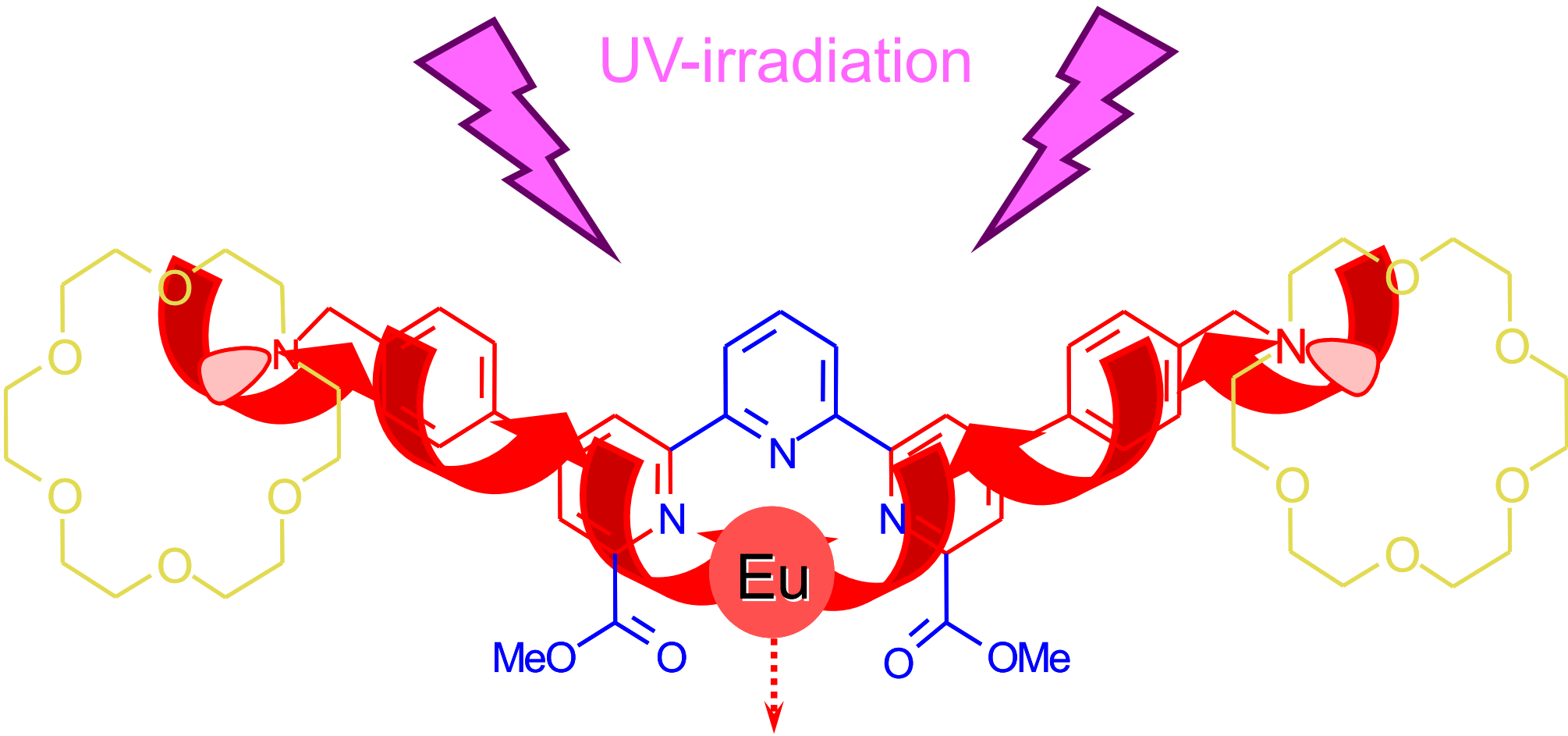
Parker, ***Chem. Soc. Rev.***, 2013,**42**, 1652-1666

