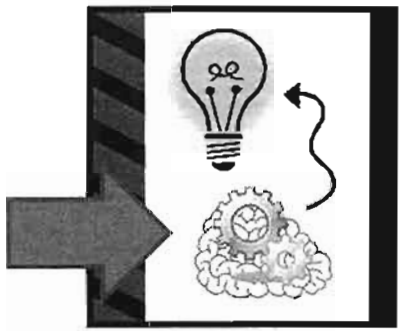
Materiales foto*luminiscentes:* *Aplicaciones*

Prof. Guillermo Orellana, UCM



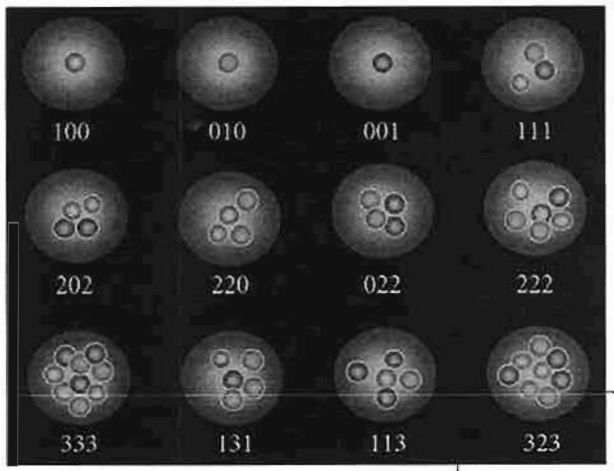
21 de Junio de 2010

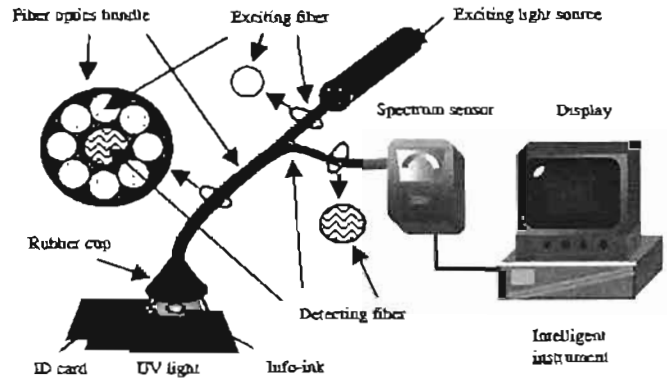
Ideal characteristics of luminescent pigments for security inks (multiplexed encoding)

- Strong, single **emission wavelength** or single narrow emission band for each individual luminescent substance;
- **Emission spectrum** independent of the exciting light (in certain range of the exciting wavelength);
- Single **light source** for all luminescent substances used in the mixture;
- **No interaction** (*energy transfer*) among different fluorescent molecules, i.e., each luminescent substance should respond to the exciting light independently;
- **No influence of matrix** material on the emission features;
- Good **miscibility** of all luminescent substances in the selected matrix material/solvent systems;
- Easy **tuneable** intensity *and* wavelength of fluorescent spectrum.

S. Chang et al., *Optics Express* **2004**, *12*, 143-147.

Multiplexed encoding with quantum dots for security inks





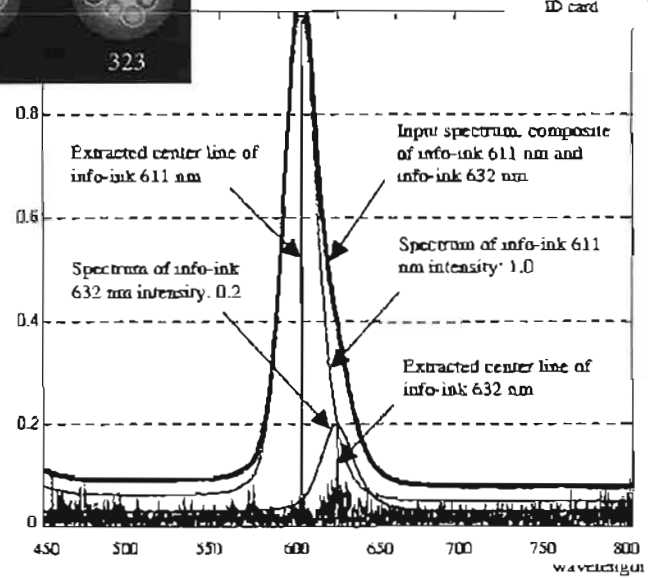


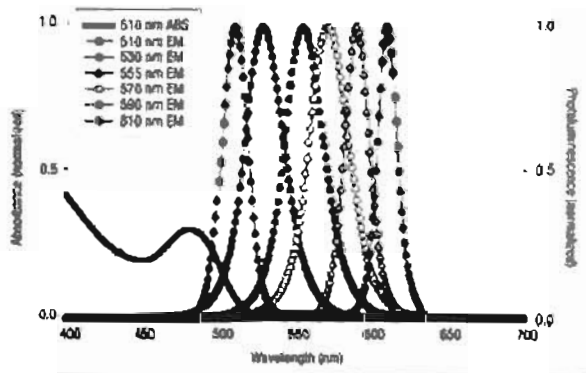
Illustration of the ***deconvolution*** procedure:

- *Noise* removal.
- Find *wavelengths* (max.) and *intensities* of individual spectra.

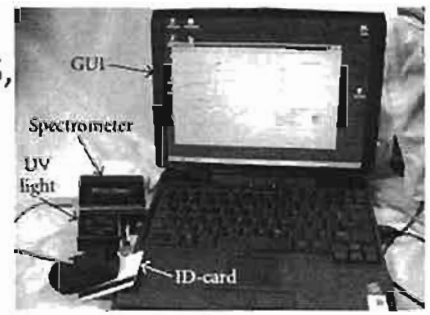
S. Chang et al., *Optics Express* **2004**, *12*, 143-147.

Advantages/disadvantages of quantum dots for multiplexed encoding of security inks

- *Nanometer* sized.
- Easy to *incorporate* in inks.
- *Photostability*.
- Excellent *tuneability*.
- Very *narrow* emission bands.
- Wide *excitation* wavelength range.



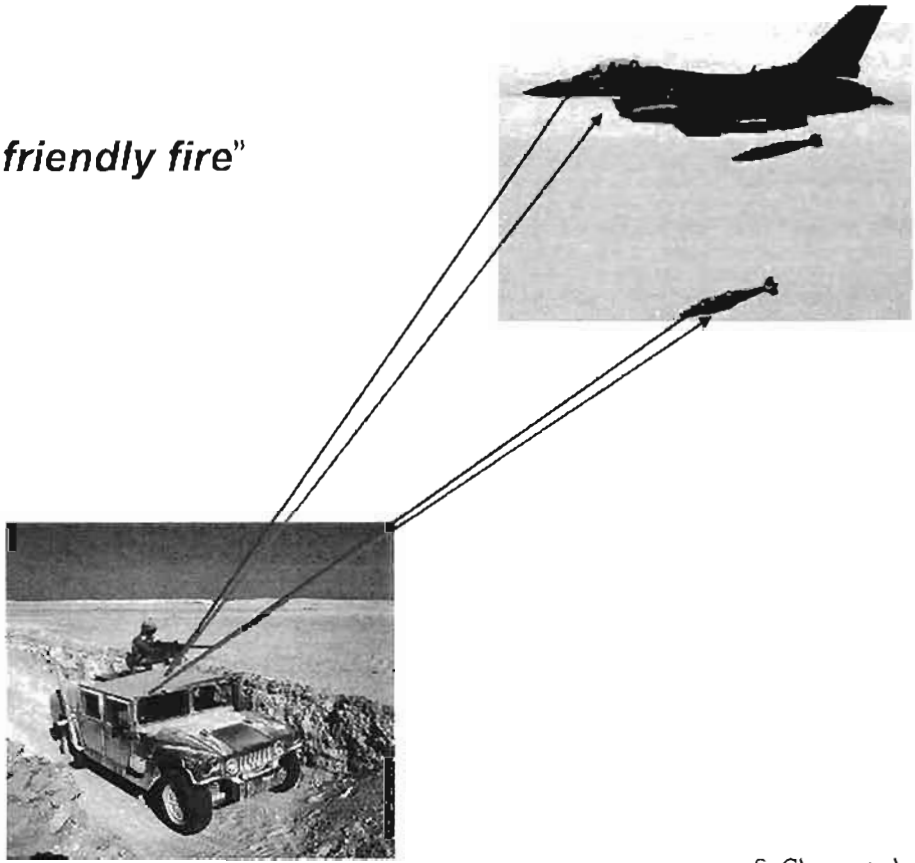
- Difficult to *handle* due to their size.
- *Toxicity* (material, size).
- Tendency to slow aggregation (*drift*).
- Sensitivity to fluorescent *interferents* (oils, polymers, additives...) due to spectrum shape changes.
- *Price* (300-600 $, 60 mg)



S. Chang et al., *J. Nanomater.* **2008**, 589532.

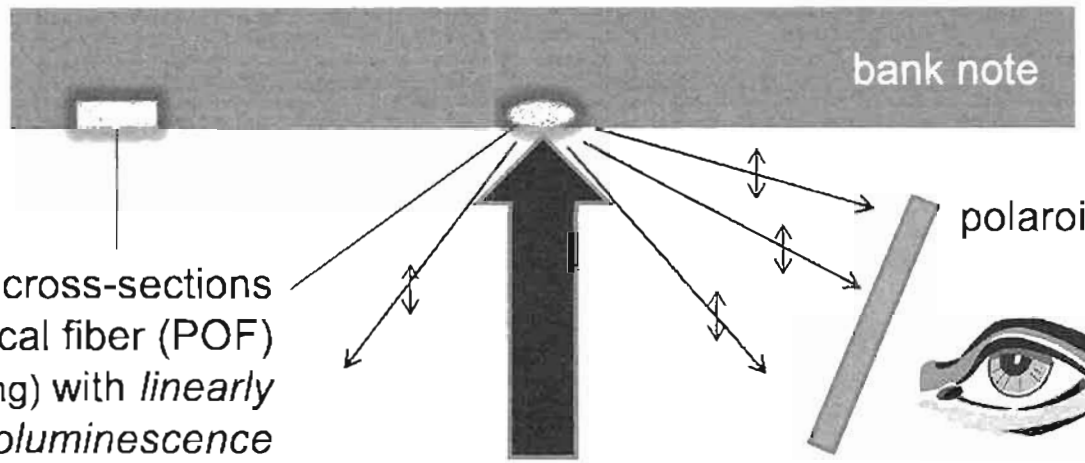
Other potential applications of quantum dots for multiplexed encoding

Avoidance of "***friendly fire***"



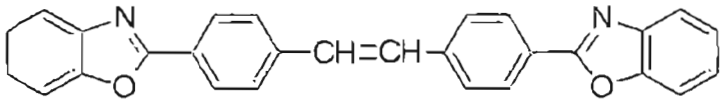
S. Chang et al., *J. Nanomater.* **2008**, 589532.

Photoluminescent optical fiber with anisotropic cross-section



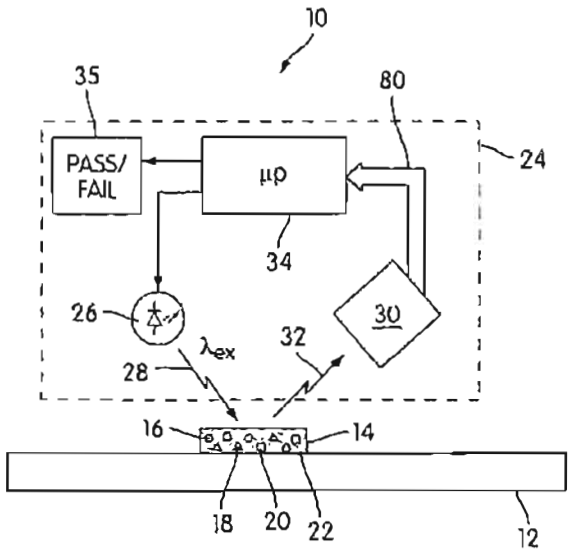
Two possible cross-sections of plastic optical fiber (POF) (3-4 mm long) with *linearly polarized photoluminescence*

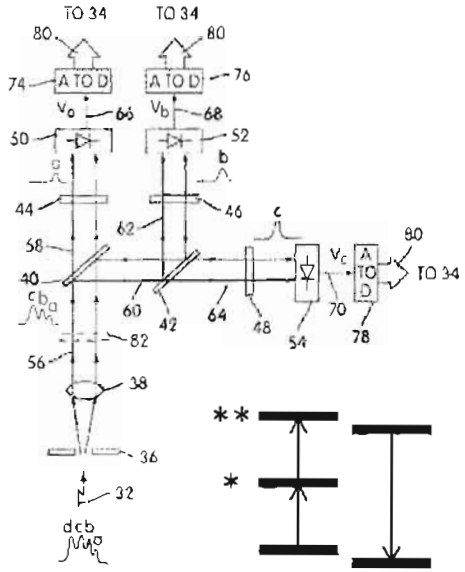
e.g. *oriented* PP doped with organic dye (*stilbene* optical brightners)

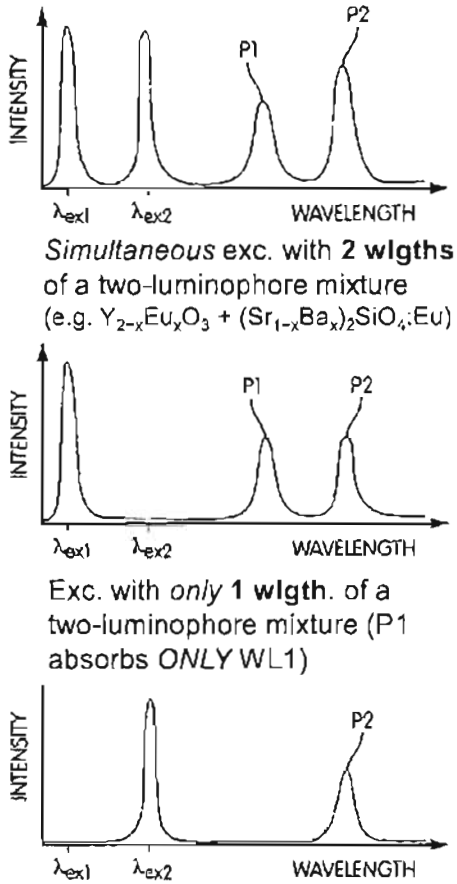


Grob & Franken (Landquart), WO2004/104277

Photoluminescent security inks with blends of up-conversion pigments







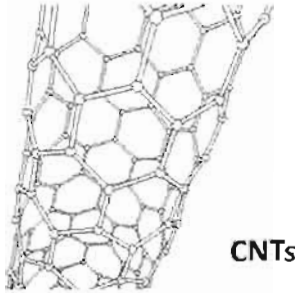
(14) **Photoluminescent ink** containing a mixture of 2-3 pigments (16) NIR absorber: **Yb(III)** compound; emitter: **Tm(III)**, **Er(III)**, **Yb(III)**

(24) **Detector** of the chosen photoluminescence property (intensity at a WL or region, ratio of PL intensities, peak WL, emission lifetime, emission rise time, emission spectrum shape, etc.)

(28) **Excitation** wavelength (380-780 nm)

Li & Yang (Intematix Corp.), US2010/0102250

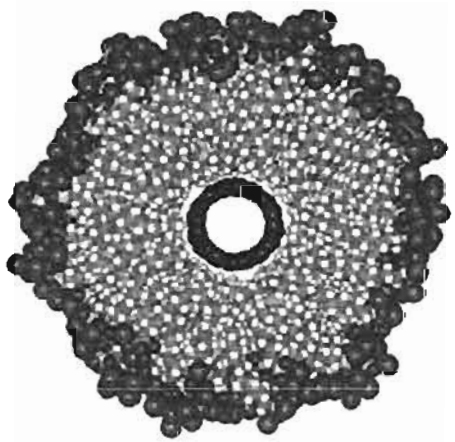
Security inks with invisible photoluminescence



CNTs

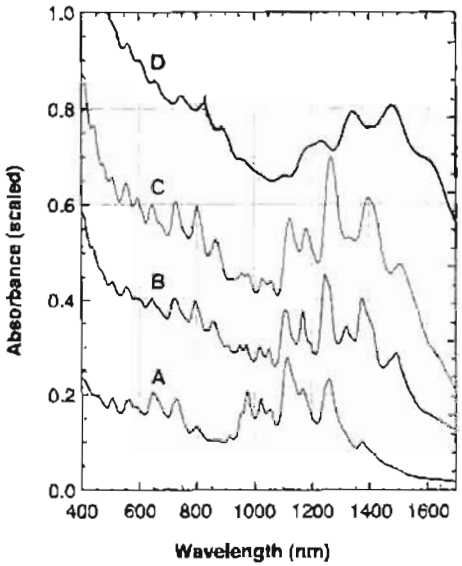
λ_{exc} = 671; λ_{em} = 1125–1700 nm

3 nm

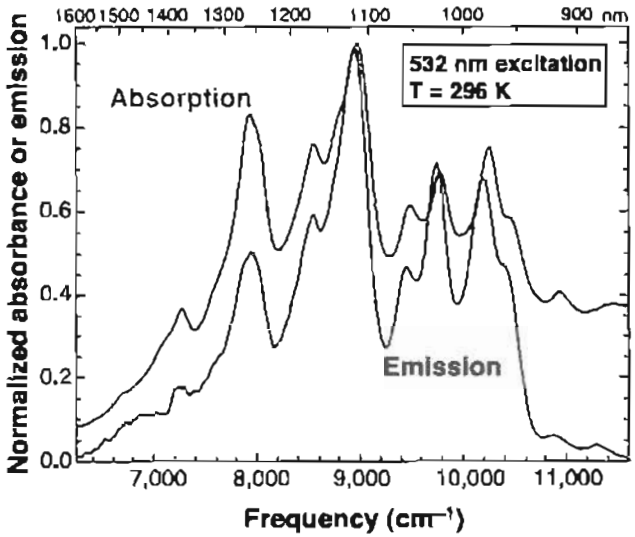


CNT protected by surfactant shell to prevent aggregation that kills photoluminescence

(O'Connell et al., *Science* **2002**, *27*, 593–596)



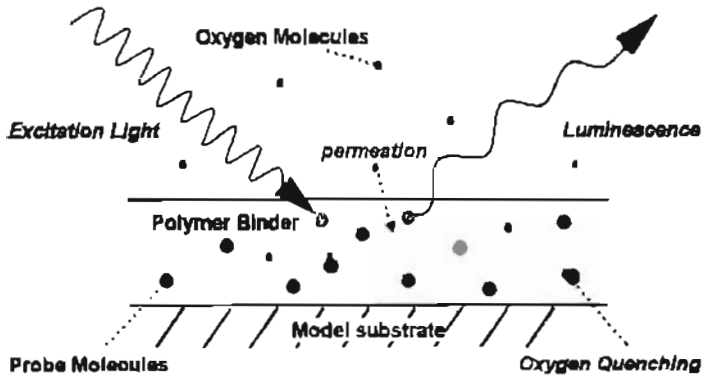
Absorption spectrum of CNT (A) individual; (D) aggregated.



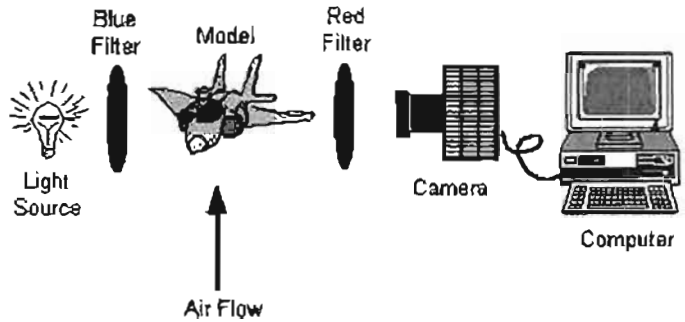
Bandgap luminescence of CNT; each size has *its own characteristic absorption and emission* wavelengths.

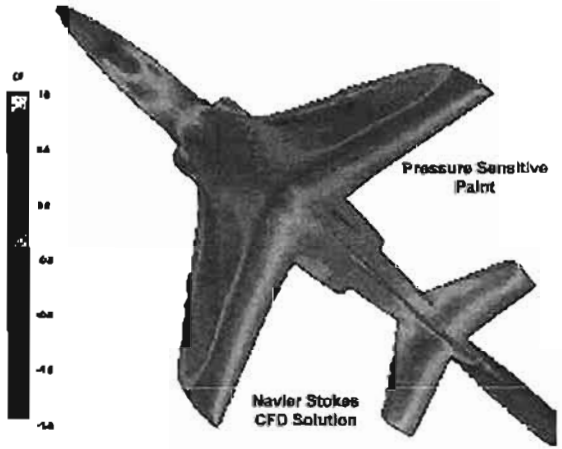
Weisman et al. (Rice Univ.), US7,682,523

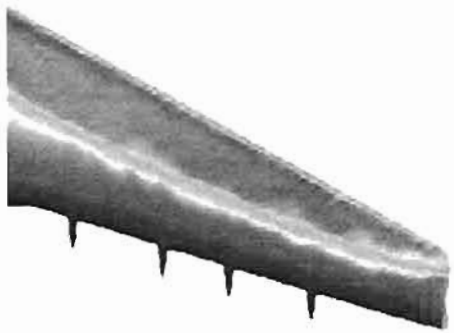
Photoluminescent pressure-sensitive paints



$$I_0/I = \tau_0/\tau = 1 + K_{SV} P_{O2}$$





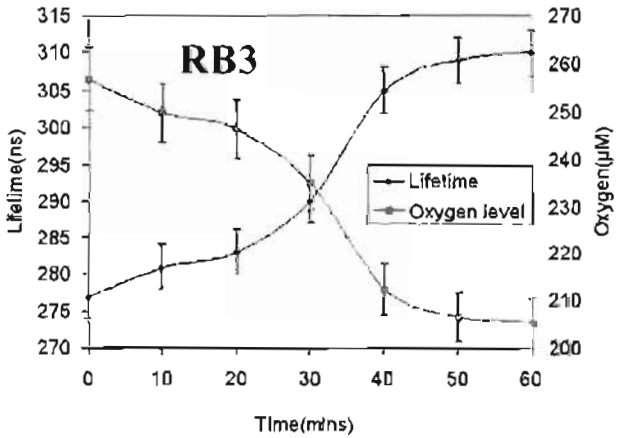


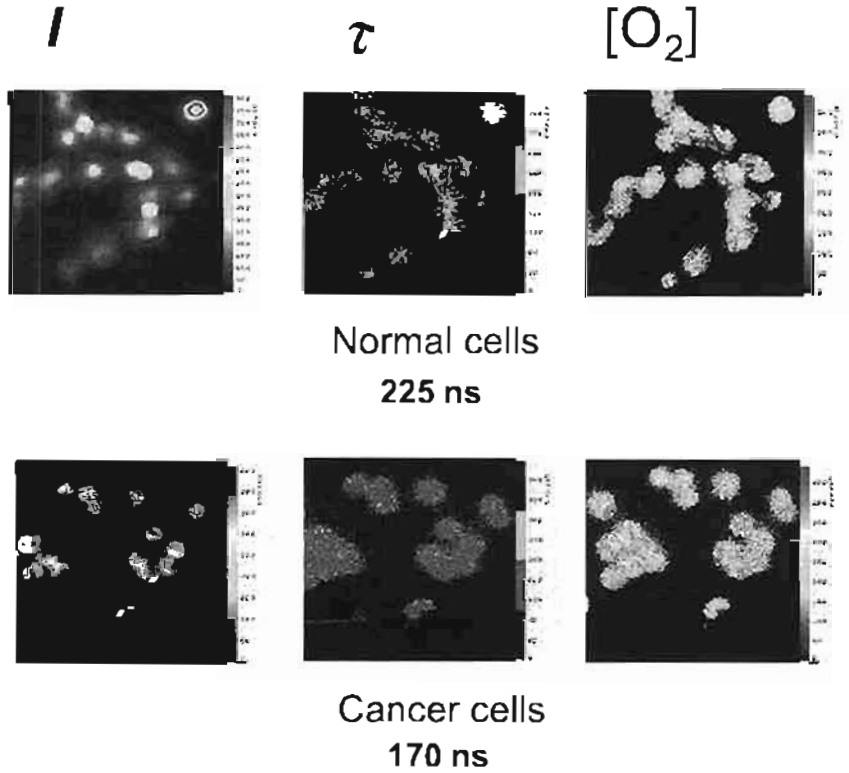
PSP on an Airbus wing

www.aerospaceweb.org

Luminescence lifetime imaging of oxygen levels in (living) cancer cells

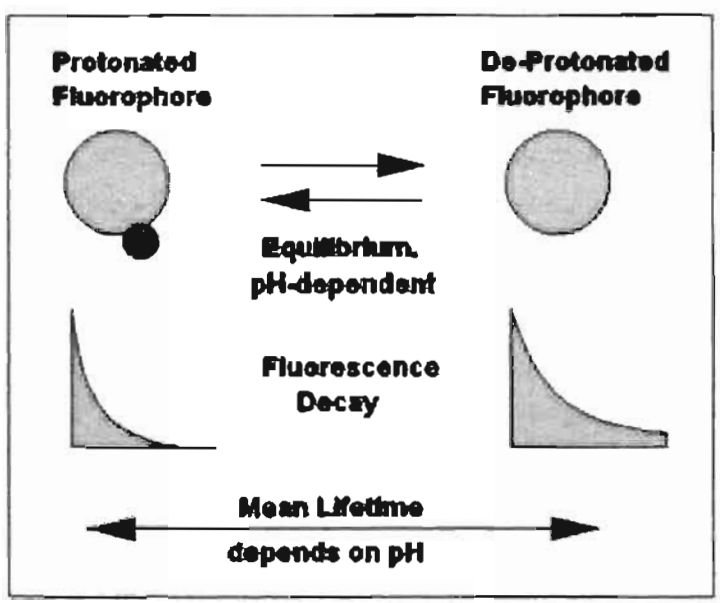
Esophageal epithelial cells

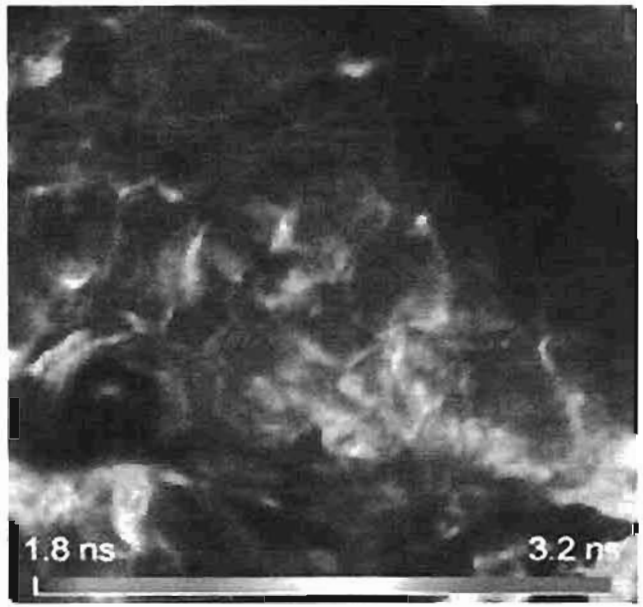




Sud, Zhong, Beer & Mycek, *Optics Express* **2006**, *14*, 4412.

Luminescence lifetime imaging of pH in skin tissue

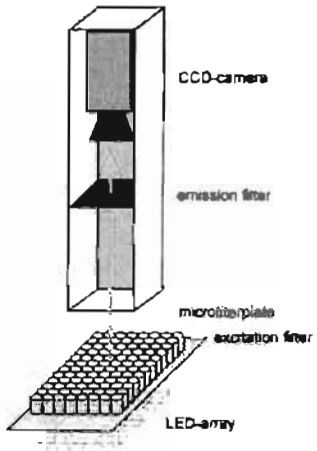


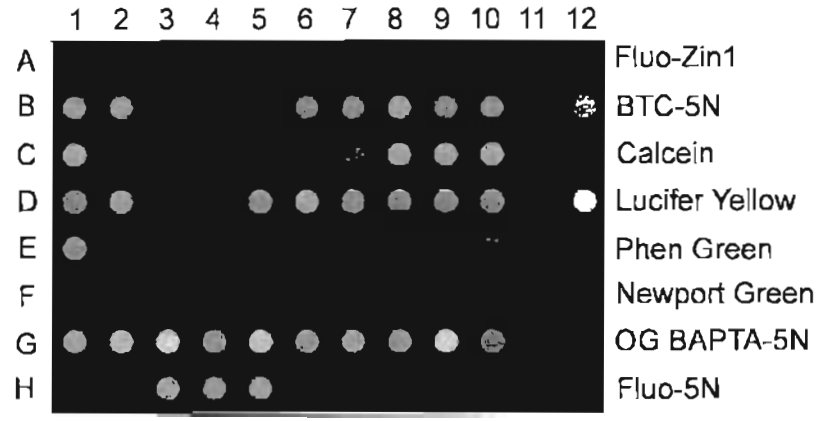


www.becker-hickl.com

Lifetime image of skin tissue stained with BCECF (a carboxyfluorescein derivative): pH gradients in the extracellular matrix of the epidermis.

