

13 Mai 2024

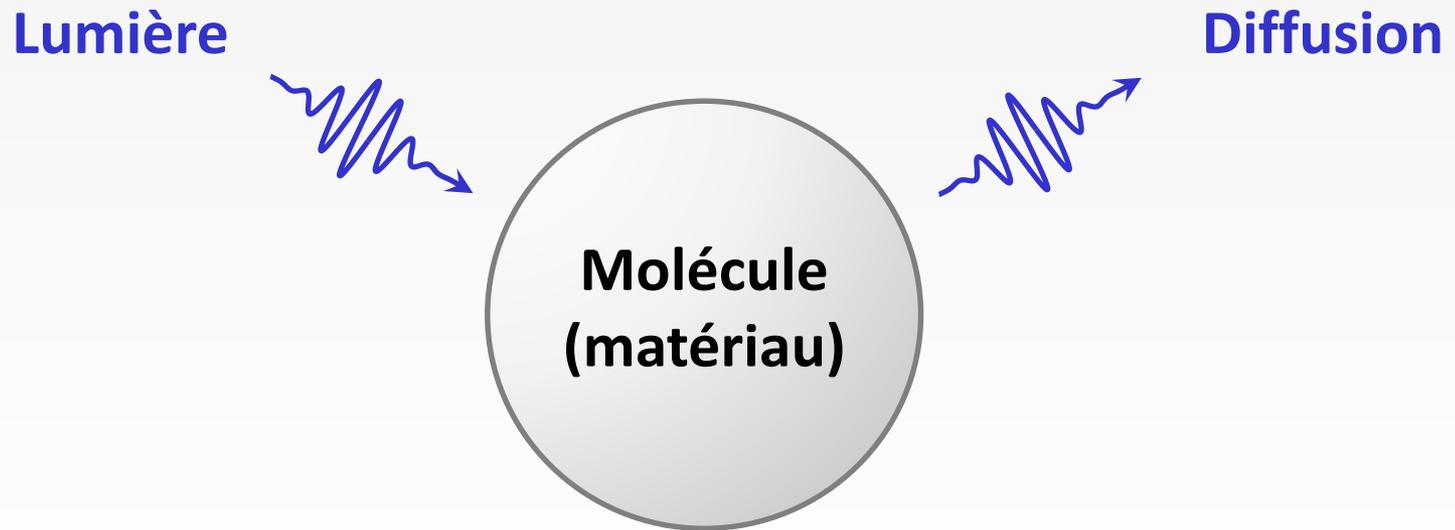
***Entre photochromisme et luminescence :
comment stimuler les molécules grâce à la lumière ?***

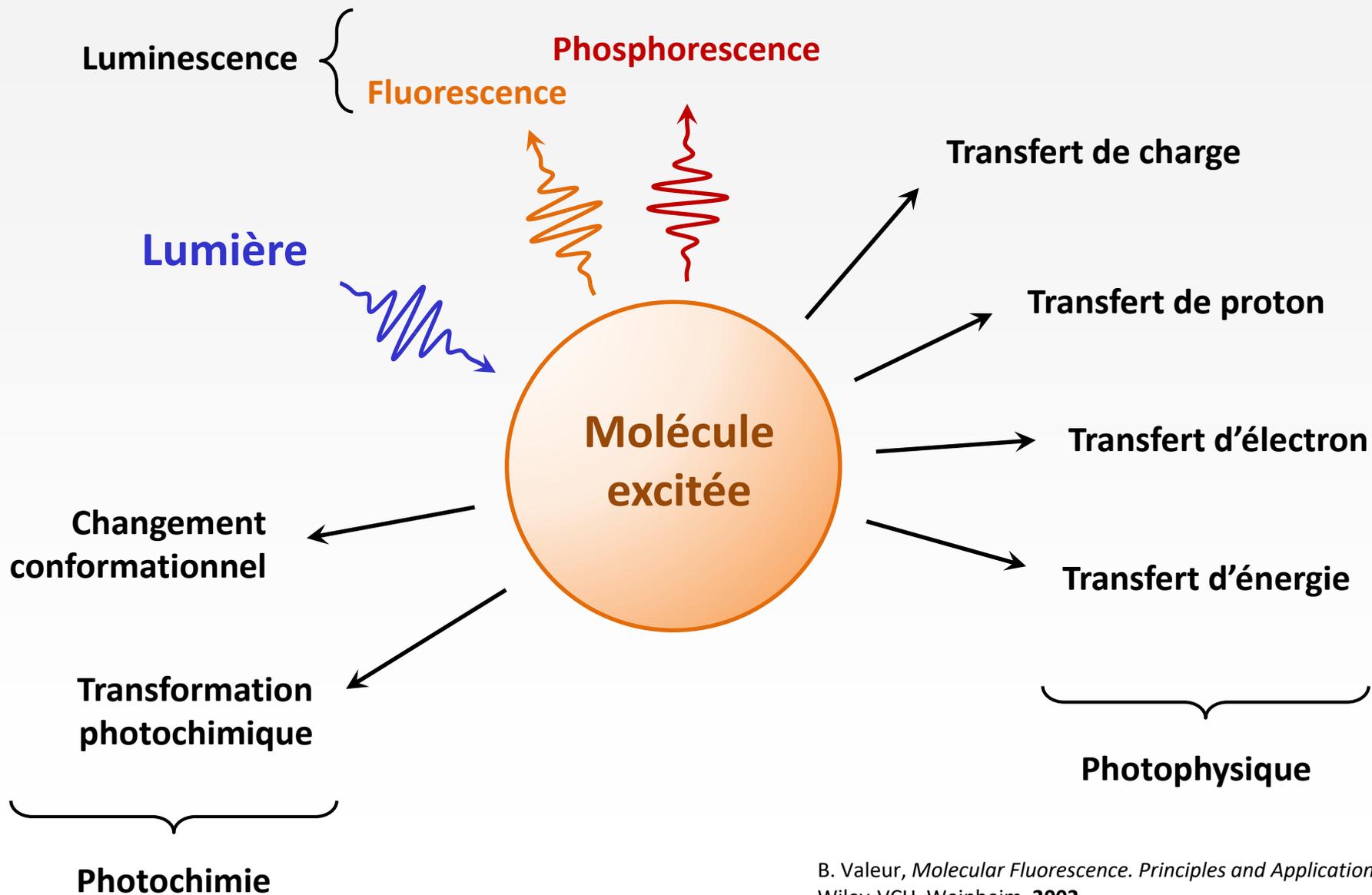
Rémi Métivier – Directeur de Recherche CNRS

école
normale
supérieure
paris – saclay



*PPSM Laboratory
(Supramolecular and Macromolecular
Photophysics and Photochemistry)
ENS Paris-Saclay
Université Paris-Saclay, France*

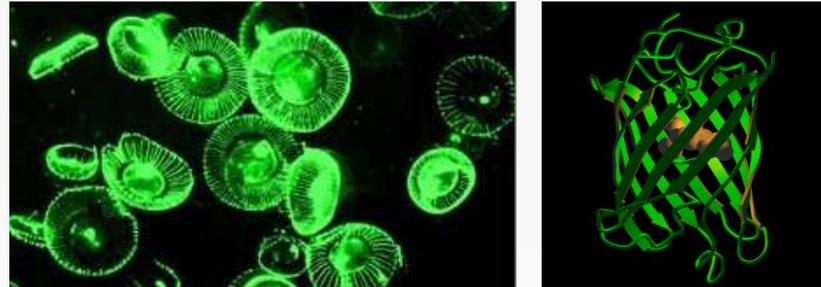




Luminescence de minéraux

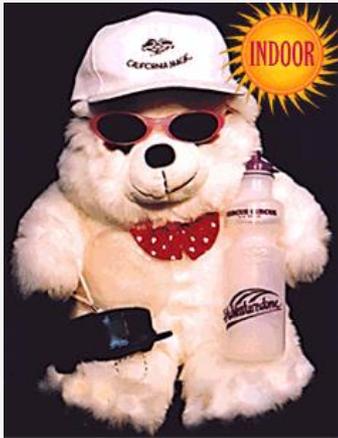


Luminescence de protéines

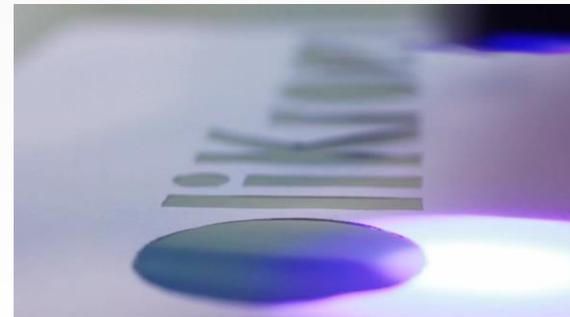


Luminescence de colorants de synthèse





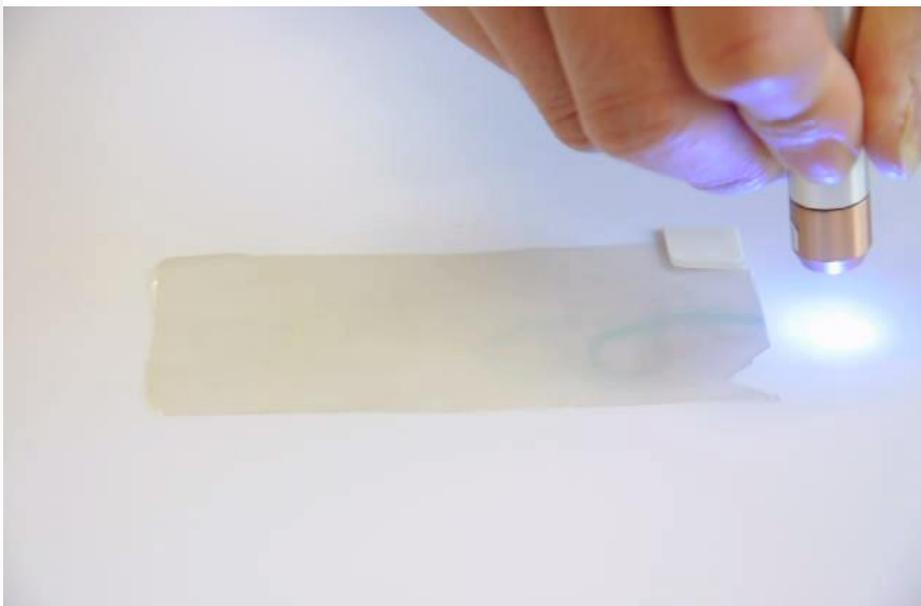
Transitions
light intelligent lenses.