Detection by removal of quenching processes



log*K* = 4.8 (MeOH)

A.P. de Silva et al., *Chem. Commun.* **1997,** 1891



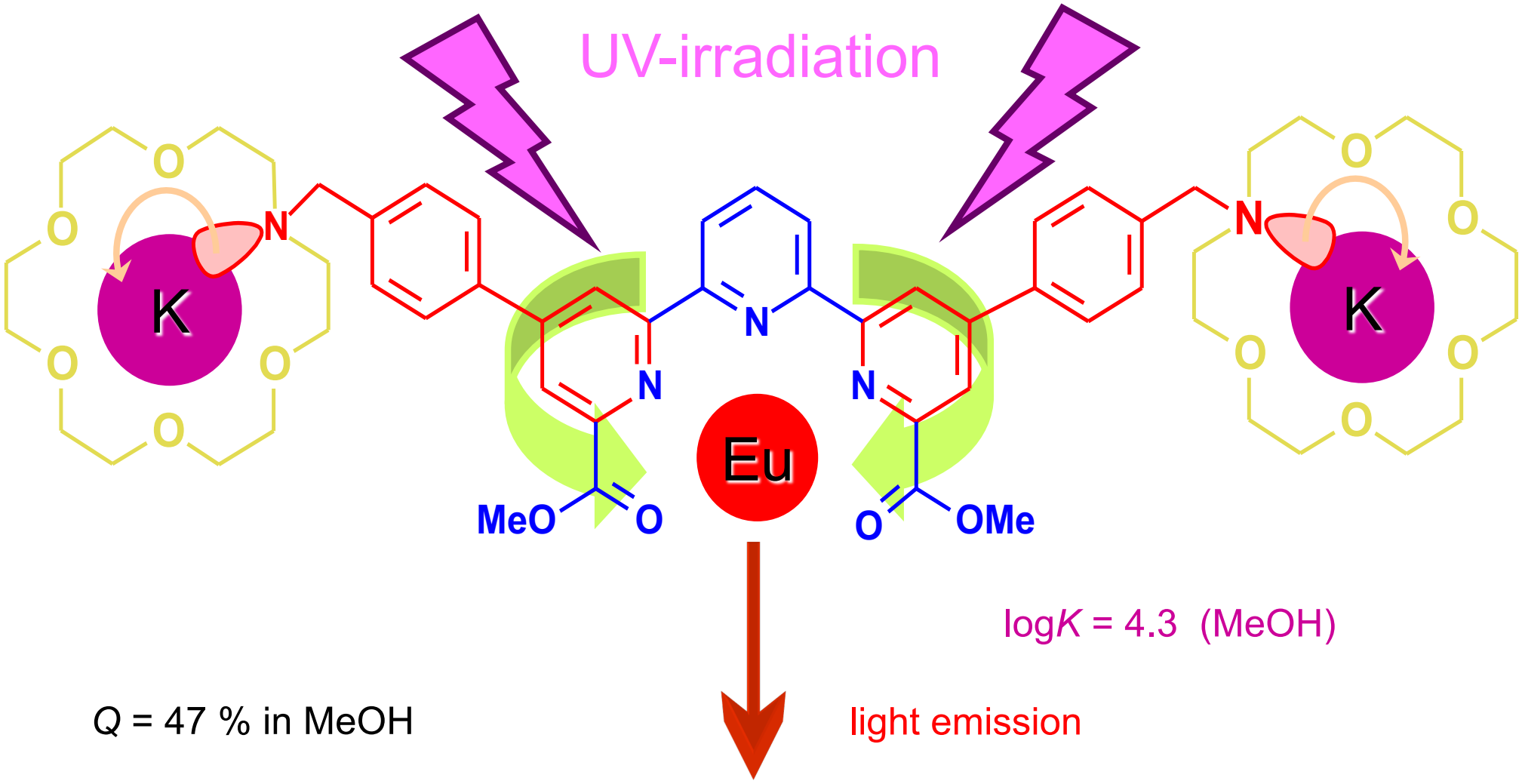
Luminescence quenched by PET (Photoinduced Electron-Transfer)

