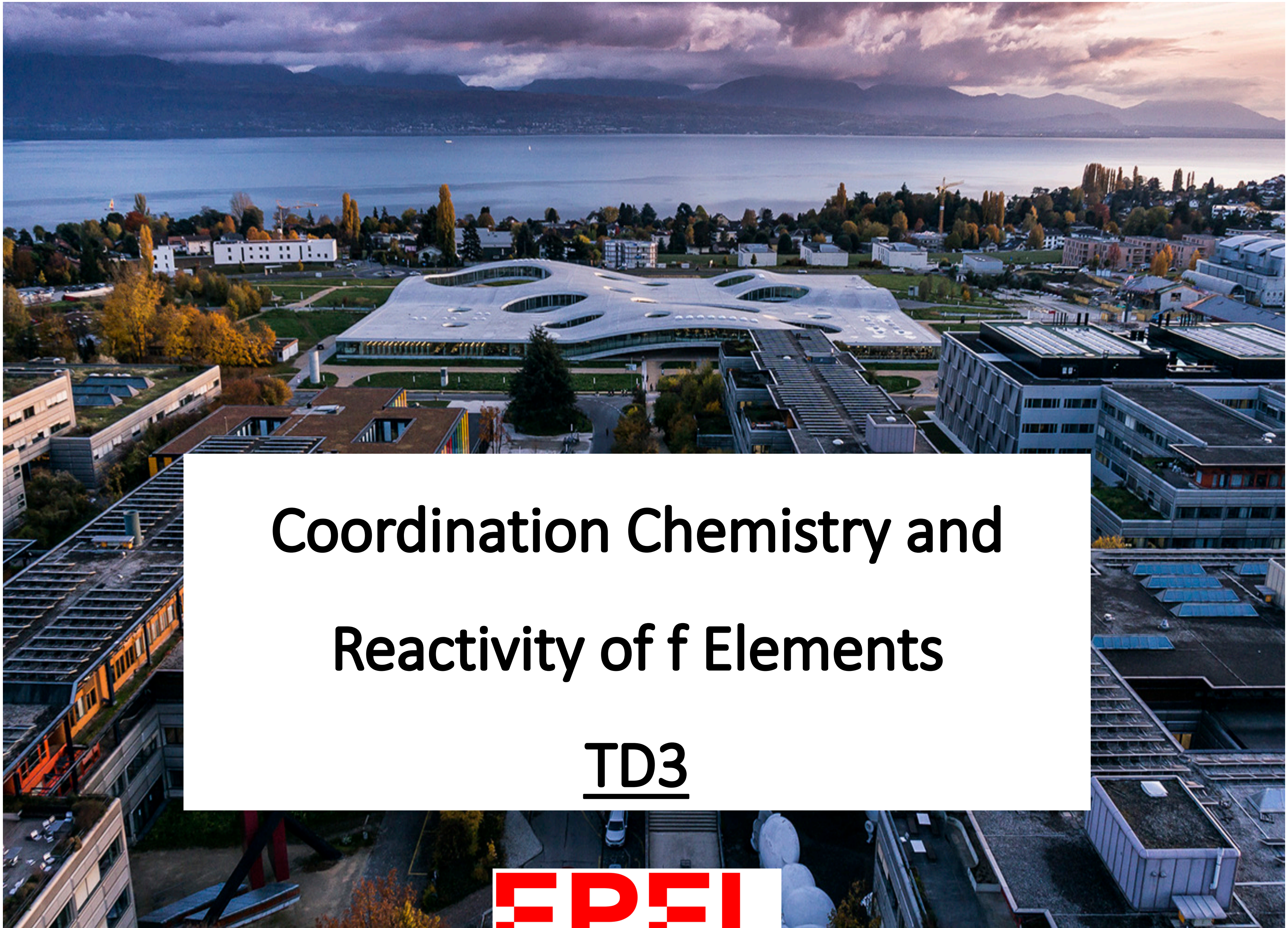


Coordination Chemistry and Reactivity of f Elements

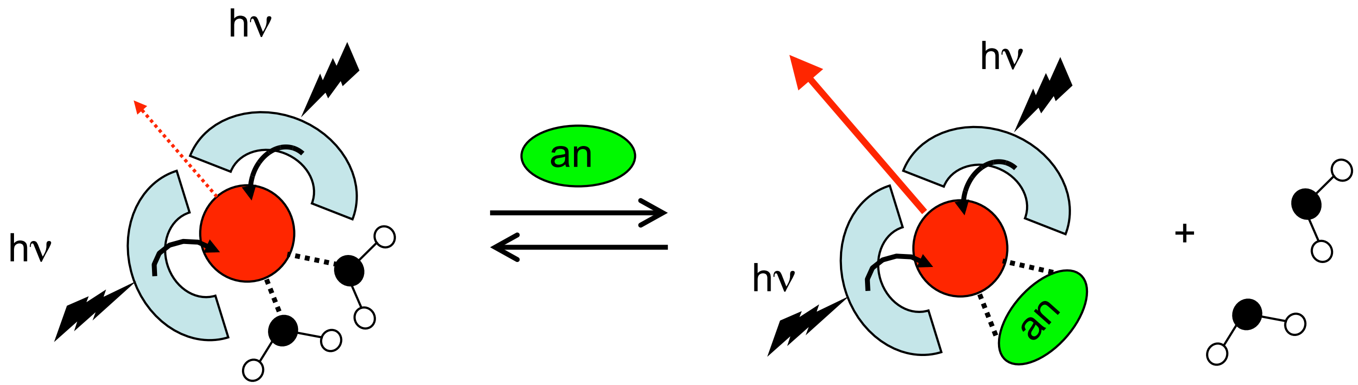
TD3

Question 1

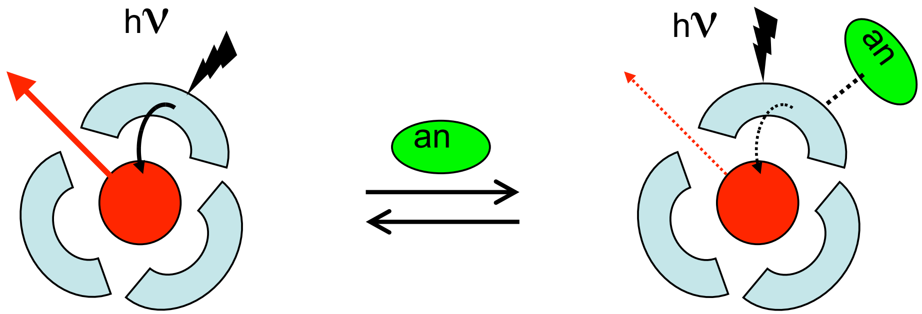