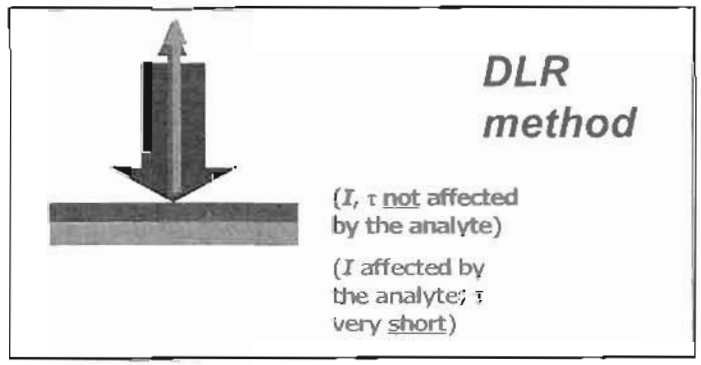
Luminescence imaging of metal ions and anion sensor arrays





⇦ (the same mixture of ions in each well of the row)

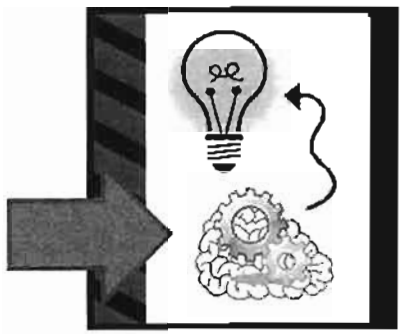
Column No.	Ca^{2+} [µM]	Cu^{2+} [µM]	Ni^{2+} [µM]	Zn^{2+} [µM]	Cd^{2+} [µM]
1	0	0	0	0	0
2	1	1	1	1	1
3	10	10	10	10	10
4	100	100	100	100	100
5	1	0	0	0	0
6	0	1	0	0	0
7	0	0	1	0	0
8	0	0	0	1	0
9	0	0	0	0	1
10	10	0	0	0	0
11	0	10	0	0	0
12	0	0	10	0	0



O. S. Wolfbeis and co-workers, *Anal. Chem.*, **2003**, *75*, 4389.

Materiales foto*luminiscentes*

Prof. Guillermo Orellana, UCM

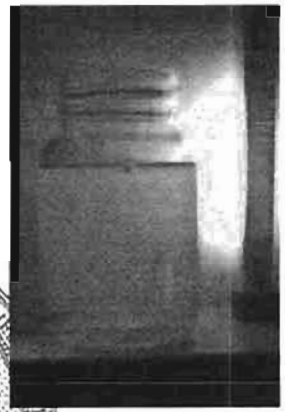


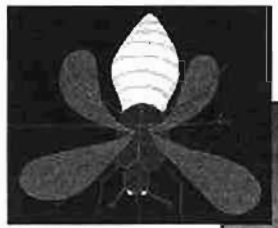
21 de Junio de 2010

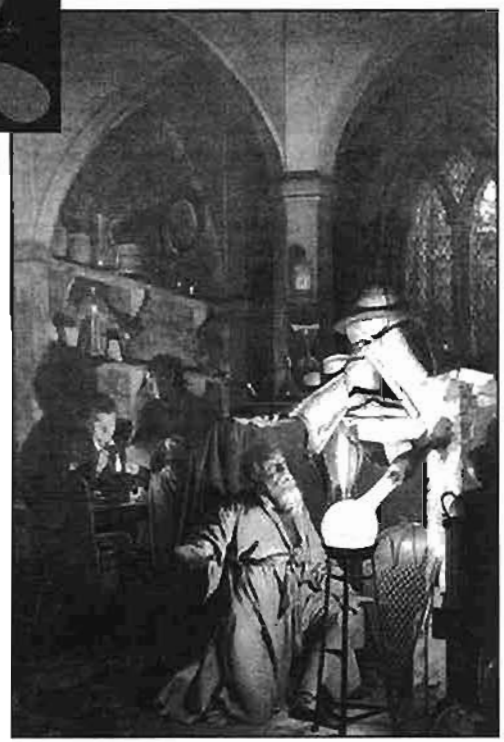
Características de los materiales "inteligentes"

- **Estímulo** al que el material inteligente responde (luz, electricidad, campo magnético, presencia de un estímulo químico,...).
- Tipo de **propiedad** (absorción, **luminiscencia**, corriente eléctrica, índice de refracción,...) que cambia en el material bajo el efecto inductor del estímulo (*respuesta*).
- Magnitud o grado de la **respuesta**
- Aplicaciones, generalidad, etc.

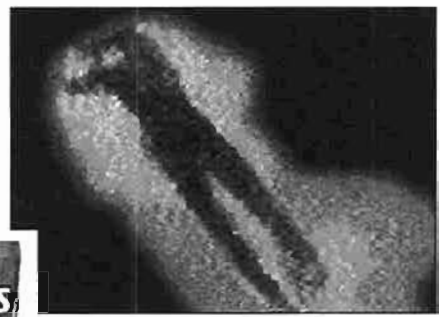
Fenómenos luminiscentes naturales







Historia Medicinal
(Sevilla, 1565)
Lignum nephriticum
¡Primer método para detección de falsificaciones!
(madera)

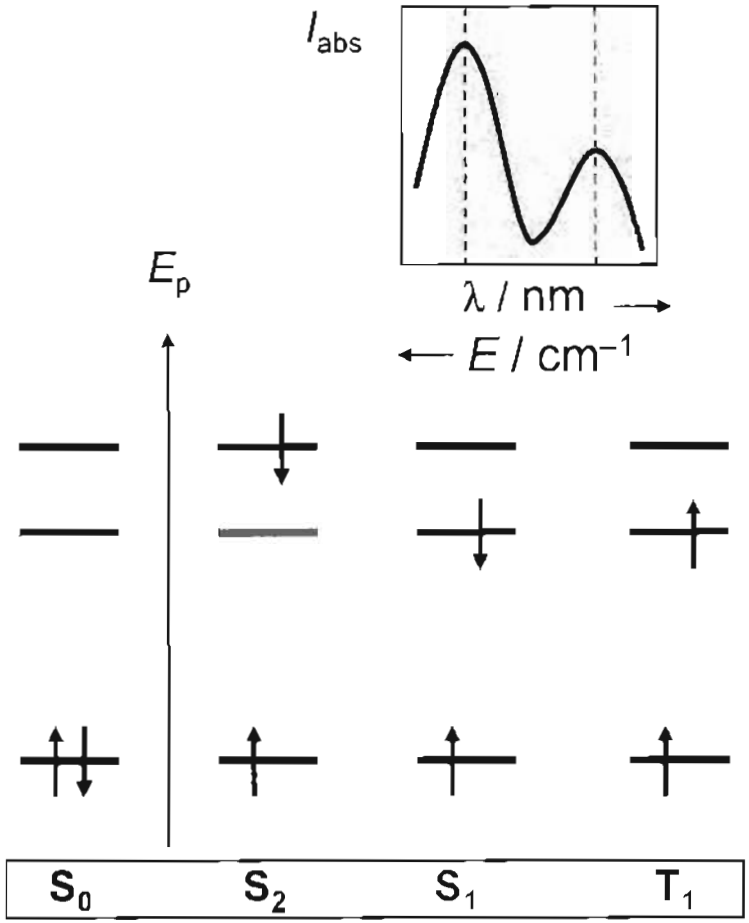


"lumen" + "essentia" = hecho de luz

Índice de la presentación

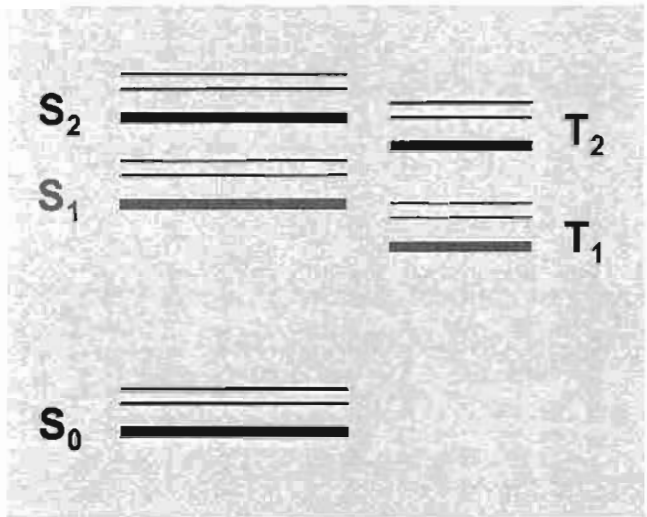
- Qué es **luminiscencia** (fluorescencia/fosforescencia)
- **Tecnología** para la medida e interrogación
- **Tipos** de compuestos y materiales luminiscentes
- Naturaleza **multi-paramétrica** de la emisión luminiscente
  - *Intensidad*
  - *Dependencia con la longitud de onda*
  - *Tiempo de vida (cinética) de la emisión*
  - *Polarización (anisotropía).*
- **Ejemplos de aplicación** (hasta donde permita el tiempo disponible)

Estados electrónicos excitados



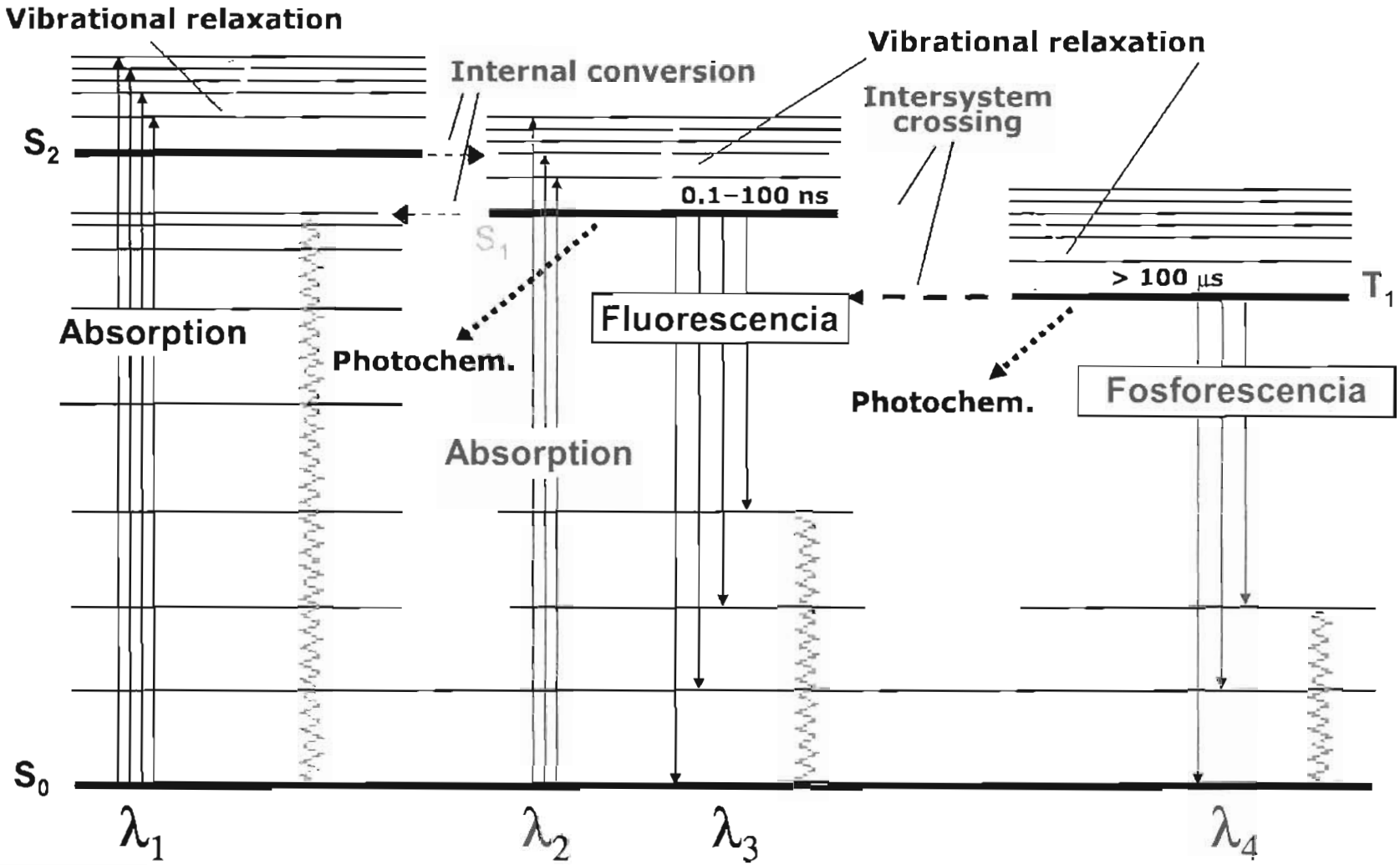
"Molecular orbitals diagram"

$$E = h\nu$$

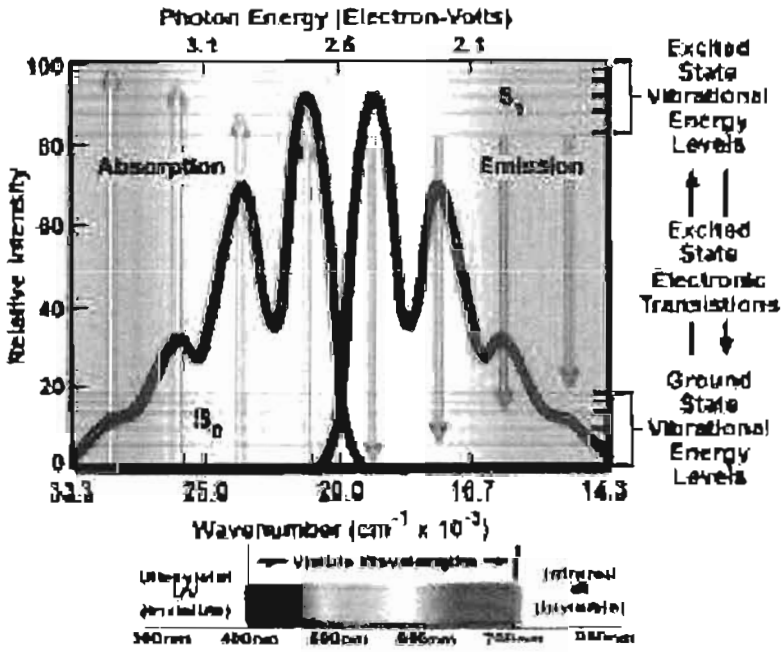


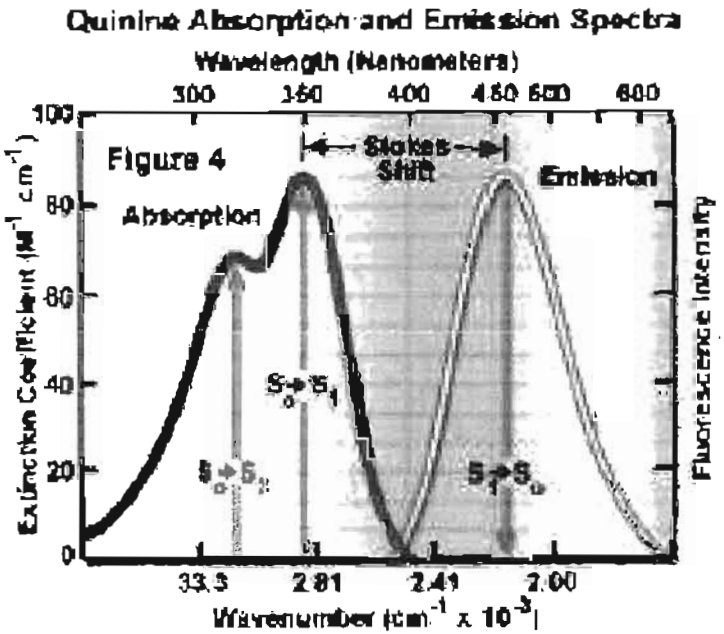
"Jablonski diagram"

¿Qué es luminiscencia?



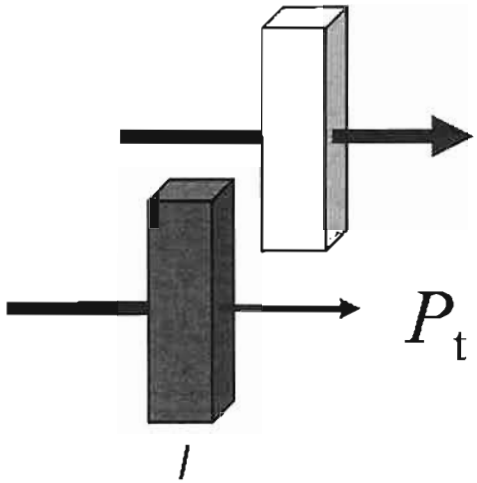
Luminescence spectrum





$$\Phi = \frac{\text{emitted photons/t}}{\text{absorbed photons/t}}$$

Luminescence- vs. absorption-based monitoring

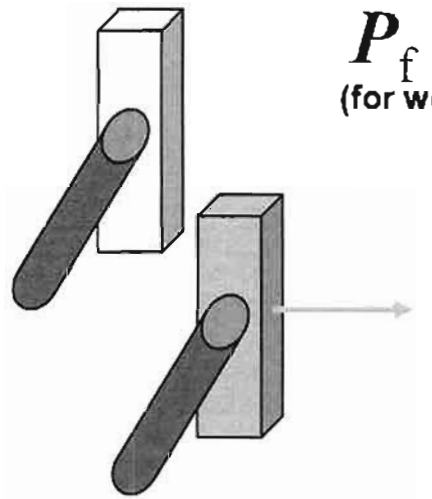


$$A = \log\left(\frac{P_0}{P_t}\right) = \varepsilon l c$$

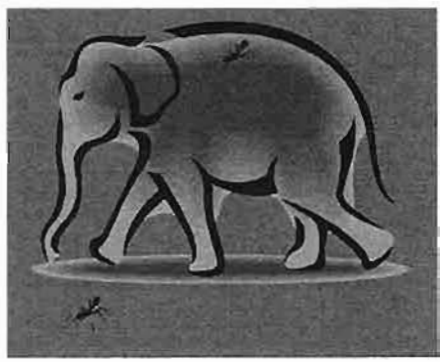
$$P_f = \kappa \varepsilon \Phi_f P_0 l c$$

(for weakly absorbing solutions)

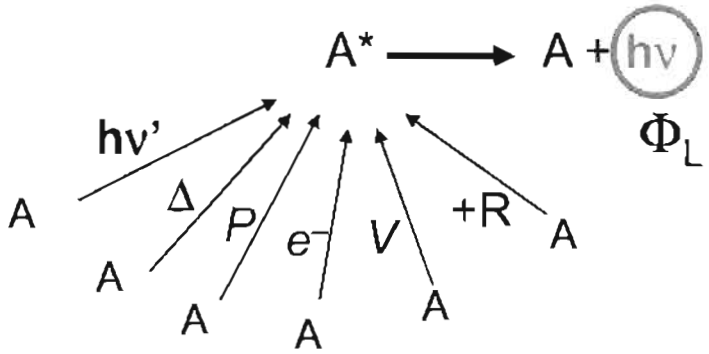
- Sensitivity
- Selectivity



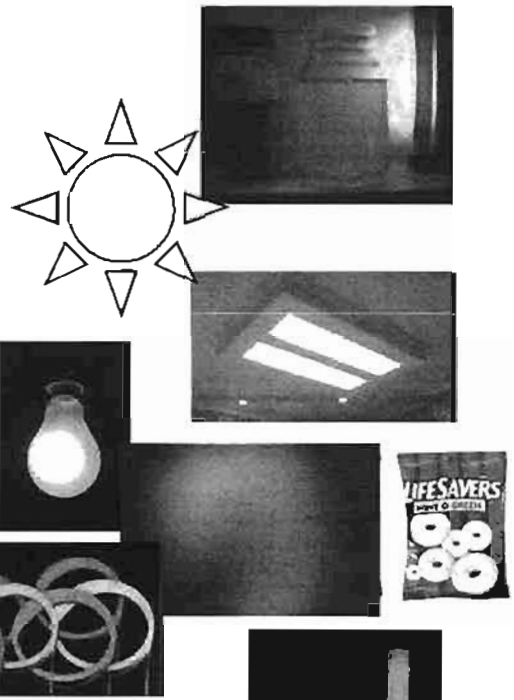
P_f



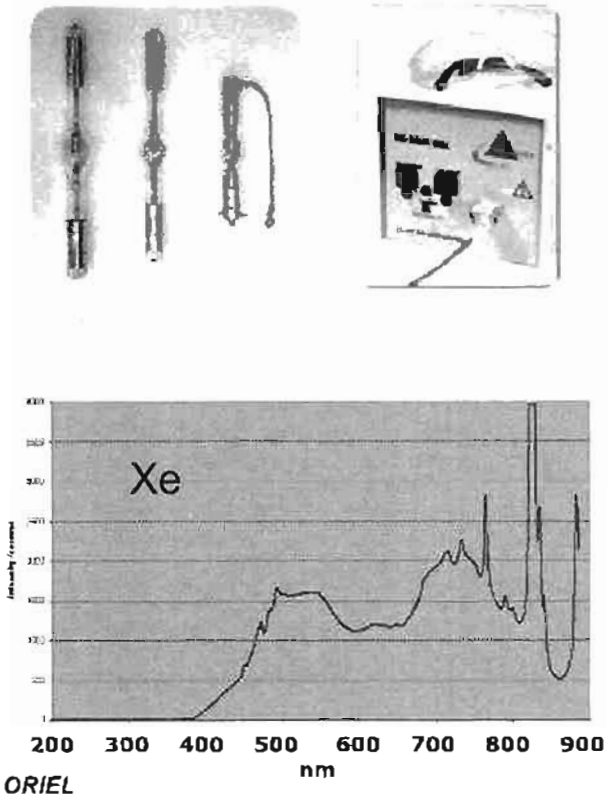
Remember: luminescence always arises from deactivation of electronic excited states

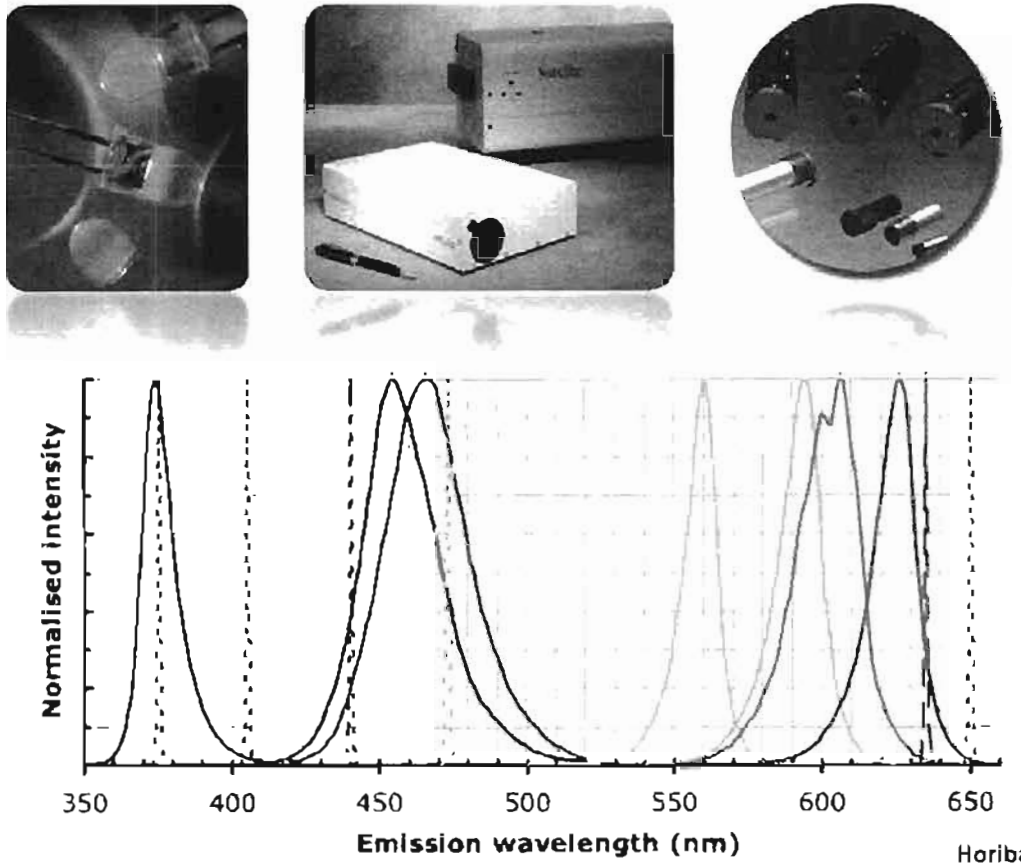


- (Photo)luminescence
- *Thermo*luminescence
- *Tribo*luminescence (*piezo*lum.)
- *Cathodo*luminescence
- *Electro*luminescence
- *Chemi*luminescence (*bio*lum.)

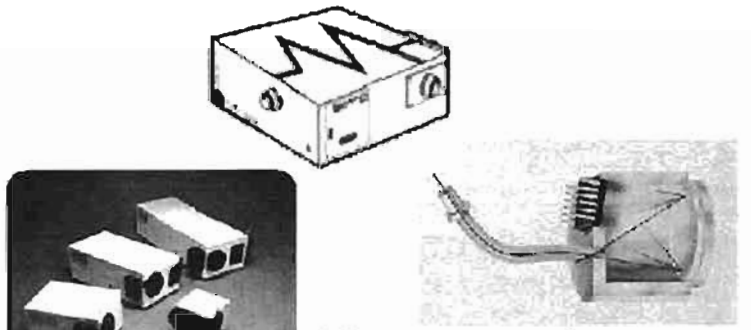


Instrumentation for luminescence measurements: light sources

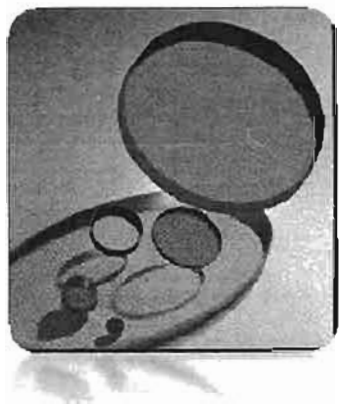




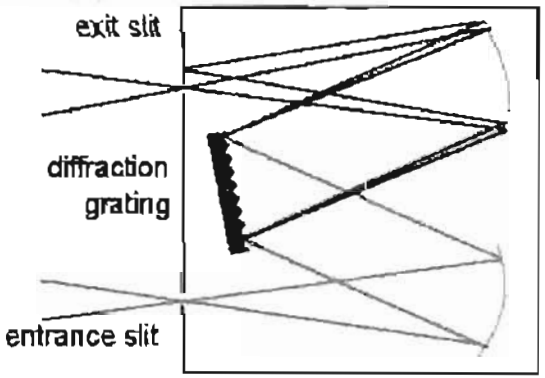
Instrumentation for luminescence measurements: wavelength selectors