$Eu^{III} \longrightarrow Eu^{II}$

Q = 2.6% in MeOH

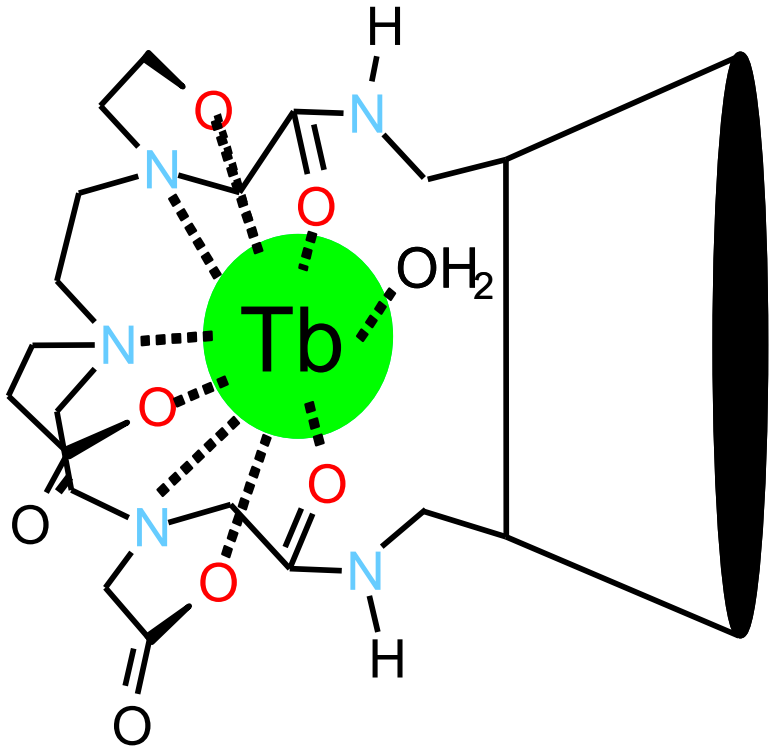
A.P. de Silva et al., *Chem. Commun.* 1997, 1891