1) What properties of the Ln(III) render them attractive for application as luminescent chemical sensors?

2) Explain the two different modes of sensing shown below and give potential applications.

I)

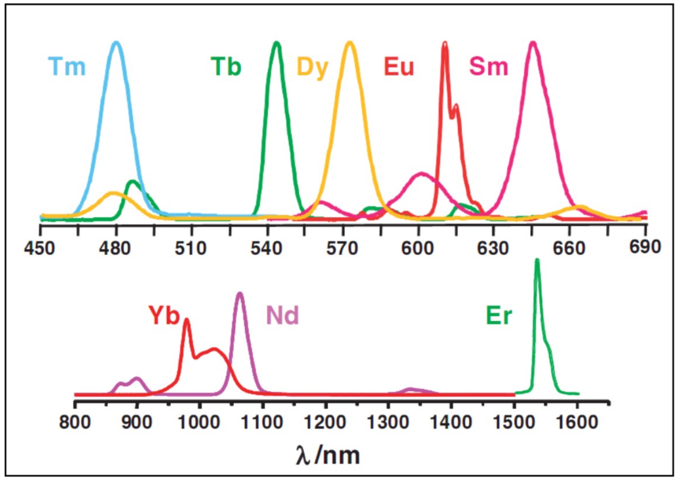


II)



