Fluorescence, Phosphorescence et autres Luminescences

Robert PANSU
pansu@ppsm.ens-cachan.fr

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Plan

- Ce que l'on voit
- Introduction historique
- Diagrammes d'énergie
- Zoologie
- La cinétique de l'état excité
- Conclusion

Applications

- Les azurants,
- Photovoltaïque, Thermoluminescence,
- Microscopie, Indicateurs, super résolution, Lasers

- L'acte chimique élémentaire, Oxymètres

Sources en français

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Historique

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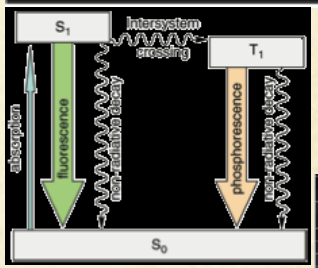

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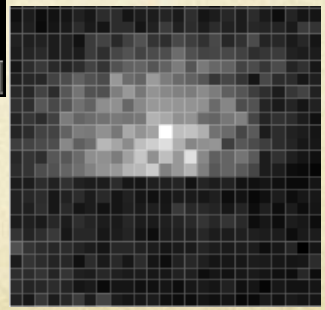

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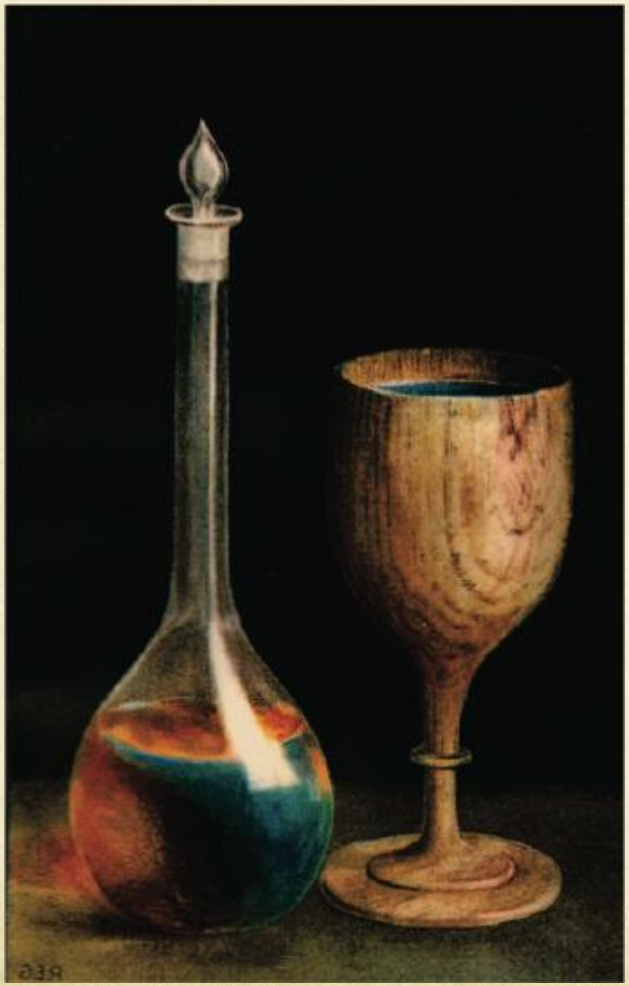
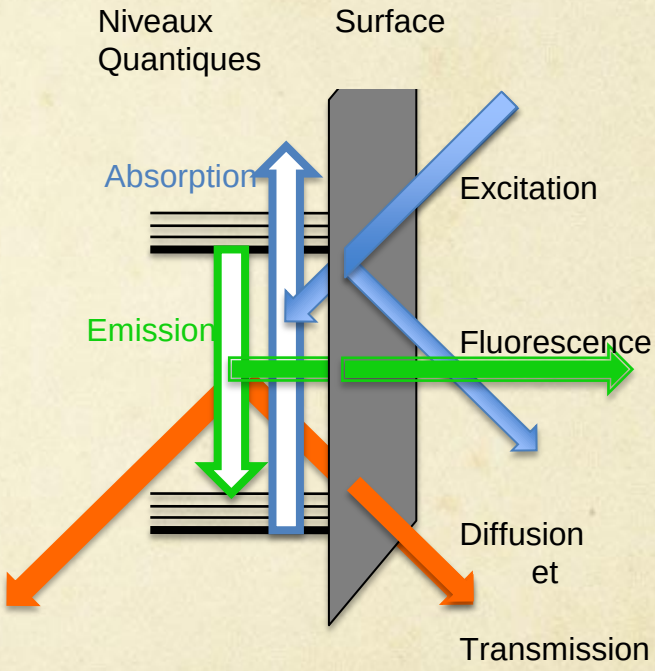
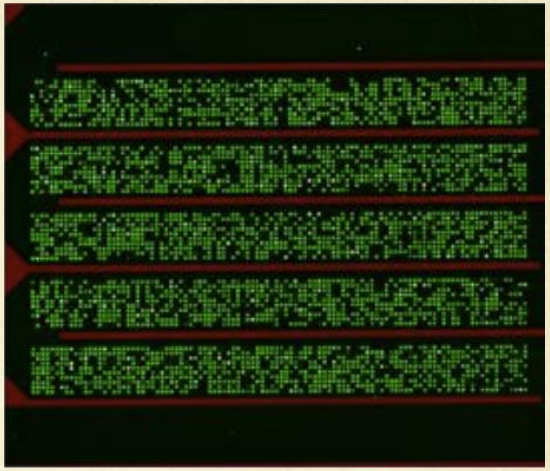
Ce que l'on voit

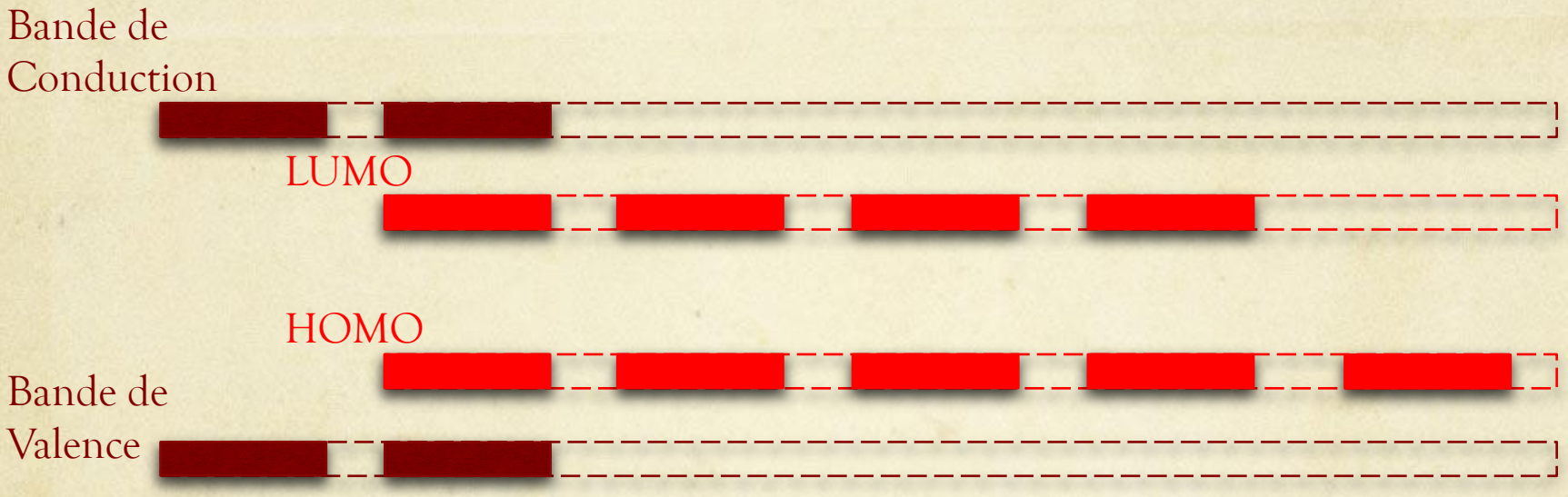




Autour de nous



Zoologie et diagramme d'énergie

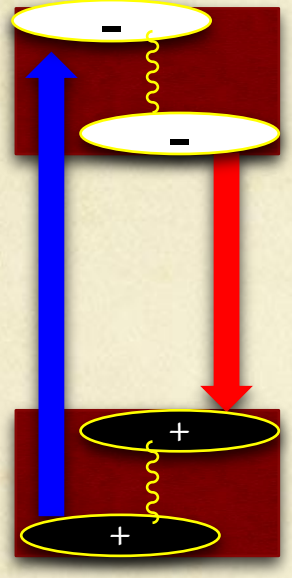


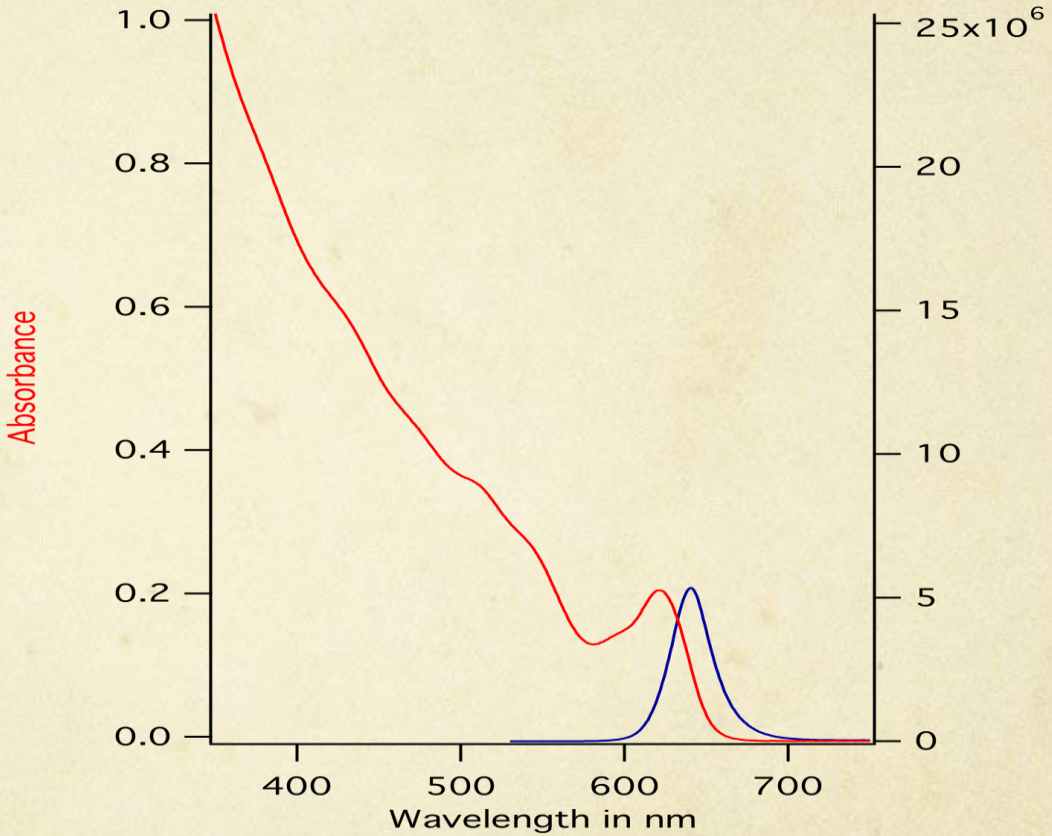
Semi Conducteurs	Défauts dans les Semi Conducteurs	Impureté dans les minéraux	Molécules fluorescentes en solution	Ions des métaux de transition	Lanthanides +3
CdSe CdSe/ZnS	ZnO	Ni, NV/Diamant	Fluorescéine Fl. Protéines	Ru^{+3},Ir^{+3} UO_2^{+2}	Tb, Eu, Dy, Nd, Er, Yb