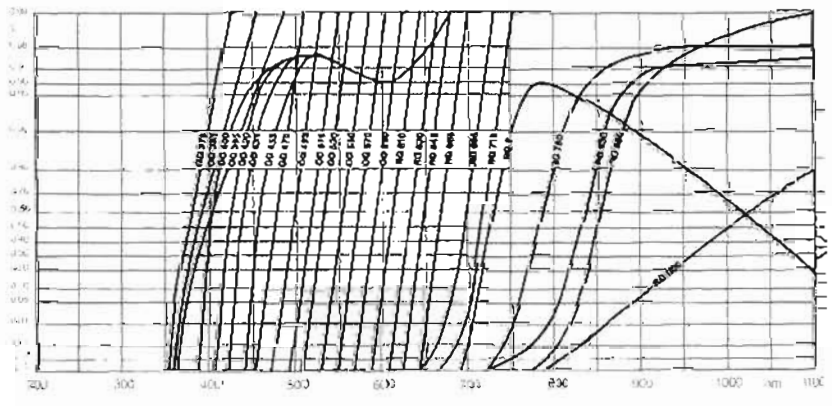
Monochromators



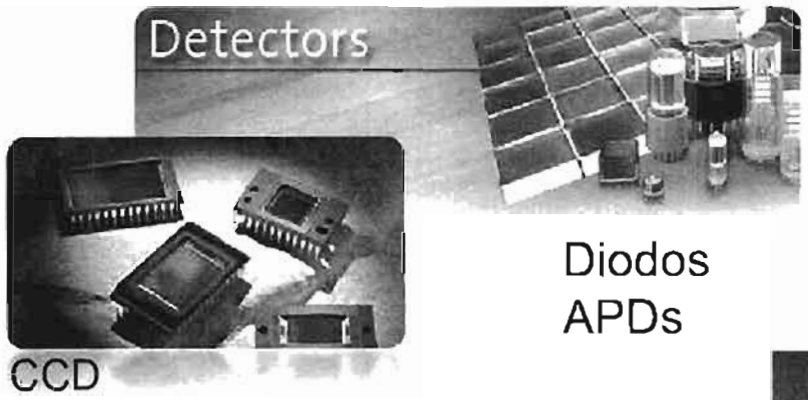
Optical filters



Schott

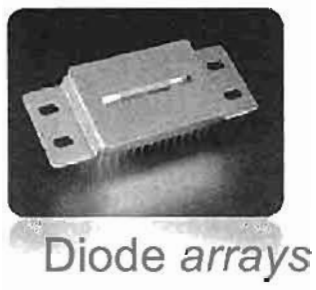


Instrumentation for luminescence measurements: detectors

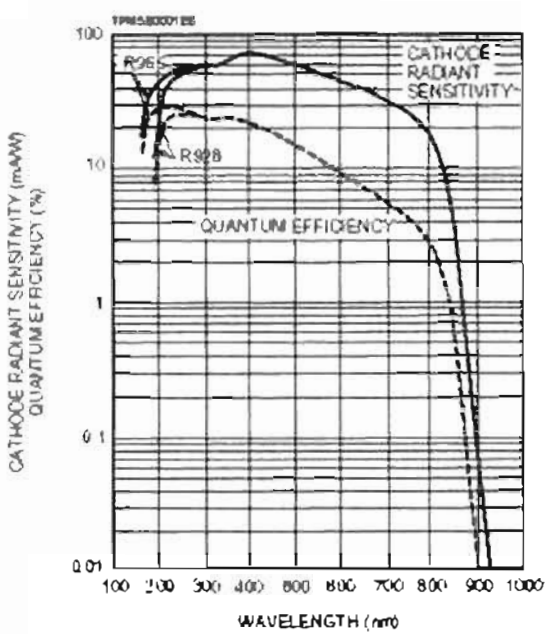


Diodos
APDs

CCD
CMOS

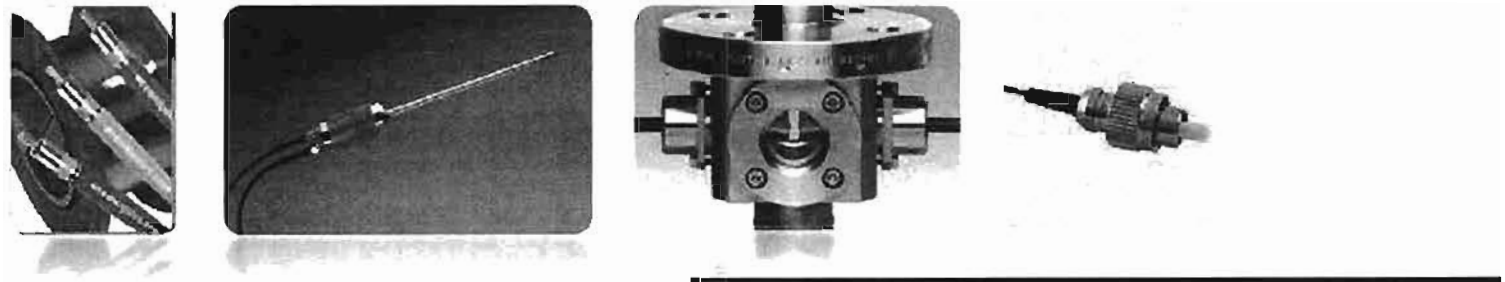


PMTs

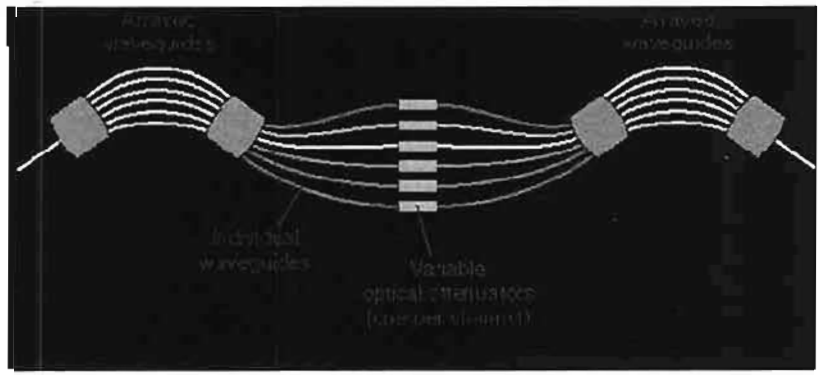


Hamamatsu

Instrumentation for luminescence measurements: light pipes & waveguides

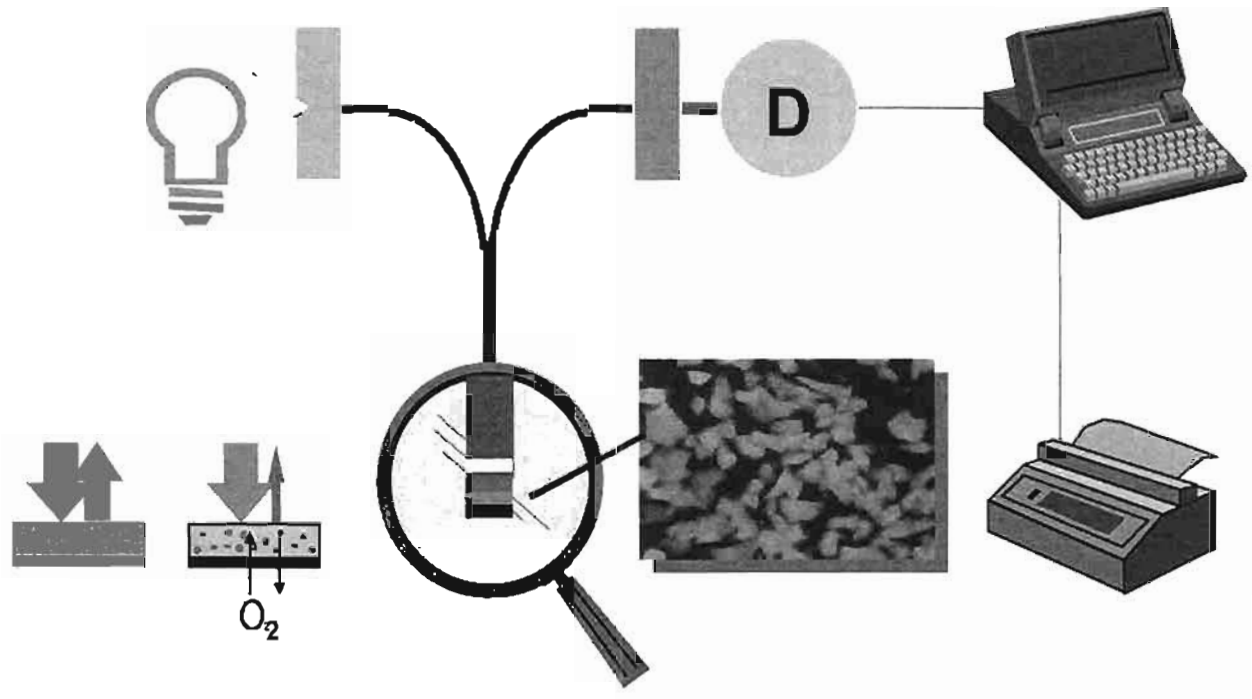


Optical fibers



Planar waveguides

Luminescent chemosensory
(indicator-, fiberoptic-based depicted)



Typical (organic) fluorophores

Common features or...

can fluorescence be predicted?

Typical (organic) fluorophores

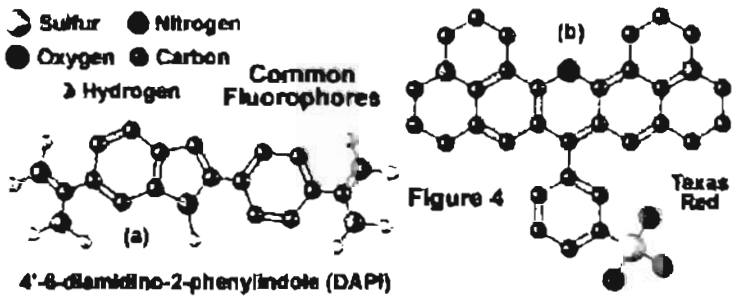
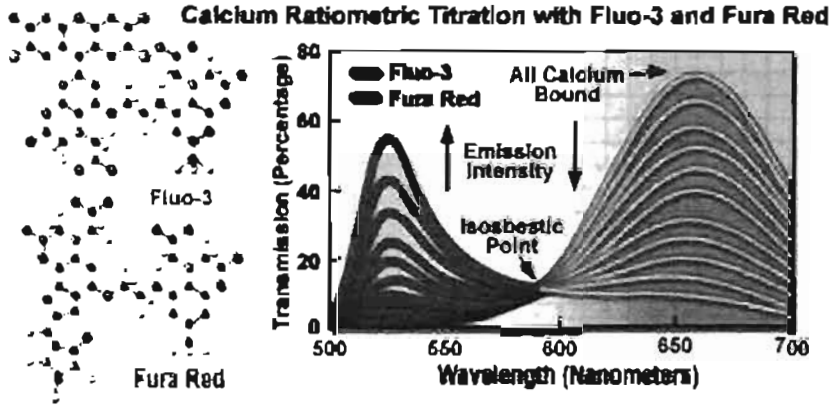
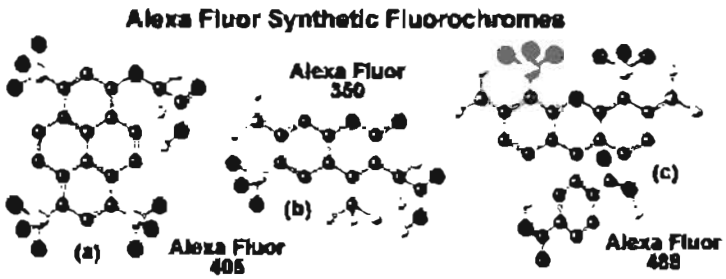
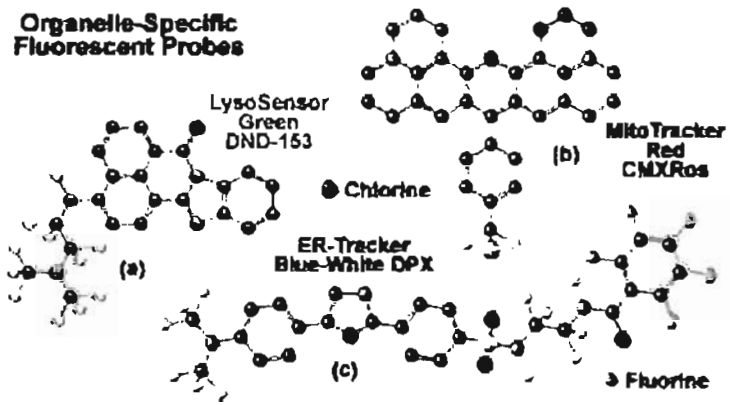


Figure 4

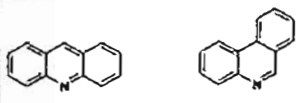
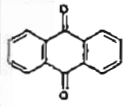
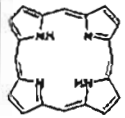
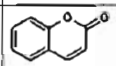
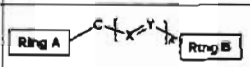


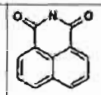
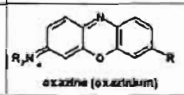
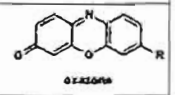
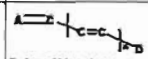
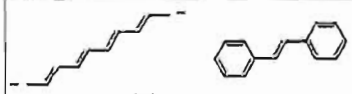
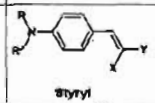
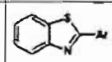
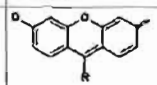




Families of organic fluorophores

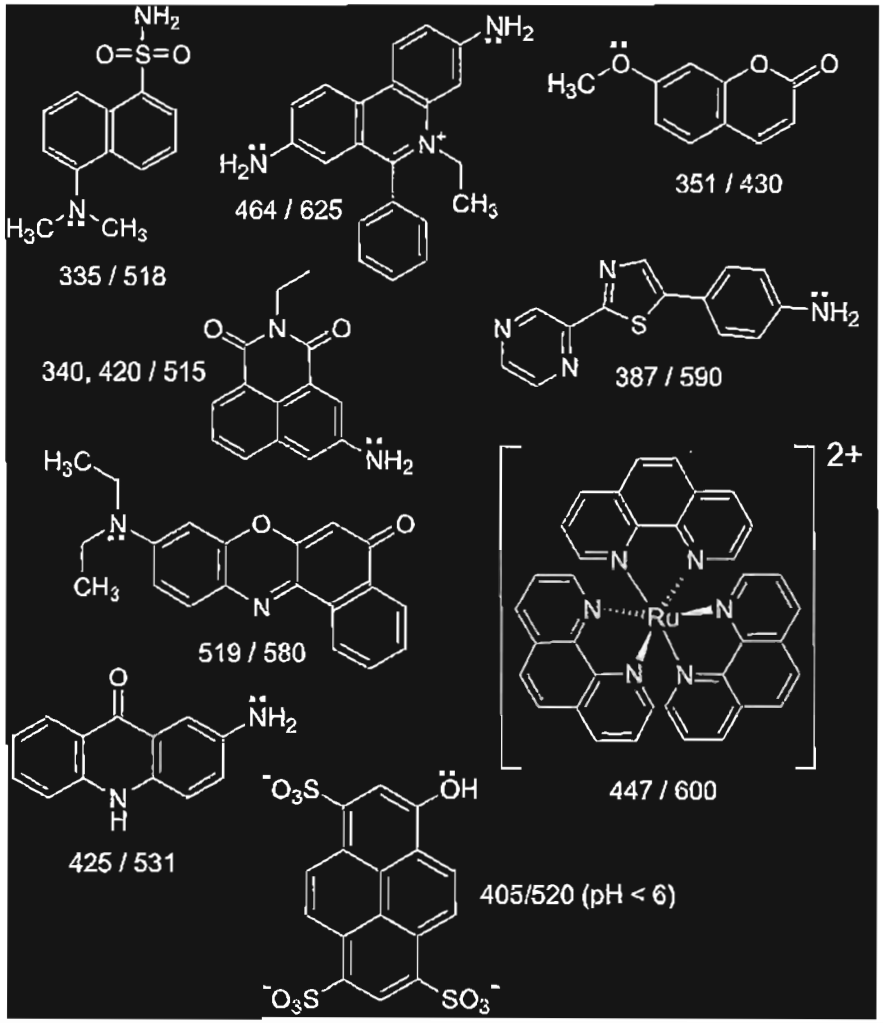
- **Table of fluorophoric substructures for classification**

Chromophore	Structure
Acridine, phananthridine	 Acridine Phenanthridine
Anthrachinone	 Anthrachinone
Aza[18]annulen	 Aza[18]annulen
Benzimidazole	 Benzimidazol
Coumarin	 Coumarin
Cyanine and azamethine	 Cyanine Ring A and B contain donor and acceptor nitrogen atom. In azamethine dyes, either X or Y is a nitrogen atoms.

Naphthalimide	 Naphthalimide
Oxazine and Oxazone	 oxazine (oxazinium)  oxazone
Oxonol	Polymethine dyes with bridges between ring systems that contain oxygen atoms.
Polymethine	 Polymethine dyes A is an electron accepter group, D is an electron donor group. Subclasses that belong to Polymethine dyes are: • Cyanine and azamethine • Oxonols • Benzimidazols • Indolens • Styryl dyes • Coumarin
Polyene	 Polyene
Styryl	 Styryl
Thiazole	 Thiazole
Xanthen	 Xanthene

Classifications refers to Conn's Biological Stains, 10th edition, R. W. Horobin, J. A. Kiernan ed., BIOS Scientific Publishers, Oxford, UK, 2002

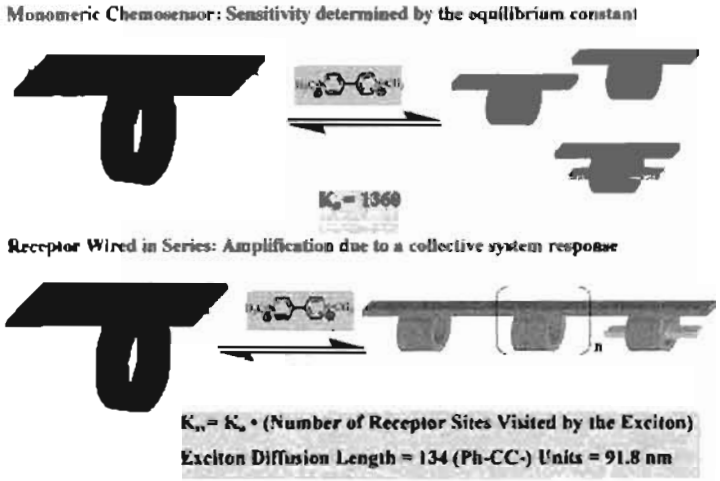
Intramolecular charge-transfer luminophores



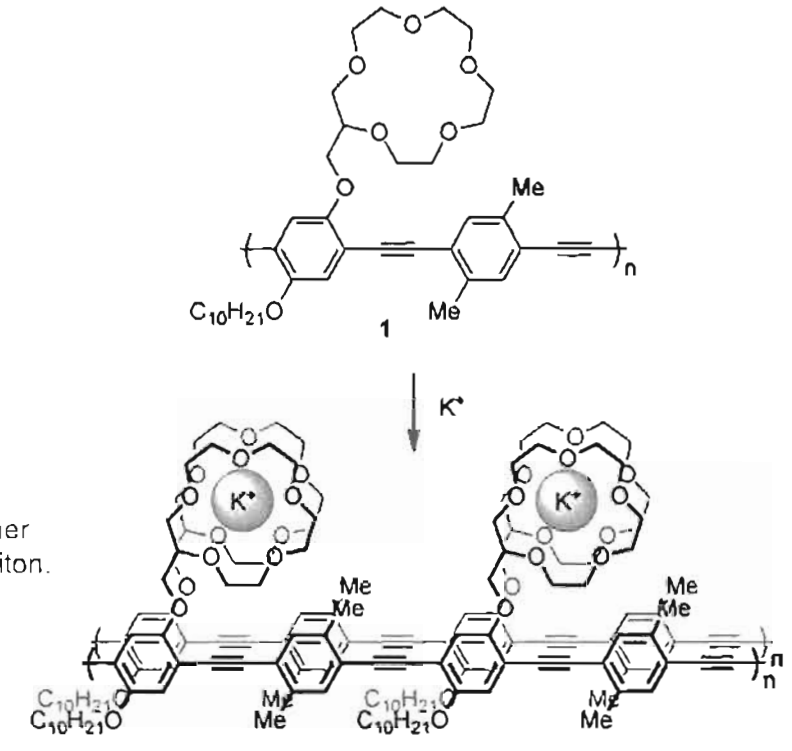
Large Stokes shift!
Sensitivity to solvent

Amplifying Fluorescent Conjugated Polymers

Excitons in AFPs are highly mobile and can diffuse throughout an isolated polymer **chain** or within an AFP solid by mechanisms that involve both *through space* dipolar couplings and *strong mixing* of electronic states.



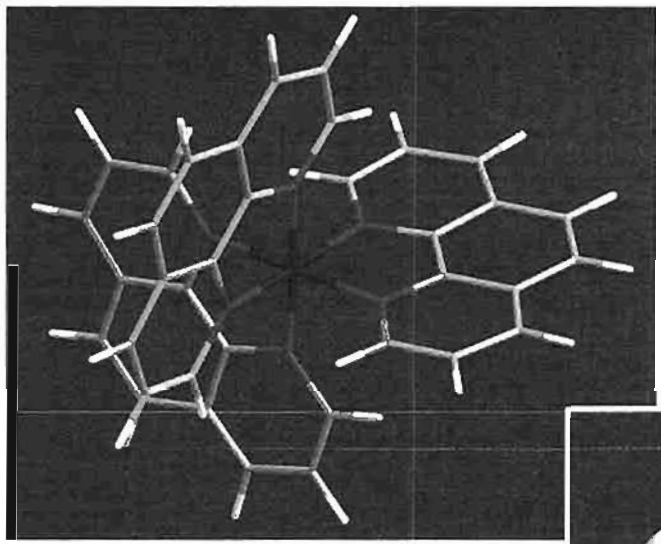
Demonstration of amplified quenching in a CP. The quencher can be bound to any of the repeating units visited by the exciton.

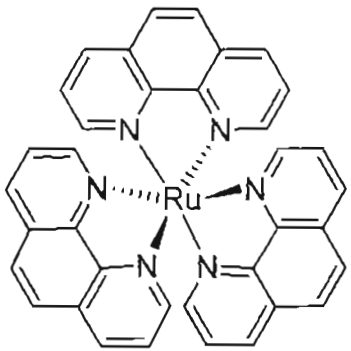


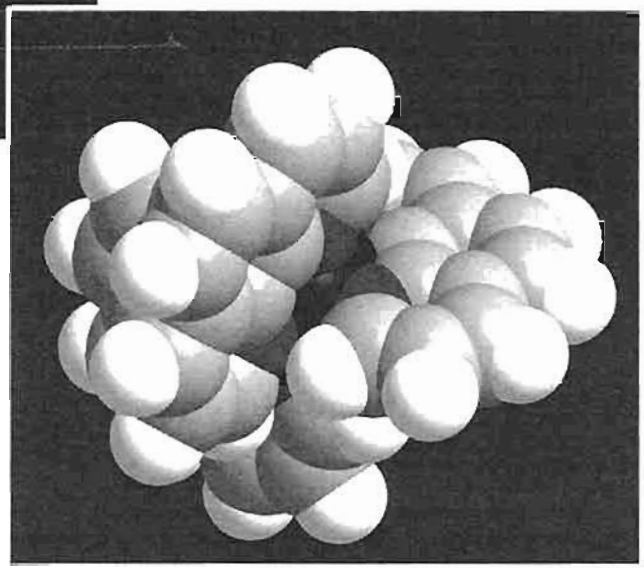
K⁺-induced aggregation of crown ether-functionalized AF polymer (emission red shift, 434 to 459, and fluorescence quenching).

Thomas, Joly & Swager, *Chem. Rev.* **2007**, *107*, 1339.

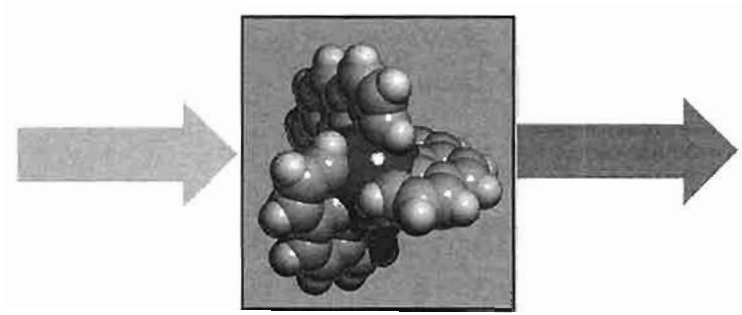
Metal-organic luminophores: Ru(II) polypyridyls







Features of the luminescent Ru(II) polypyridyls



G. Orellana & D. García-Fresnadillo, in *Optical Sensors: Industrial, Environmental and Diagnostic Applications.* Naranayaswamy and Wolfbeis, Eds., Springer (2004)

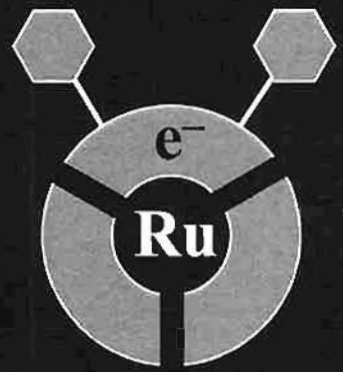
☺ *Advantages*

- **Visible absorption, strong emission**
- **Stokes' shift (150-200 nm)**
- **Long emission lifetimes (0.1 - 9 μs)**
- **(Photo)stability**
- **"Tunable" properties**
  - *towards the analyte (photochemistry/photophysics)*
  - *towards the immobilization procedure*

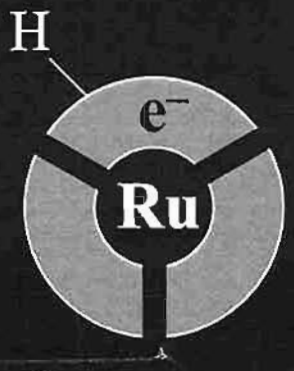
☹ *Limitations*

- **Ionic compounds**
- **Oxygen, temperature cross-talk**

Engineering of the coordinating ligands

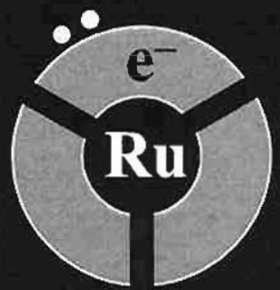


Enhanced τ
(O_2 sensitivity)

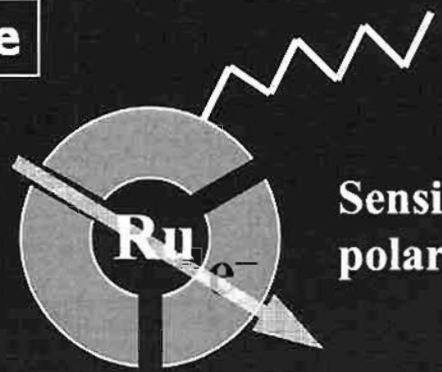


Sensitive to
BASES

^{3}MLCT excited state

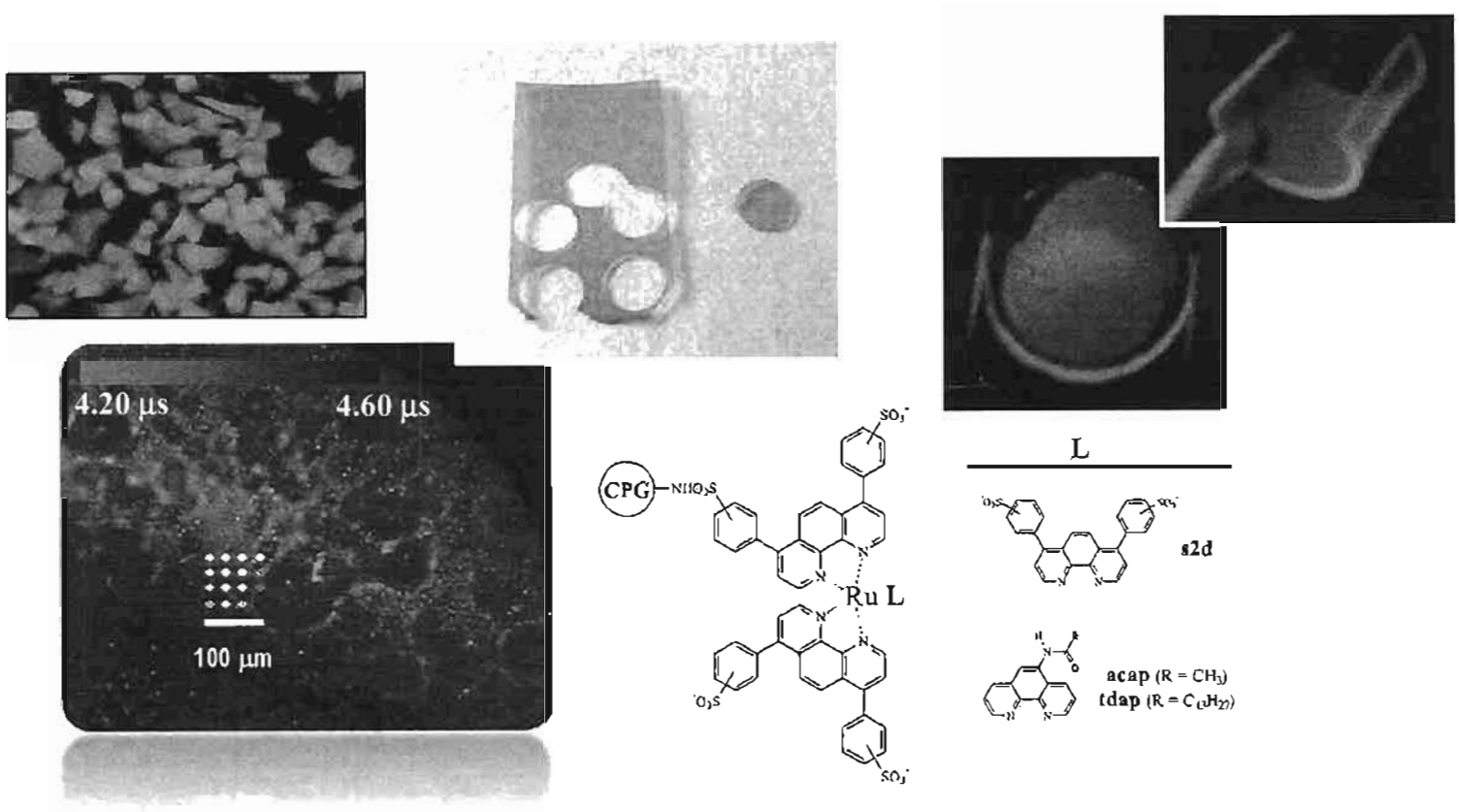


Sensitive to
ACIDS



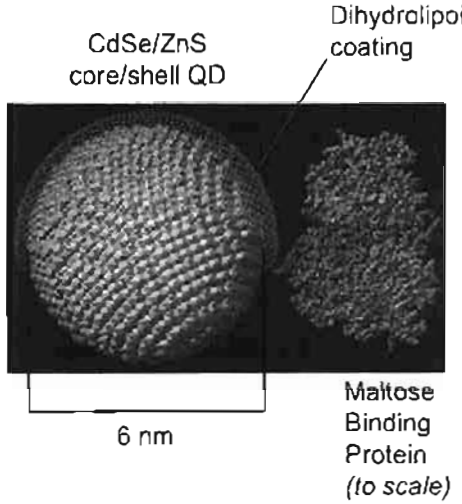
Sensitive to
polarity

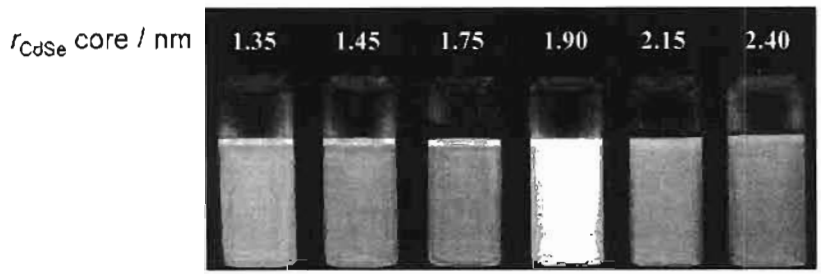
Fabrication of photoluminescent materials containing Ru(II) polypyridyls

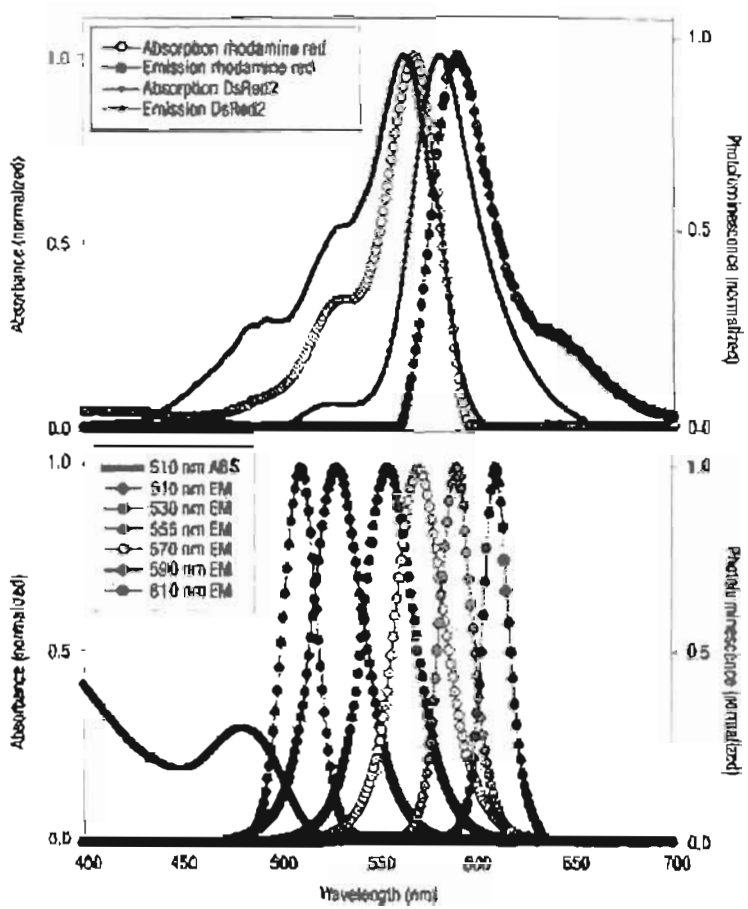


G. Orellana et al , in *Frontiers in Chemical Sensors: Novel Principles and Techniques*, G. Orellana and M.C. Moreno-Bondi (Eds.), Springer, 2005; pp. 189–225.