Detection by removal of quenching processes

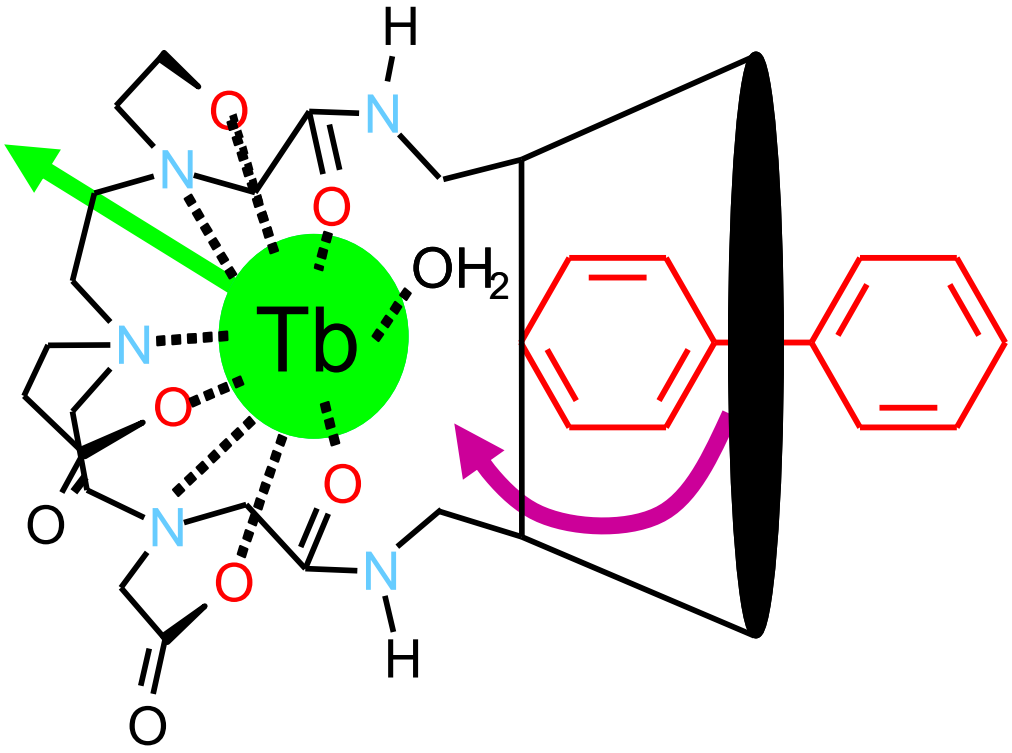


A.P. de Silva et al., *Chem. Commun.* 1997, 1891

Detection by initiation of energy transfer



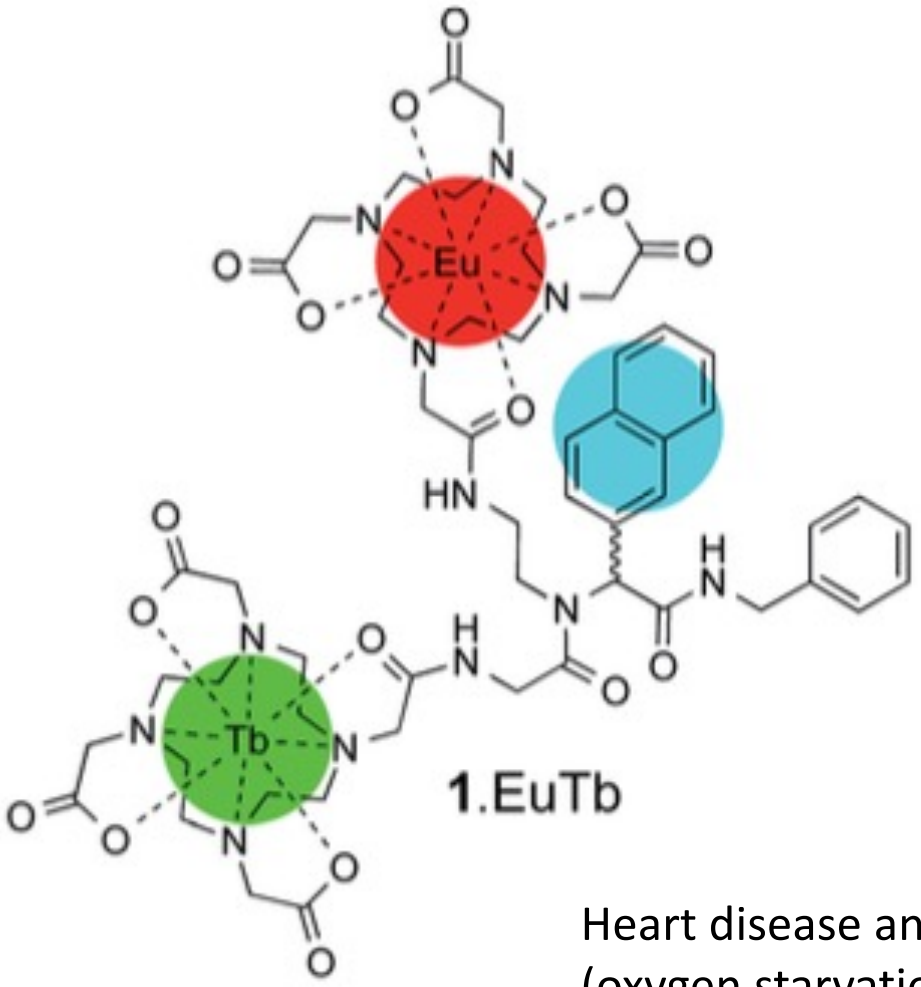
β-CD coupled to dtpa
weak Tb emission in H_2O