Semi-conducteurs

Bande de Conduction

Bande de Valence





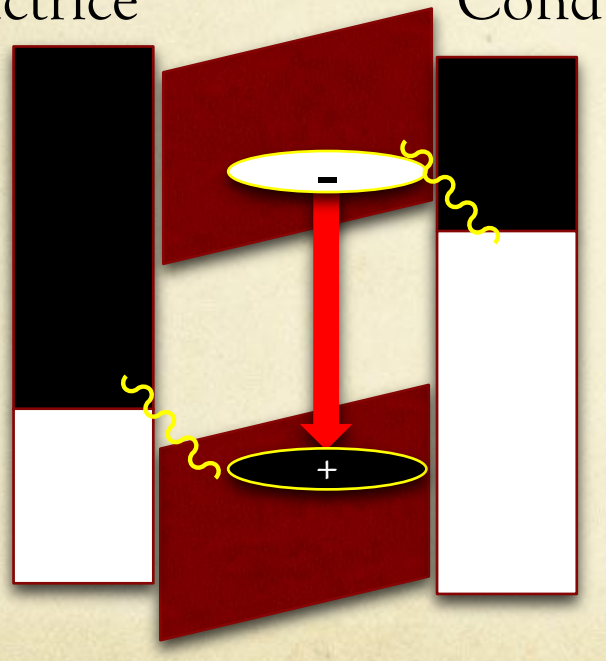
Résumé

- Photoluminescence :
  - Excitation d'un seul électron
  - Relaxation dissipative
  - Equilibre thermodynamique de l'état excité
  - Emission de photon en compétition avec les désactivations non radiatives
  - Déplacement de stokes
  - Principe de Jablonski
  - Réactivité des états excités
  - Rendement de fluorescence