Izzi [@lzzipoopi]
Instagram 2022
"PH5 - Collection UV reactive"
<https://ph5.com/collections/uv-reactive>

 **OliKrom**
SMART COLORS

Photochrome de type T

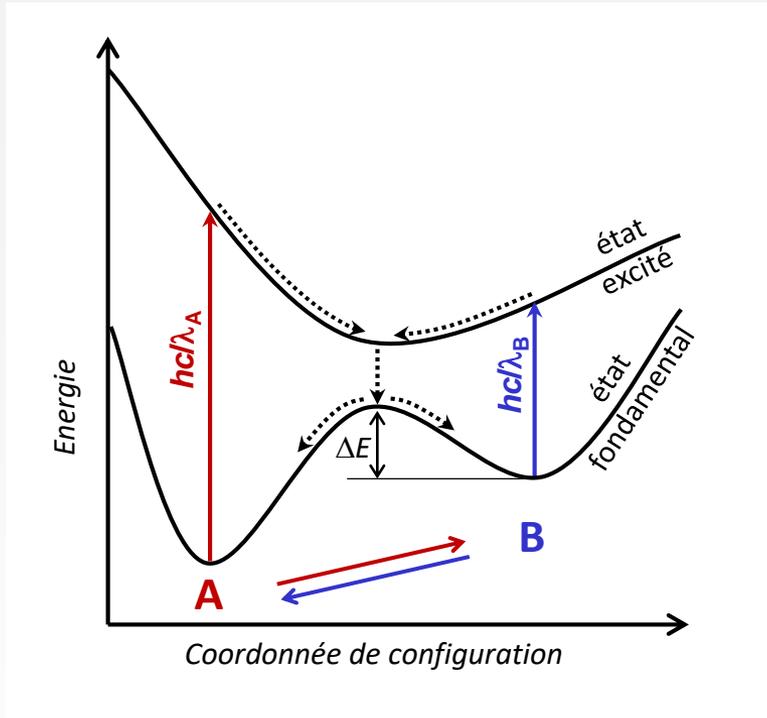


*Laboratoire du Professeur J. Abe,
Université Aoyama Gakuin, Japon*

Photochrome de type P



*Laboratoire du Professeur M. Irie,
Université Rikkyo, Japon*



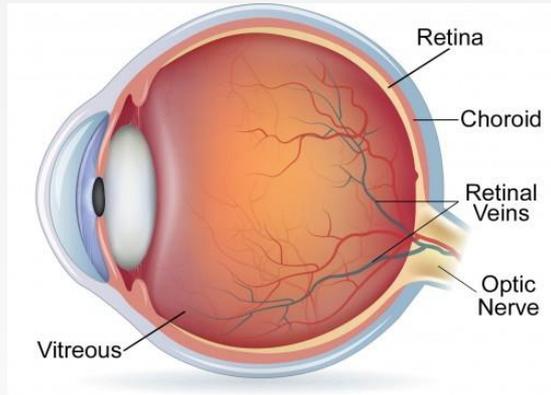
- Photochrome de type P : $\Delta E \gg kT$
- Photochrome de type T : $\Delta E \sim kT$
- Photochrome positif : $\lambda_A < \lambda_B$
- Photochrome négatif : $\lambda_A > \lambda_B$

- Rendements quantiques $\Phi_{A \rightarrow B} = \frac{\text{nombre de photoréactions } A \rightarrow B}{\text{nombre de photons absorbés par } A}$

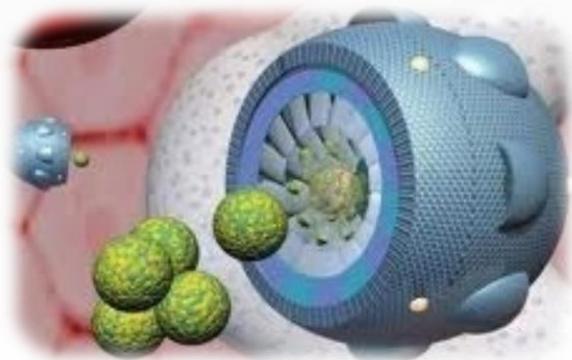
- Taux de conversion $\alpha_{A \rightarrow B} = \frac{C_B^\infty}{C_A^\infty + C_B^\infty}$ (à l'état photostationnaire)

- Vitesse de réaction
 femtoseconde / picoseconde → dynamique ultrarapide à l'état excité
 milliseconde / minute / heure → temps pour atteindre l'état photostationnaire

Biologie, santé

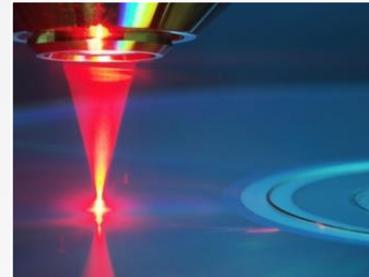


vision (rétinal)