Answer 1

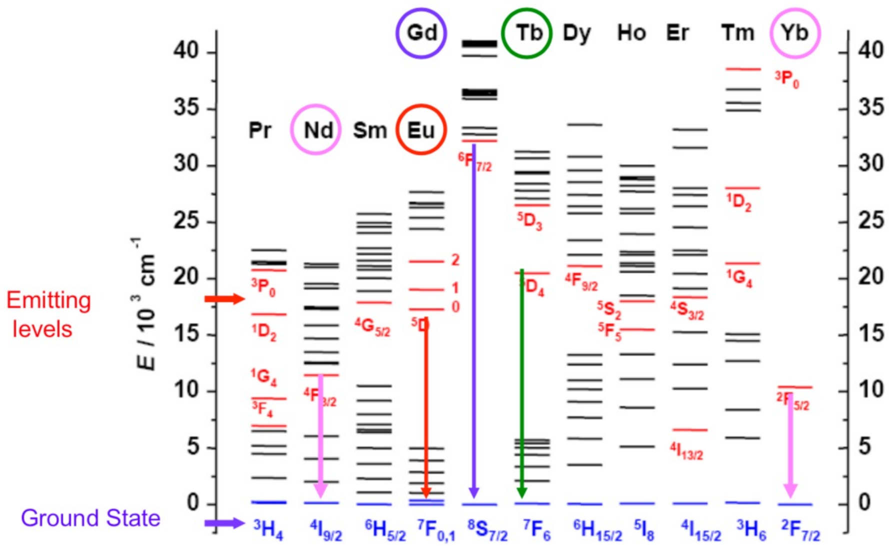
1) What properties of the Ln(III) render them attractive for application as luminescent chemical sensors?



- Recognizable line-like spectra due to f-f transitions
- Long lifetimes of excited states

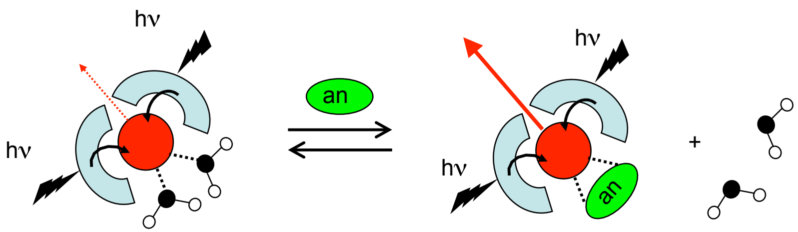
  bigger gap = longer lifetime

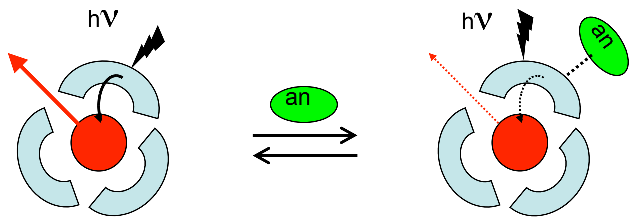
- Large stokes' shift upon ligand excitation
- High intrinsic quantum yield



Answer 1

2) Explain the two different modes of sensing shown below and give potential applications.





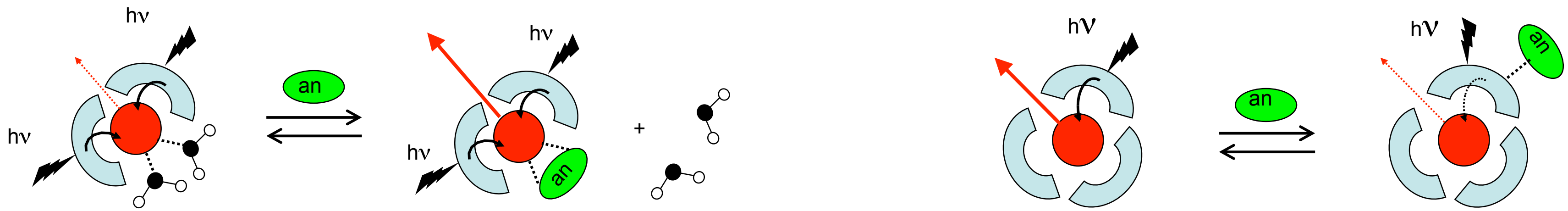
- Direct binding of the analyte
- Modifies the Ln^{III} inner-sphere coordination
- Water molecules are expelled
- Increased luminescence emission