Diode Electro Luminescente

Anode
Conductrice

Cathode
Conductrice



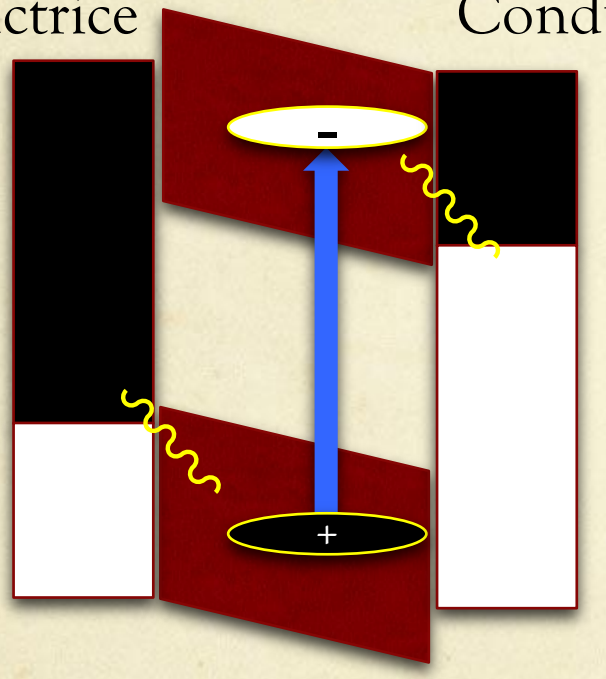
ITO

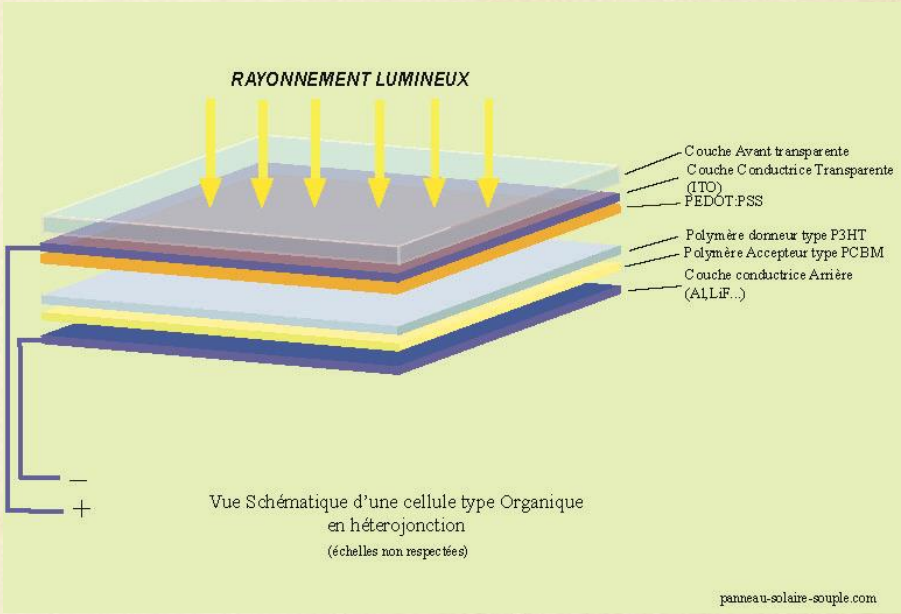
Ca

Photo-Voltaïque

Anode
Conductrice

Cathode
Conductrice



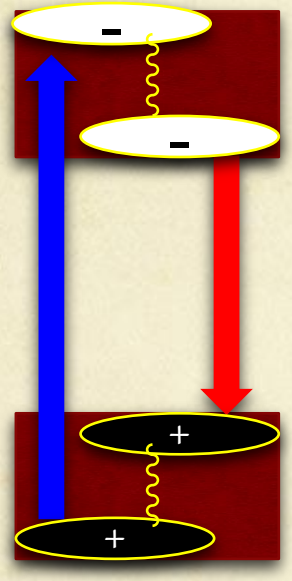


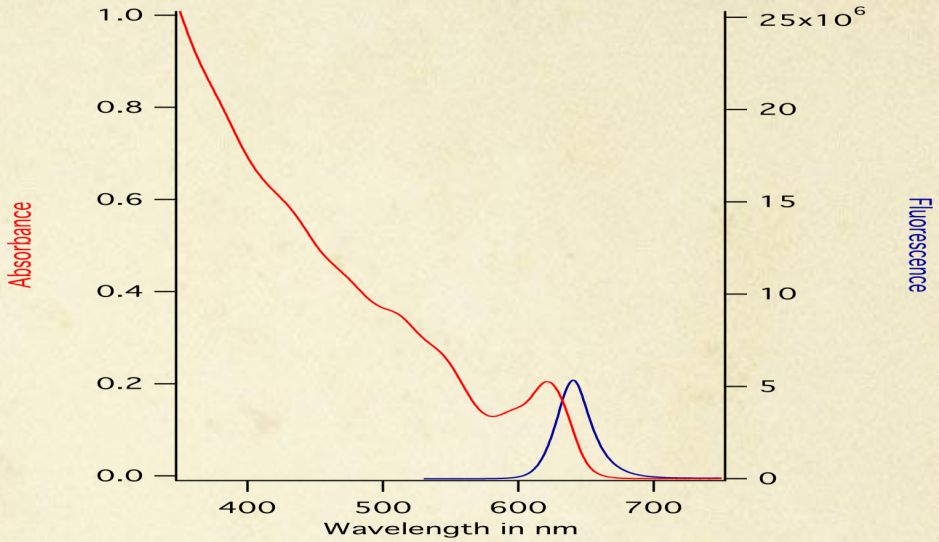
http://www.panneau-solaire-souple.com/

Semi-conducteurs

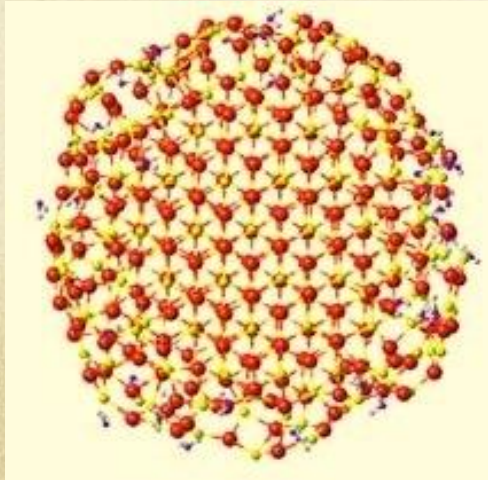
Bande de Conduction

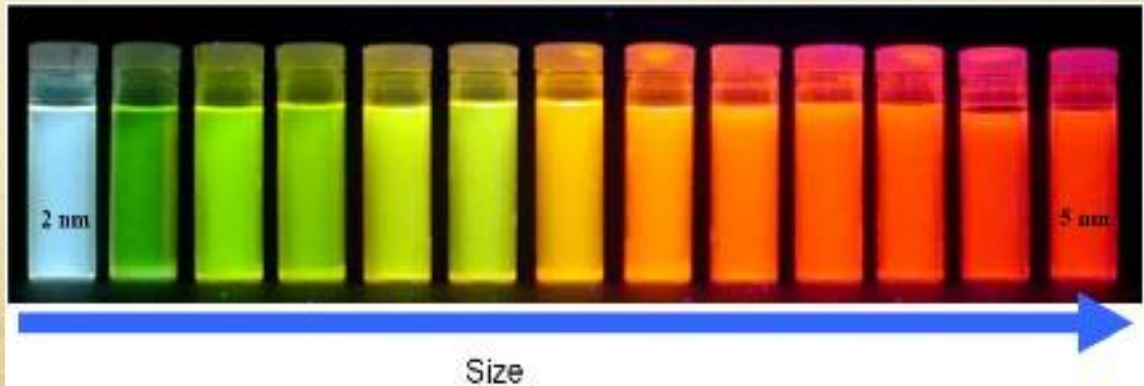
Bande de Valence



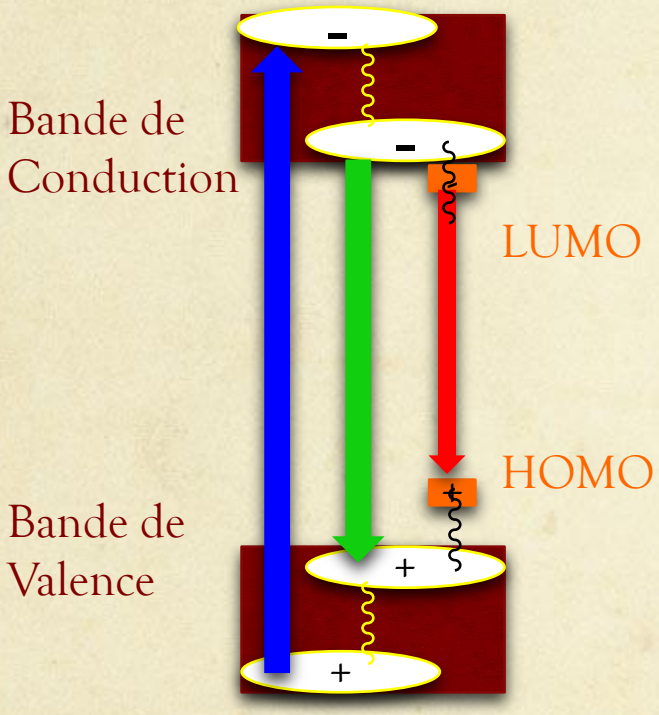


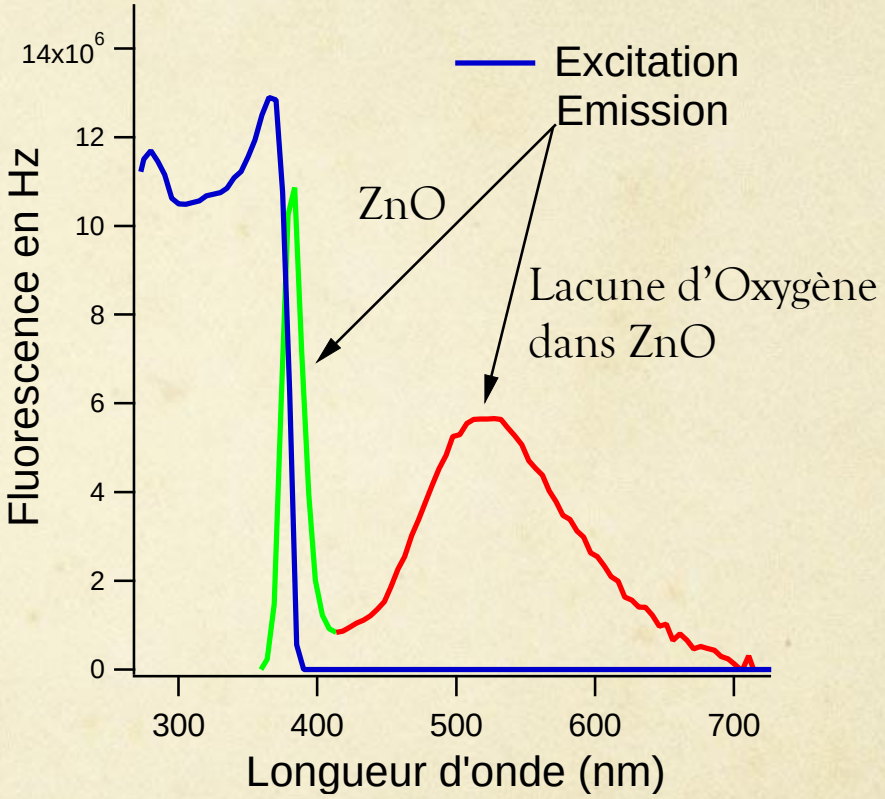
CdSe





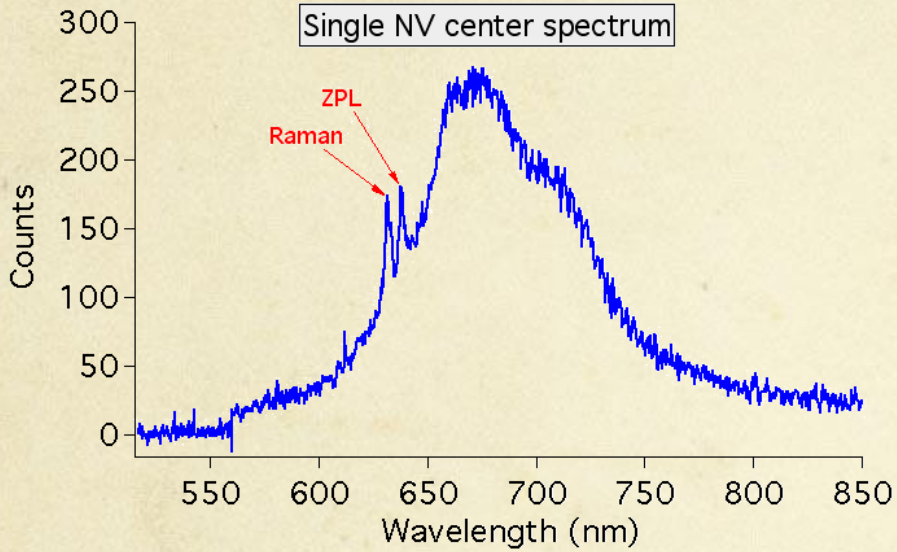
Défauts dans les Semi-conducteurs

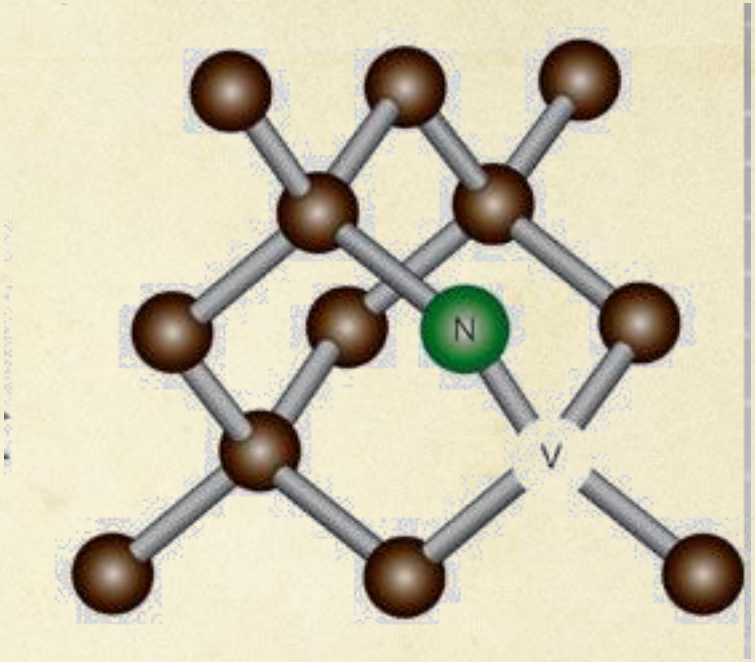




van Dijken, A. et al. J. Luminescence 2000, 90, 123.