Inorganic fluorophores: Quantum dots



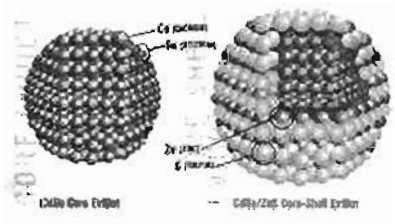


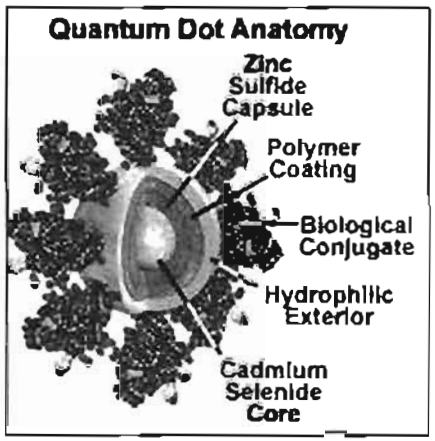


I. L. Menditz et al., *Nature Materials* **2005**, 4, 435–446.

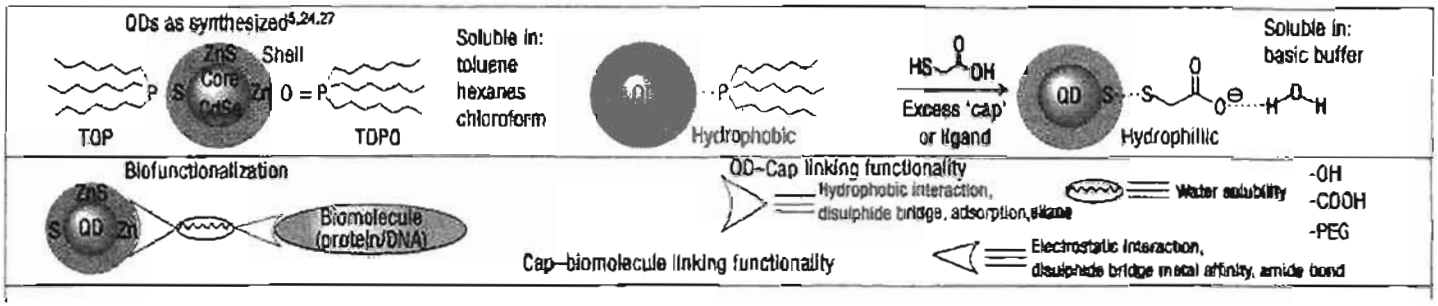
Quantum dots features (vs. organic fluorophores)

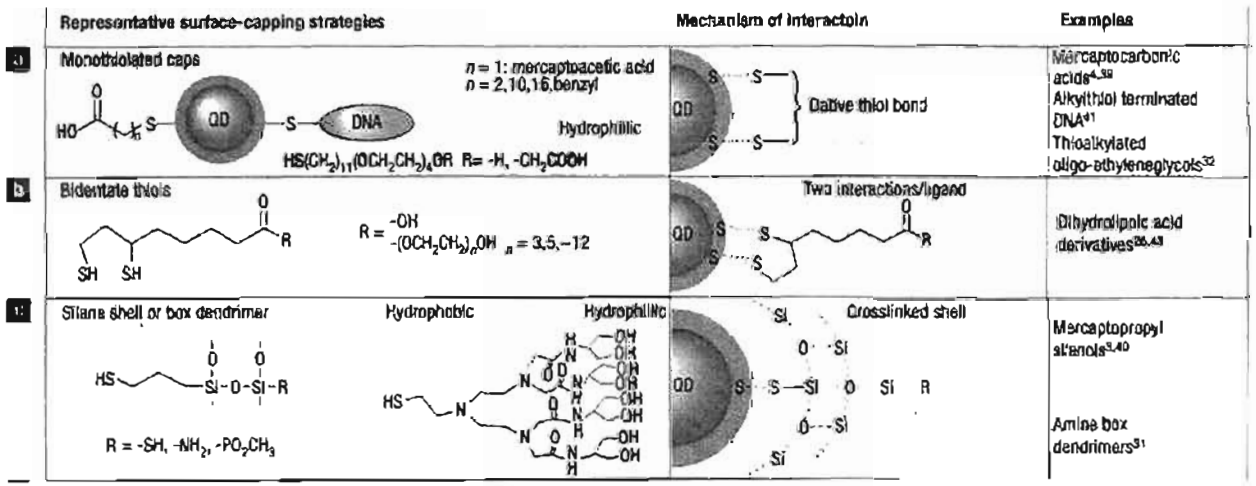
- QDs have 10–100x **absorption** coeficient.
- QDs **emission** very narrow (FWMH 30 nm, *if monodisperse!*).
- **Tuneable** emission maximum, large **Stokes shift.**
- QDs are highly **photostable**.
- Ease of **protein coating** to confer binding specificity.
- Intermittent emission (**blinking**) under continuous excitation *(Auger ionization?).*
- Metal **toxicity** and **security** issues due to particle size.





Functionalization of the quantum dots

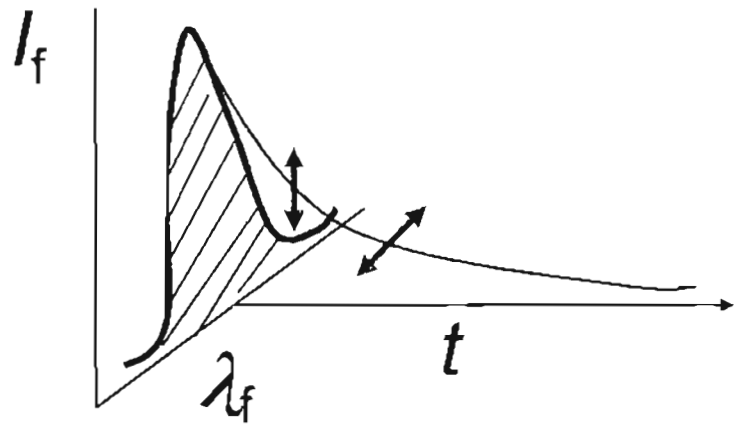




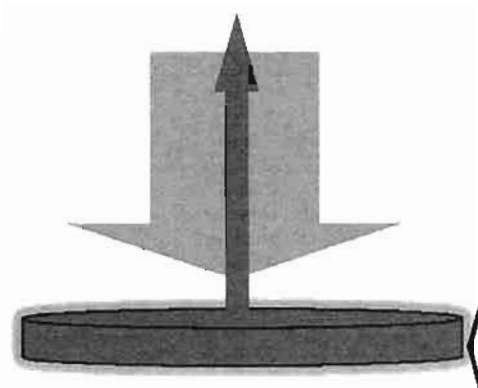
I. L. Medintz et al., *Nature Materials* 2005, 4, 435–446.

Luminescence: a multi-parametric technique

- ☑ Emission **intensity**
- ☑ Emission **spectrum**
- ☑ Emission **kinetics** ***(lifetime)***
- ☑ Emission **anisotropy** ***(polarization)***



Materials based on indicator dye *luminescence* intensity *measurements*



$$P_f = \kappa \Phi_f P_0 l c$$

(ONLY for weakly absorbing solutions!)

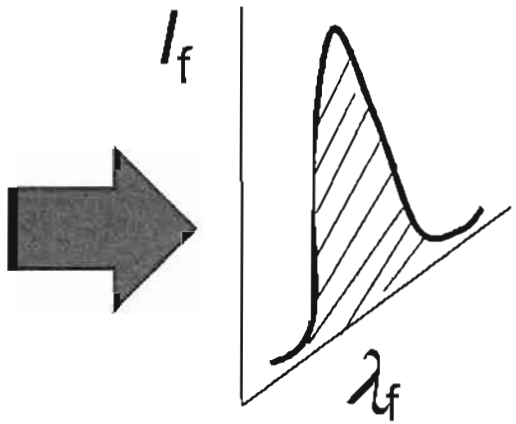
A proper design must address:

- Instrumental (κ) factors
- Indicator ε and Φ_f (concentration, thickness)
- Response time (polymer support, thickness)
- Excitation source P_0 (signal, photobleaching)
- Polymer support (light abs/scattering, analyte selectivity)

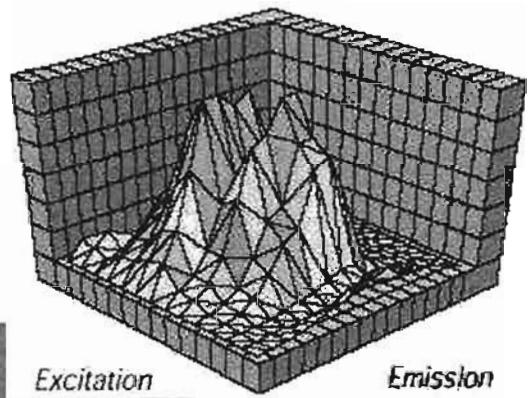
G. Orellana et al., In *Frontiers in Chemical Sensors: Novel Principles and Techniques,* Orellana and Moreno-Bondi, Eds., Springer (2005); chapter 6.

Remember: Luminescence is a multi-parametric technique

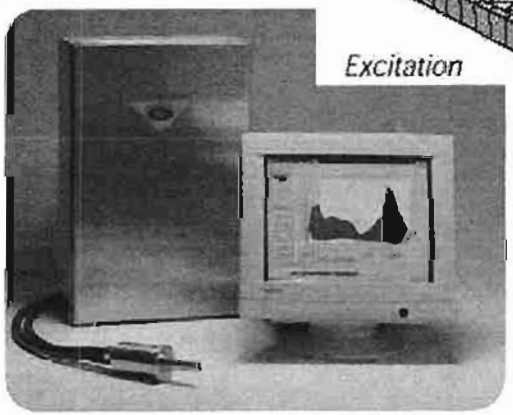
- ☑ Emission intensity
- ☑ Emission spectrum
- ☑ Emission kinetics *(lifetime)*
- ☑ Emission anisotropy *(polarization)*



Excitation-emission matrix as a source of specificity

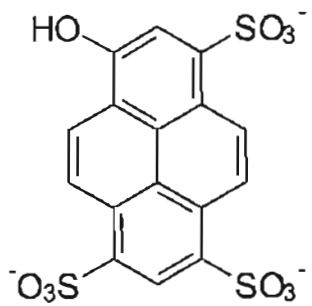


Bioview(R) system

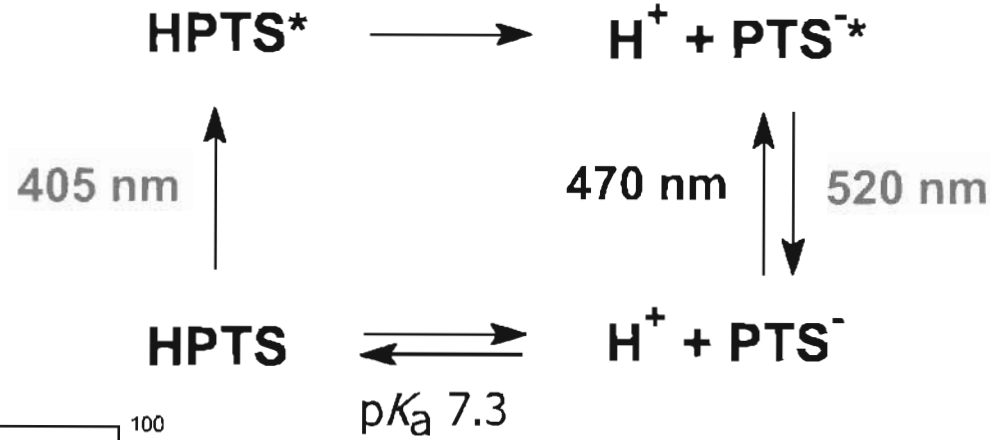


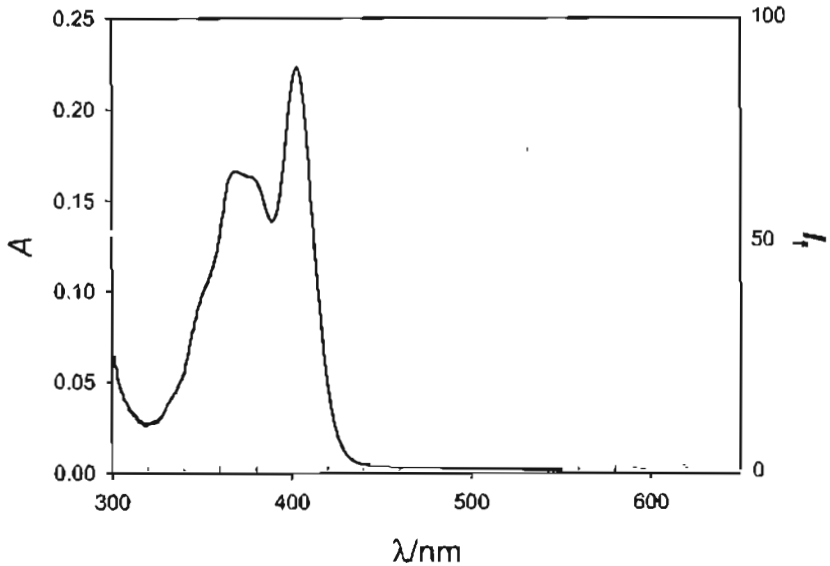
- **process control**
- **environmental analysis**

Ratiometric photoluminescent indicator dyes



HPTS



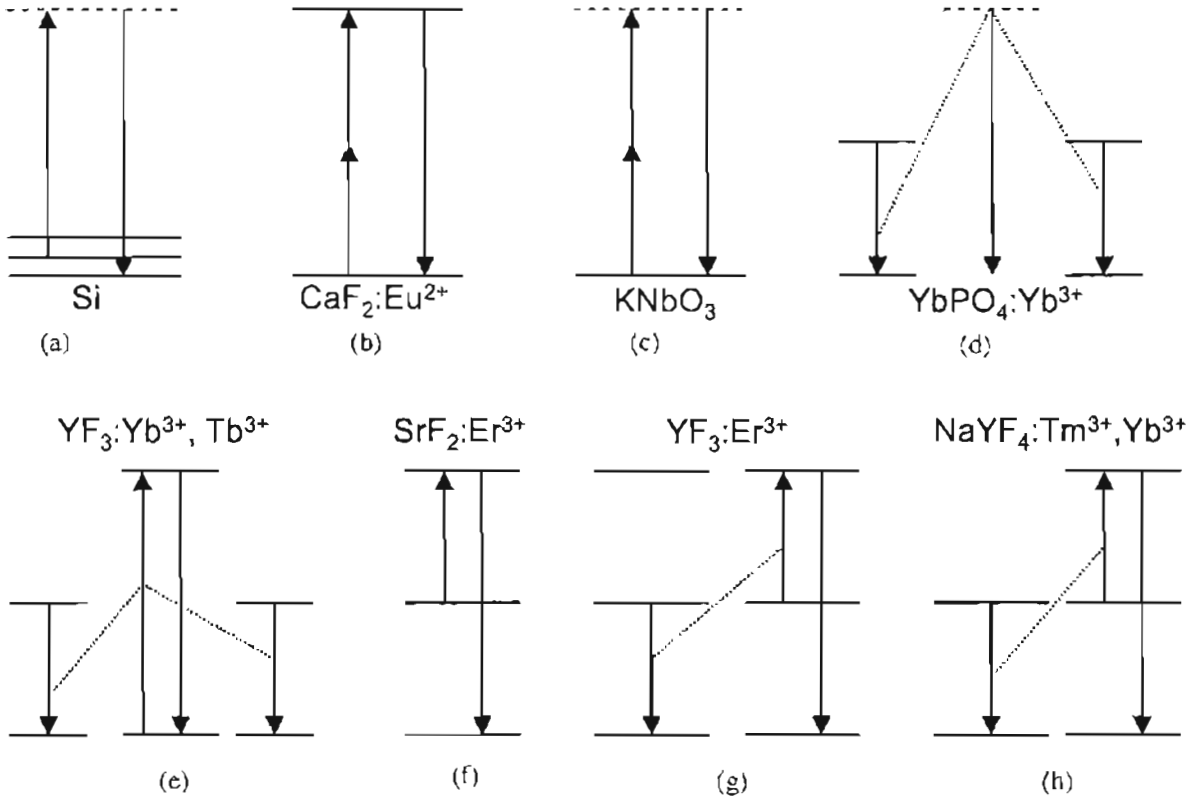


$$\text{Signal} = \frac{I_f^{(\text{ex}460)}}{I_f^{(\text{ex}405)}}$$

Photoluminescent up-conversion pigments

"Materials that are capable of absorbing photons of a certain energy E_1 and emitting photons with another energy E_2, such that $E_2 > E_1$".

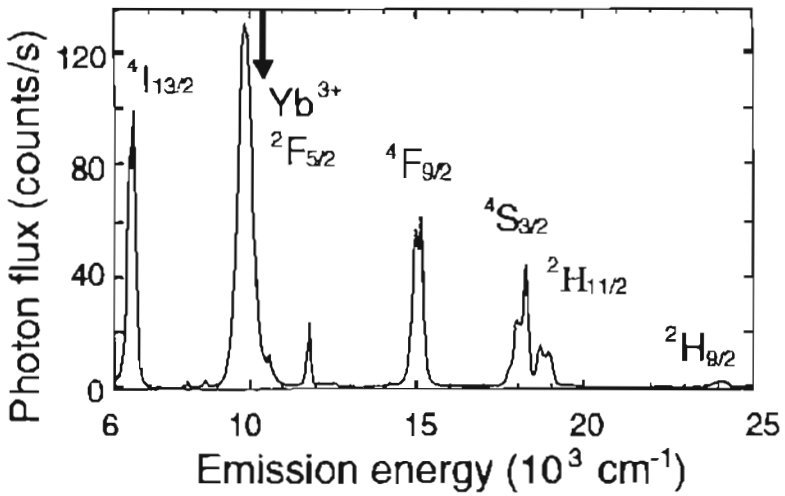
The majority of compounds that are able to perform UC involve trivalent lanthanides (Ln^{3+}) (have metastable levels of the 4f electrons)



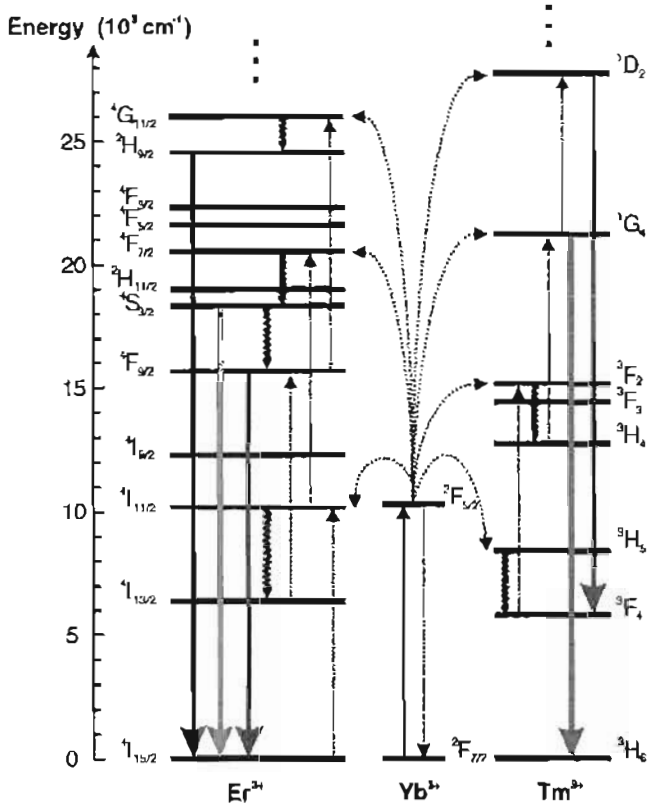
a) Anti-stokes Raman
b) Two-photon excitation
c) Second harmonic gen.
d) Cooperative luminesc.
e) Cooperative sensitization
f) Excited state absorption
g) Energy transfer up-conv.
h) Sensitized energy-transfer up-conversion

Photoluminescent up-conversion pigments

Most of the well-known upconverting phosphors contain trivalent rare earth ions as the active components, typically Pr^{3+}, Nd^{3+}, Er^{3+}, Tm^{3+}, or Yb^{3+} (typically, NIR absorption,VIS emission)

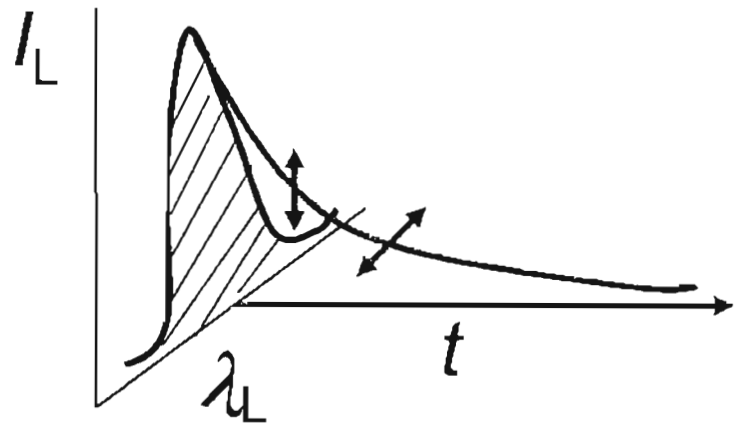


Upconversion and downconversion emission spectrum of a $NaYF_4$:Er^{3+},Yb^{3+} sample under 10 238 cm^{-1} excitation



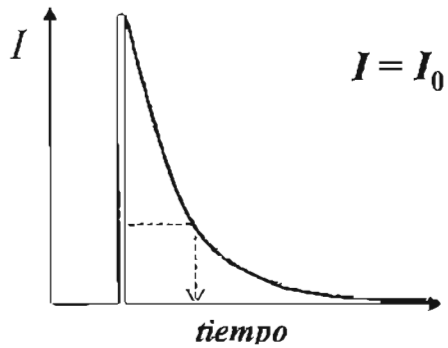
Tiempo de vida de la *luminiscencia:* *"la tercera dimensión"*

- ☑ **Intensidad** de emisión
- ☑ **Espectro** de emisión
- ☑ **Cinética** ***(tiempo de vida)*** de la emisión
- ☑ **Anisotropía** ***(polarización)*** de la emisión



Tiempo de vida de emisión

$$A^* \xrightarrow{k_{-1}} A\ (+\ h\nu)$$



$$I = I_0 \exp(-t/\tau)$$

$$\tau = \frac{1}{k_{-1}}$$

Medida de tiempo de vida de emisión

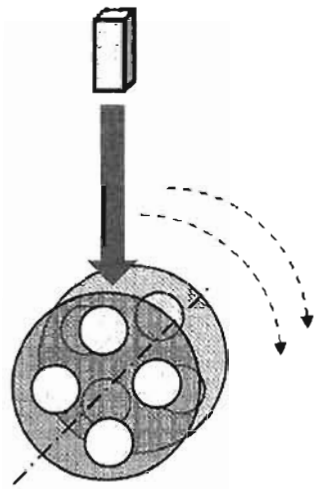
A. Técnicas con resolución temporal *(time-resolved detection techniques)*

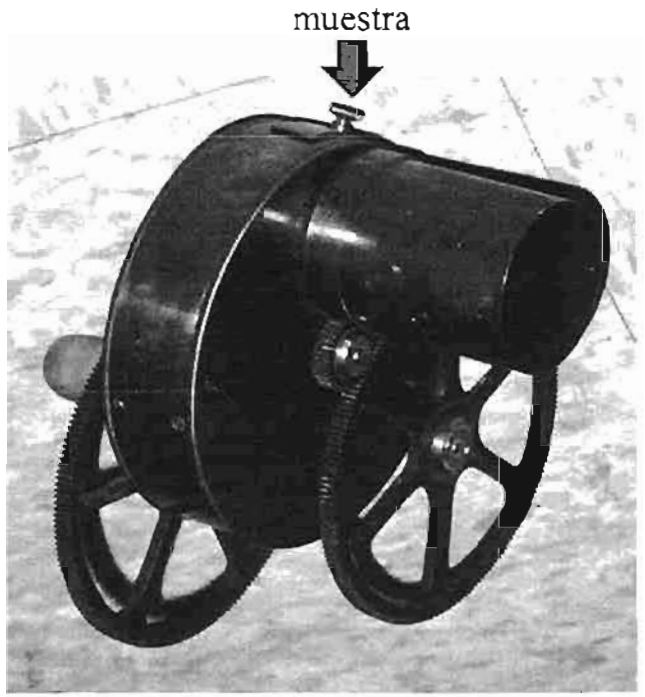
- **Excitación con lámpara *(excitation with a lamp)***
  - **lenta** ("fosforoscopios")/***slow*** *("phosphoroscopes")*
  - **rápida** (*flash photolysis* convencional)/***fast*** *(original flash photolysis)*
- **Excitación con laser pulsado** *(laser flash "photolysis", laser kinetic spectrometry)*
- **Conteo de fotones individuales correlacionados con el tiempo**
  (TC-SPC = SPT, time-correlated single photon counting = single photon timing)

B. Técnicas con resolución de fase *(phase-sensitive detection techniques)*

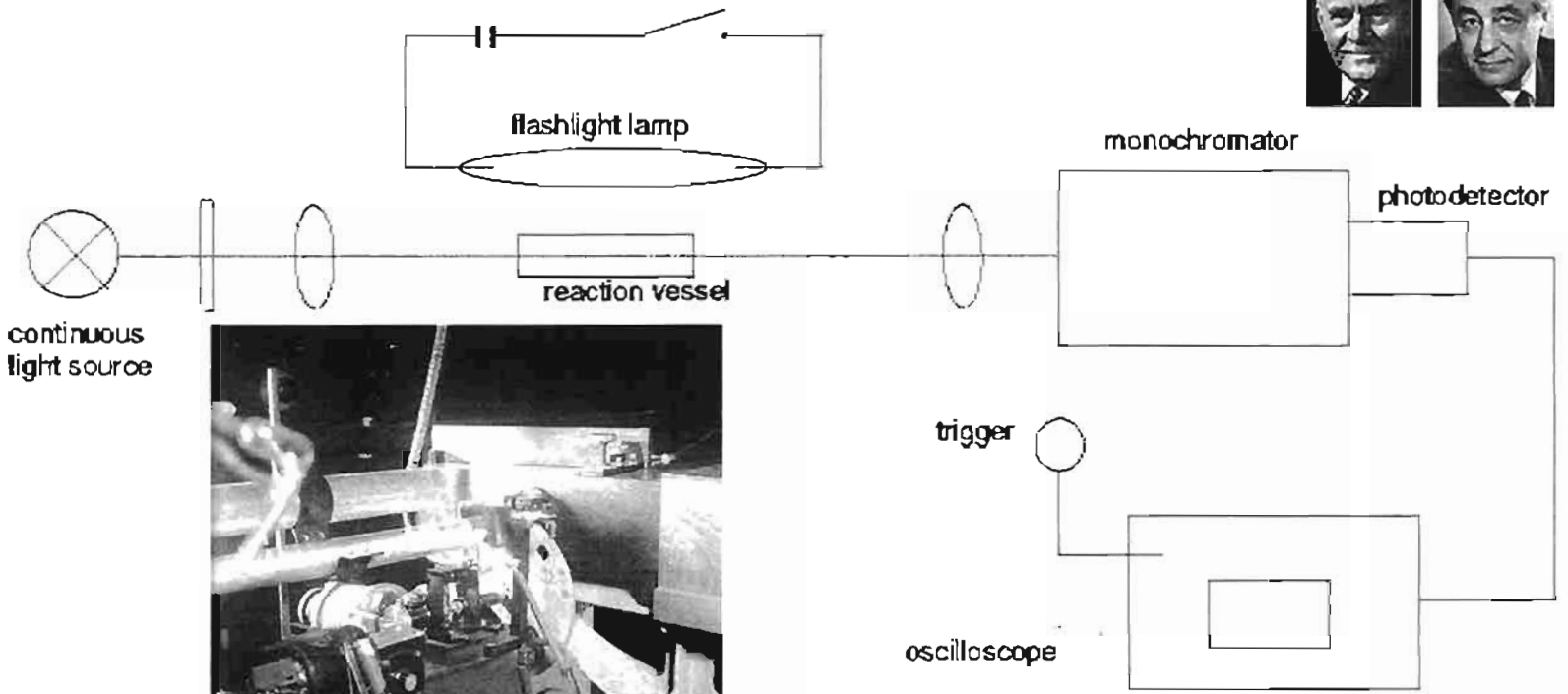
Fosforoscopio de Becquerel

Say "Becquerel" and the average physicist immediately thinks of *Henri Becquerel* (1852-1909) who discovered the phenomenon of **radioactivity** in 1896 while investigating the phosphorescence of uranium compounds. His father, ***Alexandre-Edmond Becquerel*** (1820-1891) is best known for his work on **luminescence** and **phosphorescence**; the scientific dynasty was established by his grandfather *A.C. Becquerel* (1788-1878), who developed the differential galvanometer.