Strong Tb emission in H_2O
due to efficient energy transfer
from host

Nocera et al., *Coord. Chem. Rev*. 1998, *171*, 115

Oxygen Sensors



The terbium luminescence will decrease with increasing oxygen Concentration

The europium one will be constant allowing for oxygen detection

Heart disease and stroke are consequences of ischemia (oxygen starvation), while many solid tumours have hypoxic regions in which low oxygen levels change the cellular physiology.

Faulkner 2015

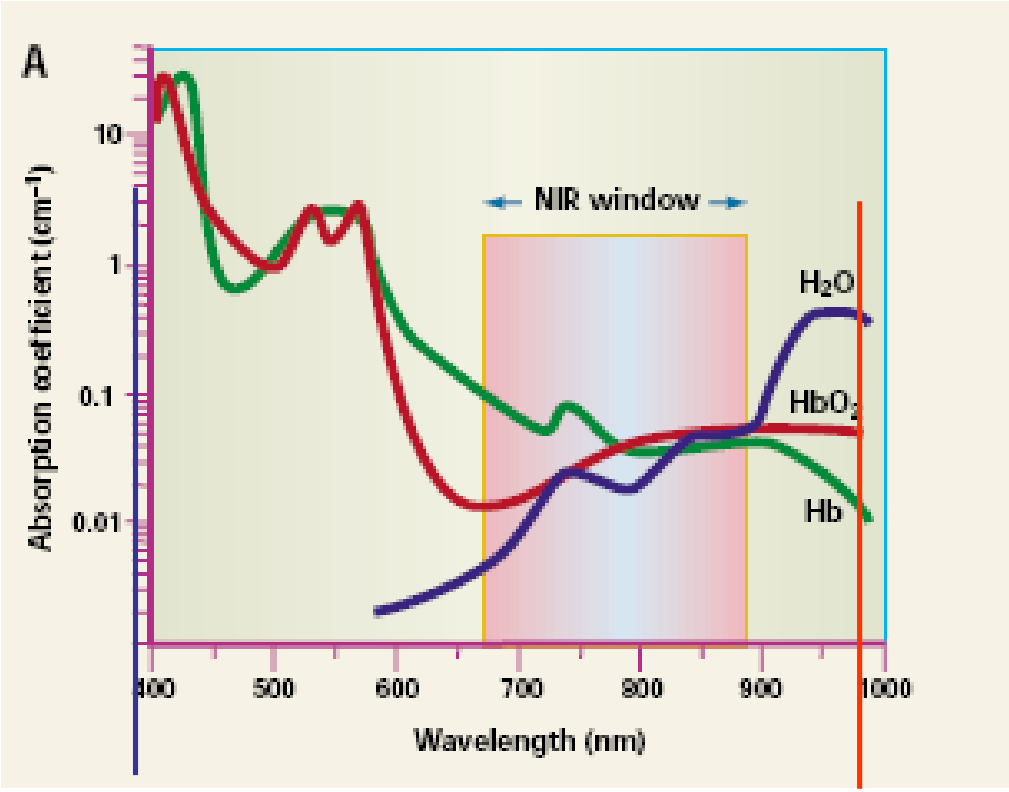
Near-Ir Luminescence

In vivo imaging

Limits of fluorescence : depth of penetration (1- 7 cm), resolution;

Advantages sensitivity (up to nm of fluorophore), non invasive

Best choice : Near Ir emitters (Yb) advantages with respect to organic fluorophores:
Resistance to photo bleaching, emission in the biological transparency window
But low quantum yields desactivation by CH, OH, NH vibrations