Impuretés dans le diamant

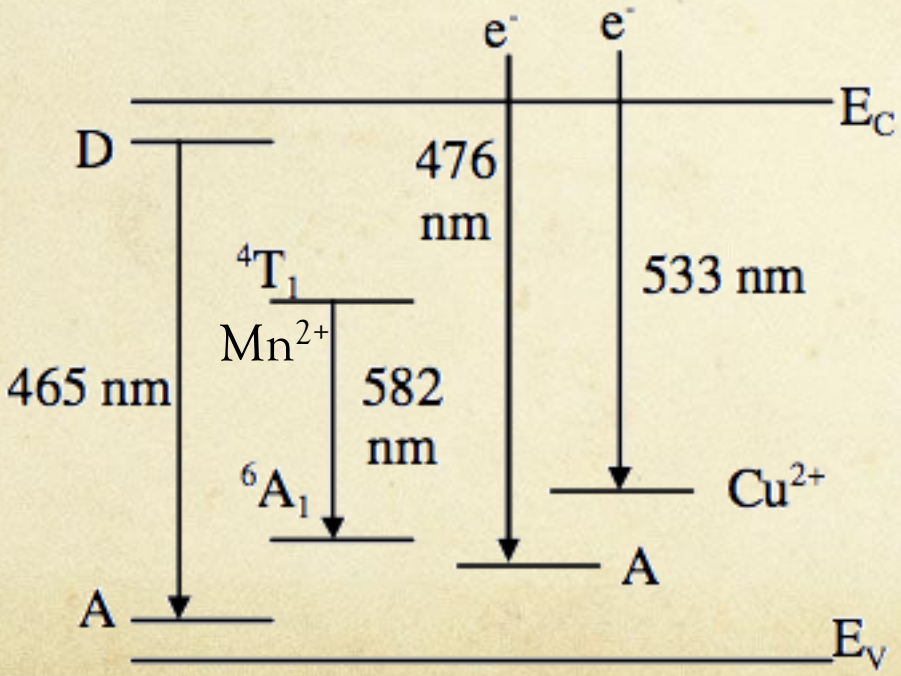


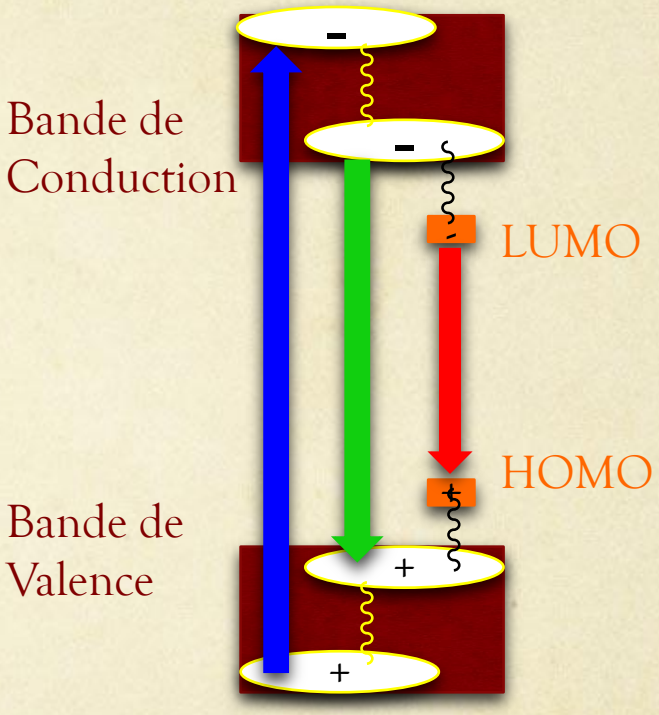


Spectroscopic and laser parameters of H3, NV and NE4 diamond color centers					
Color center	Absorption (nm)	Emission (nm)	Lifetime (ns)	Em. Width (nm)	Em. Cross-1E-20 m2
H3 V-N-V	490	525	16	60	1,6
NV N-V	565	690	13	120	3,2
NE4 V-Ni-V	670	950	27	100	6,2

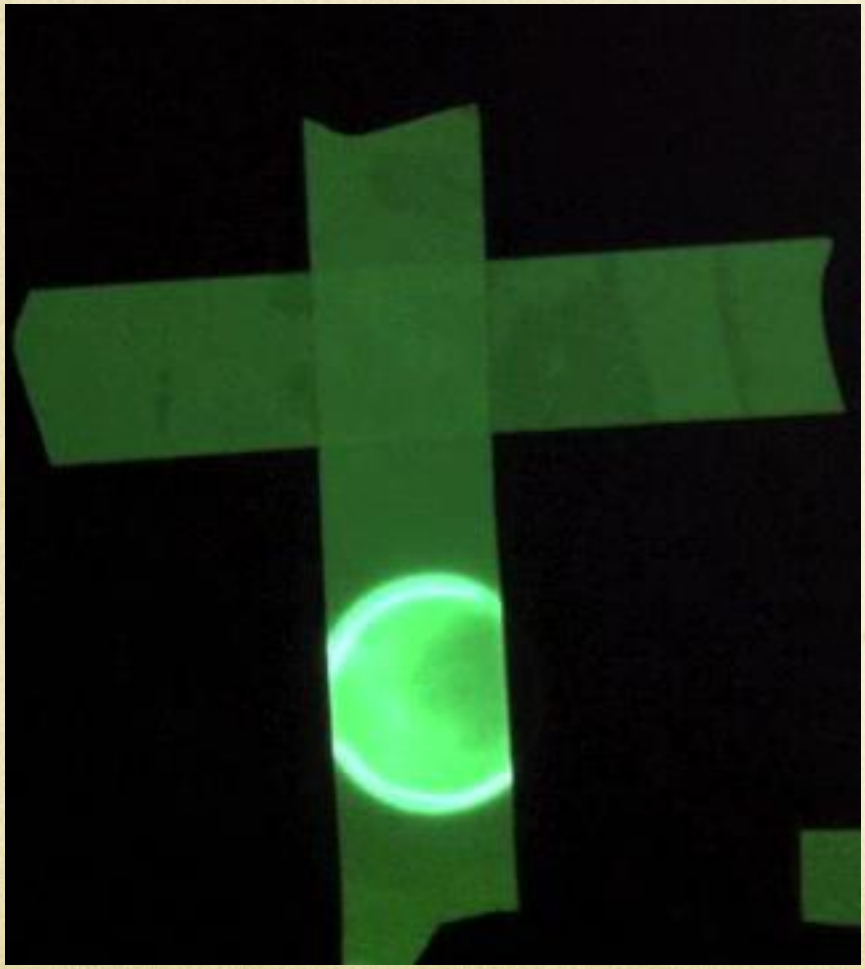
Impureté du Semi Conducteur

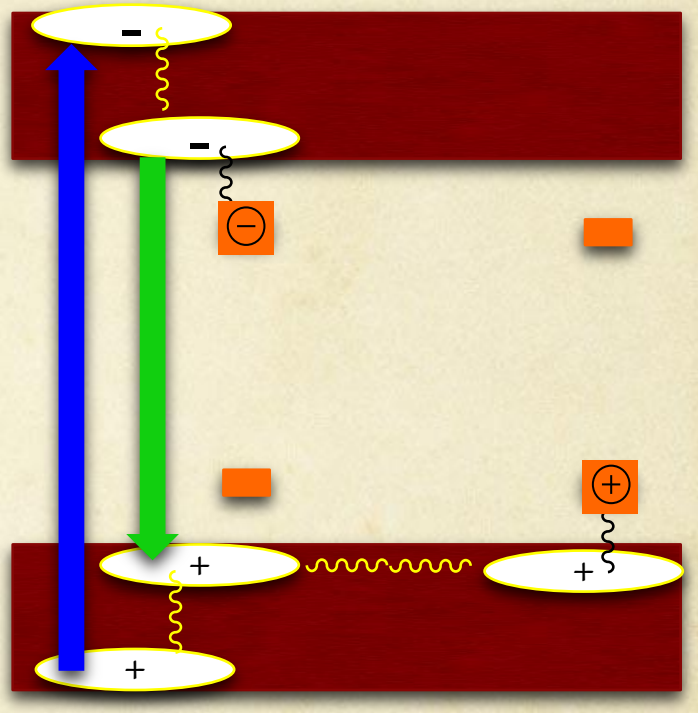
Cu^{2+},Mn^{2+},Co^{2+}/ZnS





Thermoluminescence et Photo-dépiégeage





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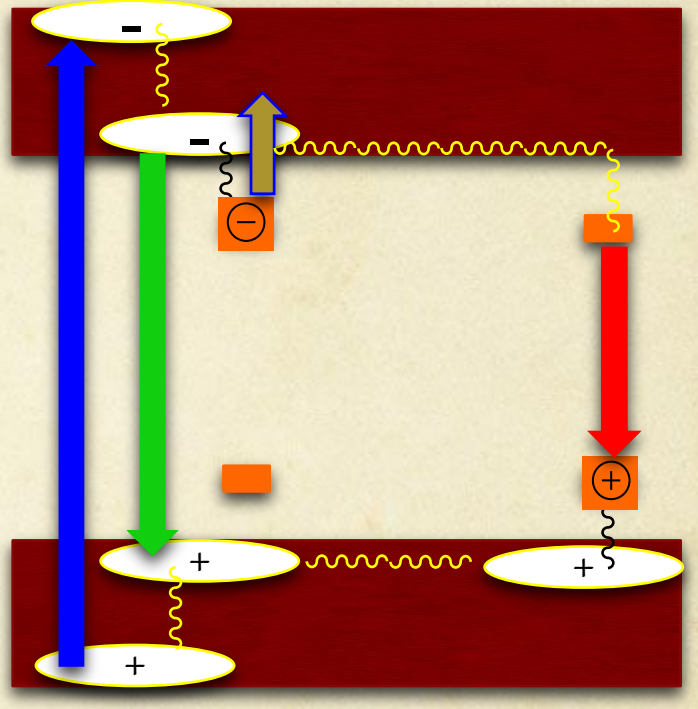
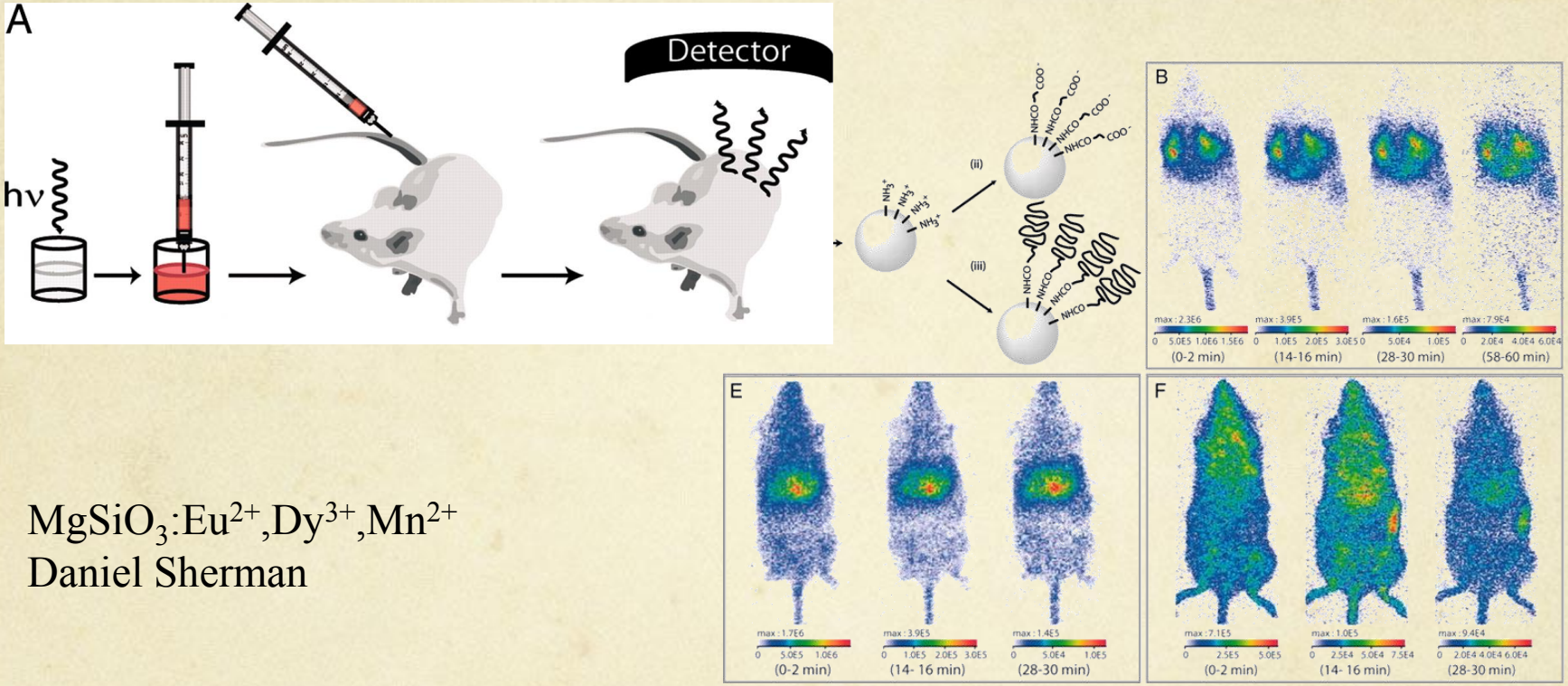
Thermoluminescence et Photo-dépiégeage



(1)Schwankner, R.; Eiswirth, M.; Venghaus, H. J. Chem. Ed. 1981, 58, 806.