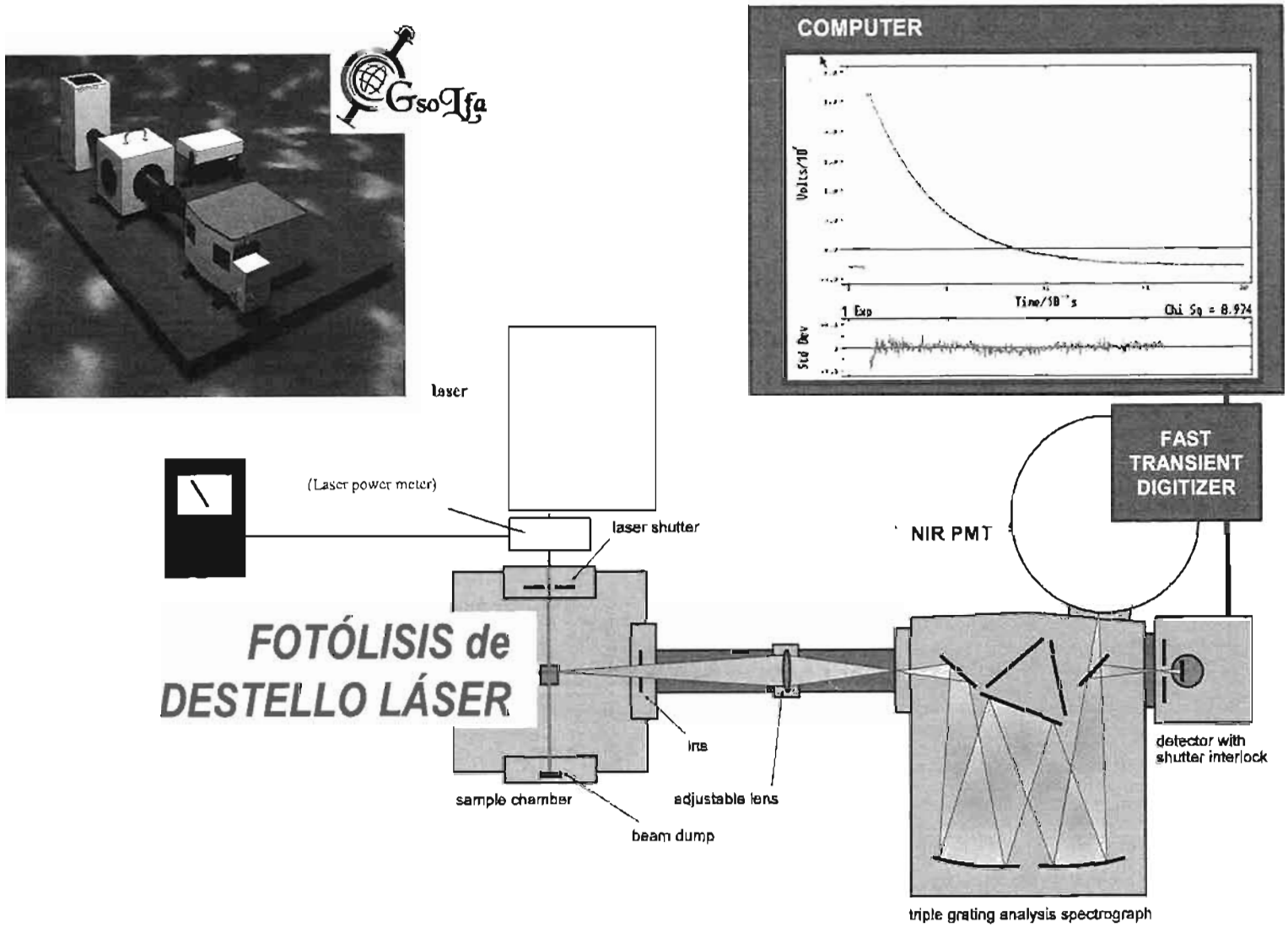
Flash photolysis



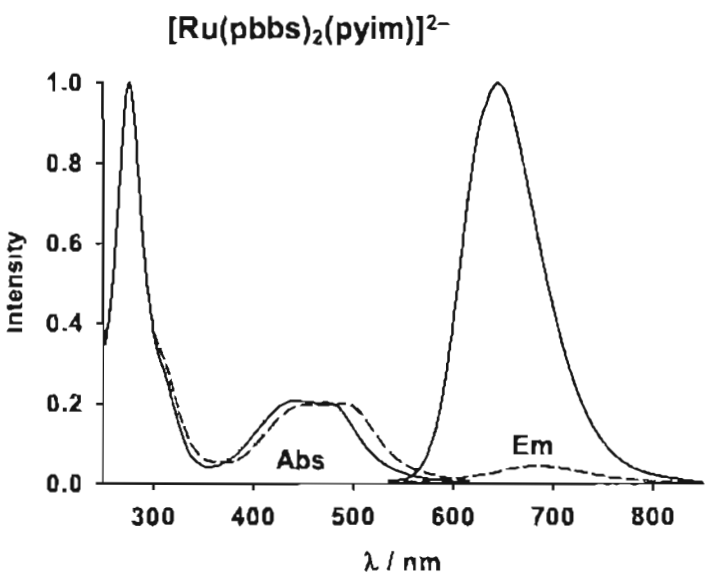
Photograph of the first flash photolysis system at Norrish & Porter laboratory (Cambridge)

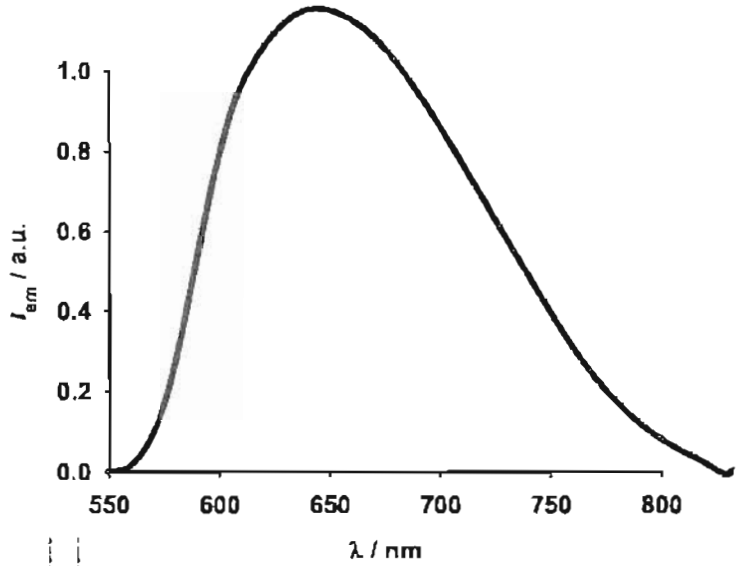
R. G. W. Norrish and G. Porter, Chemical Reactions produced by very high light intensities, *Nature*, **1949**, *164*, 658.

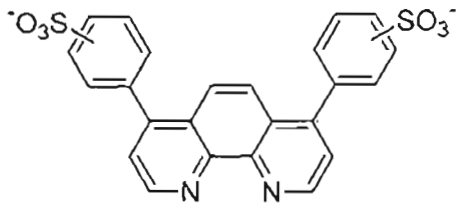
G. Porter, Flash photolysis and spectroscopy – A new method for the study of free radical reactions, *Proc. R. Soc London, Ser A*, **1950**, *200*, 284–300.


COMPUTER
Volts/10
Time/10 s
1 Exp
Chi Sq = 8.974
Std Dev
FAST
TRANSIENT
DIGITIZER
laser
(Laser power meter)
laser shutter
NIR PMT
FOTÓLISIS de
DESTELLO LÁSER
iris
detector with
shutter interlock
sample chamber
adjustable lens
beam dump
triple grating analysis spectrograph

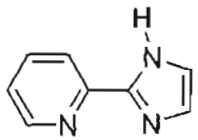
Time-resolved emission spectroscopy (TRES)



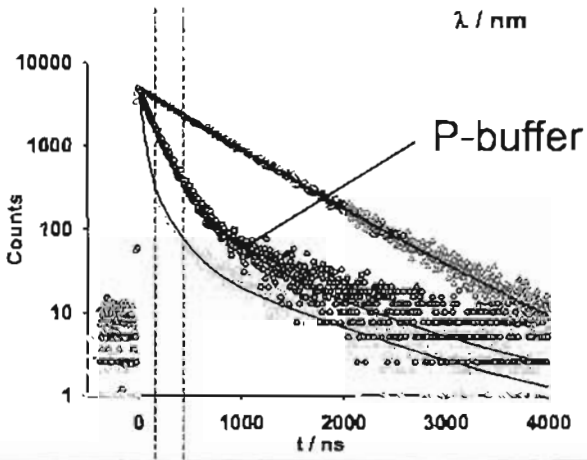




pbbs

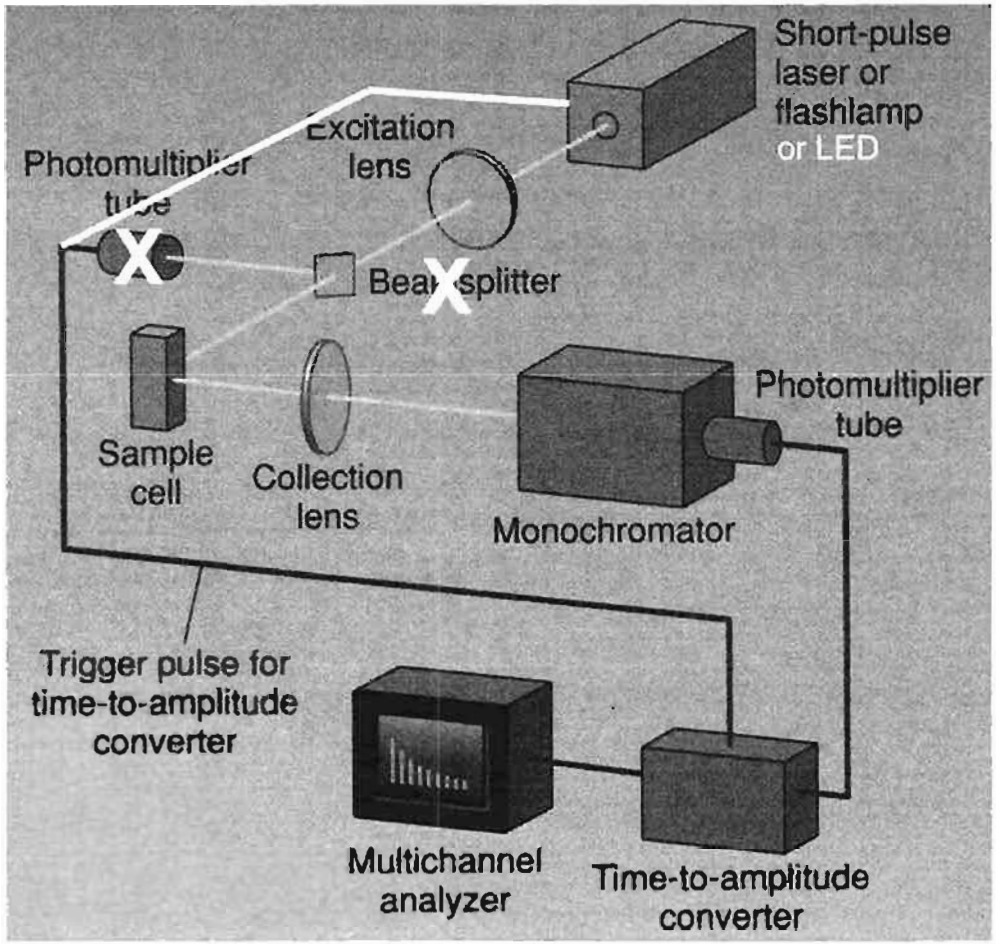


pyim

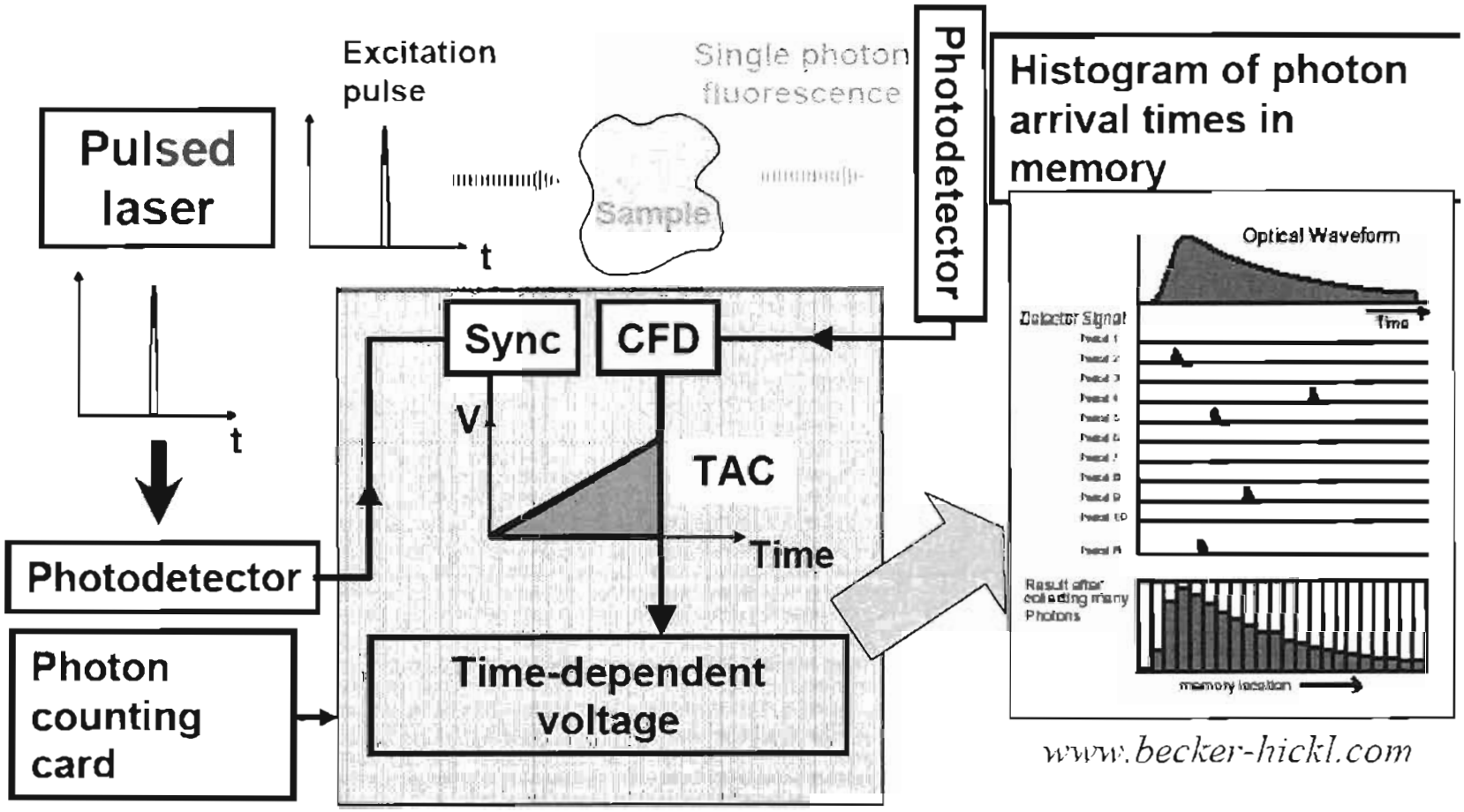


G. Orellana and co-workers, *Anal. Chem.* 2010, *82*, 5195–5204

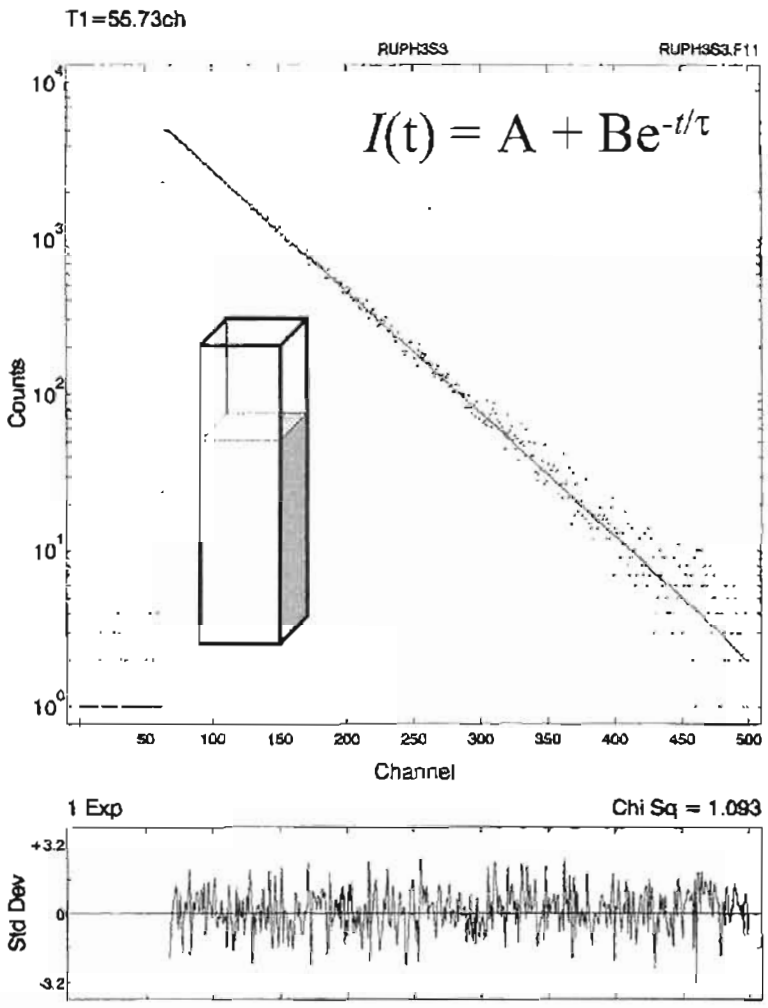
Single-photon timing (SPT, TC-SPC)

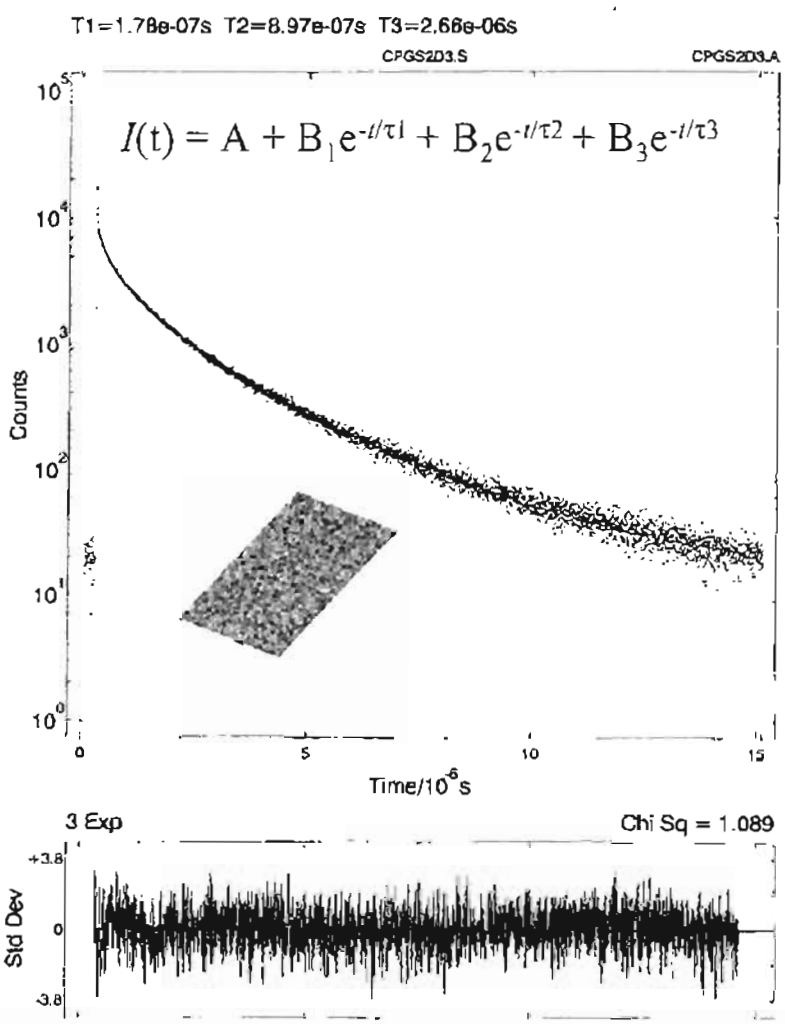


El experimento SPT



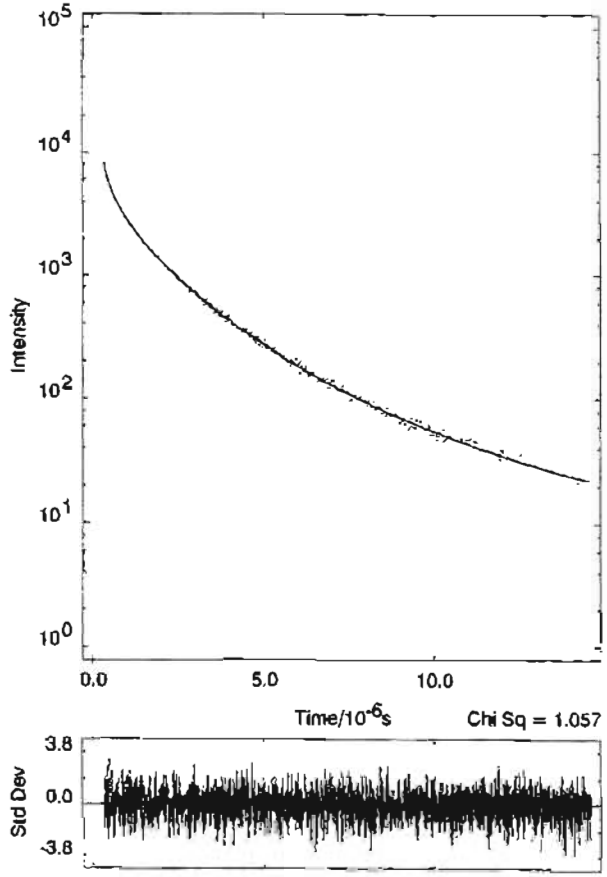
Exponencial vs. multiexponencial

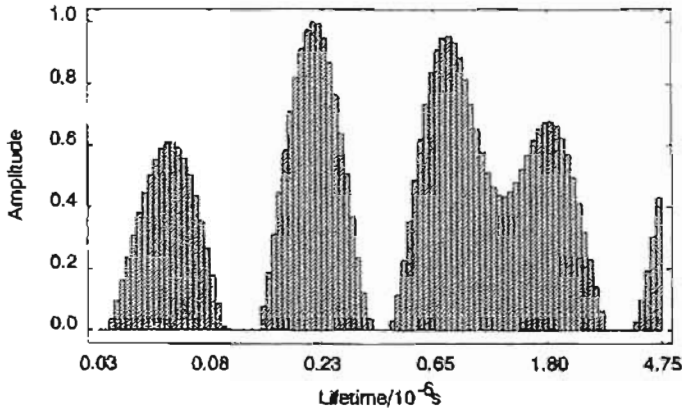




Análisis de distribución

CPGS2D3.S CPGS2D3.DNH
Ex=379nm ExPol=No Em=625nm EmPol=No Temp=25.8 C
CPG-Ru(s2d)3





DISTRIBUTION ANALYSIS

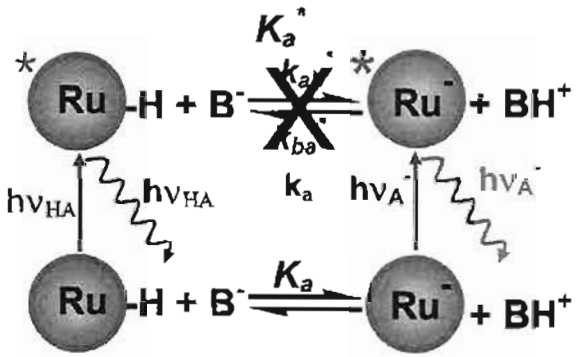
Analysis Mode : High Res

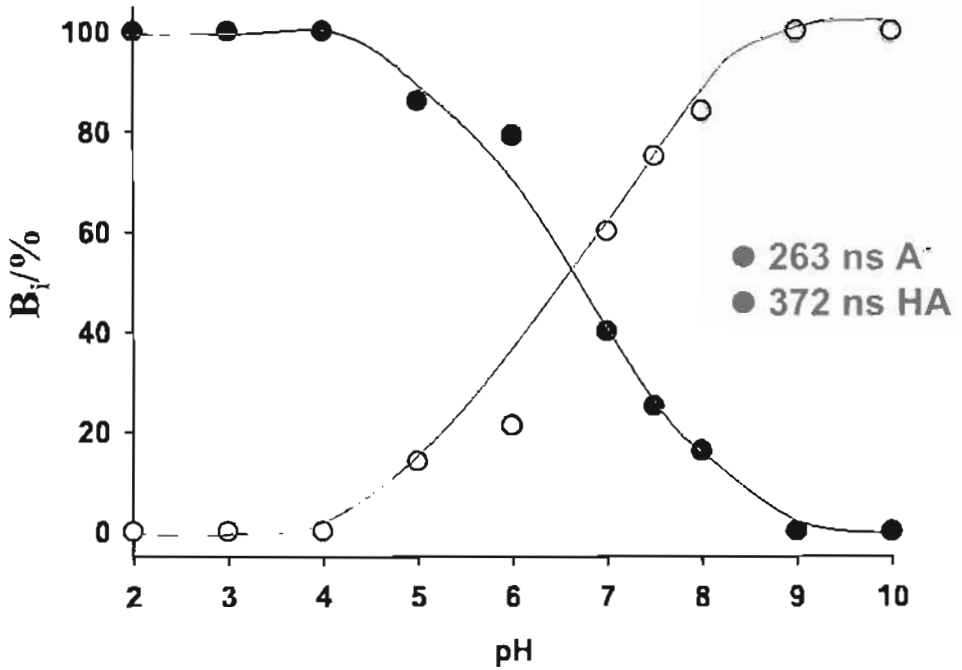
Peak Statistics :