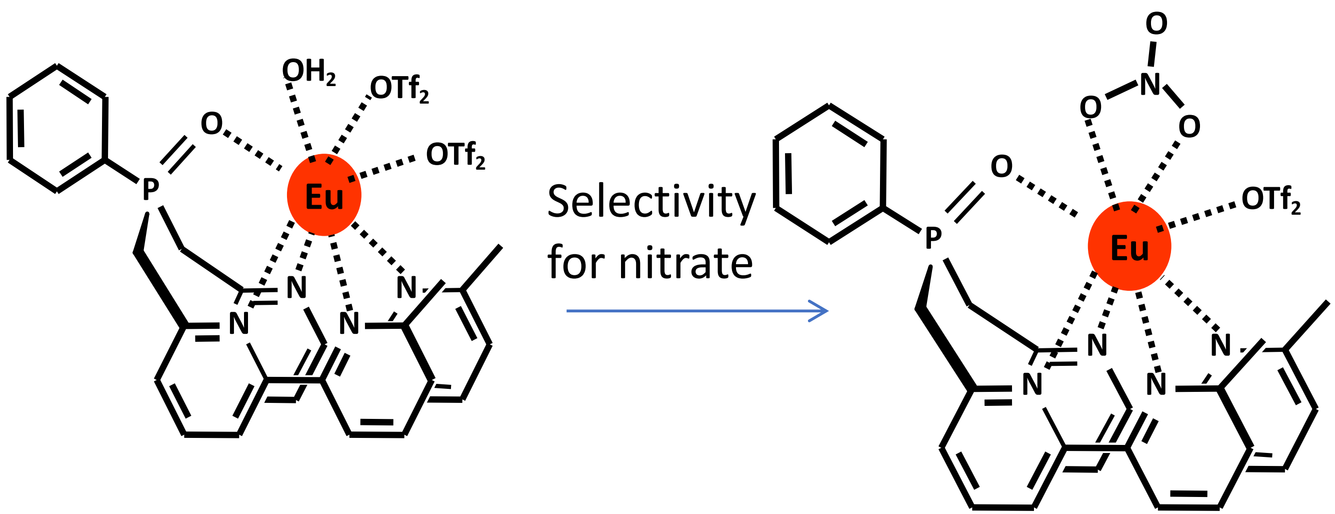
- Binding of the analyte to the ligand
- Initiate or quench an energy transfer process from the ligand to the metal ion
- Results in a quenching or enhancement of the metal-centered luminescence

EPFL

Answer 1

2) Explain the two different modes of sensing shown below and give potential applications.





Possible application: detection of **coordinating anions** such as nitrate

Question 2

1) Indicate the key design principles for the development of biological tags based on lanthanides.

Answer 2

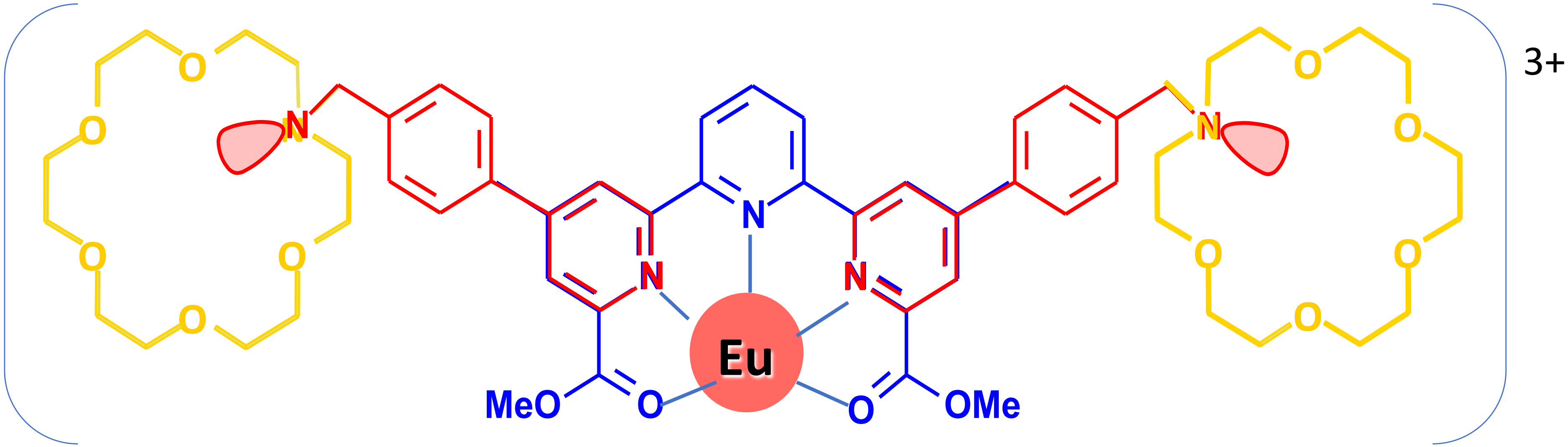
1) Indicate the key design principles for the development of biological tags based on lanthanides.