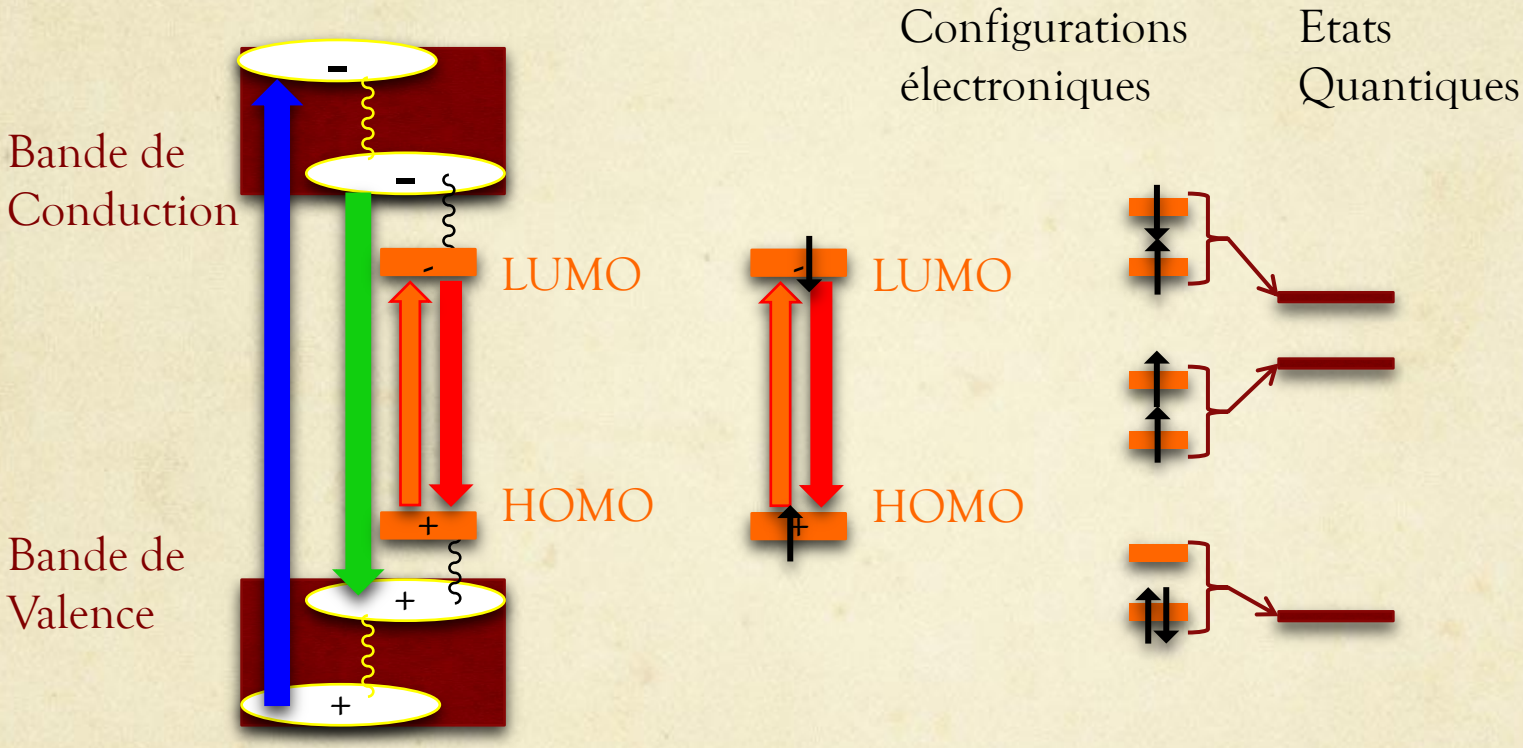
Fonctionnalisation de surface et vectorisation



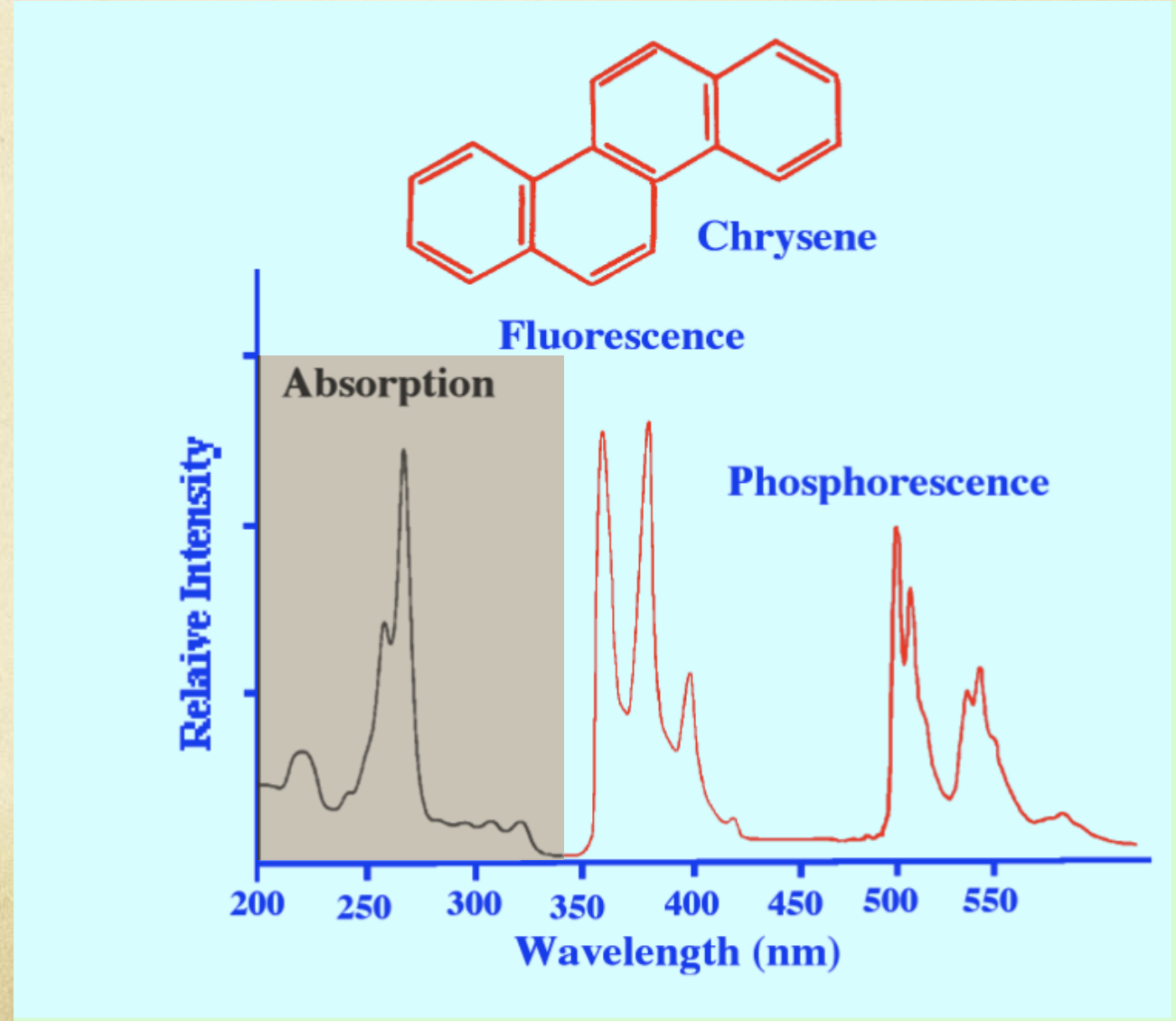
$MgSiO_3:Eu^{2+},Dy^{3+},Mn^{2+}$
Daniel Sherman