	Mean Lifetime	Std Dev	Rel %
T1	5.866e-08s	1.297e-08s	1.34
T2	2.225e-07s	4.695e-08s	7.74
T3	7.741e-07s	1.798e-07s	28.56
T4	1.831e-06s	4.072e-07s	47.57
T5	4.629e-06s	2.622e-07s	14.80

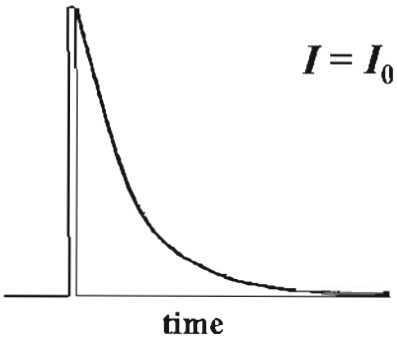
Análisis global

$$I(t) = A + B_1 e^{-t/\tau 1} + B_2 e^{-t/\tau 2}$$

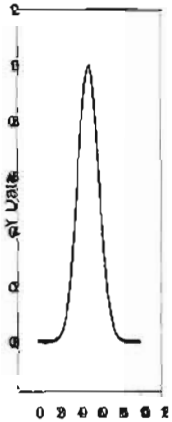




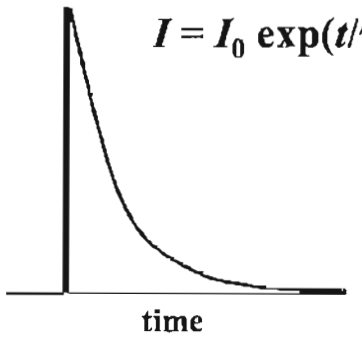
Medida de tiempos de vida cortos: deconvolución de la señal



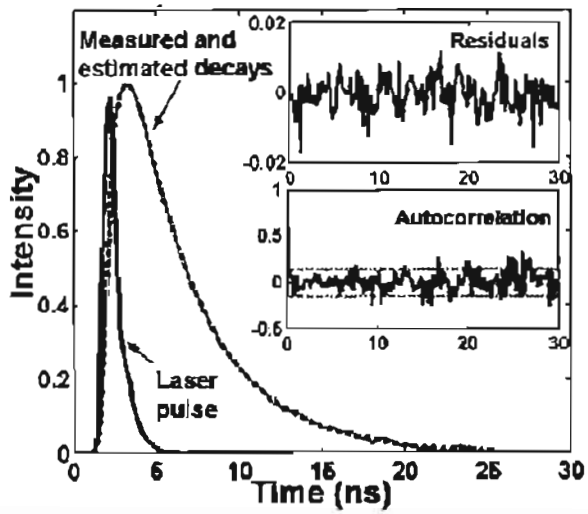
$I = I_0 \exp(t/\tau)$



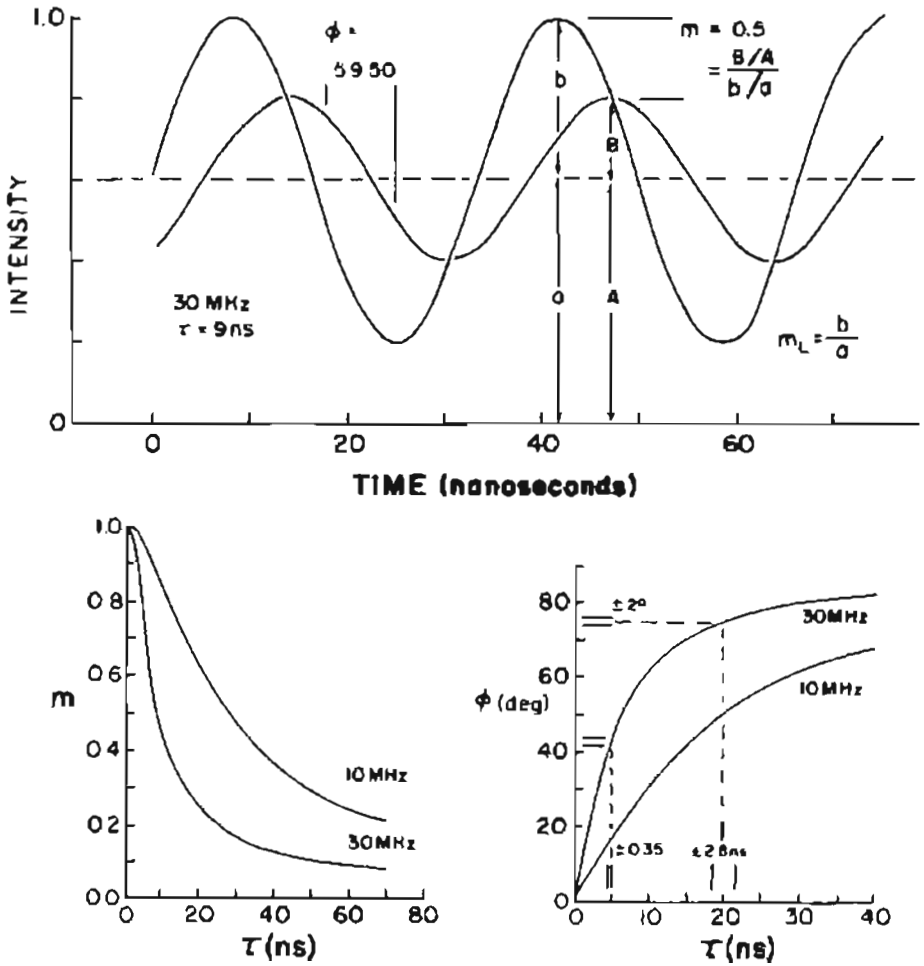
$\otimes$



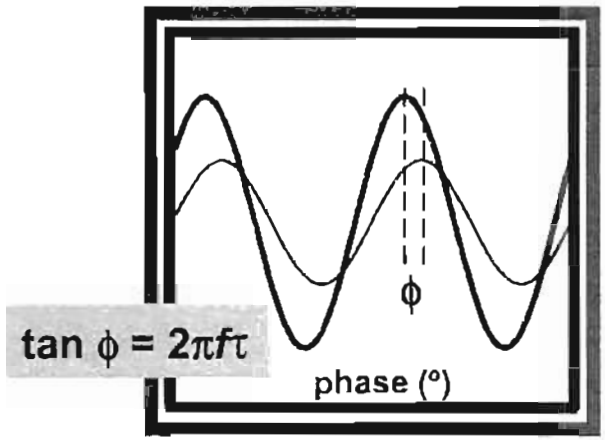
$I = I_0 \exp(t/\tau)$

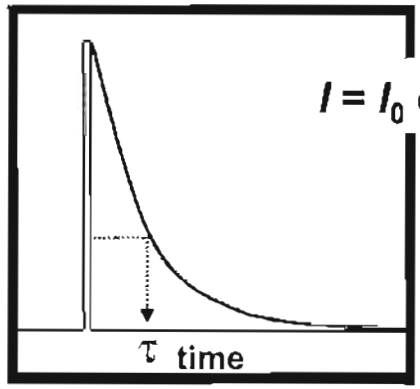


Detección sensible a la fase



Luminescence lifetime (emission kinetics)





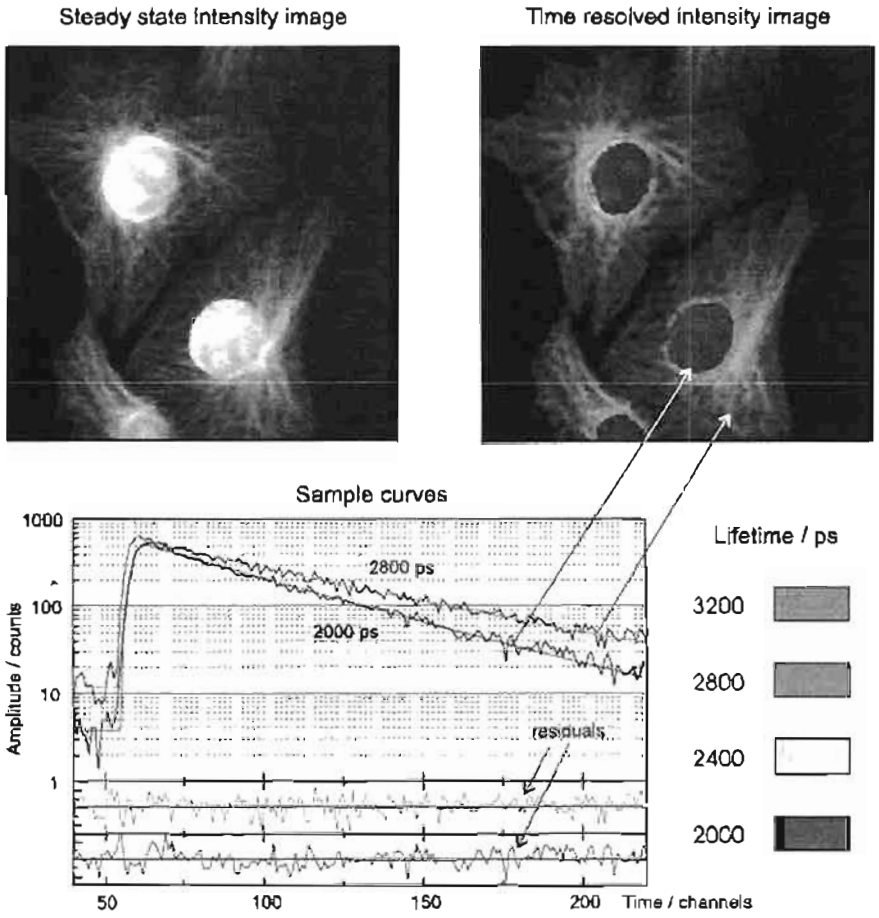
$I = I_0 \exp(t/\tau)$

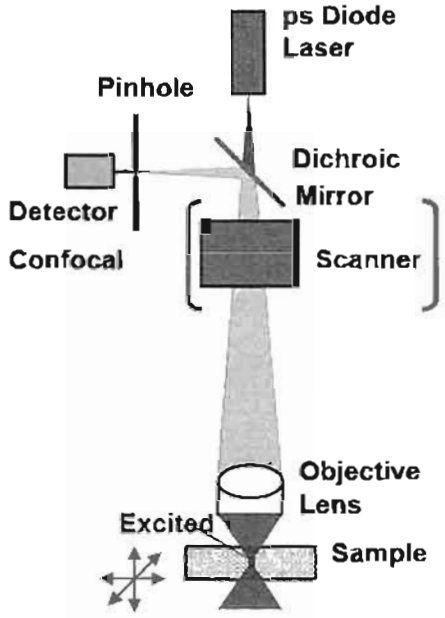
$\tau = 1/k$

- *No interference* from the **ambient light**.
- *No effect* of the **indicator leaching** or **bleaching**.
- *No effect* of the **excitation source intensity** or **photodetector aging**.

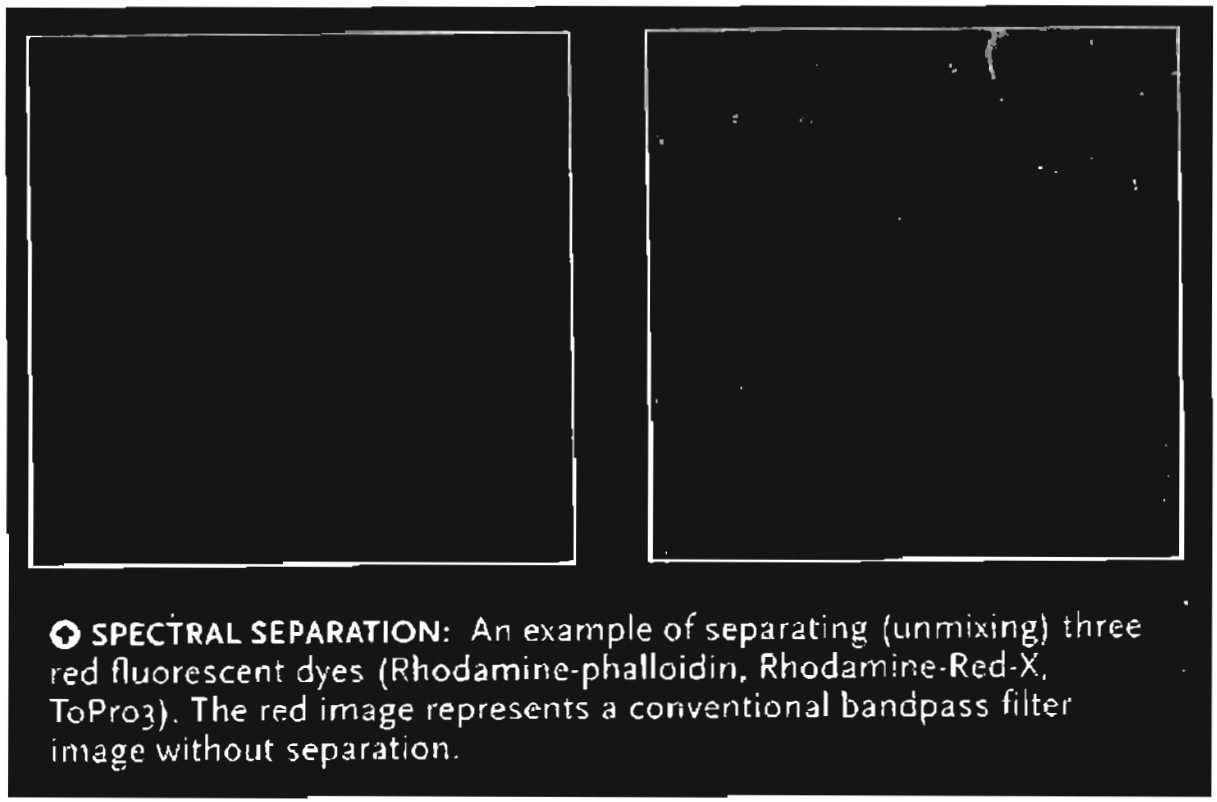
- *More simple* acquisition and data processing *electronics* due to the **limited bandwidth** of the sinusoidal tone(s) used for excitation of the luminescence.
- Possibility of using **cheaper** electro-optic components.

Fluorescence lifetime imaging (FLIM)





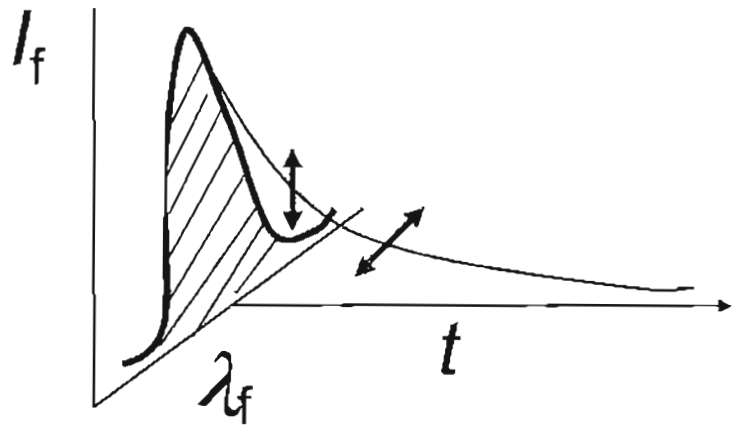
Fluorescence lifetime imaging (FLIM)



SPECTRAL SEPARATION: An example of separating (unmixing) three red fluorescent dyes (Rhodamine-phalloidin, Rhodamine-Red-X, ToPro3). The red image represents a conventional bandpass filter image without separation.

Luminescence: a multi-parametric technique

- ☑ Emission **intensity**
- ☑ Emission **spectrum**
- ☑ Emission **kinetics** ***(lifetime)***
- ☑ Emission **anisotropy** ***(polarization)***

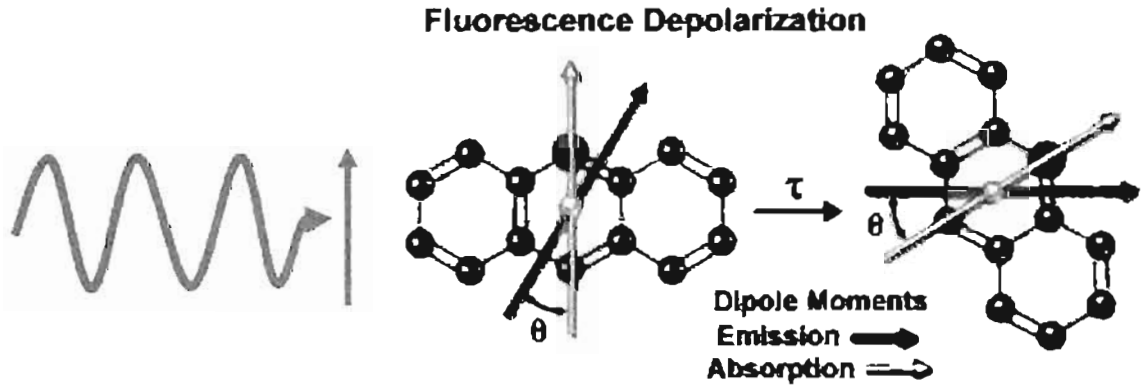


Luminescence polarization (anisotropy)

- When a population of luminophores is illuminated by a **linearly polarized** incident **light**, those whose transition moments are oriented in a direction close to that of the electric vector of the incident beam are **preferentially** excited (*photoselection*).

- Because the distribution of excited luminophores is **anisotropic**, the emitted luminescence is also anisotropic.

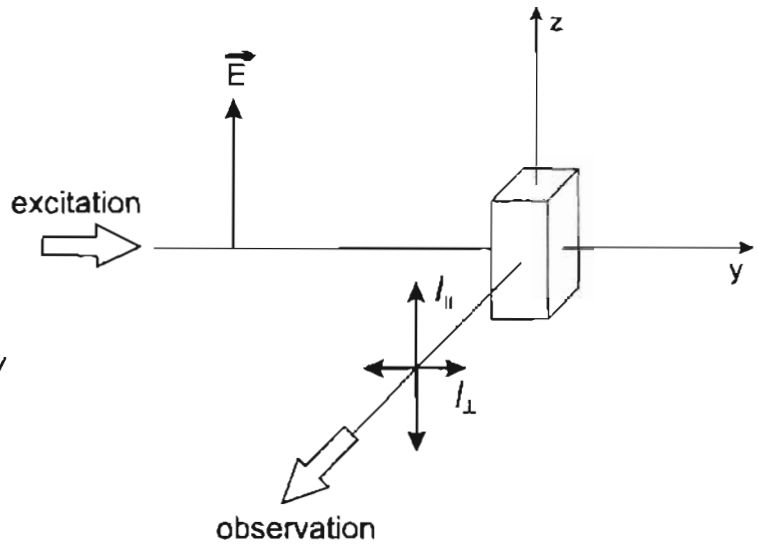
- Any change in direction of the transition moment *during the lifetime* of the excited state will cause this anisotropy to decrease, i.e. will induce a partial (or total) **depolarization** of luminescence.



Luminescence polarization (anisotropy)

Causes of fluorescence **depolarization**

- *non-parallel* absorption and emission transition moments
- torsional *vibrations*
- Brownian *motion*
- to another molecule with different orientation. *transfer of the excitation energy*



Fluorescence polarization measurements can thus provide useful *information* on molecular mobility, size, shape and flexibility of molecules, fluidity of a medium, and order parameters.

polarization ratio

$$p = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

emission anisotropy

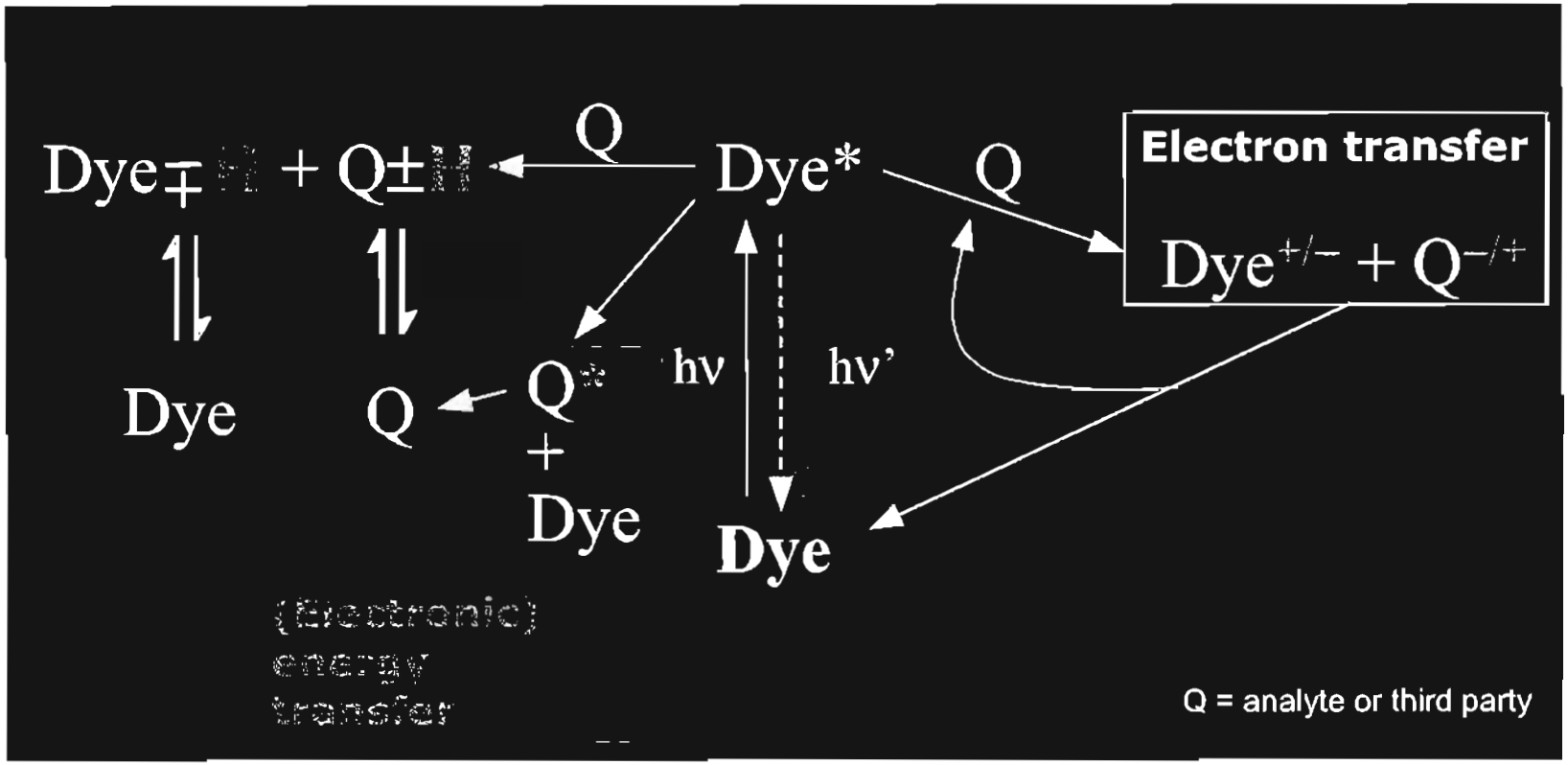
$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}}$$

$I_{tot} = I_{\parallel} + 2I_{\perp}$

$$r = \frac{2p}{3 - p}$$

Principles of reversible *luminescence sensing by photochemical quenching processes*

"Quenching": a decrease or total extinction of the fluorophore emission due to an external agent

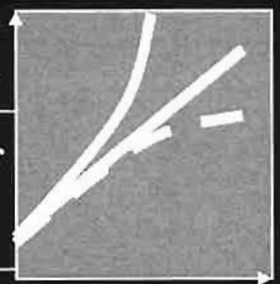


Luminescence lifetime-based sensing by photochemical quenching processes

$I^* + A \rightarrow I^+ + A^-$ $\qquad$ $I^* + A \rightarrow I^- + A^+$

$D^* + A \rightarrow D + A^*$

$$\frac{\tau_0}{\tau} = 1 + K_{SV}[Q]$$



$I^* + HB \Leftrightarrow B + HI^*$

$\uparrow\downarrow k_I$ $\qquad$ $k_{HI}\downarrow\uparrow$

$I + HB \Leftrightarrow B + HI$

$$pK_a^* = pK_i + \log(\tau_{HI}/\tau_I)$$

(ONLY if equilibrium in the excited state is established!)

Radioluminiscencia

WELCOME TO SMART

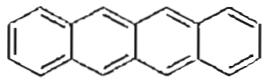
HOTOCH OMIC

MATERIALS !!!

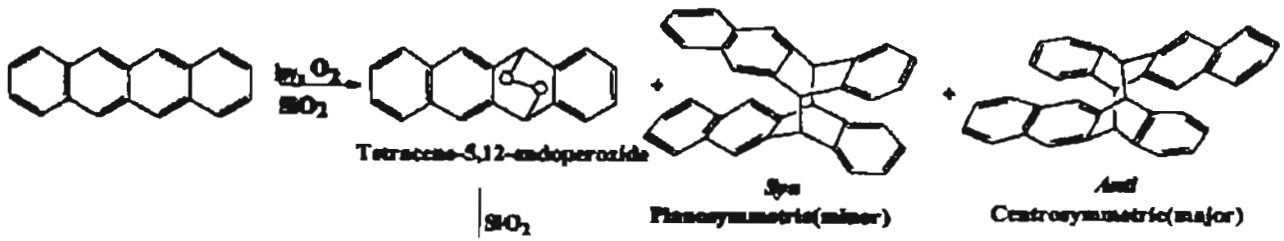
Materiales fotocrómicos

- **Concepto de fotocromismo**
- **Tipos de compuestos y materiales fotocrómicos**
  - Inorgánicos
  - Orgánicos
- **Aplicaciones de materiales fotocrómicos a diferentes productos / tecnologías**

J. Fritzsche, *Compt. Rend. Acad. Sci. (Paris)* **1867**, *69*, 1035.



cambio de color *inducido por la luz* y que es **reversible**



Concepto de fotocromismo *phos-chroma* = luz y color

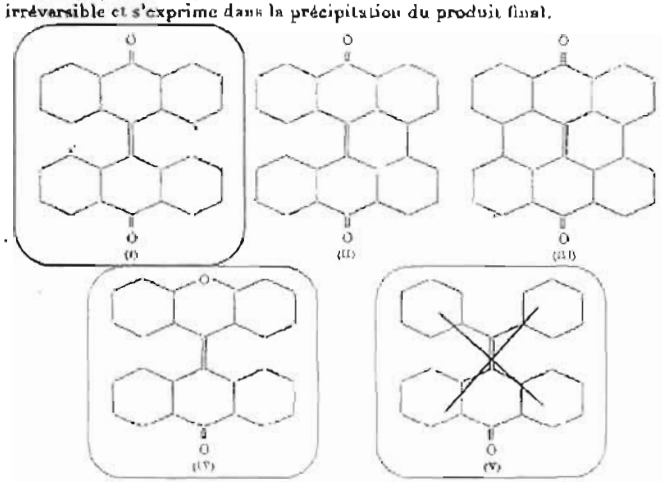
SÉANCE DU 30 OCTOBRE 1950. 903

les éprouvettes sont passives très rapidement et le restent, quel que soit leur état de surface initial. Il en est ainsi pour l'acide sulfurique $d = 1,4$ additionné de 2000 ppm d'acide nitrique à 30°C ou de 20000 à 90°C.

CHIMIE PHYSIQUE. — *Photochromie dans la série de la bianthrone.* Note (*) de M. YEHUDA HIRSHBERG, présentée par M. Antoine Lacassagne.

Dans un travail récent (1) nous avons décrit en détails la thermochromie des dérivés de la bianthrone (I) et de quelques substances apparentées. Dans l'étude de ces phénomènes, un effet additionnel a été observé que nous voudrions décrire ici, sans discuter sa base théorique.

Si une solution de bianthrone est irradiée par la raie 3650 Å à — 60° C, sa couleur verte se change en rouge brunâtre. L'effet est très net déjà après une minute d'irradiation. Il est d'un caractère transitoire et réversible, car en réchauffant la solution à la température ordinaire on récupère la bianthrone inaltérée. Evidemment, ce phénomène est différent de la réaction photochimique qui se produit à température ordinaire et qui donne l'hélianthrone (II) et la naphthodianthrone (III) (2). Cette dernière réaction est irréversible et s'exprime dans la précipitation du produit final.



(*) Séance du 9 octobre 1950.
(1) HIRSHBERG, LÖWENTHAL, BERGMANN et PULLMAN, *Bull. Soc. Chim.* (sous presse).
(2) BROCKMANN et MUHLMANN, *Ber.*, 83, 1950, p. 348.

904 ACADÉMIE DES SCIENCES.

La xanthylidène-anthrone (IV) montre le même comportement. A — 70° et en une minute, la couleur verte assez faible de la solution devient très intense; la couleur disparaît en réchauffant, et la substance peut être récupérée quantitativement à partir de la solution. A température ordinaire, l'irradiation produit un précipité insoluble.