→ luminescent Ln(III) Probes

- Highly stable complexes → polydentate ligands
- The ligand should incorporate a chromophore for antenna effect
- Triplet state energy is close to the energy of the higher excited states.
- Rigid ligand architecture is important in the presence of the same chromophore

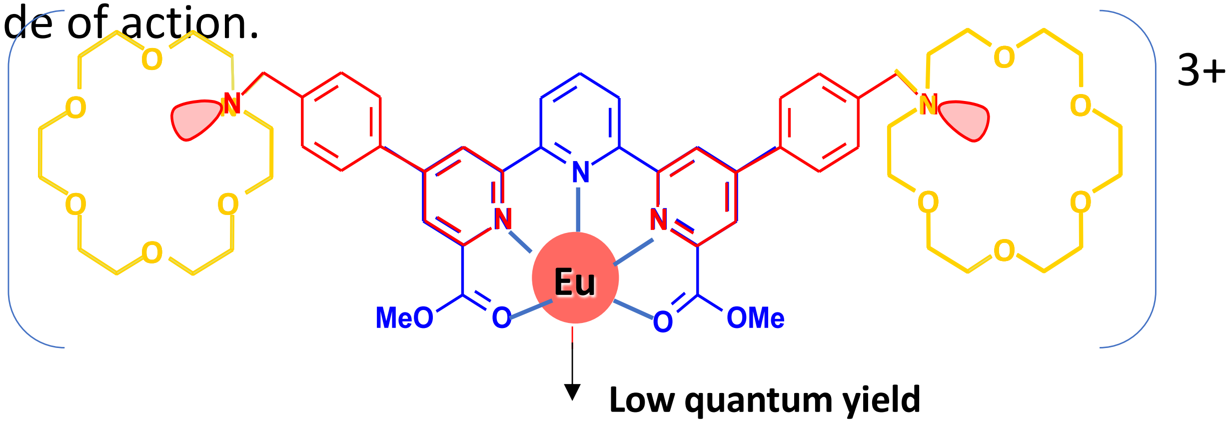
Question 3

1) The europium complex below becomes luminescent in the presence of potassium. Explain the mode of action.



Answer 3

1) The europium complex below becomes luminescent in the presence of potassium. Explain the mode of action.

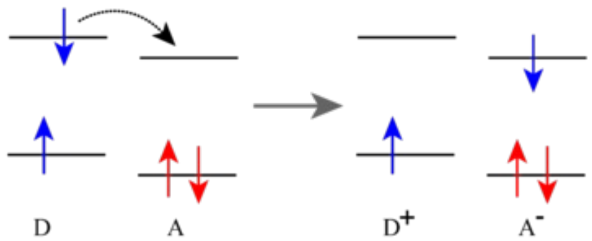


Low quantum yield
No light emission

PET = photoinduced electron transfer

→ Excited electron is transferred from donor to acceptor

→ This can lead to redox reaction occurring in excited state



L + hv → L*

Eu^{3+} + L* → $\mathbf{Eu^{2+}}$ + L^+

When potassium is bound to the N lone pair, electrostatics and the deconjugation of N lone pair with pi-system make PET thermodynamically unfavorable

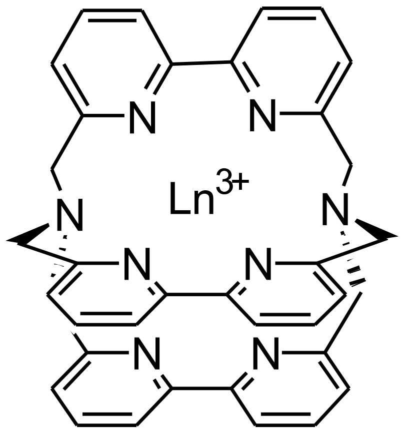
→ **Main pathway is fluorescence**

EPFL

Question 4

A) Explain the concept of FRET (**Foster Resonance Energy Transfer**) also known sometimes in an abuse way as Fluorescence Resonance Energy Transfer

B) The bpy.bpy.bpy cryptate was originally used in the commercial DELFIA Kit. What are the disadvantages of this system and how could it be improved?