le Masne de Chermont Q et al. PNAS 2007;104:9266-9271

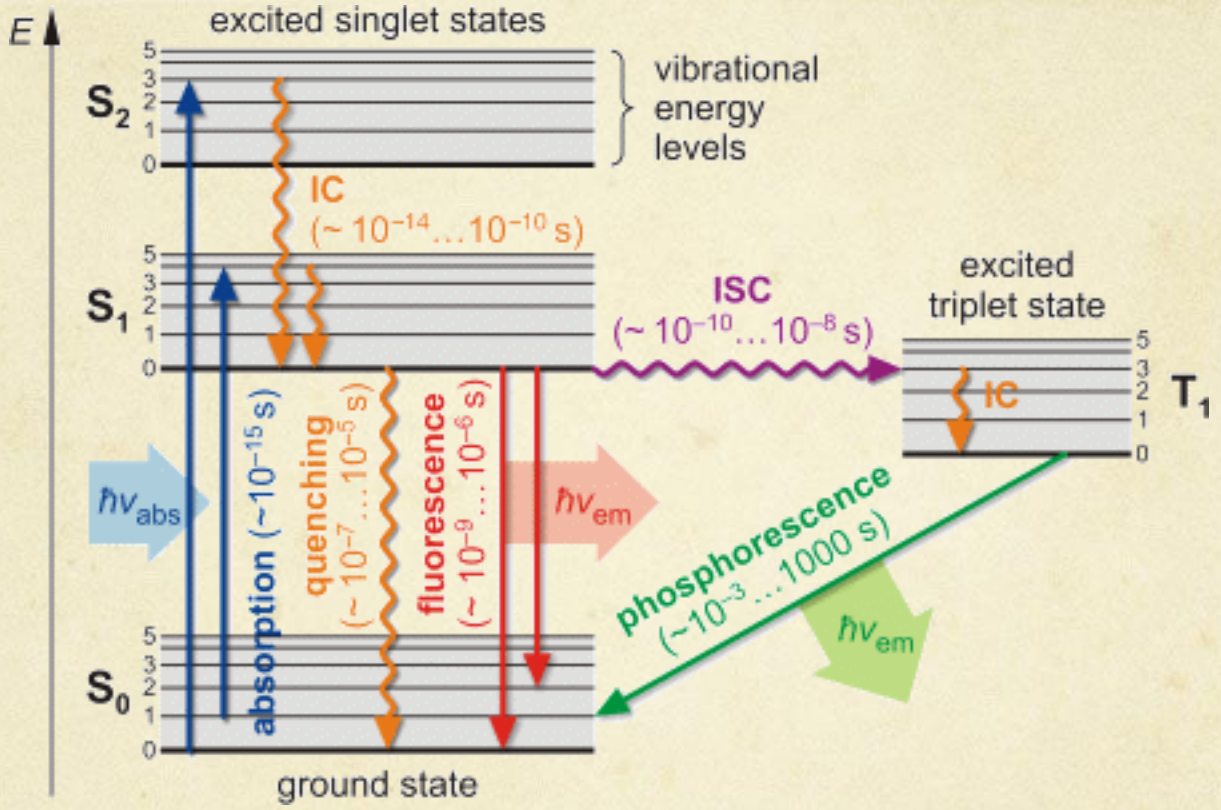
Fluorescence et Phosphorescence des molécules organiques



Fluorescence et Phosphorescence des molécules organiques



Fluorescence et Phosphorescence des molécules organiques



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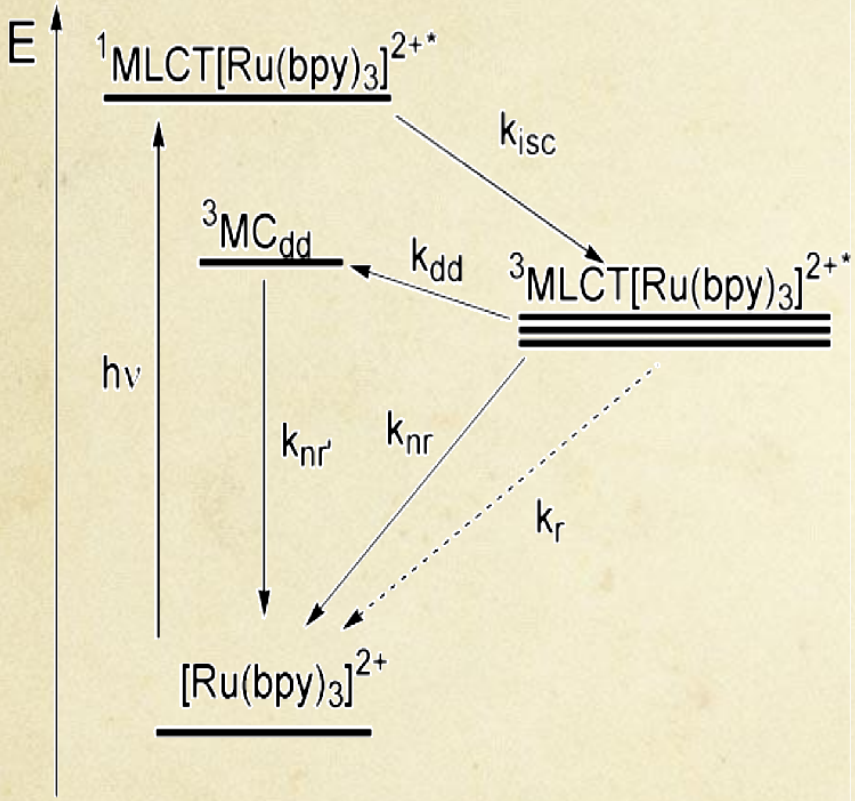
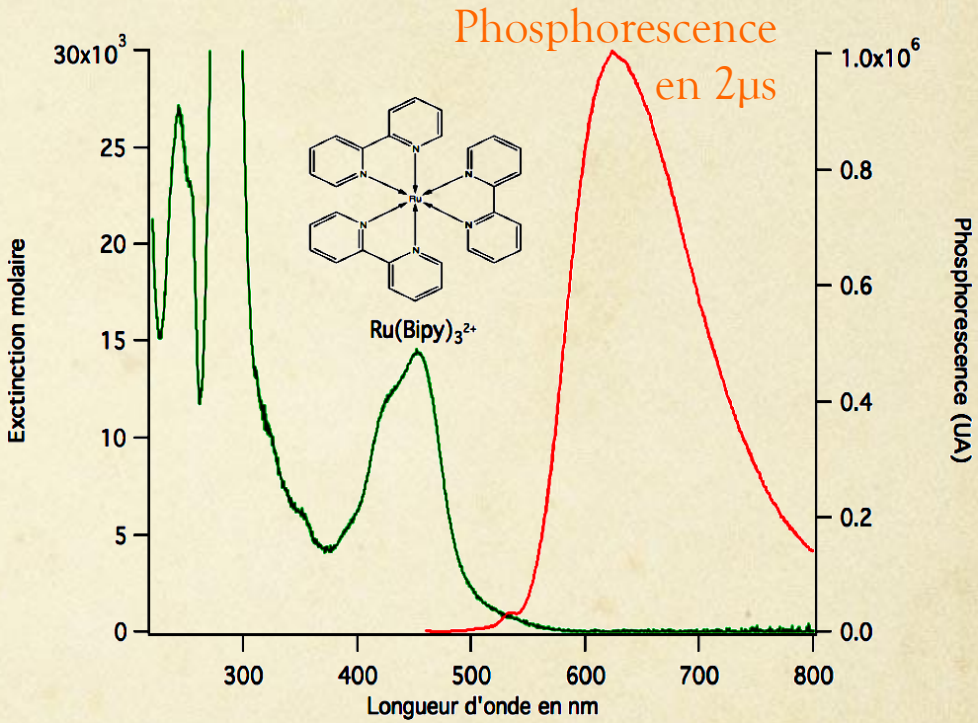
Complexe de Ru^{+3} et Ir^{+3}





Maruszewski, K. et al. (1993) *JACS* ***115 (18) 8345-50.***

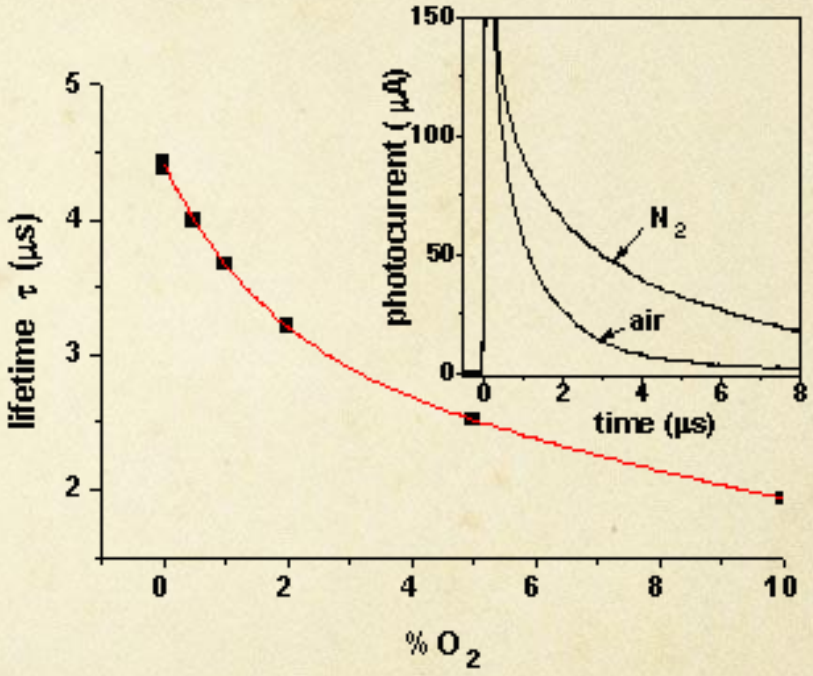
Détection O_2

$T_1 \rightarrow S_0$ k_{nr}

$T_1 \rightarrow S_0 + hv$ k_{phos}

$T_1 + {}^3O_2 \rightarrow S_0 + {}^1O_2$ k_{dif}

$$\frac{d[T]}{dt} = -(k_{nr} + k_{phos})[T] - k_{diff}[O_2][T]$$



Fluorescence, Phosphorescence et autres luminescences
la « Phosphorescence » de Cu,Mn,Co/ZnS

http: IUPAC > Gold Book > alphabetical index > phosphorescence :

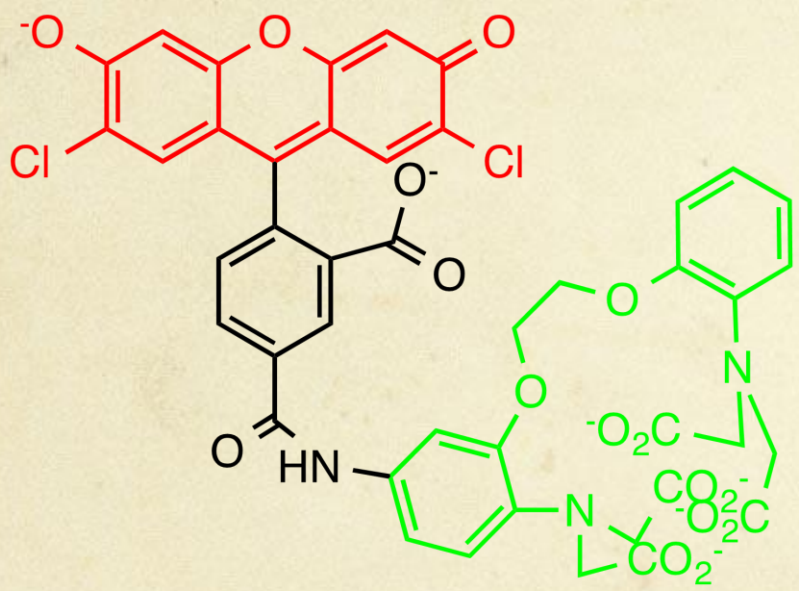
The term has been used to describe long-lived luminescence. The term designates luminescence involving change in spin multiplicity.