nano-médicaments

Matériaux

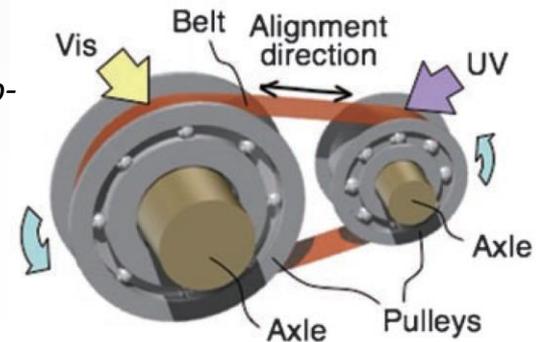


*stockage
optique de
l'information*

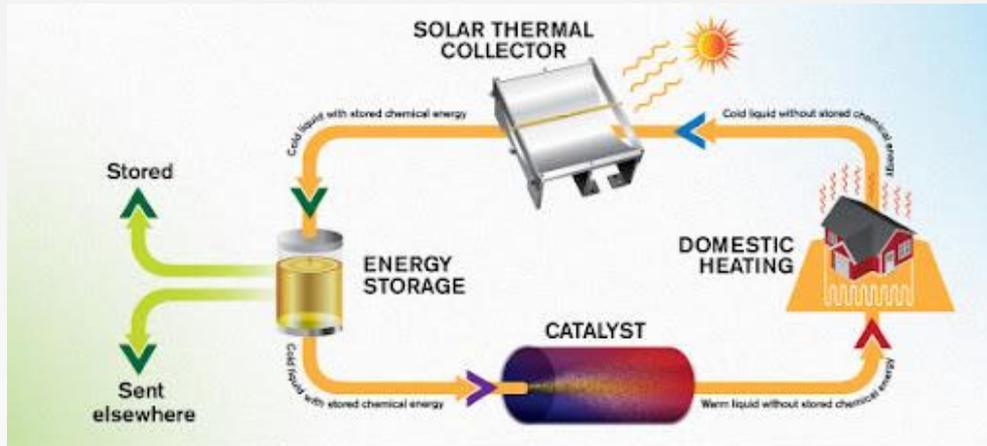
*surfaces
activables*



*micro-photo-
mécanique*

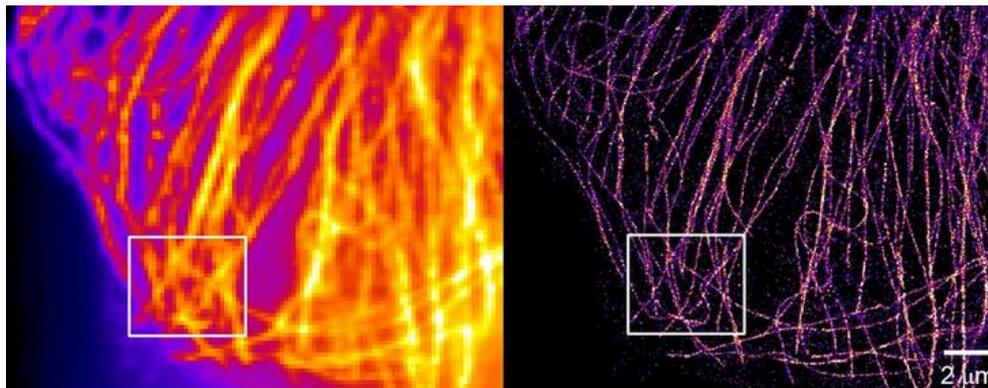


Énergie



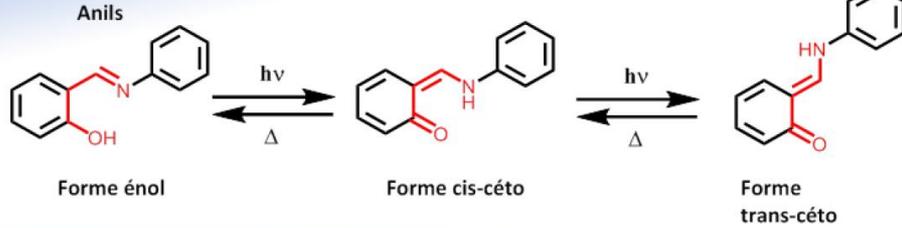
*stockage
de l'énergie solaire*

Imagerie

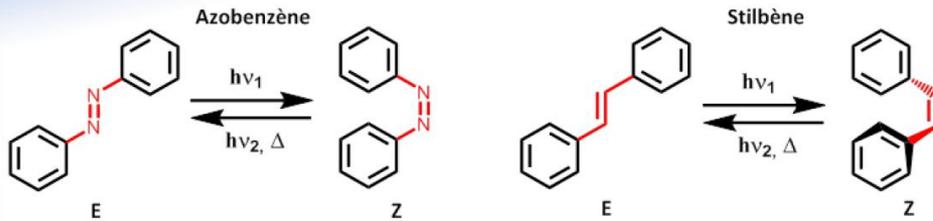


*imagerie
super-résolution*

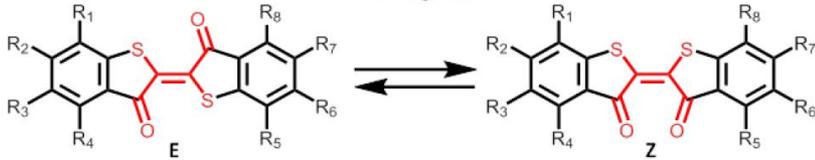
Phototautomérisation



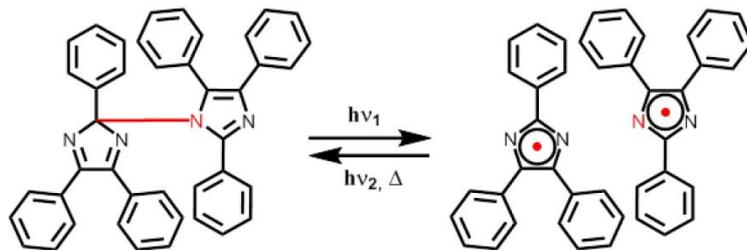
Photoisomérisation E/Z



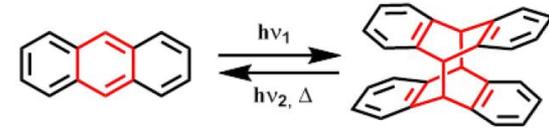
Thioindigoïdes



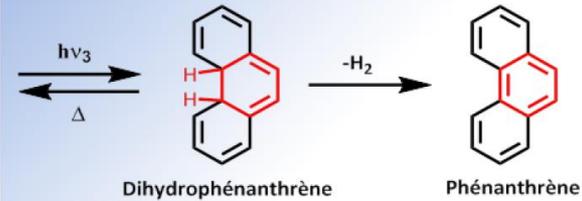
Coupure homolytique



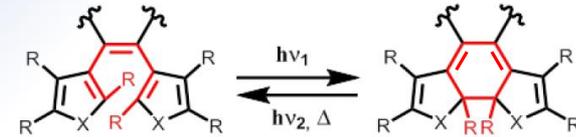
Photocycloaddition



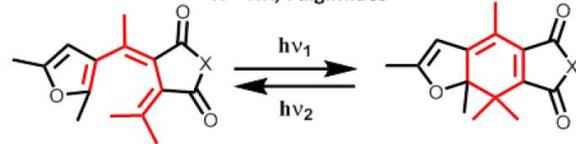
Cyclisation



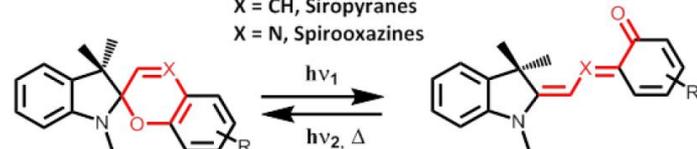
Diaryléthènes



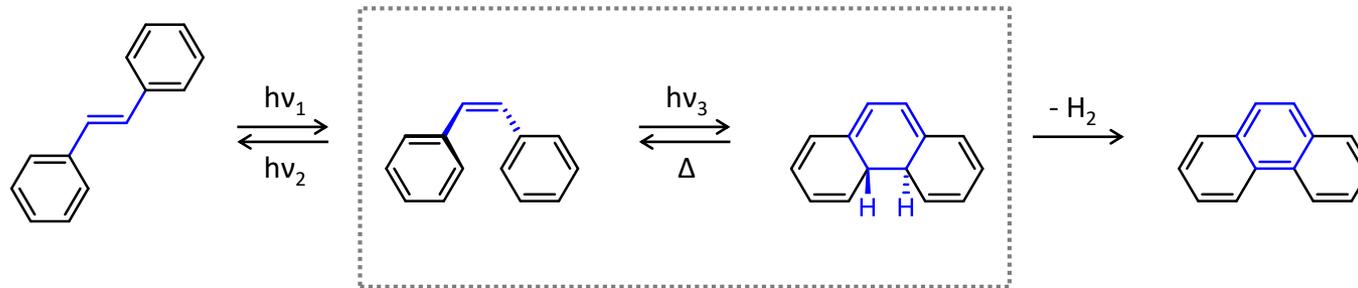
X = O, Fulgides
X = NR, Fulgimides



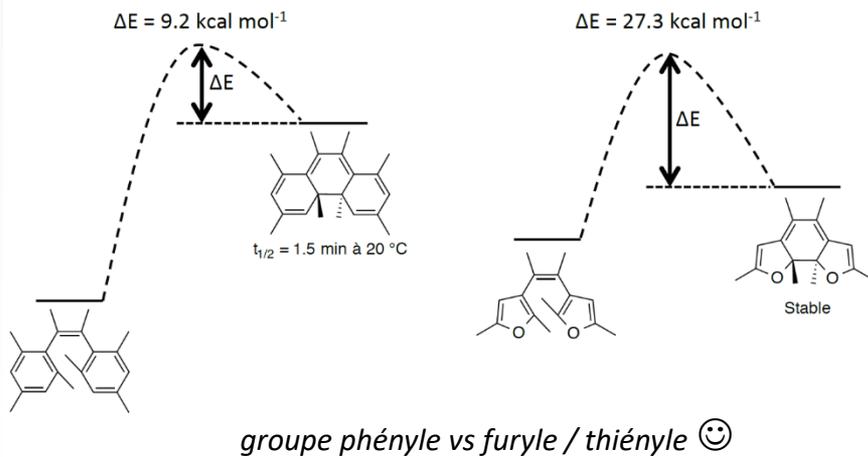
X = CH, Spiropyranes
X = N, Spirooxazines



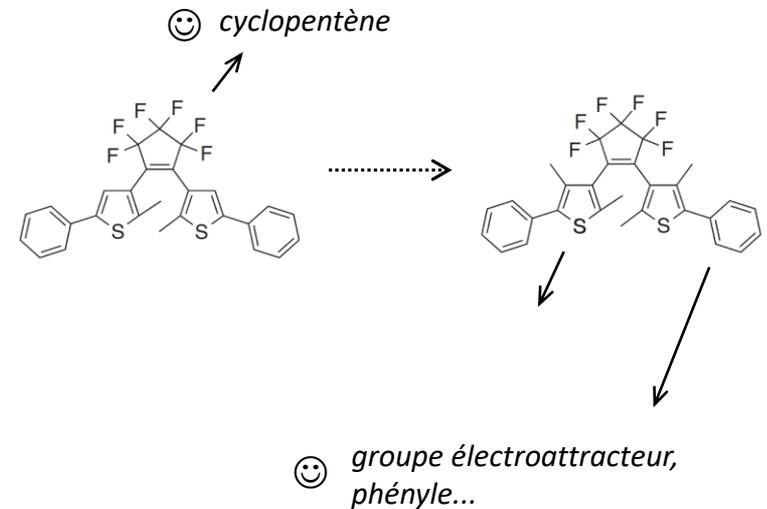
Photoisomérisation du stilbène...



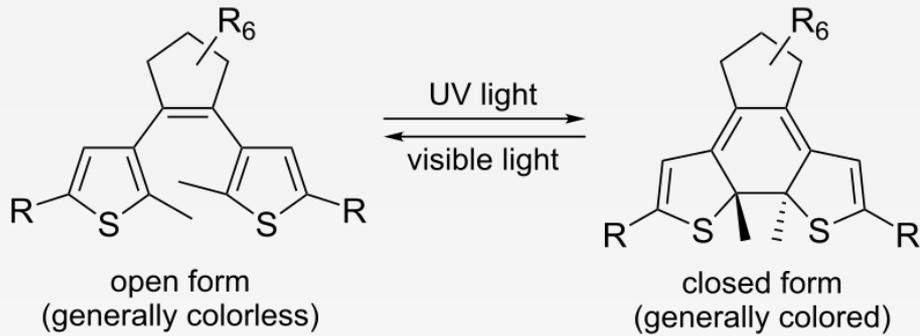
Réversibilité et "bistabilité"



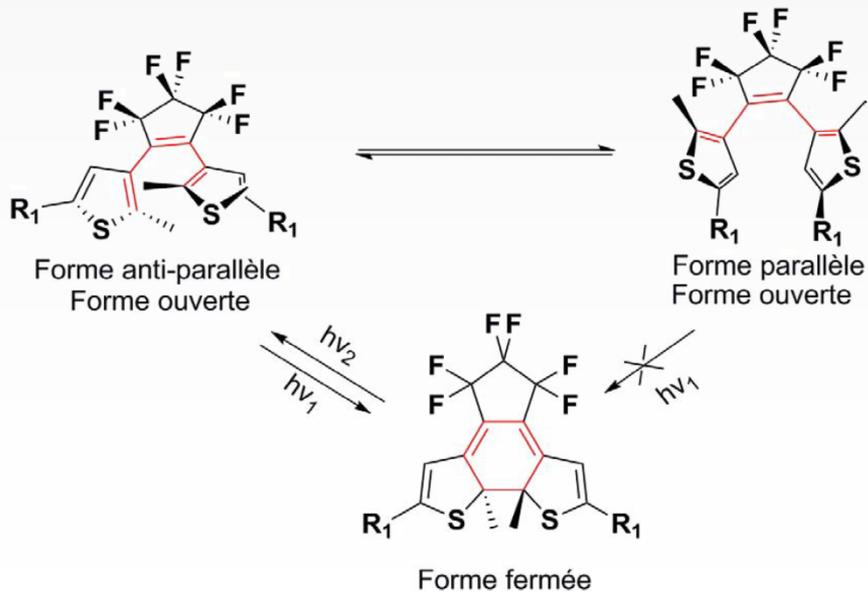
Amélioration de la "résistance à la fatigue"



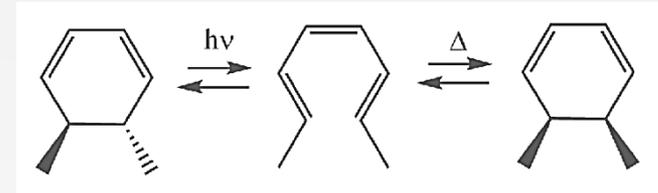
Réaction photochrome



Formes parallèle / anti-parallèle

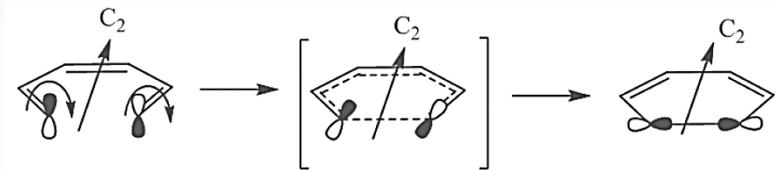


Électrocyclization (4n+2) conrotatoire

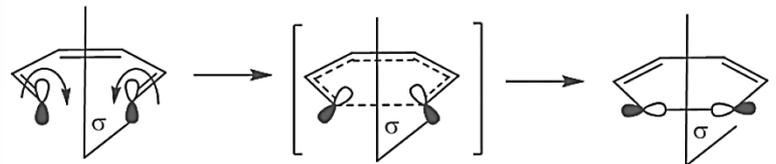


Règles de Woodward-Hoffmann (1965)

Nb d'électrons π	Thermique	Photochimique
4n	conrotatoire	disrotatoire
4n+2	disrotatoire	conrotatoire



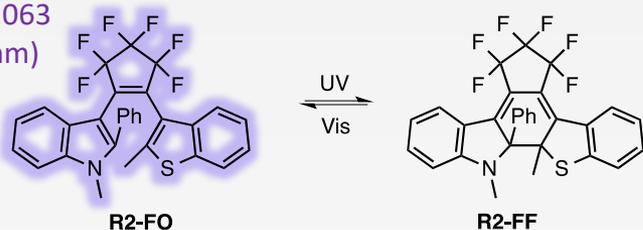
conrotatoire



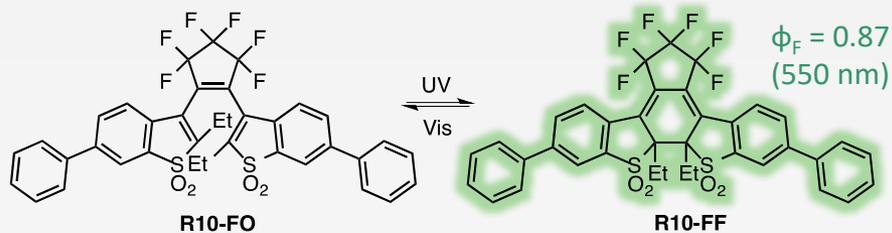
disrotatoire

Catégorie 1: diaryléthènes intrinsèquement fluorescents

$\phi_F = 0.063$
(433 nm)



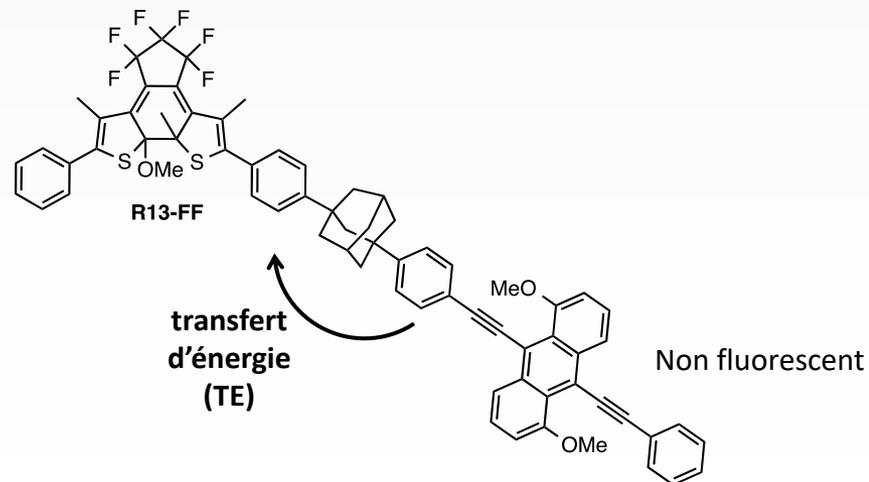
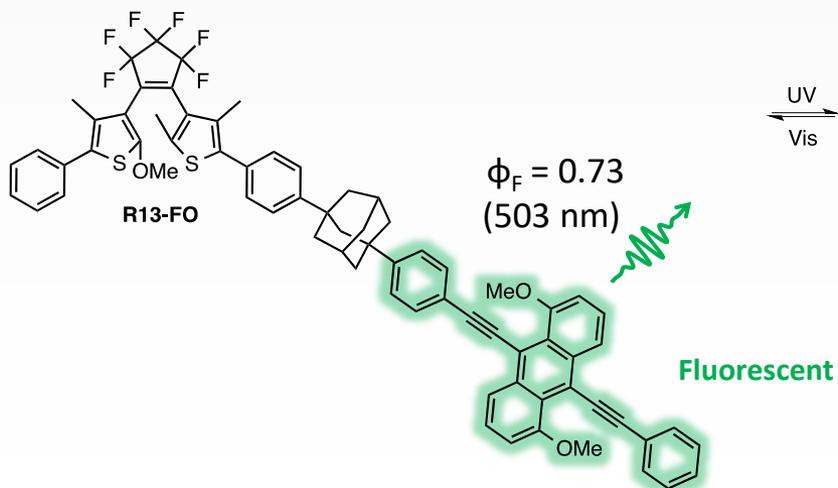
Yagi, Irie, *Bull. Chem. Soc. Jpn.* **2003**, 76, 1625



$\phi_F = 0.87$
(550 nm)