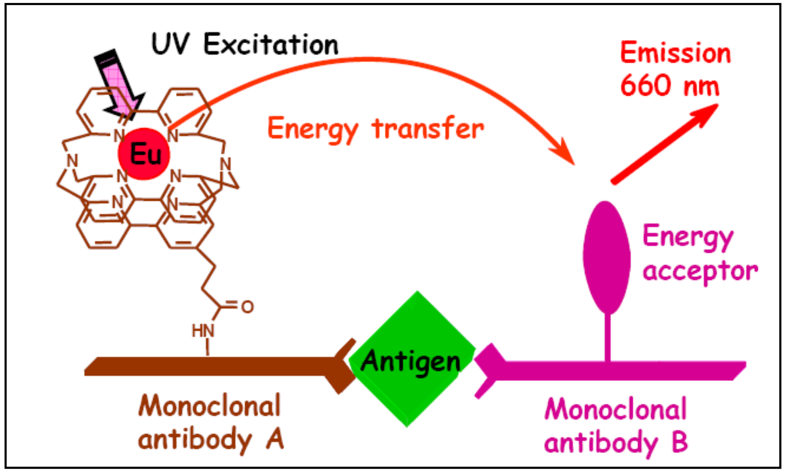


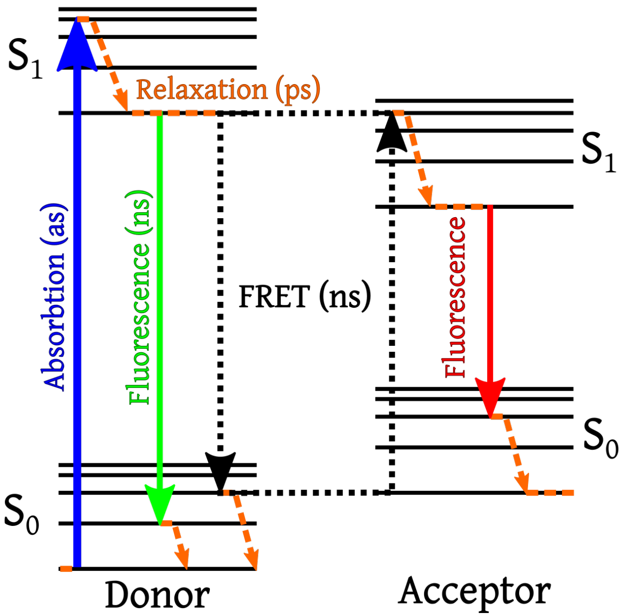
Bipy.bipy.bipy

Answer 4

A) Explain the concept of FRET (Foster Resonance Energy Transfer).

- Energy transfer between two light sensitive molecules
- Donor in excited state to an acceptor
- Through nonradiative processes





- Long-lived luminescence of the organic acceptor sensitized by the lanthanide complex

- Much **more intense and visible** compared to **short-lived** luminescence of the **acceptor** and the **weaker emission** of the **Lanthanide complex**

Answer 4

B) The bpy.bpy.bpy cryptate was originally used in the commercial DELFIA Kit. What are the disadvantages of this system and how could it be improved.

- Quantum yield is low due to **water binding** and **PET process**

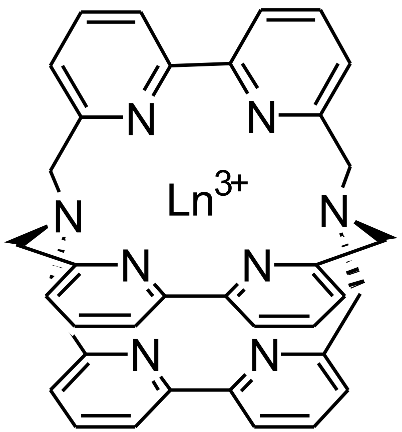
Addition of fluorides

This can increase the Q up to 10 %

compare to 0.02 % without

Smaller cavity minimizes PET process

Ionic radius of Eu(II) is larger than Eu(III)



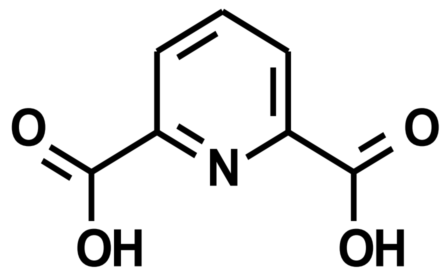
Bipy.bipy.bipy

Question 5

A)Draw the structure of the complex $[Eu(dpa)_3]K_3$ and the scheme of formation of the complex from the ligand in water . In the solid state the luminescence lifetime of the complex is 1.67 ms

In the concentration range 1–1.7 × 10^{-4} M, for the complex $[Eu(dpa)_3]^{3-}$ a lifetime $\tau_{obs}(H_2O)$ = 1.56 ± 0.02 ms was measured in water and a lifetime of $\tau_{obs}(D_2O)$ = 3.0 ± 0.1 ms, was measured in D_2O. Explain why. Explain also why the value of lifetime is lower in water than in the solid state.