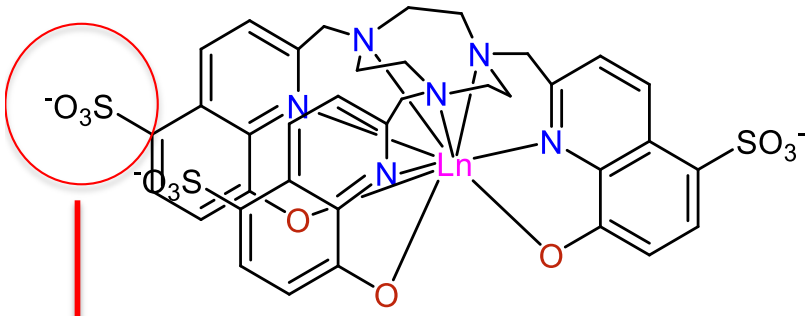


370 nm

976 nm

R. Weissleder. *nature biotechnology* (19) 2001 , 316

Near-IR emitting 8-hydroxyquinoline-based Complexes



[Ln(thqtcn-SO_3)]$^{3-}$

solubility

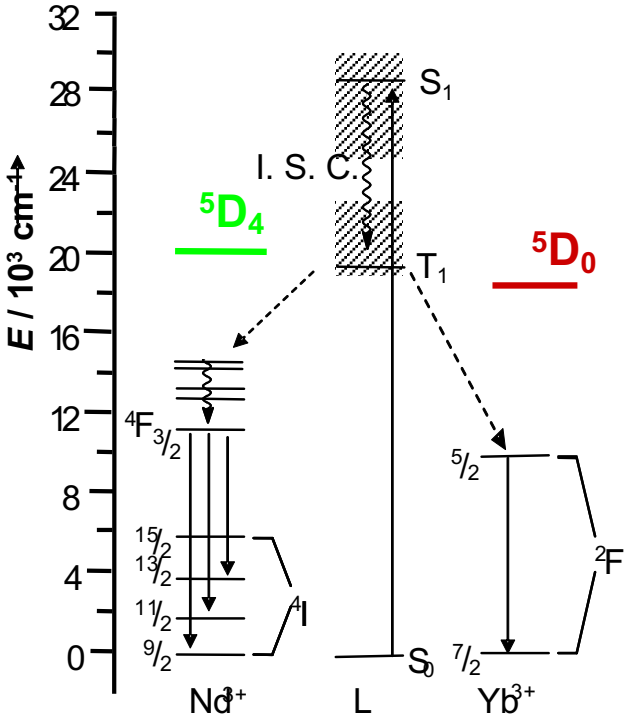
- Hydroxyquinoline good sensitizer of Ln in the near-IR region

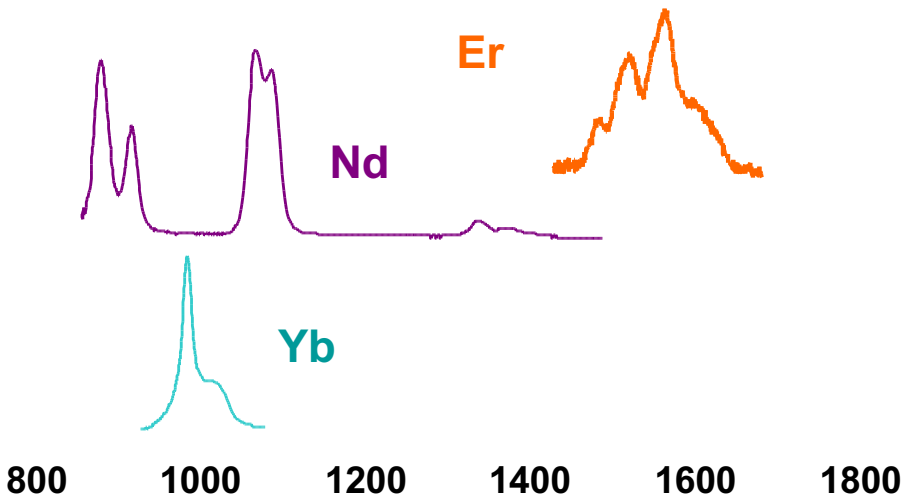
- Rigid 1:1 complexes in solution with q = 0