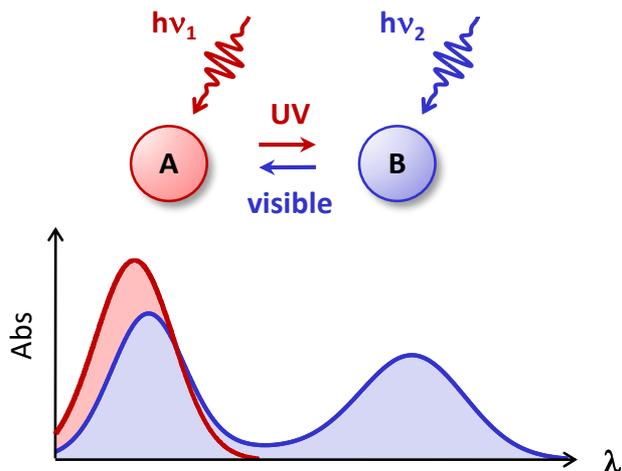
Irie, Morimoto *et al. Photochem. Photobiol. Sci.* **2012**, 11, 1661

Catégorie 2: diaryléthènes couplés à des fluorophores

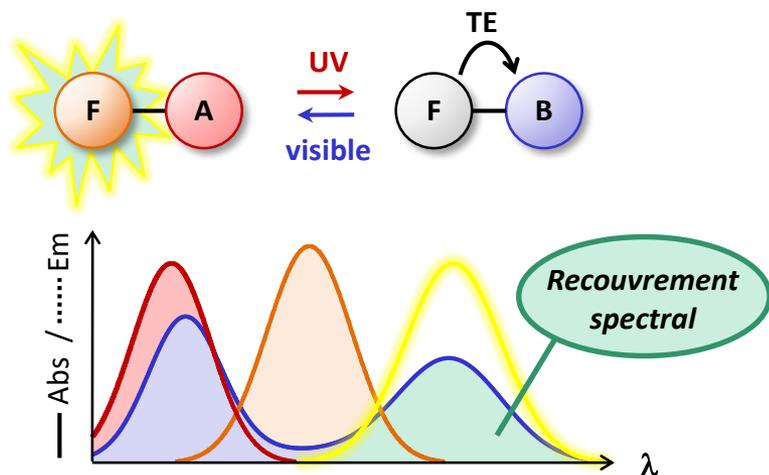


Irie, Fukaminato, Kawai *et al. Nature* **2002**, 420, 759; *J. Am. Chem. Soc.* **2004**, 126, 14843

Photochromisme

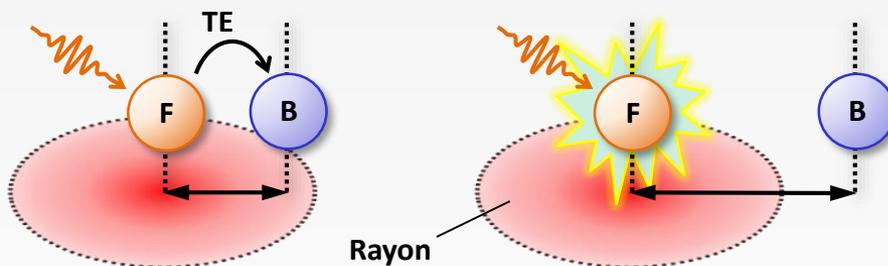


Couplage photochromisme-fluorescence



Processus de transfert d'énergie (mécanisme de Förster)

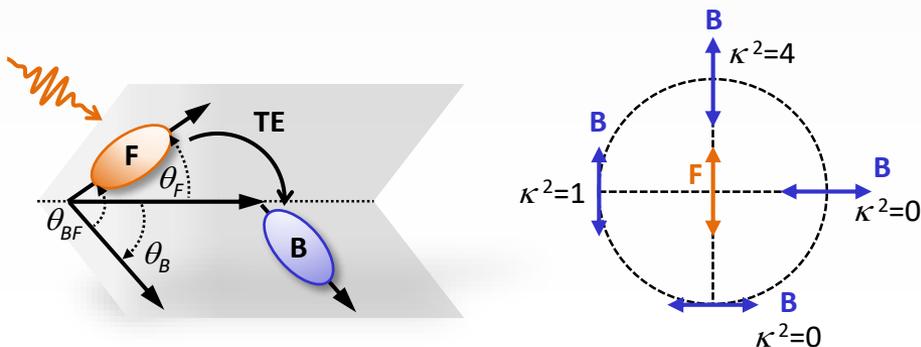
- Paramètre n°1: Recouvrement spectral
- Paramètre n°2: Distance interchromophorique



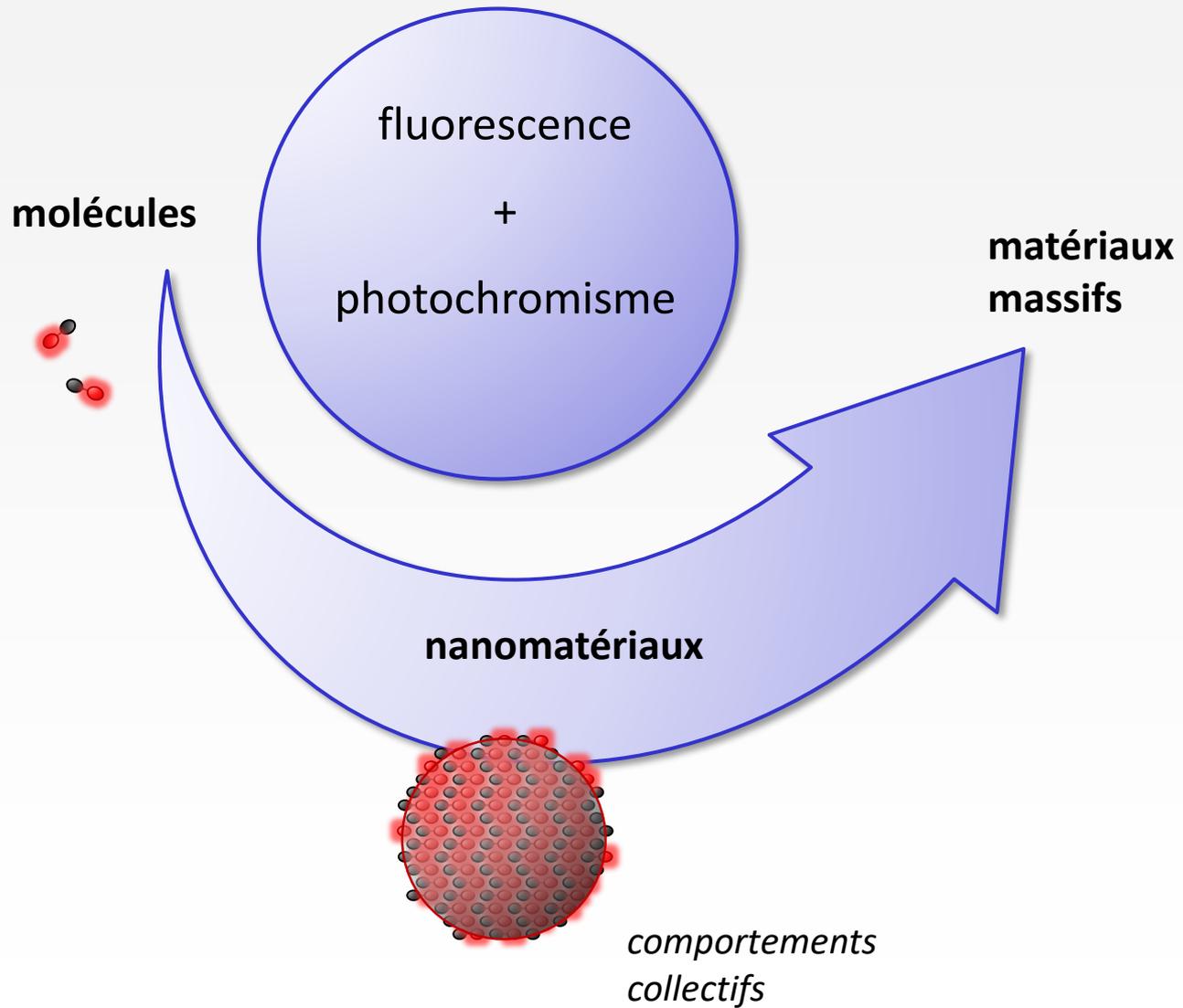
Rayon de Förster :

$$R_0 = 0.2108 \left[\kappa^2 \Phi_D^0 n^{-4} \int_0^\infty I_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda \right]^{1/6}$$

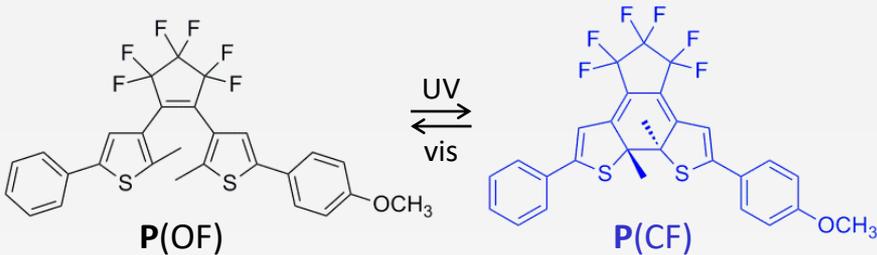
- Paramètre n°3: Orientation relative



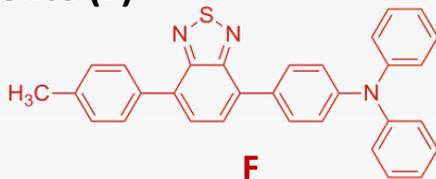
Facteur d'orientation : $\kappa^2 = (\cos\theta_{BF} - 3\cos\theta_B\cos\theta_F)^2$



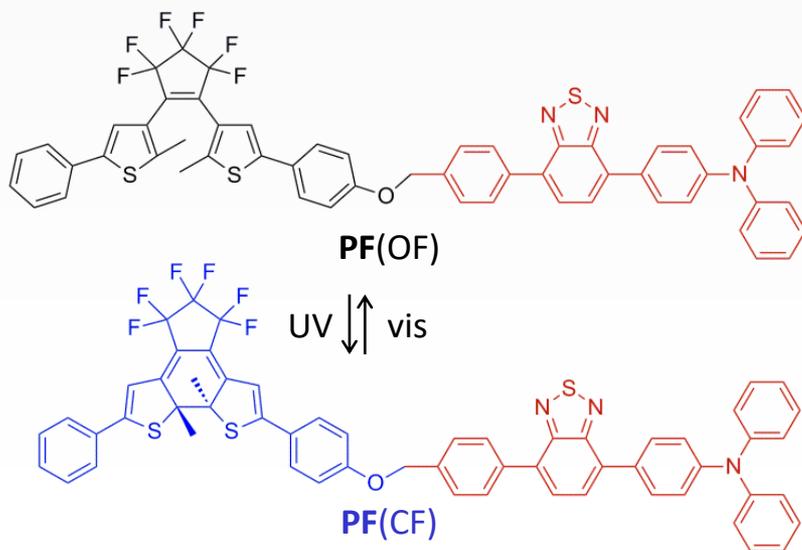
Unité photochrome (P)