En raison du fait que les bianthrones substituées en 4.4' ne présentent pas de thermochromie à température élevée (1), il est intéressant de remarquer qu'elles se comportent comme la bianthrone (I) quand on irradie leurs solutions à — 60° :

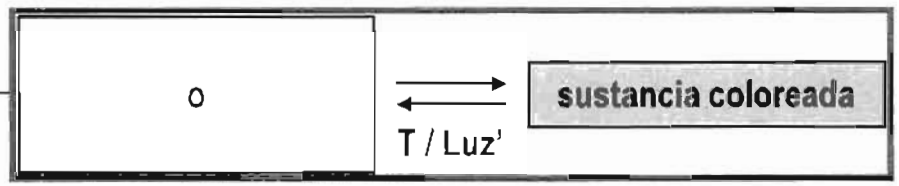
Diméthoxy-4.4' bianthrone : verdâtre → vert foncé ;
Diméthyl-4.4' bianthrone : verdâtre → bleu foncé;
Dibromo-4.4' bianthrone : vert jaunâtre → vert foncé.

A la température ordinaire, ces trois substances ne sont pas affectées par une irradiation de durée moyenne.

L'effet est limité aux bianthrones et à la xanthylidènanthrone; les benzhydrylidène-anthrones (V) ne le présentent pas.

Estudiado desde *mediados del sXIX*
- iluminación con luz UV-Visible
- cambio de color o aparición del mismo
- transformación rápida
- reversible (con temperatura o luz)
- reproducible con otros colorantes...

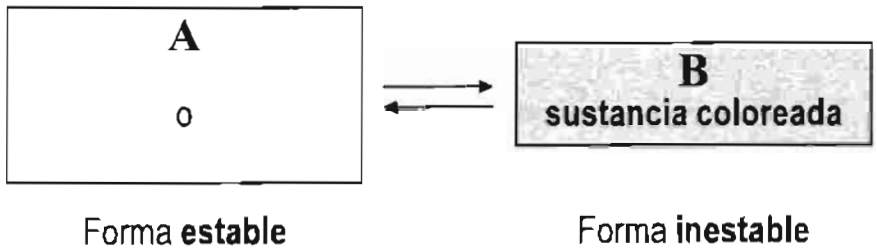
... pero no con todos... ¿con cuáles?

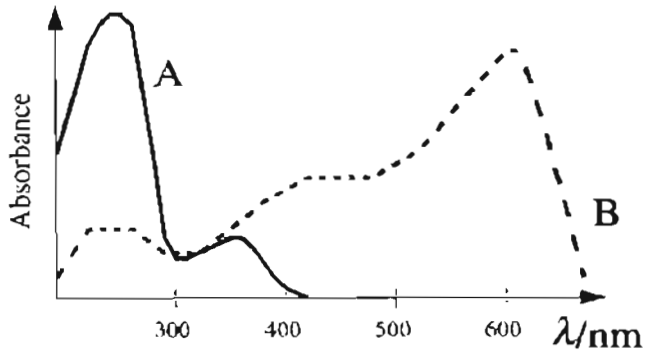


Compt. Rend. Acad. Sci. (Paris) 1950, 231, 903-904. Chem. Eur. J. 2006, 12, 3345-3354.

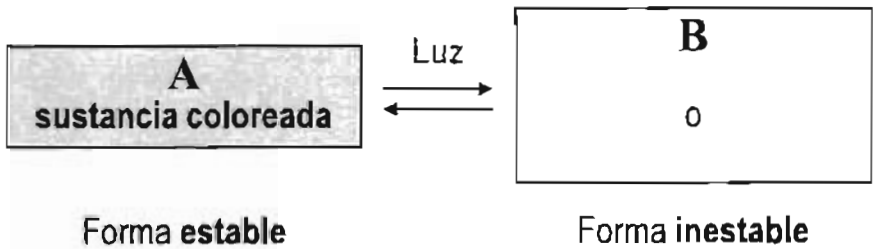
Tipos de fotocromismo

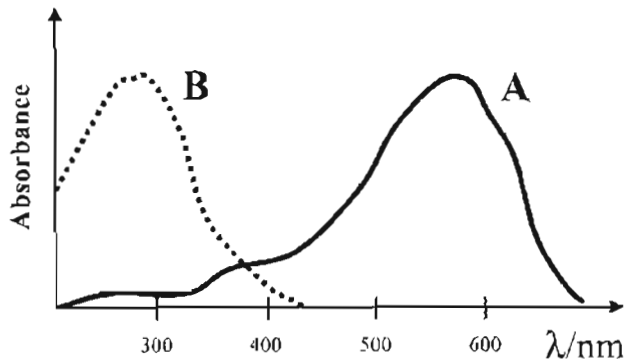
FOTOCROMISMO POSITIVO





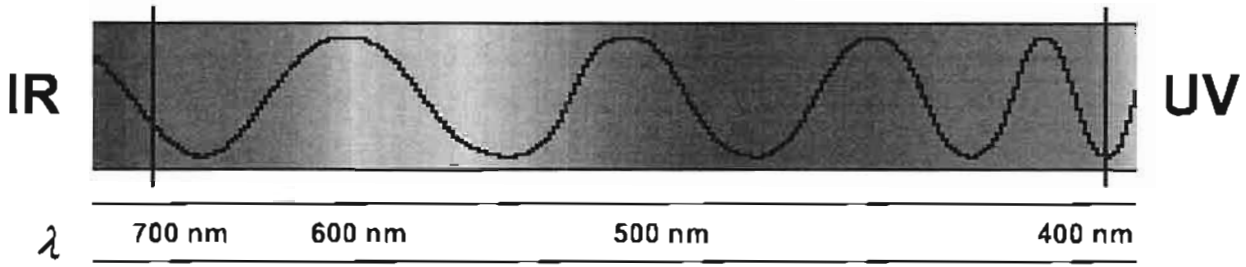
FOTOCROMISMO NEGATIVO O *INVERSO*





[1] *Pure Appl. Chem.* 2001, *73*, 639-665.

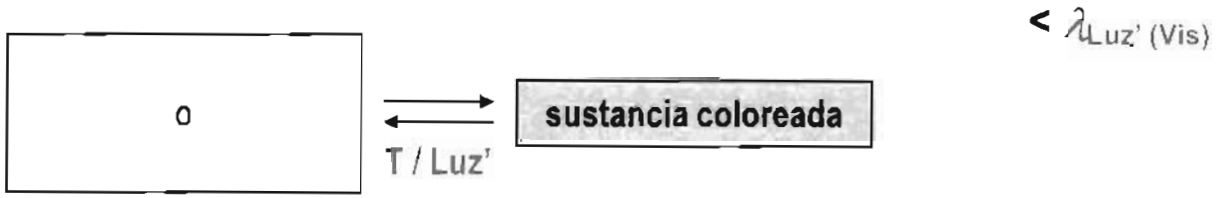
El espectro de luz visible y su color...



La luz absorbida y el color observado...

λ Wavelengths absorbed (nm)	Observed color
380–460	yellow
380–500	orange
440–560	red
480–610	purple
540–650	blue
380–420 and 610–700	green

Tipos de fotocromismo



- Tipo T: *revierte térmicamente*
  - Más usados en ***aplicaciones convencionales***:

  Lentes oftálmicas
  Decoración
  Textiles
  Tintas y barnices
  Impresión de seguridad

- Tipo P: *revierte fotoquímicamente*
  - Más usados en ***aplicaciones tecnológicas***:

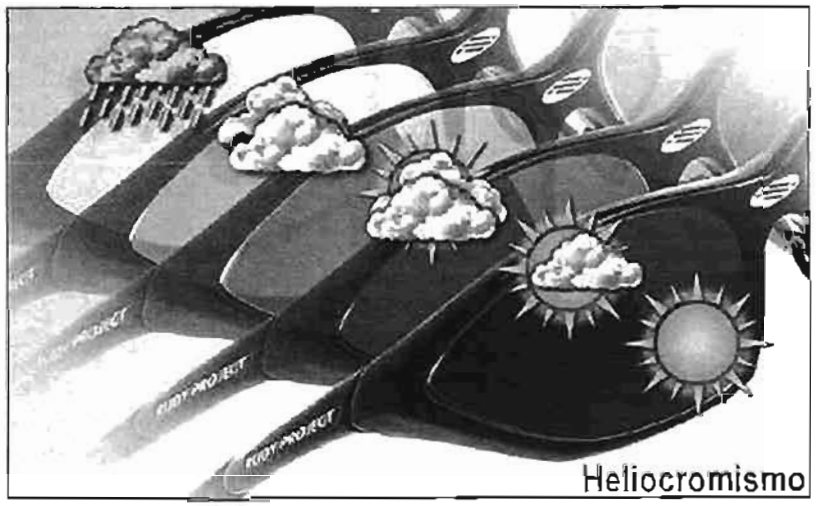
  Superficies / Movimiento mecánico
  Colorantes funcionales en:
  - *Electrónica*
  - *Química*
  - *Comunicación / Transducción*
  - *Computación ...*

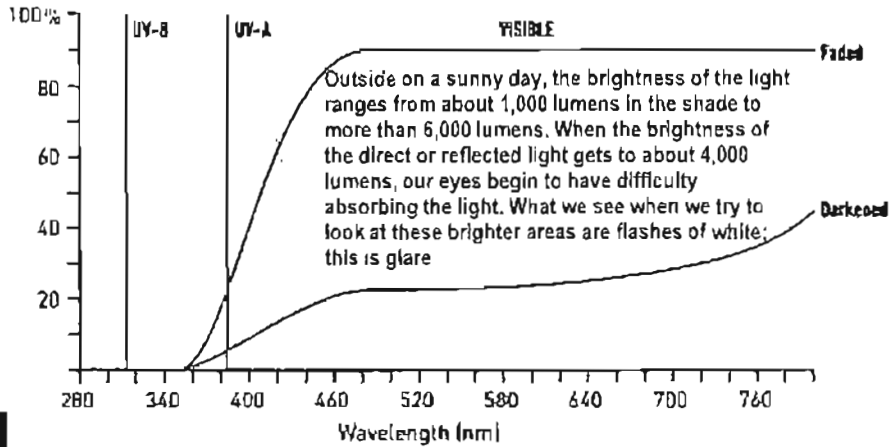
  interruptores o aparatos moleculares optoelectrónicos
  (molecular switches / devices)

J. Color. Technol. 2009, 125, 249-261.

Comercialización de los primeros materiales fotocrómicos, 1960s

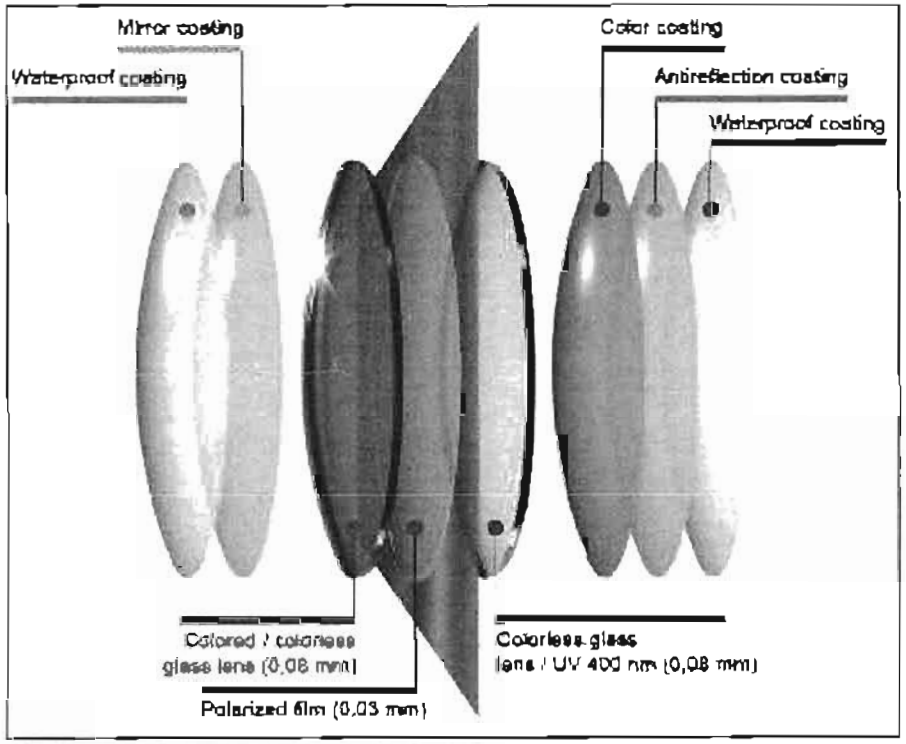
Stanley Donald Stookey He was a research director at **Corning Glass Works** for 47 years doing R & D in glass and ceramic development. His inventions include Fotoform, CorningWare, Cercor, Pyroceram and Photochromic Ophthalmic glass eyewear

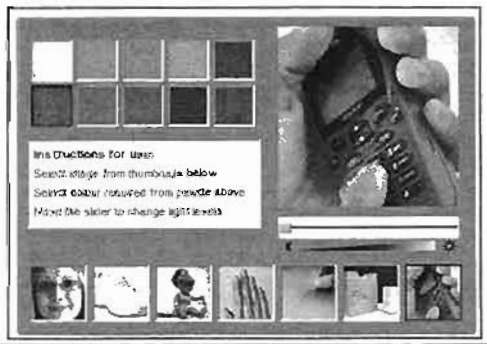


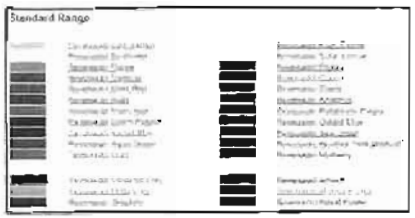


I+D+i en materiales fotocrómicos 1960/2010

- Al principio se utilizaron materiales inorgánicos: **vidrio** y **haluros de plata**
- Modernamente se usan **plásticos** y **colorantes orgánicos**
  - Más robustos
  - Más ligeros
- Actualmente se están desarrollando **múltiples aplicaciones**



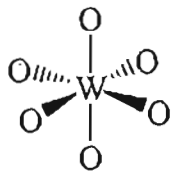


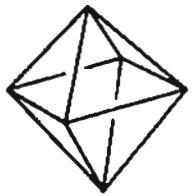


Now you see it – now you don't...
Attention-grabbing effects involving the sudden generation or dissapearance of colour in response to light

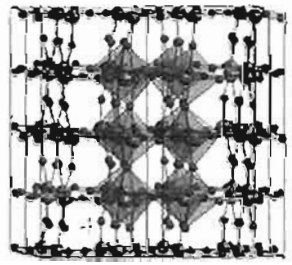
Color. Technol. 2009, 125, 249-261.

Materiales fotocrómicos inorgánicos: WO_3





Material semiconductor basado en óxido metálico



Efecto fotocrómico observado en películas delgadas de material amorfo (nanopartículas de 1-5 nm Ø)

- Existencia de defectos estructurales superficiales (vacantes de O y cationes W^{n+} no equivalentes) que conducen a la separación de cargas + y e^-
- Los e^- estabilizados son los responsables de la absorción del fotón
- WO_3 amorfo presenta mejor fotocromismo que el cristalino debido a su mayor cantidad de defectos
- El calor o la presencia de O_2 disminuyen el fotocromismo
- La presencia de medios próticos (agua, alcohol) aumenta el fotocromismo

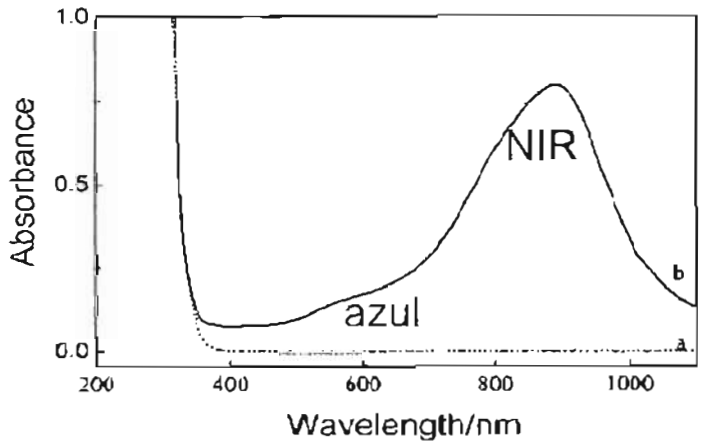


Fig. 1 UV-vis absorption spectra of tungsten oxide film: (a) before and (b) after UV-light irradiation. The film was prepared from the oxide colloid with a 0.3 M concentration of oxalic acid and pH ~ 1.[47]

[47] J. Mater. Chem. 2007, 17, 4547-4557

Materiales fotocrómicos inorgánicos: WO_3

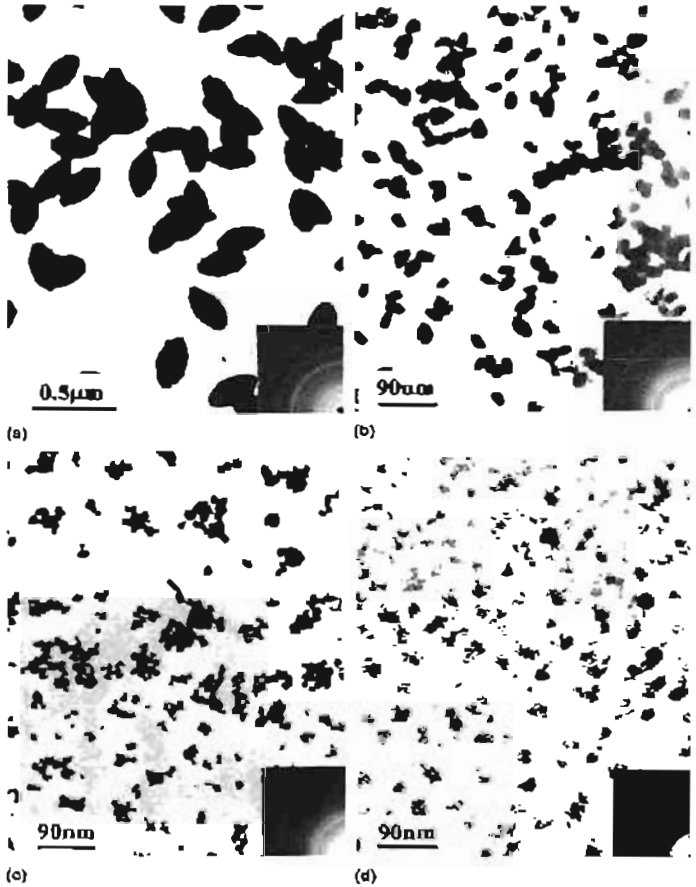


Fig. 3 TEM micrographs and electron diffraction patterns of nanocrystalline oxide films prepared from colloid solutions with different oxalic acid concentrations: (a) 0.1, (b) 0.3, (c) 0.4, and (d) 0.8 M.[47]

- A menor Ø de partícula se desplaza el máximo de absorción hacia menores λ

- A menor Ø de partícula son más amorfas, aumentando el fotocromismo

- La mayor concentración de oxalato atrapa los huecos (vacantes de O) suprimiendo la recombinación electrón-hueco

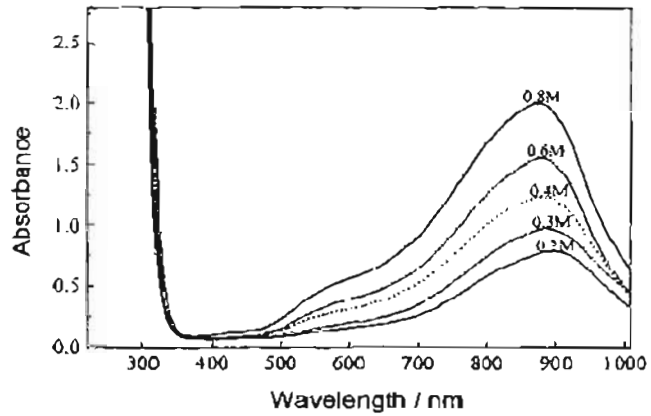


Fig. 2 UV-vis absorption spectra of tungsten oxide film with different oxalic acid concentrations after UV-light irradiation, where the pH was fixed at 1.[47]

Materiales fotocrómicos inorgánicos: WO_3

El efecto fotocrómico se puede mejorar mediante dopaje con nanopartículas de Au o de otros óxidos (MoO_3, ZnO)

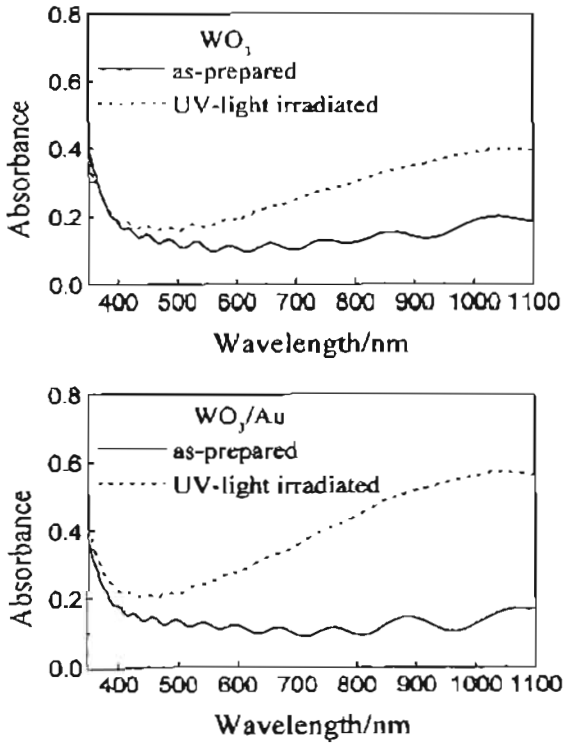


Fig. 5 Absorption spectra for thin films of WO_3 and WO_3–Au before and after UV-light irradiation for 3 min in air.[56]

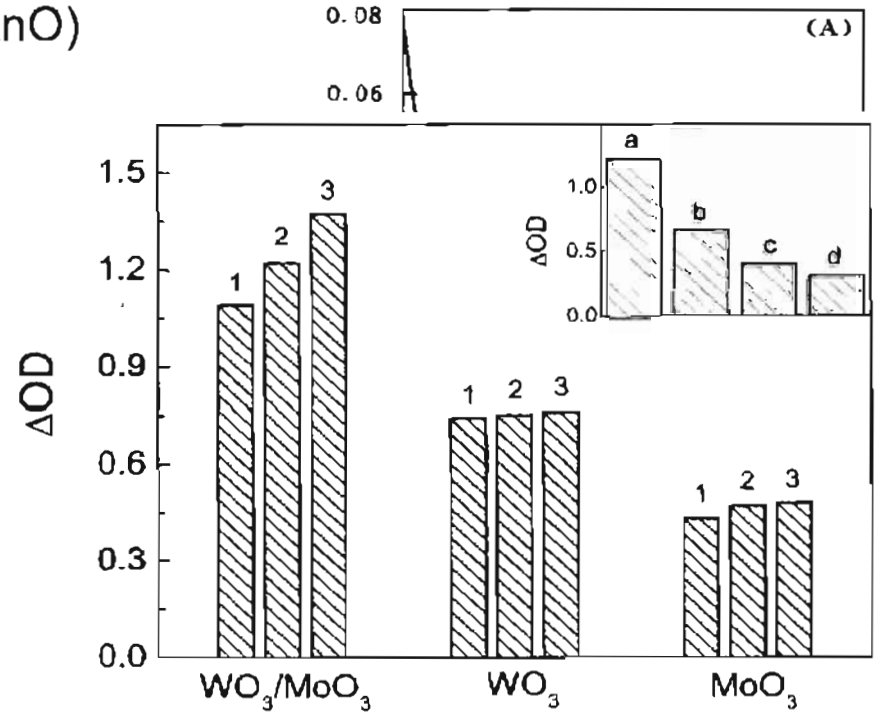


Fig. 7 Photochromic response at 800 nm of 92% WO_3–8% MoO_3, WO_3, and MoO_3 thin films after 5 min UV-light irradiation in N_2 in different vol% of C_2H_5OH vapor: (1) 0.25%, (2) 0.5%, and (3) 1%. Inset: photochromic response of a 92% WO_3–8% MoO_3 thin film in 0.5 vol% vapors of (a) ethanol, (b) methanol, (c) *n*-propanol, and (d) isopropanol.[80]

after 1 min UV-light irradiation. Inset shows the dependence of $\Delta OD_{WO3-ZnO}/\Delta OD_{WO3}$ at 900 nm on the concentration of ZnO.[33]

Materiales fotocrómicos inorgánicos: WO_3

Reversibilidad del efecto fotocrómico

- En general del WO_3 presenta alta fatigabilidad tras la primera decoloración térmica ⇒ 1 ciclo

- La combinación de WO_3 con moléculas orgánicas (sales de amonio $R–NH_3^+$) mediante autoensamblaje de capas permite obtener materiales híbridos con las ventajas de ambos tipos de compuestos:

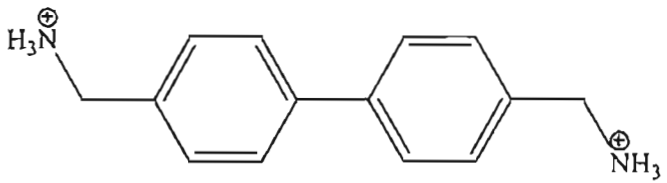
  Inorgánicos: fortaleza, estabilidad térmica, resistencia química

  Orgánicos: ligereza, flexibilidad, versatilidad

- La presencia de los grupos amonio forma puentes de H que facilitan la separación hueco/e^- aumentando el fotocromismo y permitien aumentar el nº de ciclos

- Al poner las muestras coloreadas en aire a la oscuridad revierten al color inicial

(la presencia de O_2 destruye las vacantes de O, más rápidamente al calentar)



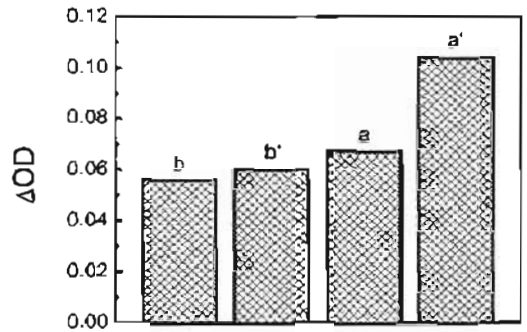
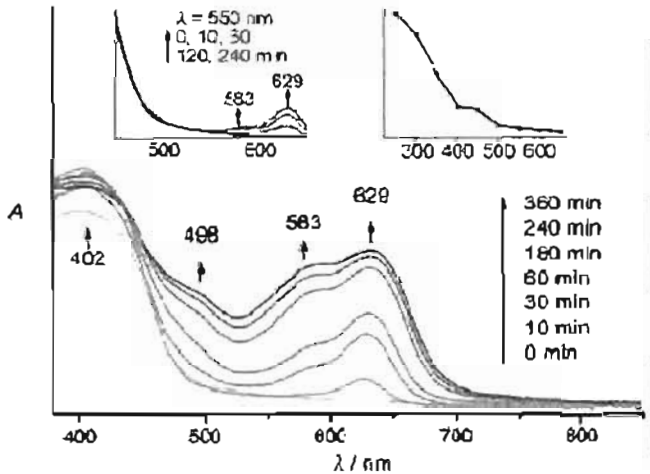
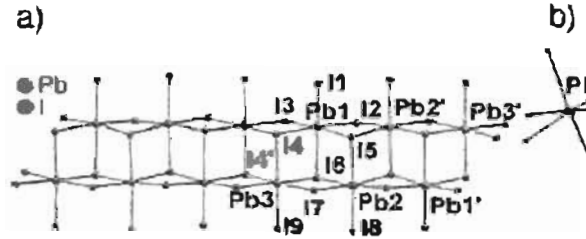


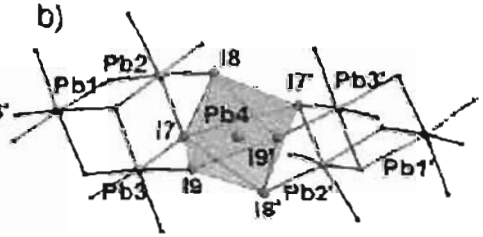
Fig. 13 Photochromic response at 900 nm of (a, a') a 28-layer WO_3–1,10-DAD SAM film and (b, b') a 40-layer WO_3–4,4'-BAMBp SAM film. (a,b): As-prepared or bleached films; (a',b'): the films after 3 min UV-light irradiation in air.[103]

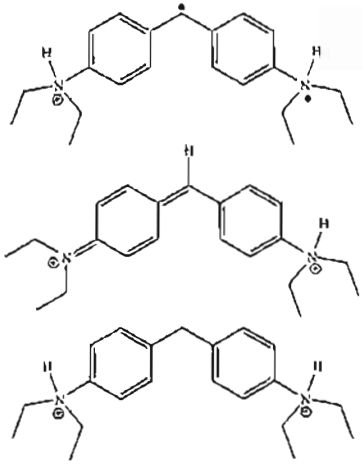
Materiales fotocrómicos híbridos inorgánico/orgánico: iodoplumbatos

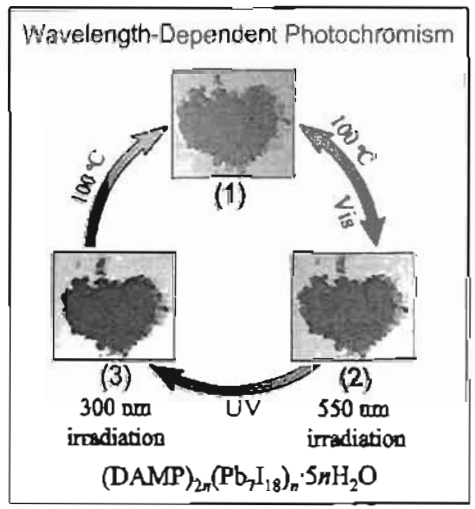
Material semiconductor híbrido basado en haluro metálico











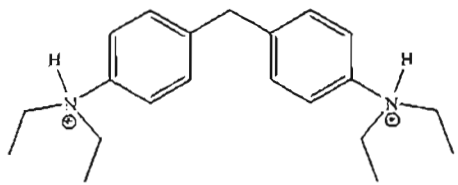
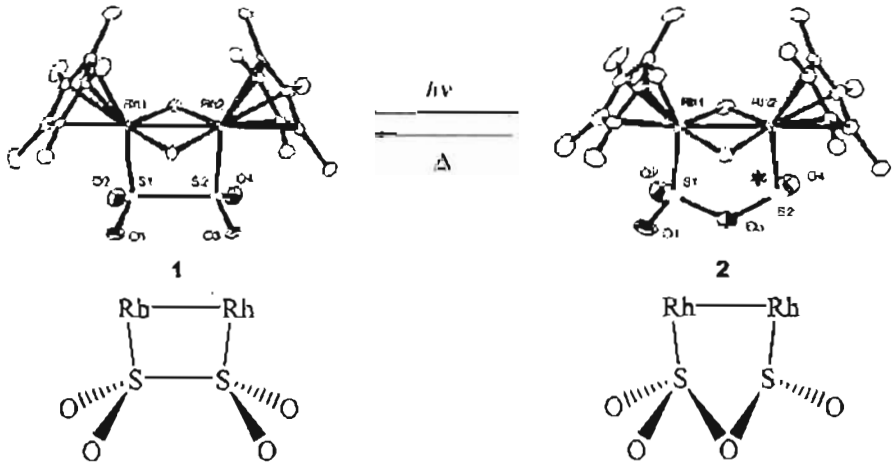


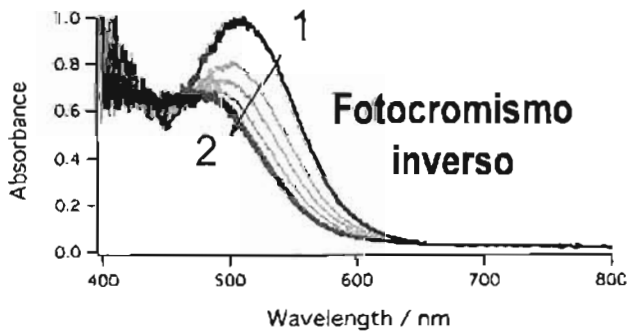
Figure 4. Spectral and color changes of the title compound upon repeated irradiation at 300 nm at 25°C. Left inset: Spectral changes of the compound upon repeated irradiation at 550 nm at 25 °C. Right inset: Plot of absorbance at 498 nm after irradiation at various wavelengths for 10 min. The powder samples of **1**, **2**, and **3** are shown on the right.