Calculate the value of the number of coordinated water molecules for the complex in water and indicate how the value can be explained.



dpaH_2

Answer 5

Draw the structure of the complex $[Eu(dpa)_3]^{3-}$ and the scheme of formation of the complex from the ligand in water . In the solid state the luminescence lifetime of the complex is 1.67 ms

No bound water molecules in the solid state→ high lifetime

$$q = 1.05 \cdot \Delta k_{\text{obs}} \quad \text{with } \Delta k_{\text{obs}} = k_{\text{obs}}(\text{H}_2\text{O}) - k_{\text{obs}}(\text{D}_2\text{O})$$

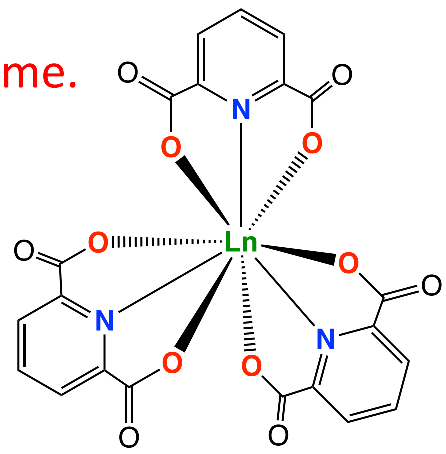
$q = 0.32 \pm 0.02$ in water

Since one dpa^{2-} ligand replaces three water molecules in the inner coordination sphere of Eu^{III}, this corresponds to the presence of 11% ± 1% of $[Eu(dpa)_2]^{-}$.

The tris-ligand complex partially dissociates in water leading to lower lifetime.

$$[Eu(H_2O)_9]Cl_3 + 2\ H_2dpa \xrightarrow{4\ KOH} [Eu(dpa)_2(H_2O)_3]K + 3\ KCl$$

$$[Eu(H_2O)_9]Cl_3 + 3\ H_2dpa \xrightarrow{6\ KOH} [Eu(dpa)_3]K_3 + 3\ KCl$$



Question 6

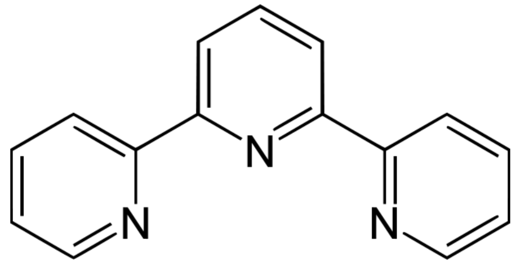
A) Complete the following equations and indicate what is the geometry of the final complex.

B) Indicate which of the formed complexes is the most luminescent and why.

$[Tb(H_2O)_9]Cl_3$ + 2 terpy $\xrightarrow[\text{(non-coordinating solvent)}]{}$

$[Tb(H_2O)_9]Cl_3$ + 3 terpy $\xrightarrow[\text{(non-coordinating solvent)}]{}$

C) Indicate the colour of luminescence



terpy

Answer 6

A) Complete the following equations and indicate what is the geometry of the final complex.

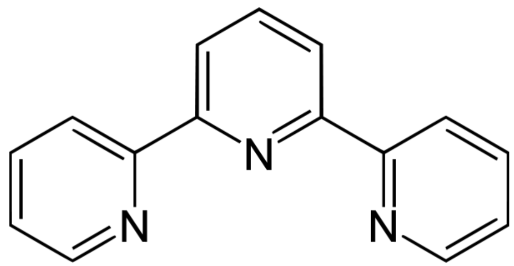
$[Tb(H_2O)_9]Cl_3 + 2\ \text{terpy} \xrightarrow{\text{(non-coordinating solvent)}} [Tb(terpy)_2(H_2O)_3]Cl_3 + 6\ H_2O$

$[Tb(H_2O)_9]Cl_3 + 3\ \text{terpy} \xrightarrow{\text{(non-coordinating solvent)}} [Tb(terpy)_3]Cl_3 + 9\ H_2O$

Geometry: tricapped trigonal prismatic

B) Indicate which of the formed complexes is the most luminescent and why.