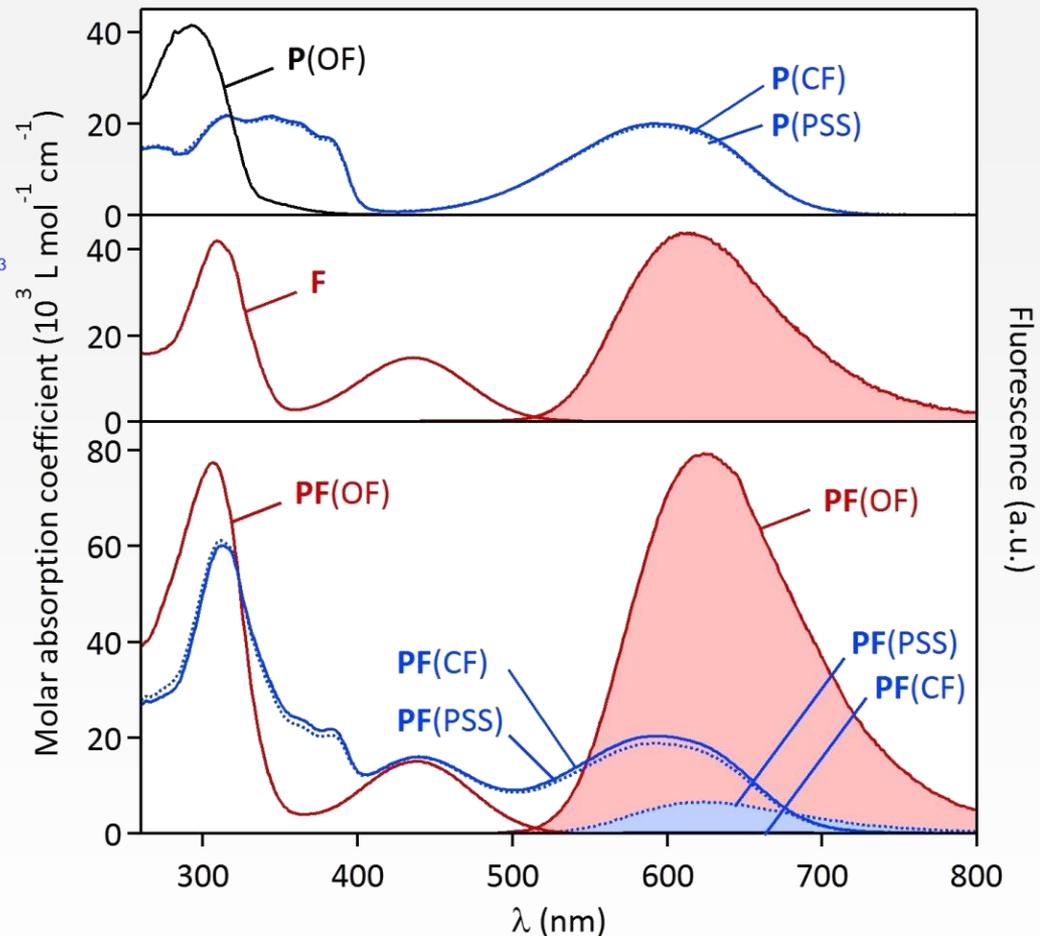
Unité fluorescente (F)



Dyade photochrome-fluorescente (PF)



(Synthèse : T. Fukaminato, Kumamoto Univ.)



Dyade PF en solution dans le THF

$$\Phi_F = 0,67$$

$$\tau_F = 7,8 \text{ ns}$$

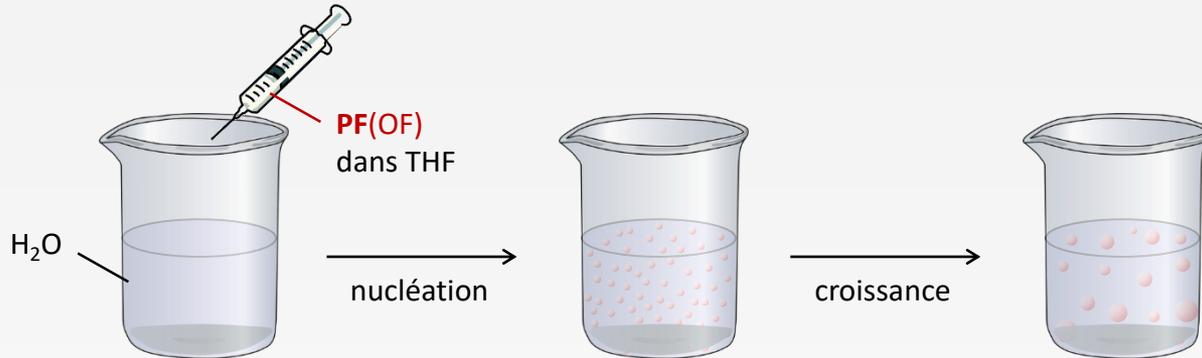
$$\Phi_{TE} > 0,99$$

$$\Phi_{o \rightarrow c} = 0,46$$

$$\Phi_{c \rightarrow o} < 0,01$$

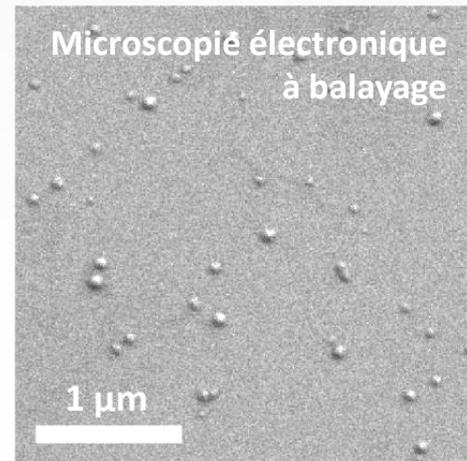
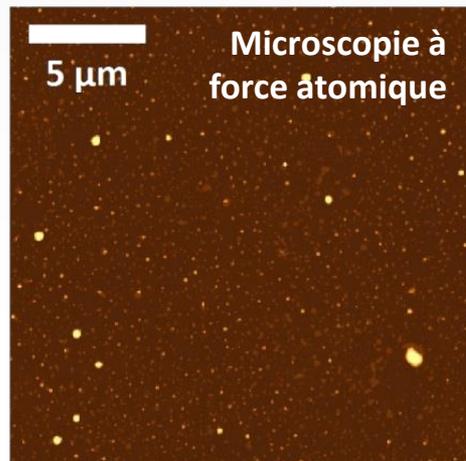
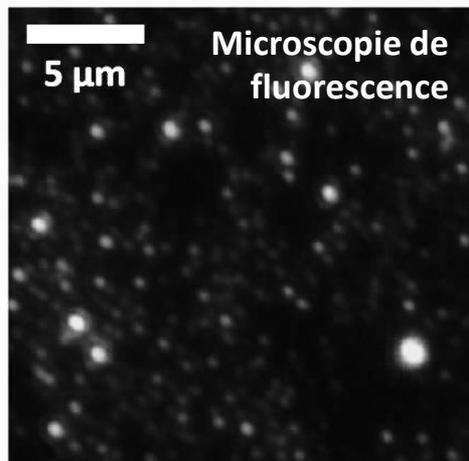
$$\alpha_{313 \text{ nm}} = 0,90$$

Méthode de re-précipitation pour préparer des nanoparticules

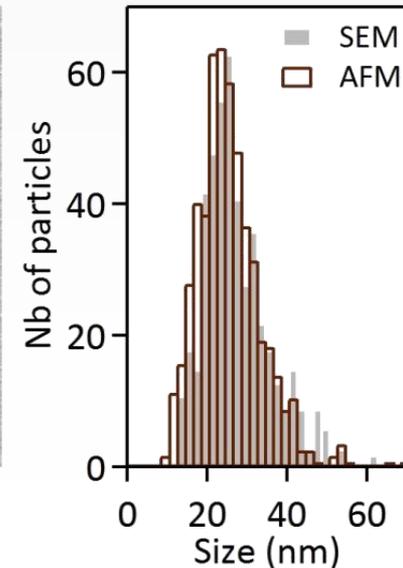


Fukaminato, Ishida, Su, Nakatani, Métivier in *Photosynthetic responses in molecules and molecular aggregates*, Miyasaka H., Matsuda K., Abe J., Kawai T. (eds.), Springer, 2020.