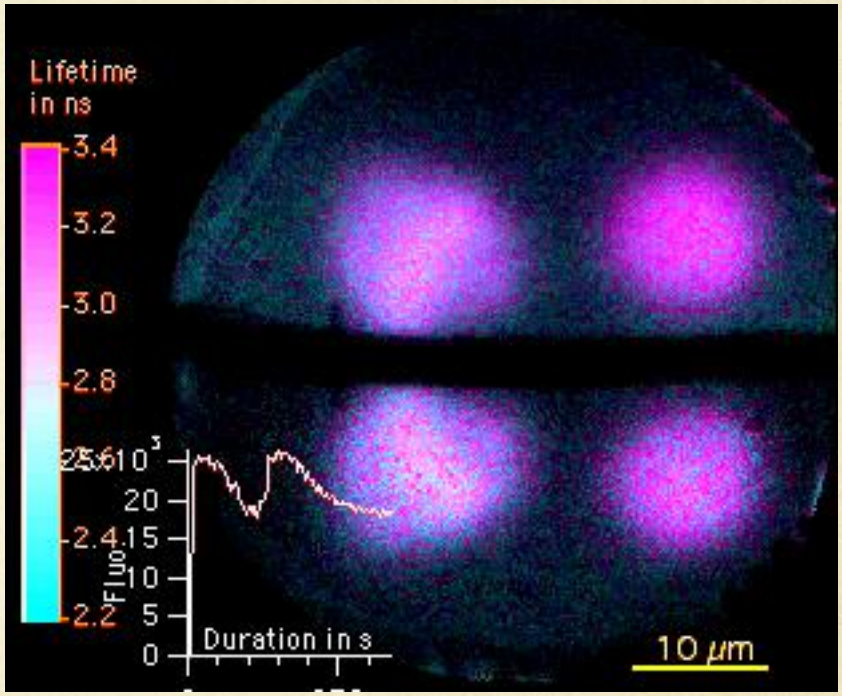
	Cu/ZnS	**Mn/ZnS**	**Co/ZnS**
Luminescence longue	☺	☺	☺
Non conservation du Spin	??	☺ $^4T_1 \rightarrow {}^6A_1$	☹ $^4T_1 \rightarrow {}^4A_2$
Thermo luminescence	☺	☺	
Photo dépiégeage	☺		
	??	Phosphore-scence Retardée	Fluorescence Retardée

Applications

AGRICULTURES & TERRITOIRES
CHAMBRE D'AGRICULTURE HÉRAULT

Indicateurs fluorescents

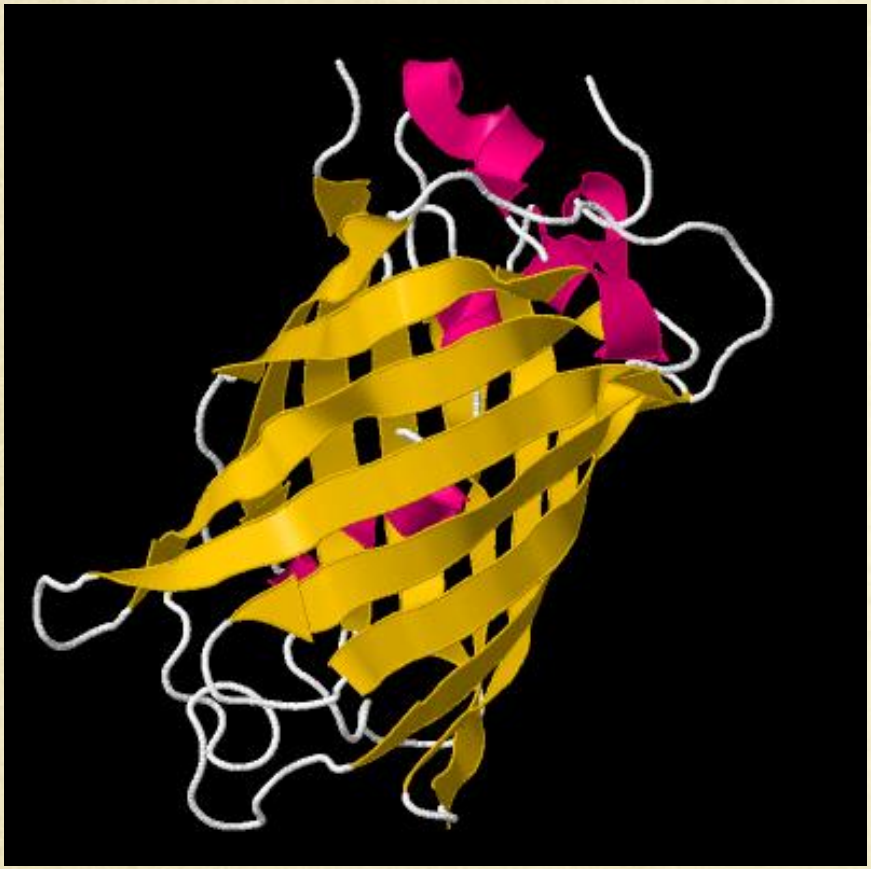


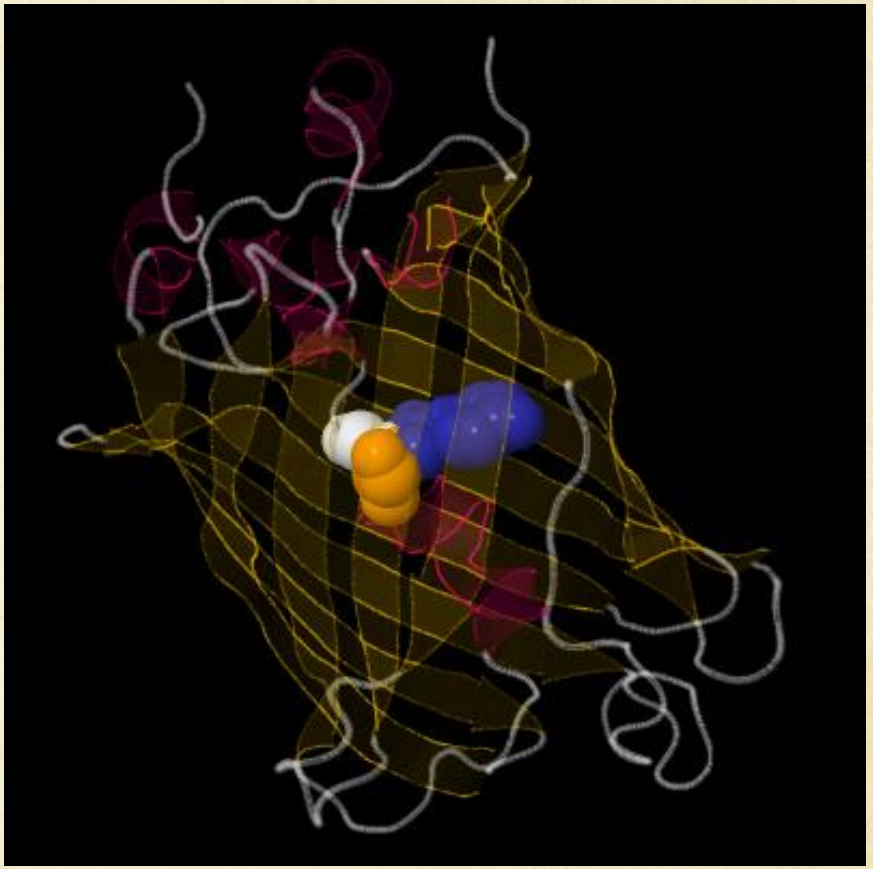


Tsien, R. Y. Biochemistry 1980, 19, 2396.

Valeur, B. http://www.theses.fr/?q=%22Fluoroionophore%22

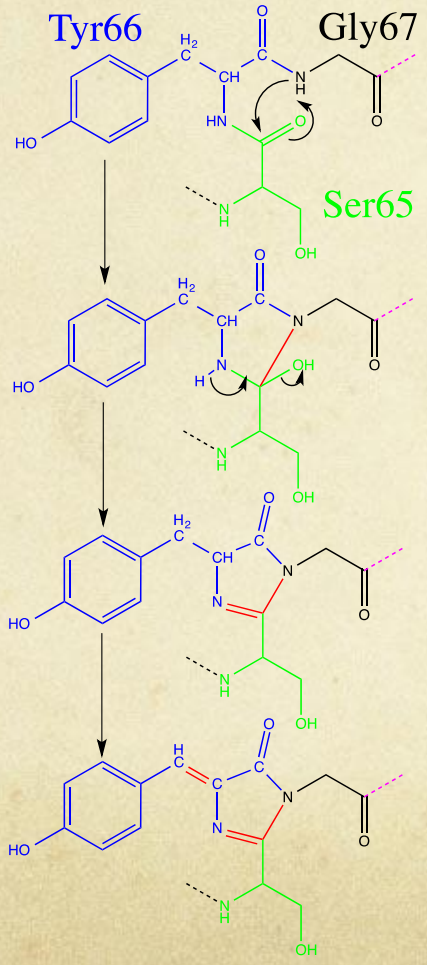
Les protéines fluorescentes

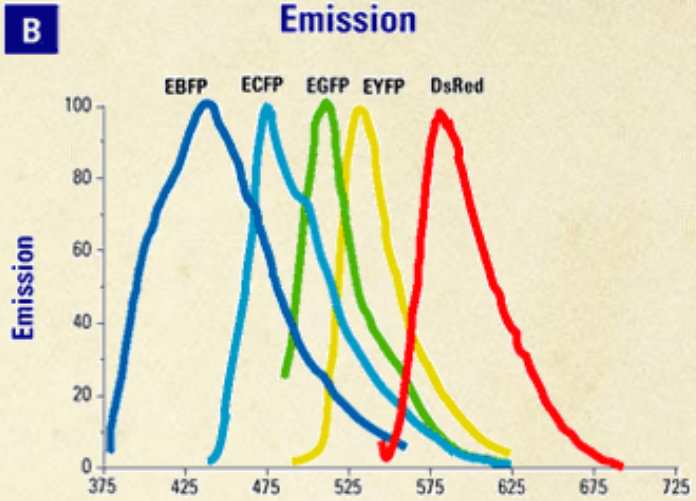


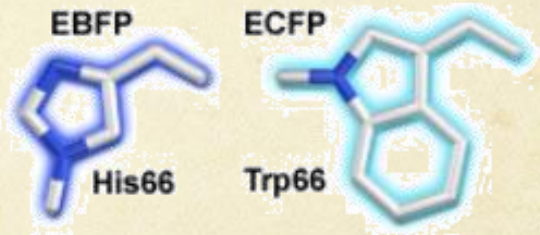


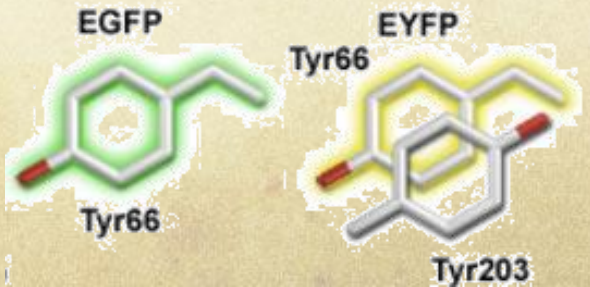
http://www.librairiedemolecules.education.fr/molecule.php?idmol=323