The second one is the most luminescent, due to **none coordinated water molecules** (desactivation of luminescence by vibrations in the first complex)



terpy

C) Indicate the colour of luminescence

Green

Question 7

A) Give advantages and disadvantages of MRI an fluorescence imaging

B) Which Ln is the best for application of fluorescence imaging in vivo and why?

C) Indicate what kind of fluorophore are needed and give an example.

D) What are the different requirements for the application of lanthanide complexes for in vivo Imaging?

Answer 7

A) Give advantages and disatvantages of MRI an fluorescence imaging

MRI: - High resolution
- Low sensitivity
- Deep penetration

Fluorescence : - High sensitivity
- No resolution
- Low penetration

B) Which Ln is the best for fluorescence imaging application in vivo and why?

Yb: - Near IR emission has deeper penetration
- Emits in the biological transparency → Window (650-900 nm)

Answer 7

C) Indicate what kind of fluorophores are needed and give an example.

The **triplet state should be compatible** (higher but not too much) with the emitting state of Yb (hydroxyquinolinate). Ideally we should suppress C-H bond that desactivates Yb luminescence

D) What are the different requirement for the application of lanthanide complexes for in vivo Imaging?

-High stability -High solubility -High relaxivity for MRI contrast agents

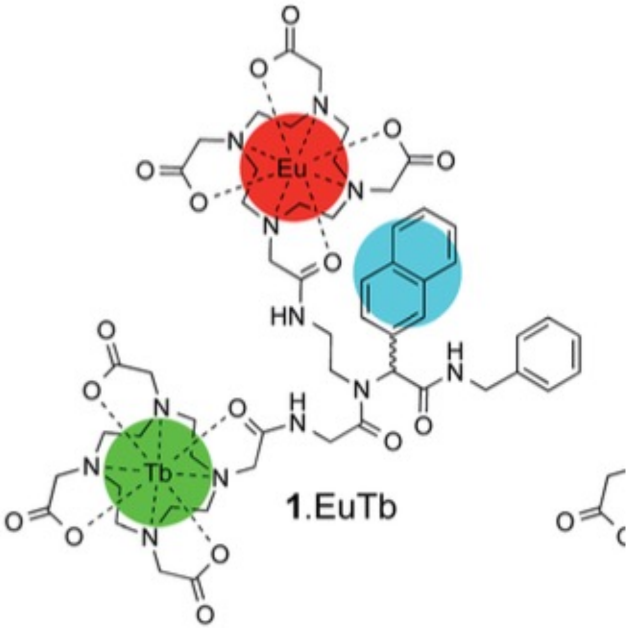
-High quantum yield -Excitation in the visible (low energy) for fluorescence

Question 8

Suggest a possible design for building an oxygen sensor indicating the element of design required . Indicate why such sensor is needed.

Answer 8

Suggest a possible design for building an oxygen sensor indicating the element of design required . Indicate why such sensor is needed.



We need to combine a Luminescent Tb complex for which the luminescence is quenched by oxygen, a chromofore and a Eu complex as standard

Used to **detect oxygen level**: 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.

Question 9

A) What are « non classical » lanthanides(II)?

B) Indicate examples of ligands that have allowed the isolation complexes of these elements

C) Indicate how the complex is prepared and why and draw the structure for $[NdI_2(THF)_5]$

EPFL

Answer 9

A) What are « non classical » lanthanides(II)?

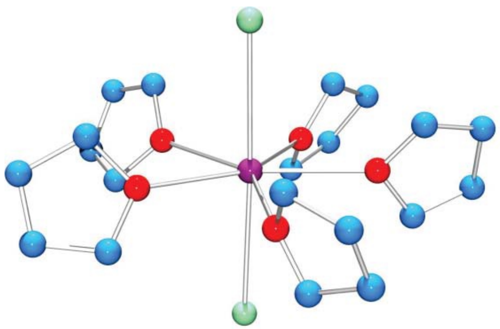
All except Sm, Eu, Yb

B) Indicate examples of ligands that have allowed the isolation complexes of these elements

I^-, bulky amides , bulky aryloxides
"$[Ln\{N(SiMe_3)_2]$"

C) Indicate how the complex is prepared and why and draw the structure

Is prepared at low T to avoid disproportionation to Nd^0 and Nd^{3+} or ring opening of THF



$[NdI_2(THF)_5]$

It is prepared by oxidation of the metal with I_2

Controlled stoichiometry is important to avoid formation of NdI_3

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If you have any questions about these exercises you can send a mail to :

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Arsene: fang-che.hsueh@epfl.ch