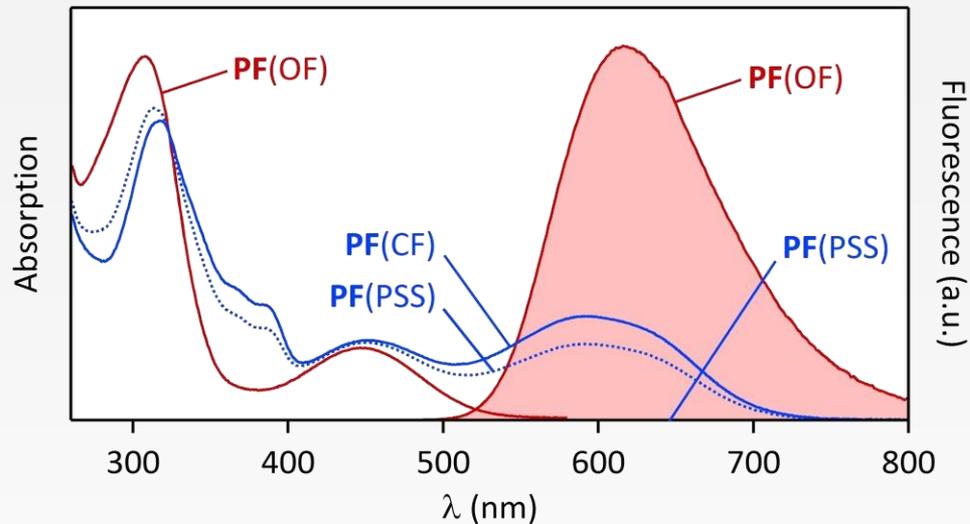
Caractérisation des nanoparticules



$$\varnothing = 25 \pm 10 \text{ nm}$$



Propriétés photophysiques en suspension colloïdale

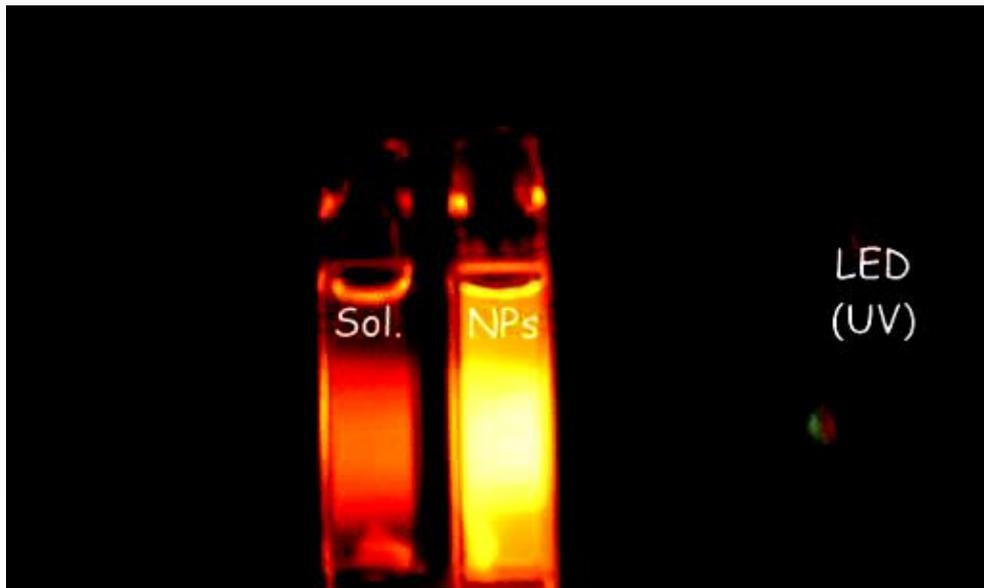


➔ **Dyade PF en nanoparticules**

$\Phi_F = 0,65$
 $\langle \tau_F \rangle = 7,8\text{ns}$

$\alpha_{313\text{nm}} = 0,73$

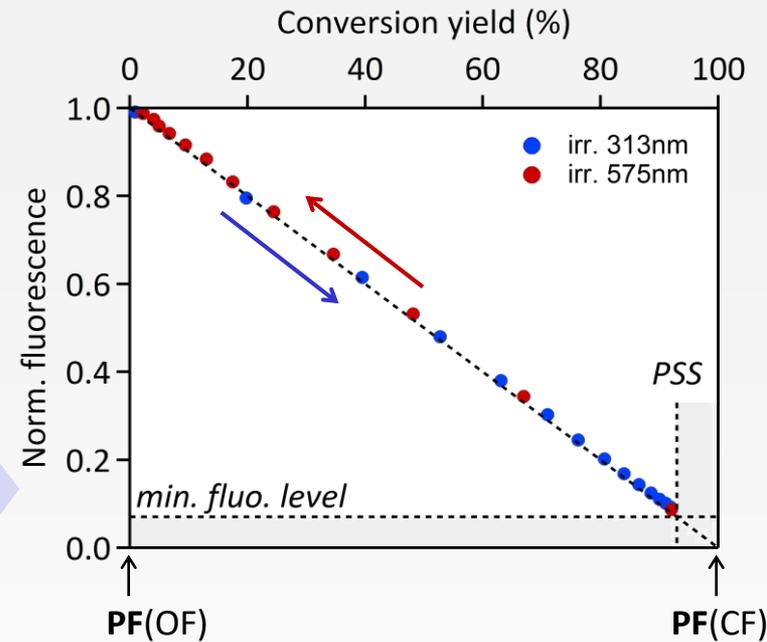
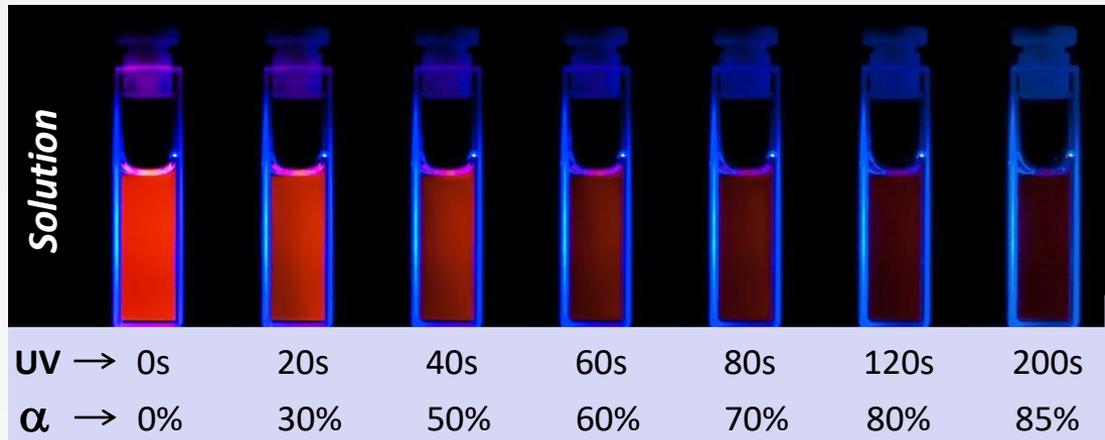
➔ **Extinction complète de fluorescence** ?



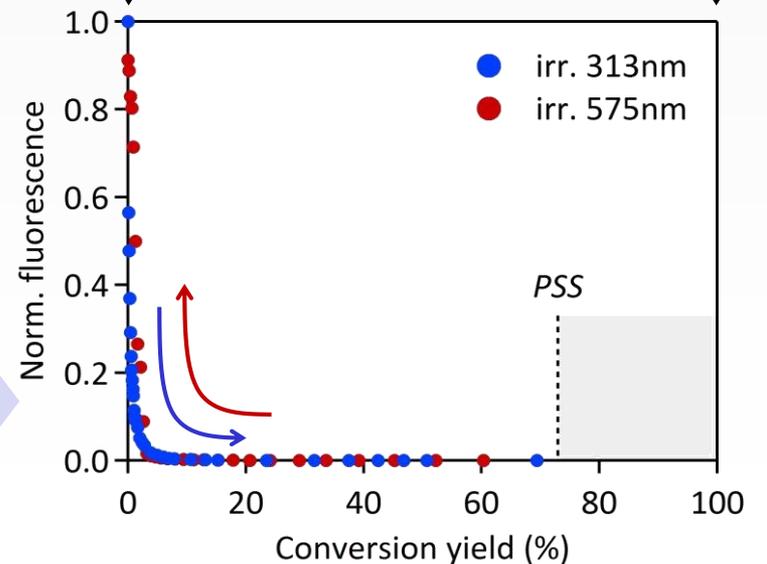
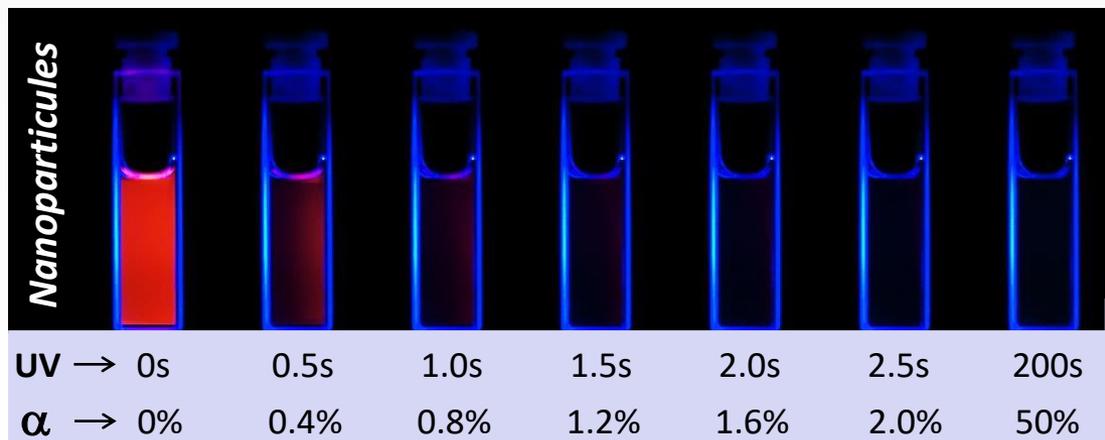
(vidéo : Prof. T. Fukaminato, Kumamoto Univ.)

Amplification géante de la photocommutation de fluorescence 19/27

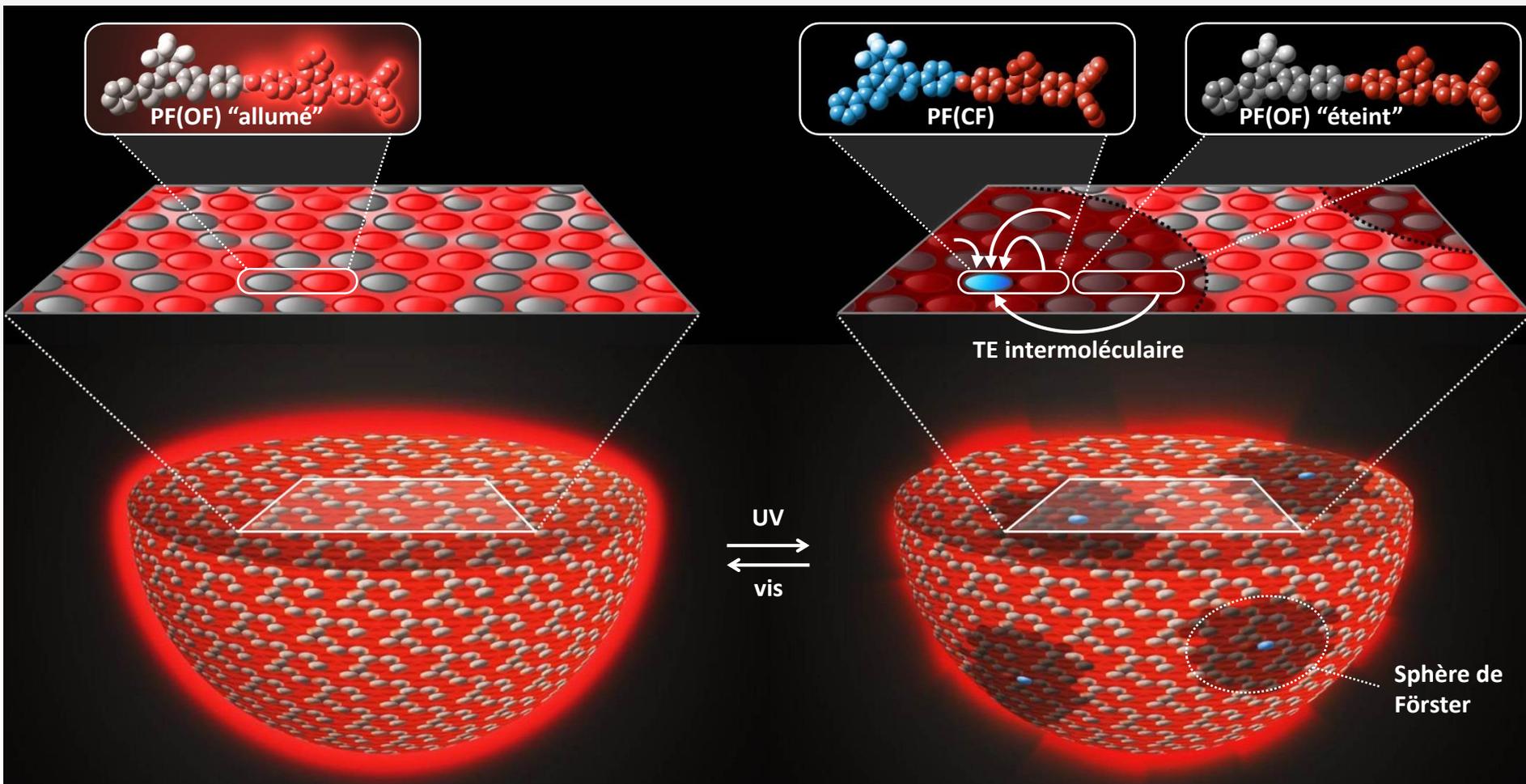
Comportement en SOLUTION



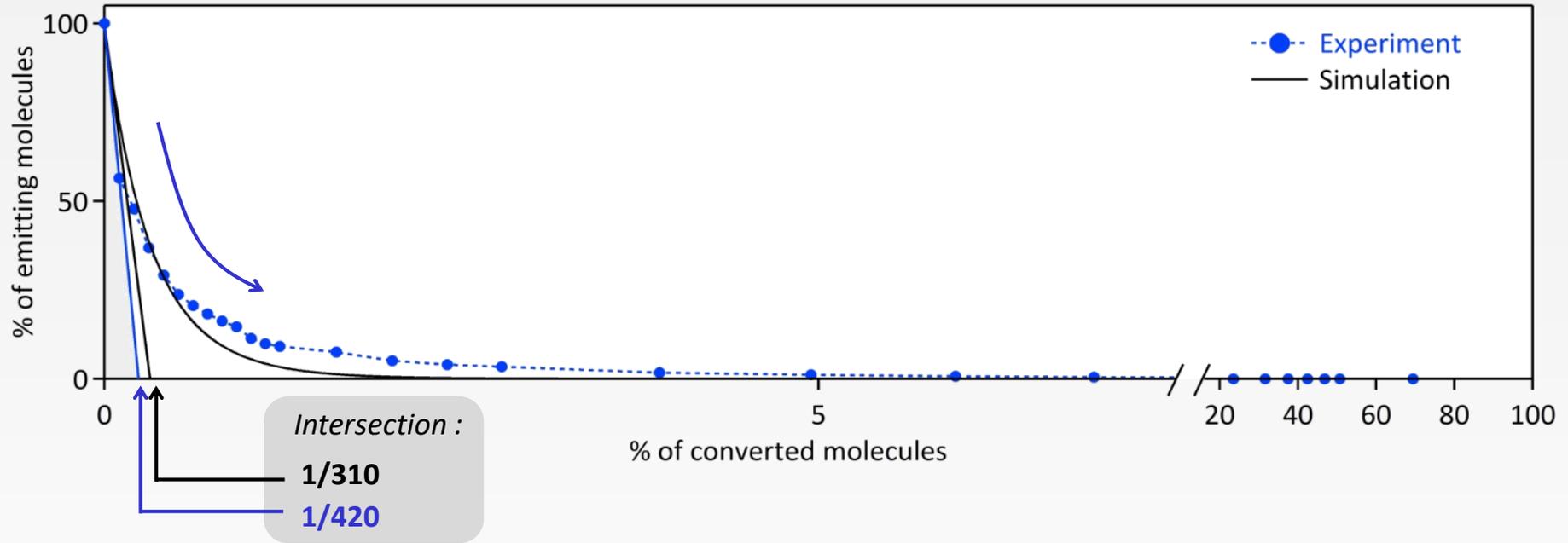
Comportement en NANOPARTICULES



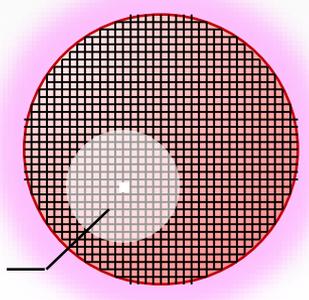
Amplification géante de la photocommutation de fluorescence 20/27