Protéines fluorescentes

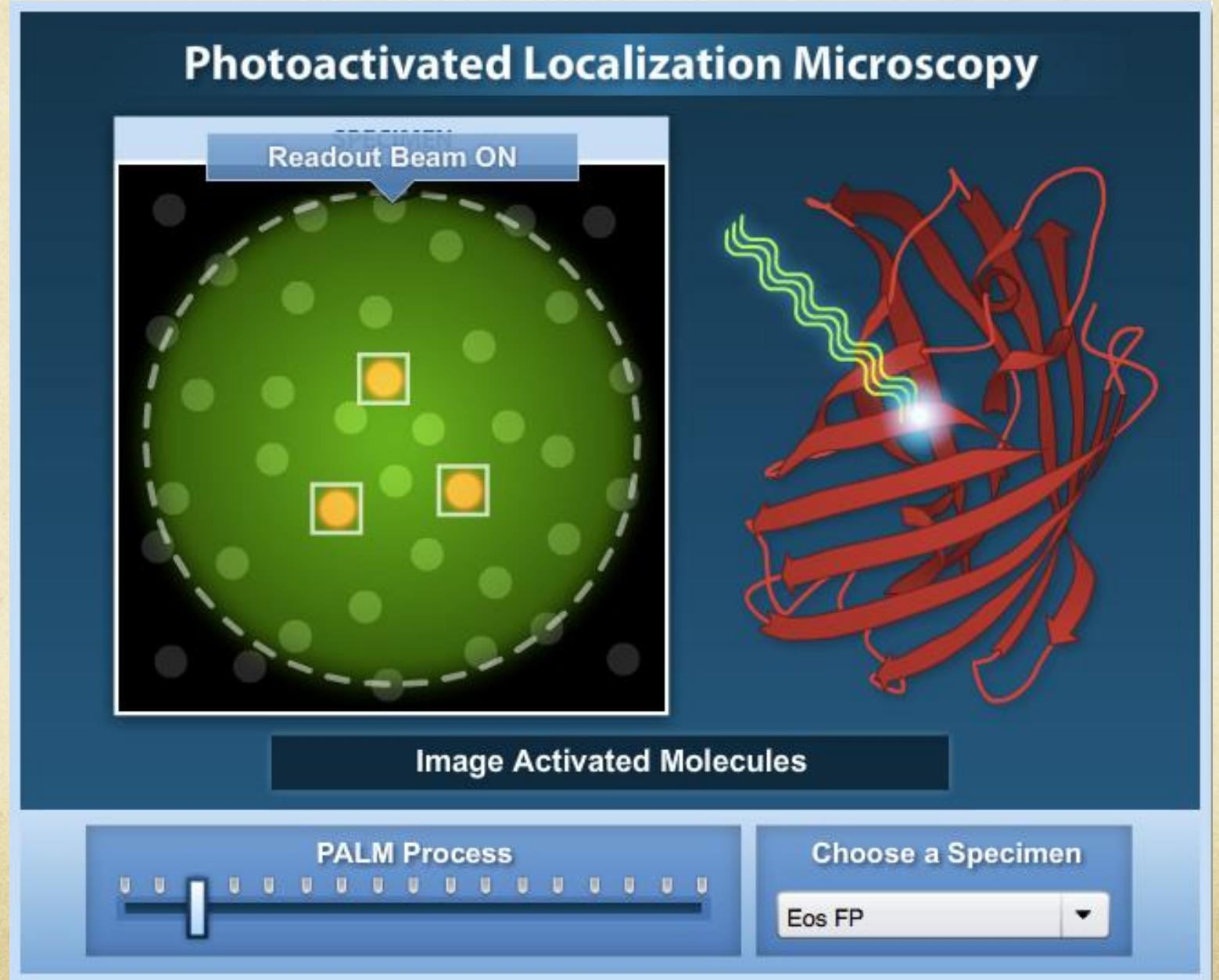








La super résolution

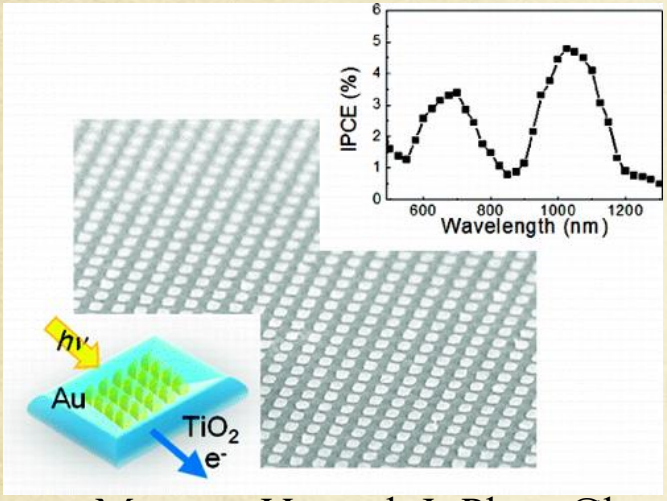


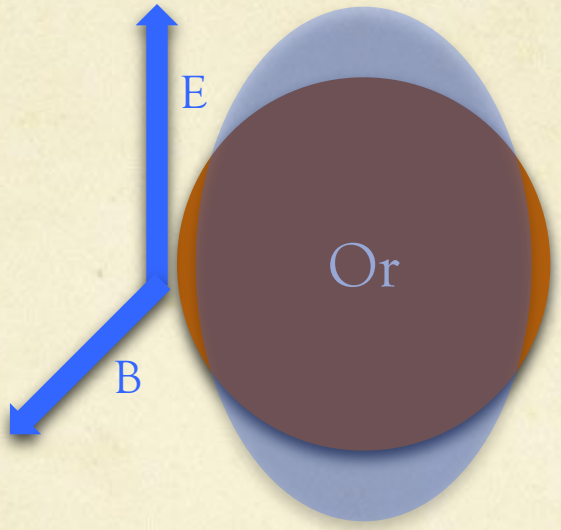
Conclusions

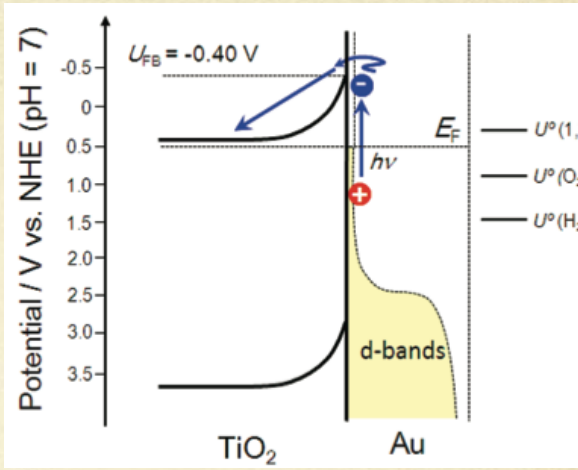
- Les diagrammes d'énergie permettent de décrire
  - Le déplacement de Stokes
  - Luminescence indépendante du mode d'excitation
  - Concept commun avec l'électronique
- De nombreuses applications
- Les prochains matériaux luminescents

Perspectives

- Plasmon







Misawa, H. et al. J. Phys. Chem. Letters 2010, 1, 2031.

- Thermo-Luminescence

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- d

Distribution of populations

m:number of quenching sites, p: occupation probability, n: number of quenchers,

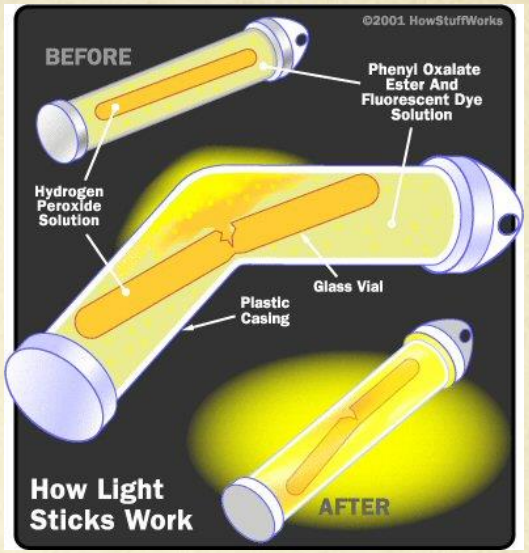
$$I_f(t) = I_f(0) \sum_{n=o}^{m} C_m^n p^n (1-p)^{m-n} \exp\left(-k_f t - n\int g(u)du\right)$$

$$I_f(t) = I_f(0)\exp(-k_f t)\left(p + (1-p)\exp\left(\int g(u)du\right)\right)^m$$

$$Ln\left(\frac{I_f(t)}{I_f(0)}\right) \rightarrow -k_f t - m\int_o^t k_Q(u)du \qquad as\ p \rightarrow 1$$

$$Ln\left(\frac{I_f(t)}{I_f(0)}\right) \rightarrow -k_f t + mp\left\{\exp\left(-\int_o^t k_Q(u)du\right) - 1\right\} \qquad as\ p \rightarrow 0$$

Chimi- Bio- Luminescence



http://tpe-luminescence.blogspot.fr