LogKGd = 19.2, kinetically inert

λ_{ex} = 340-450 nm

^{3}S = 585 nnm



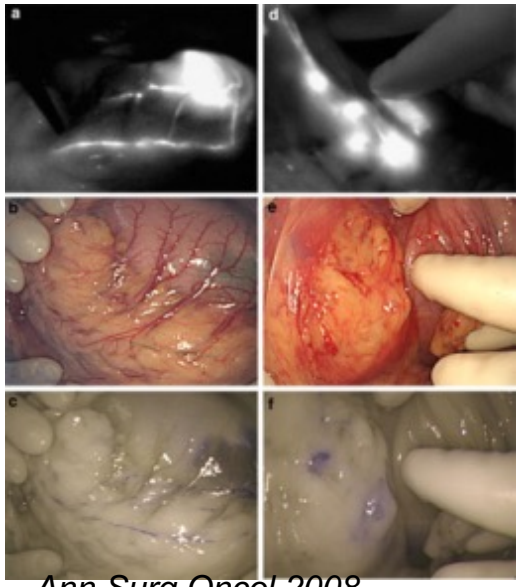


Nd	0.02 %	0.05%
Yb	0.14%	0.55%
Er	-%	0.006%
	(H_2O)	(D_2O)

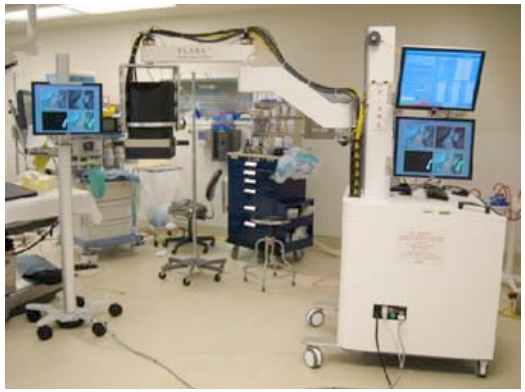
Inorg. Chem. **2009**, *48*, 4207-4218.

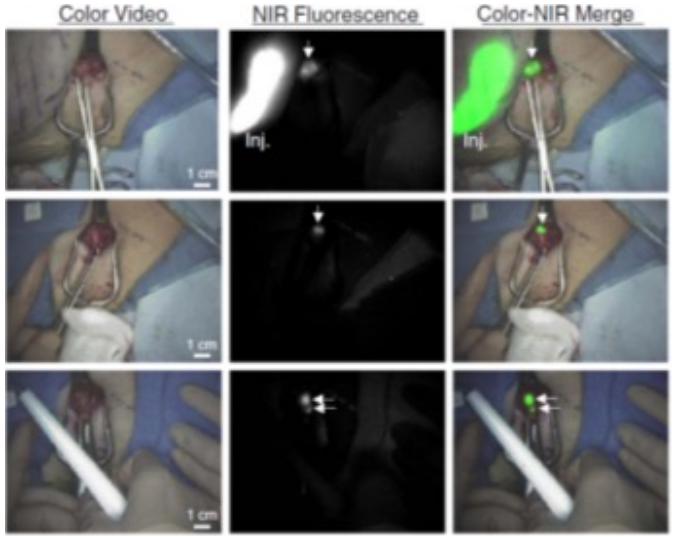
Intra-operative surgery

Fluorescence-guided sentinel node biopsy with ICG



Ann Surg Oncol 2008





Ann Surg Oncol 2009

Summary

-Basic principles of luminescence

-Principle of luminescence in lanthanide compounds

-The importance of antenna effect in applications

-Basis of design of highly luminescent complexes

-Main application in material science and in biomedecine