Amplification géante de la photocommutation de fluorescence 21/27

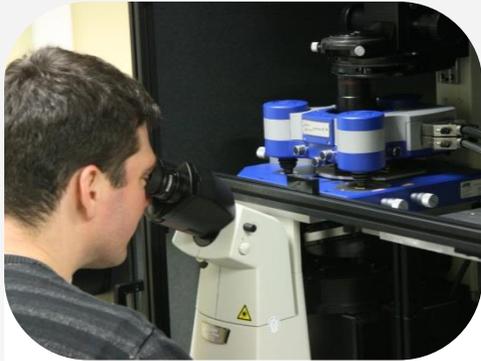


Simulation numérique

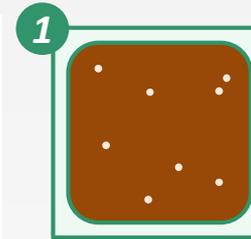
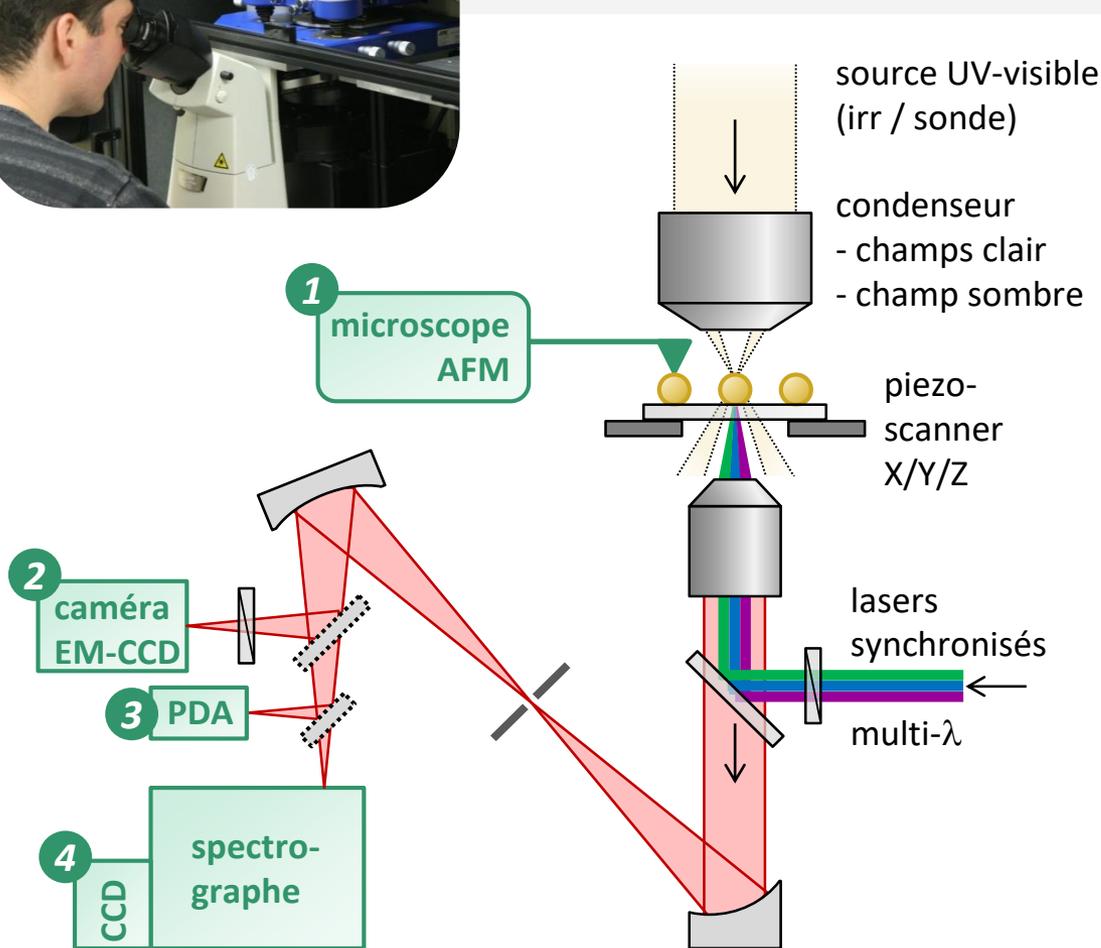
- ① Nanoparticule subdivisée en unités élémentaires
 n molécules dans la sphère de Förster ($R_0 = 4,9\text{nm}$)

- ② Probabilité pour une molécule donnée d'être "ON": $(1 - \alpha_{CF})^n$
- ③ Intégration sur l'ensemble de la nanoparticule

Calcul du facteur d'amplification

- ① Nombre de fluorophores éteint par "quencheur"
 $\rightarrow \Phi_1 = 420$ (exp) or 310 (calc)
- ② Nombre de photons absorbés nécessaires pour éteindre 90% de la fluorescence
 150 photons vs. 7000 molécules
 $\rightarrow \Phi_2 = 40$

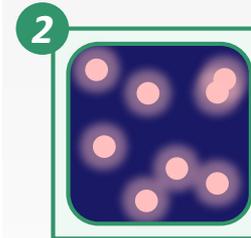


Microscope optique + microscope à force atomique



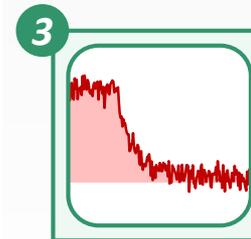
Module AFM

- imagerie topographique
- mécano-stimulation + détection



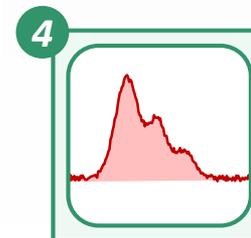
Caméra amplifiée

- imagerie champ large
- détection d'objets individuels



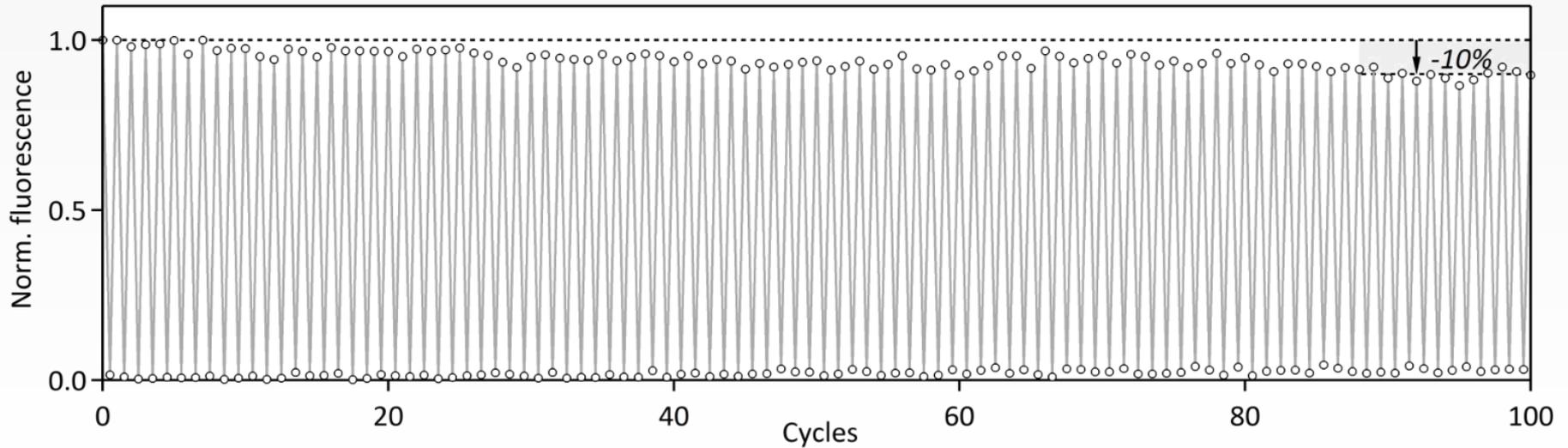
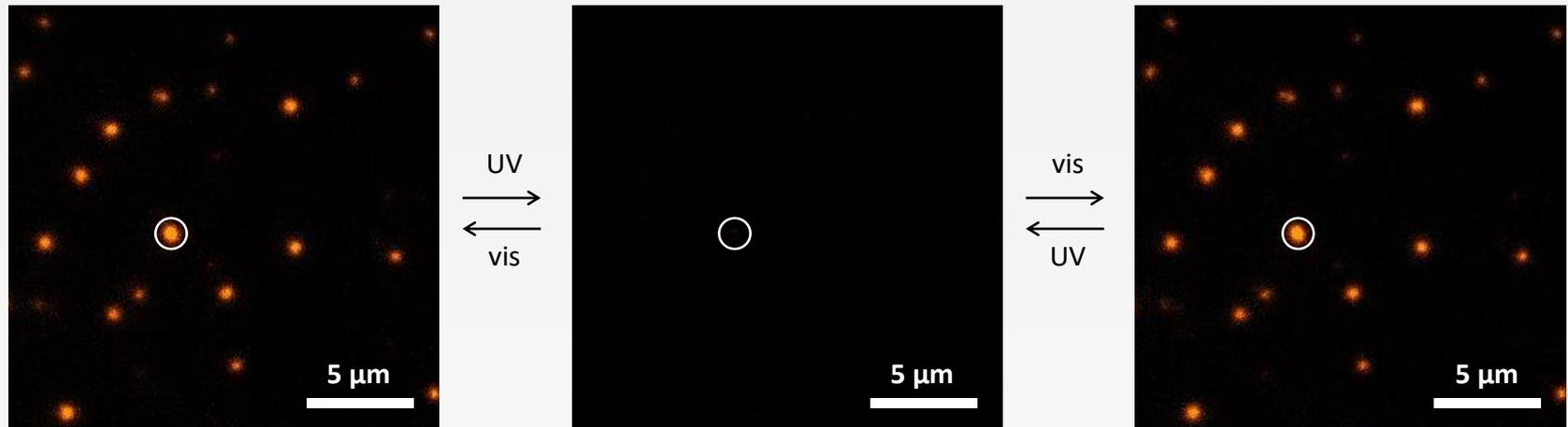
Compteur de photons

- imagerie confocale
- durées de vie
- photocommutation



Spectrographe UV-visible

- imagerie hyperspectrale
- absorption, fluorescence, diffusion



Excellent contraste

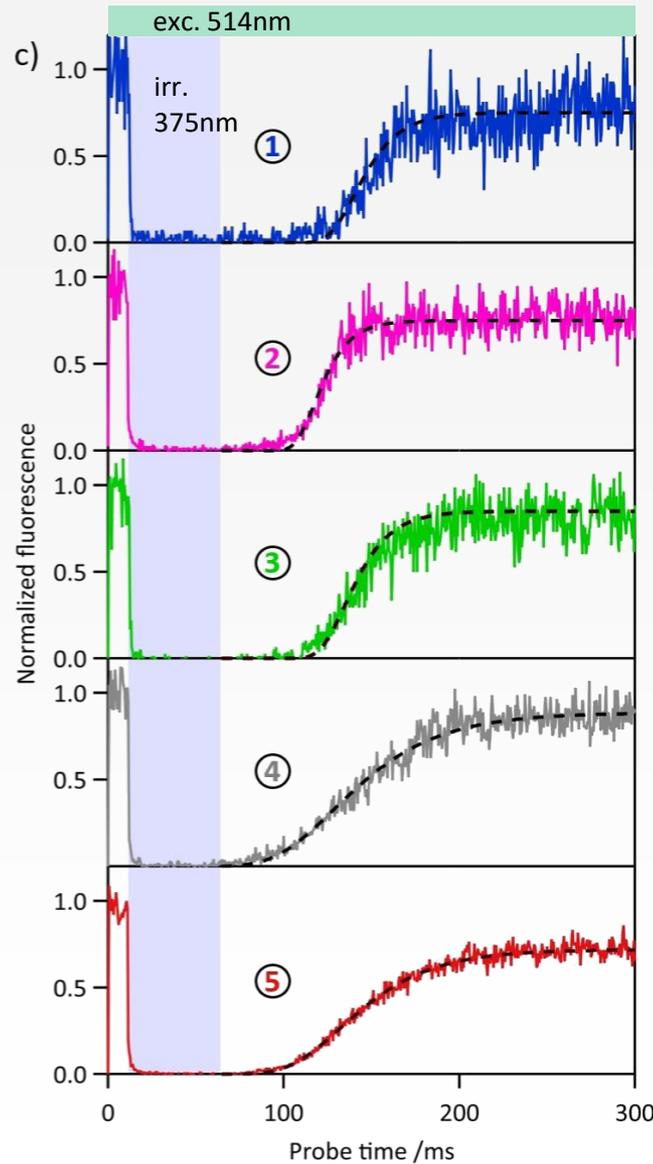
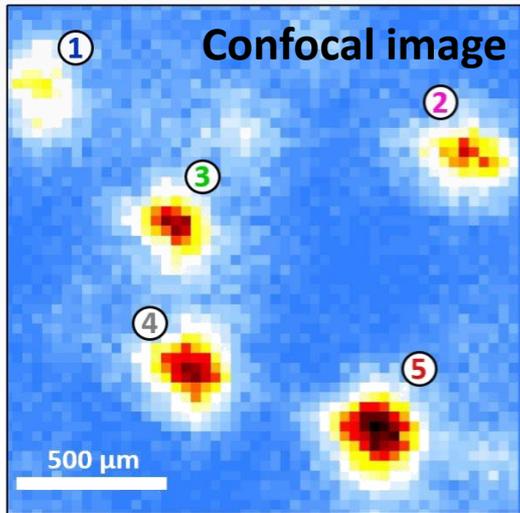
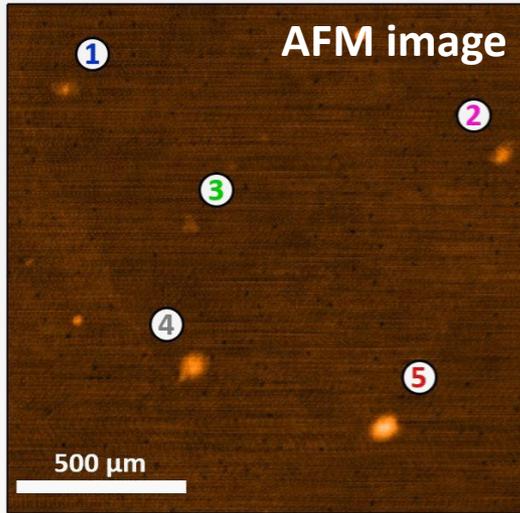
→ 600:1 après 20 cycles

Forte brillance

→ $\sim 10^8 \text{ L mol}^{-1}\text{cm}^{-1}$

Bonne résistance à la fatigue

→ -10% après 100 cycles



Observation

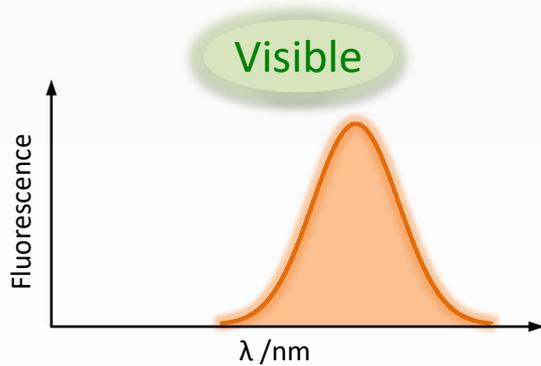
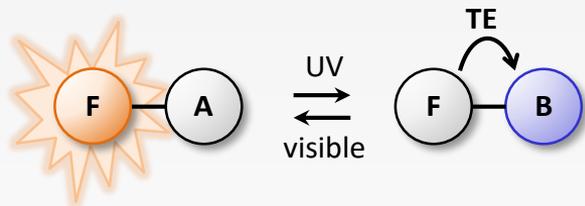
- **ON → OFF**
~ 3ms (irr. 375nm)
- **OFF → ON**
~ 70ms (irr. 514nm)
+ profil sigmoïdal



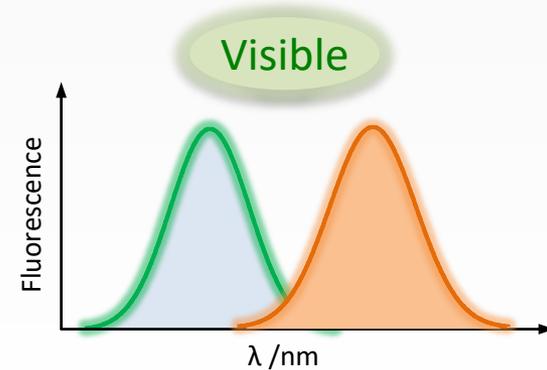
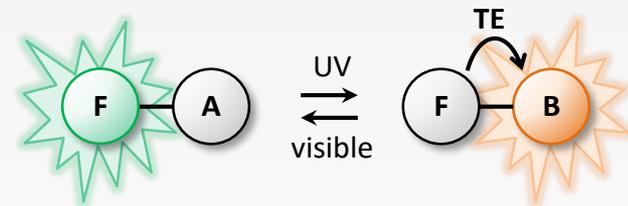
Photophysique

- **Amplification géante**
de la photocommutation
- **Effet de seuil** de la transition OFF → ON
- **Photocinétique** contrôlée par effet d'antenne

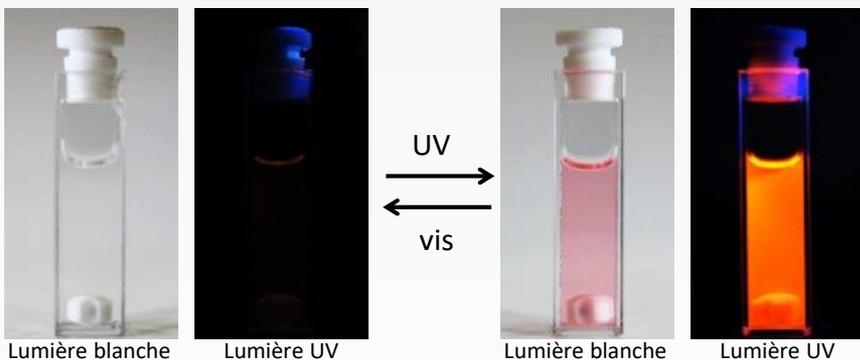
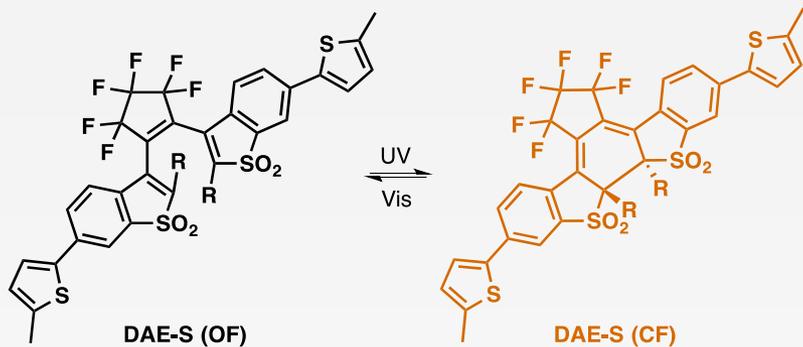
Photocommutation de fluorescence de type "ON-OFF"



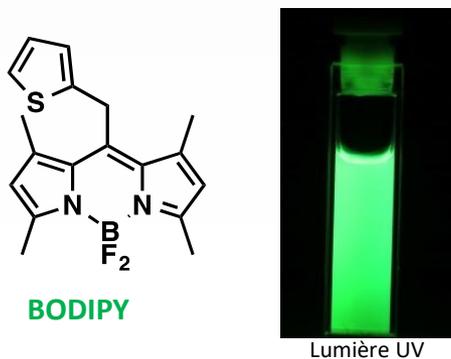
Photocommutation de fluorescence "multi-émission"



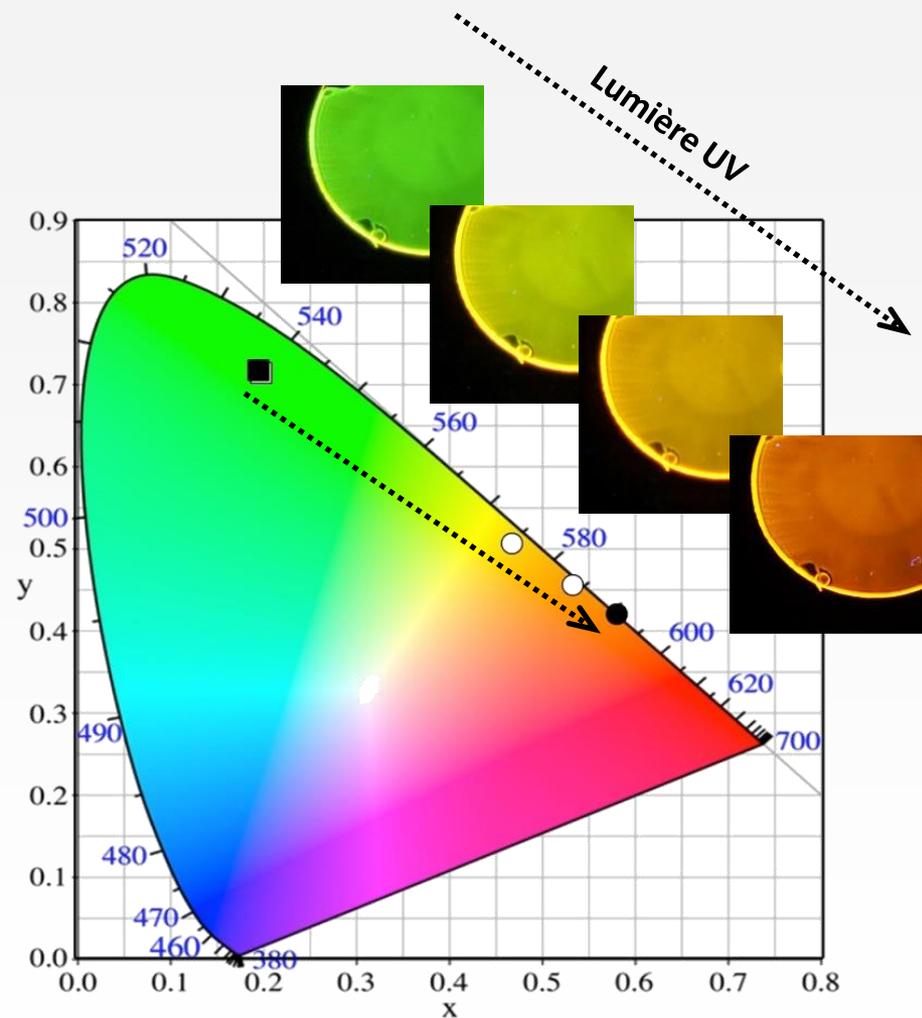
Diaryléthène fluorescent (orange)



Fluorophore (vert)



Films polymers comportant les deux unités



Étudiants & collègues

- Dr. J. Su
- Dr. S. Maisonneuve
- Dr. C. Pavageau
- Dr. M.-T. Do
- Dr. E. Barrez
- Dr. N. Fabre
- A. Brosseau
- L. Chocron
- Dr. G. Laurent
- Prof. J. Xie
- Prof. K. Nakatani

Collaborateurs

- Prof. T. Fukaminato
(Kumamoto Univ., Japan)
- Dr. P. Yu (Univ. Paris-Saclay)

Soutiens