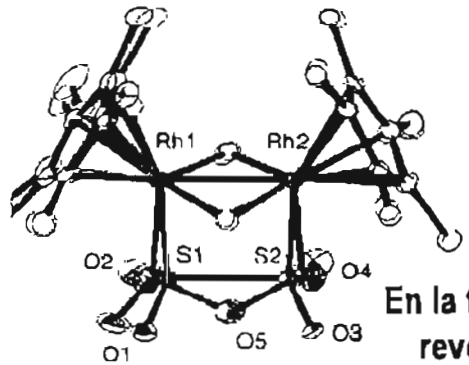
Angew. Chem. Int. Ed. 2008, 47 4149-4152.

Materiales fotocrómicos híbridos: complejos organometálicos

Complejo dinuclear de Rh





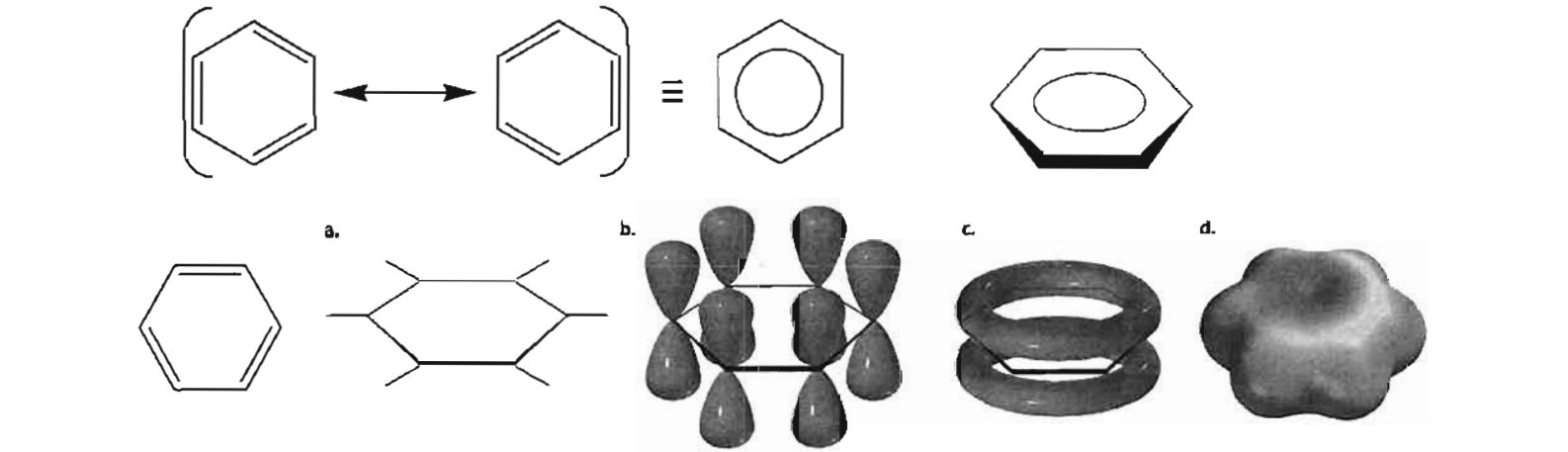


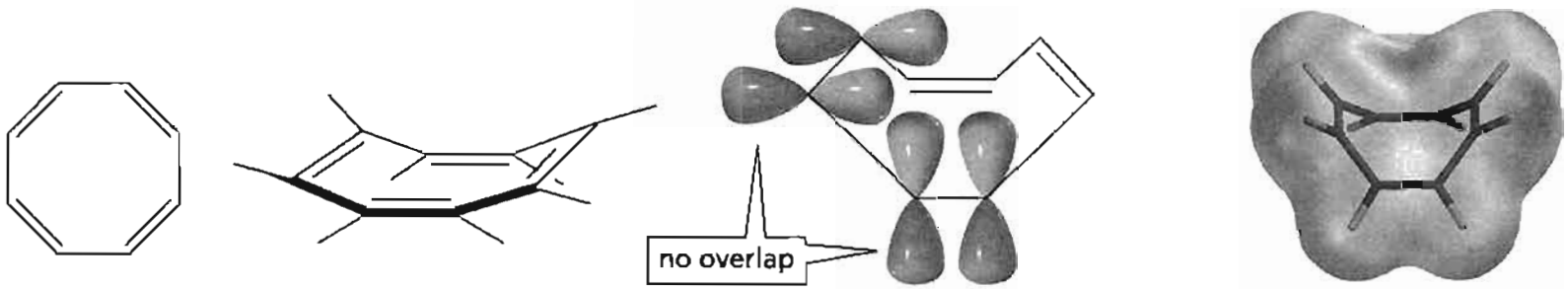
Irradiation time-resolved UV-vis spectra of **1** (blue) to **2** (red) in micro-crystalline powder

(1) *Angew. Chem. Int. Ed.* 2006, 45, 6473-6476.

En la transformación reversible la red cristalina se reorganiza y varía su volumen un 1%

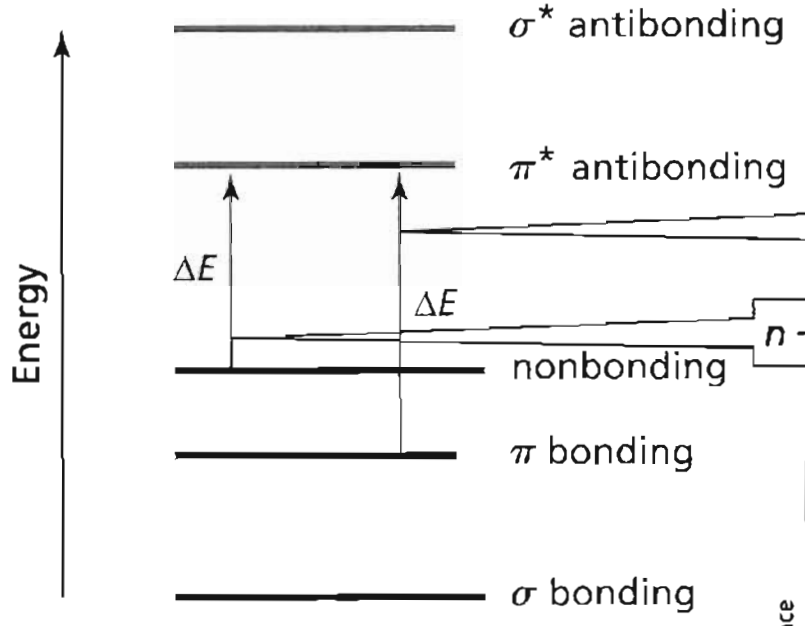
Materiales fotocrómicos orgánicos: unos fundamentos de Q. Org. ...





cyclooctatetraene

Materiales fotocrómicos orgánicos: unos fundamentos de Q. Org. ...

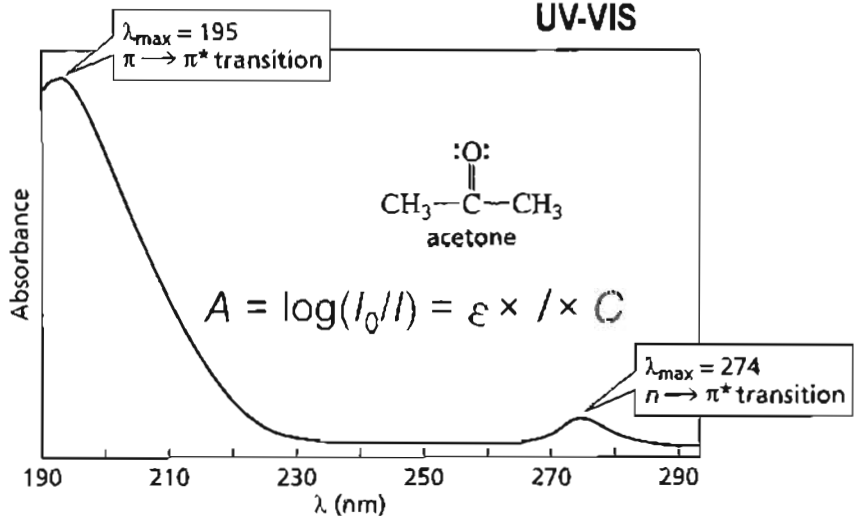


La luz UV y/o VIS pueden causar distintos tipos de transiciones electrónicas

$\pi \longrightarrow \pi^*$ transition

$n \longrightarrow \pi^*$ transition

Los compuestos orgánicos con e^- π (dobles enlaces) presentan espectros de absorción de luz UV-VIS

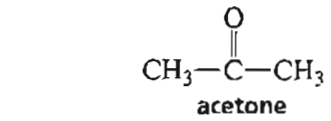


Se observan bandas de absorción VIS en el espectro si el compuesto absorbe luz visible (tiene color)

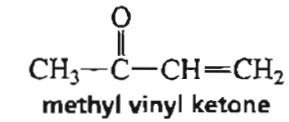
Se observan bandas de absorción UV en el espectro si el compuesto absorbe luz UV (no tiene color)

Materiales fotocrómicos orgánicos: unos fundamentos de Q. Org. ...

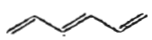
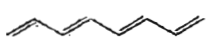
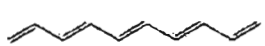
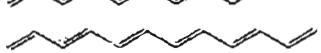
Effecto de la conjugación en λ_{max}

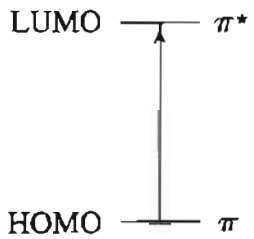


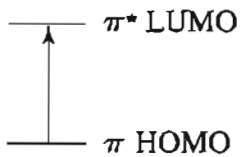
$n \longrightarrow \pi^*$ λ_{max} = 270 nm
$\pi \longrightarrow \pi^*$ λ_{max} = 187 nm



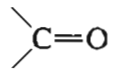
λ_{max} = 324 nm
λ_{max} = 219 nm

Table 8.3 Values of λ_{max} and ε for Ethylene and Conjugated Dienes		
Compound	λ_{max} (nm)	ε
$H_2C{=}CH_2$	165	15,000
	217	21,000
	256	50,000
	290	85,000
	334	125,000
	364	138,000

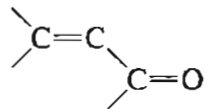




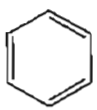
nonconjugated π electrons

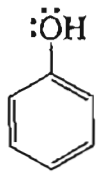


conjugated π electrons

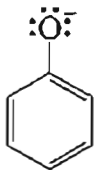


λ_{max} y ε se incrementan al aumentar el nº de dobles enlaces conjugados

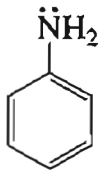

benzene
255 nm



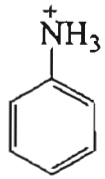
phenol
270 nm



phenolate ion
287 nm



aniline
280 nm



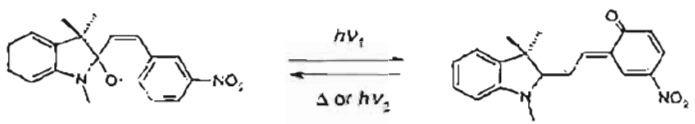
anilinium ion
254 nm

λ_{max} y ε también varían en función de los grupos de átomos (grupos funcionales) unidos a los dobles enlaces conjugados

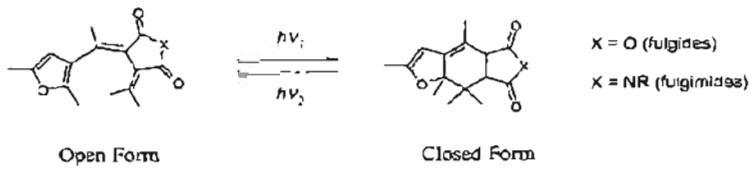
Materiales fotocrómicos orgánicos

- Reacciones **pericíclicas** (6 e⁻ π) entre *moléculas isómeras*

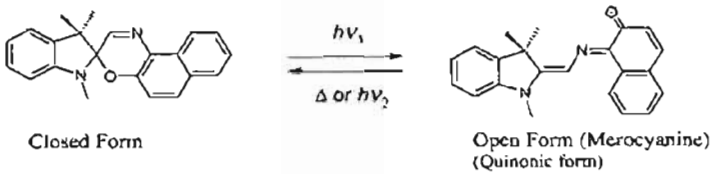
Spiropyrans



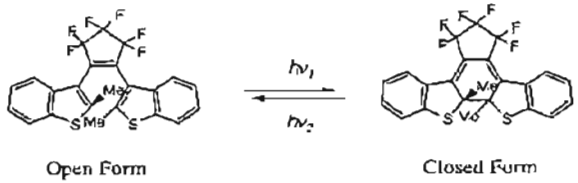
Fulgides and fulgimides



Spirooxazines

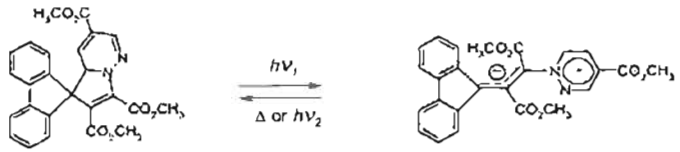


Diarylethenes and related compounds



Chromenes

Spirodihydroindolizines

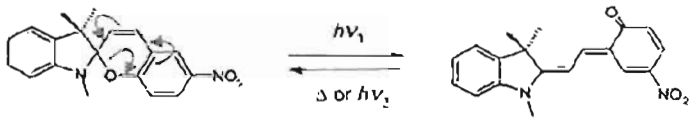


🗀 *Pure Appl. Chem.* 2001, 73, 639-665.

Materiales fotocrómicos orgánicos

- Reacciones **pericíclicas** (6 e^- π) entre *moléculas isómeras*

Spiropyrans



Closed Form

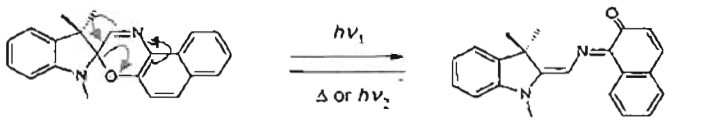
Open Form (Merocyanine)
(Quinonic form)

Fulgides and fulgimides

Open Form

Closed Form

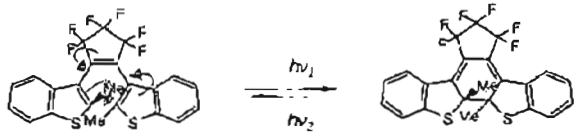
Spirooxazines



Closed Form

Open Form (Merocyanine)
(Quinonic form)

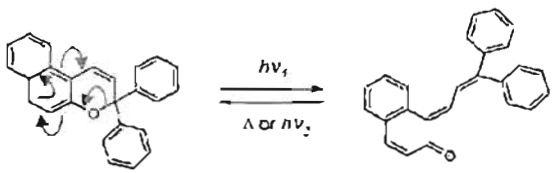
Diarylethenes and related compounds



Open Form

Closed Form

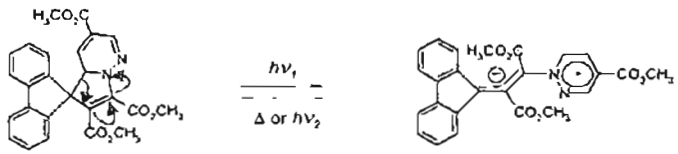
Chromenes



Closed Form

Open Form

Spirodihydroindolizines



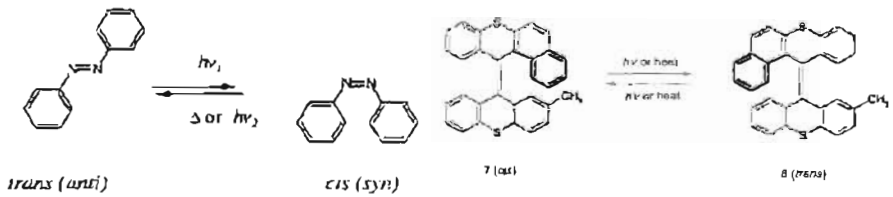
Closed Form

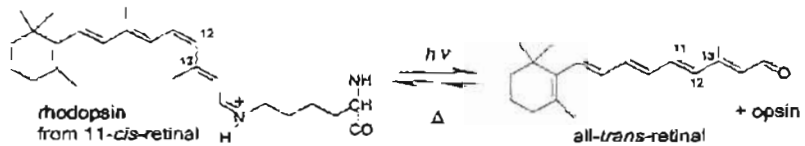
Open Form

Materiales fotocrómicos orgánicos

• Isomerización *cis-trans*

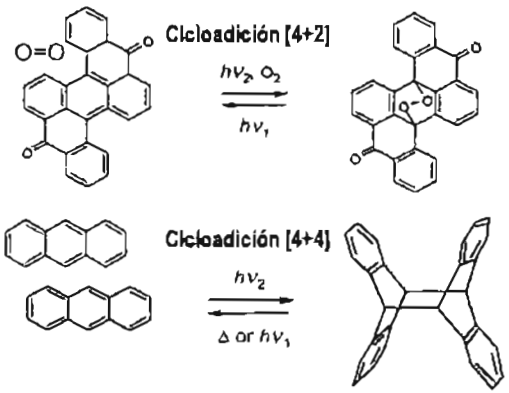
Azo compounds





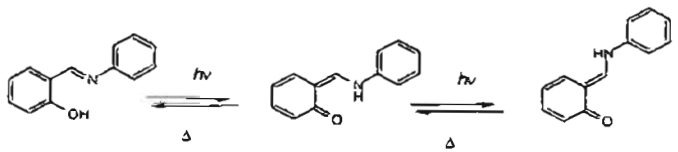
• Reacciones pericíclicas (6 e⁻ π)

Polycyclic aromatic compounds



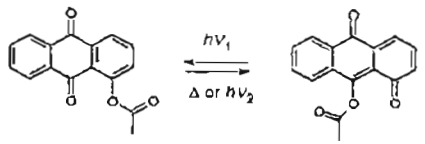
• Transferencia protónica (H^+)

Anils and related compounds (hydrogen transfer)



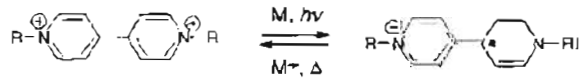
• Transferencia de grupo funcional

Polycyclic quinones (periaryloxyquinones)



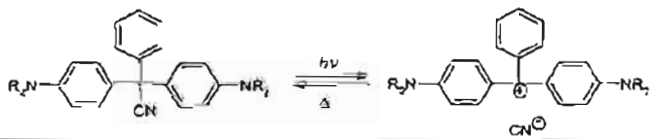
• Transferencia electrónica (e^-)

Viologens



• Disociación

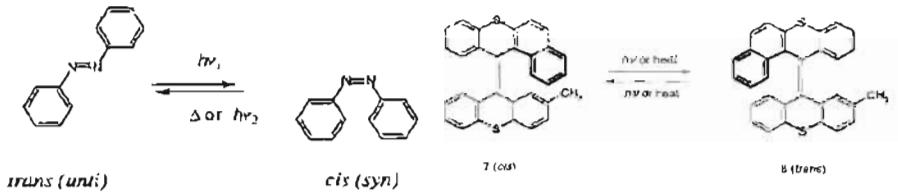
Triarylmethanes



Materiales fotocrómicos orgánicos

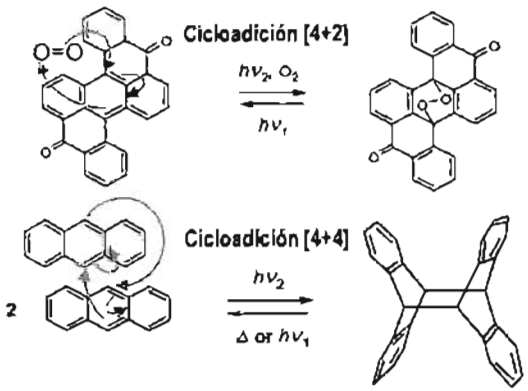
• Isomerización *cis-trans*

Azo compounds



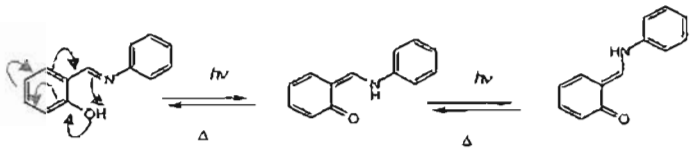
• Reacciones pericíclicas (6 e⁻ π)

Polycyclic aromatic compounds



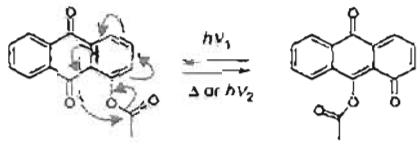
• Transferencia protónica (H^+)

Anils and related compounds (hydrogen transfer)



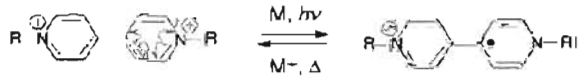
• Transferencia de grupo funcional

Polycyclic quinones (periaryloxyquinones)



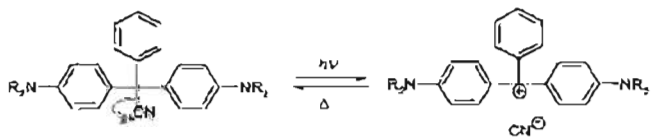
• Transferencia electrónica (e^-)

Viologens



• Disociación

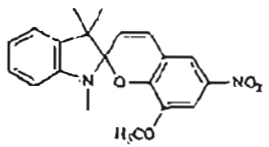
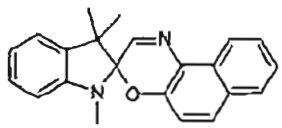
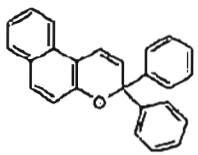
Triarylmethanes



Parámetros fotocrómicos importantes

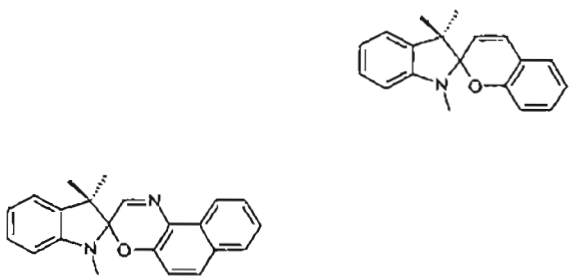
- **Colorabilidad**, $A_0(\lambda)$
  Capacidad para desarrollar color tras un pulso de luz, $A_0(\lambda) = k_{(I_0)} \times \Phi_{col} \times \varepsilon_B \times C_A$
- **Fatiga**
  Disminución de la capacidad de fotoactivación con el tiempo por la degradación del colorante (típicamente por oxidación) ⇒ disminuye nº ciclos de activación
- **Vida media**
  En irradiación continua, t^* o $t_{1/2}$
  Tiempo que tarda en alcanzar la mitad de la absorbancia inicial
  $t_{1/2} = \Delta A_0{}^{max}{}_{\lambda}/2$
- **Constante cinética de decoloración térmica**
  Cinética de 1er orden, k_Δ

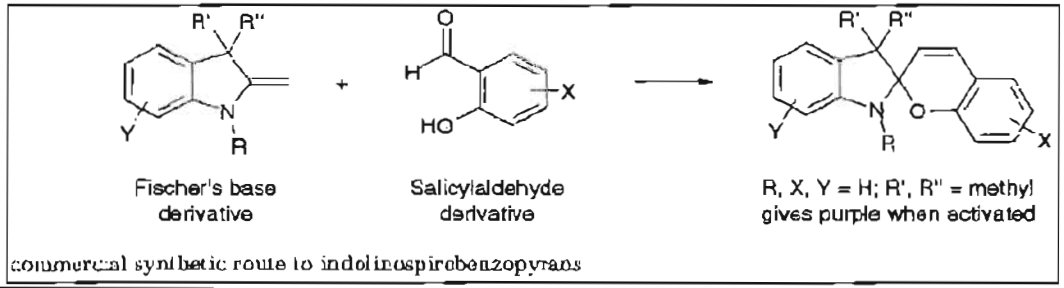
Table 1. Photochromic parameters in diluted toluene solutions.

Compound (2.5×10^{-5}M) in toluene	Colored Form λ_{max}/nm	$A_0(\lambda)$ $t\to0$	k_Δ /s^{-1}	$t^*_{(A_{1/2})}$
 6-nitro-8-methoxy BIPS	615	4.6	0.02	7.5 min
 1,3,3-trimethylspiro[indoline-naphthoxazine]	594	1.08	0.54	8.5 h
 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran	432	0.84	0.09	7.5 h

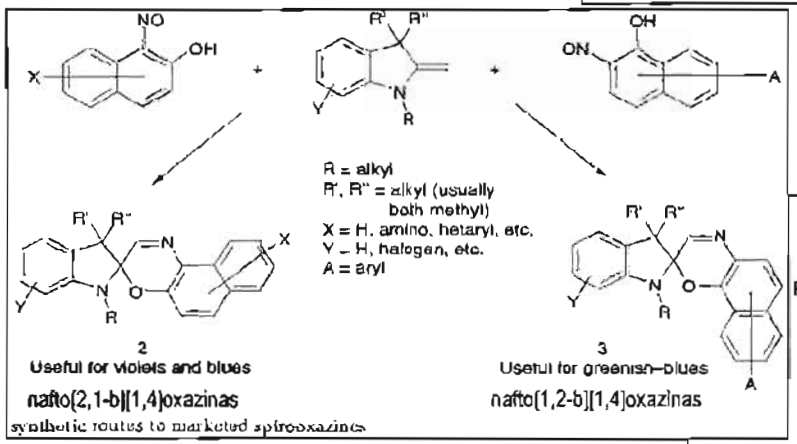
Características de colorantes fotocrómicos industrialmente importantes

- Alta eficiencia de **fotocoloración** por luz UV / Vis
- **Decoloración** moderadamente eficiente por calor / luz
- Fotodegradación poco eficiente ⇒ ***Estable***
- Facilidad de **síntesis** en cantidad suficiente

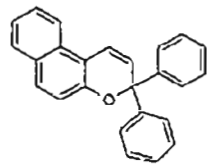


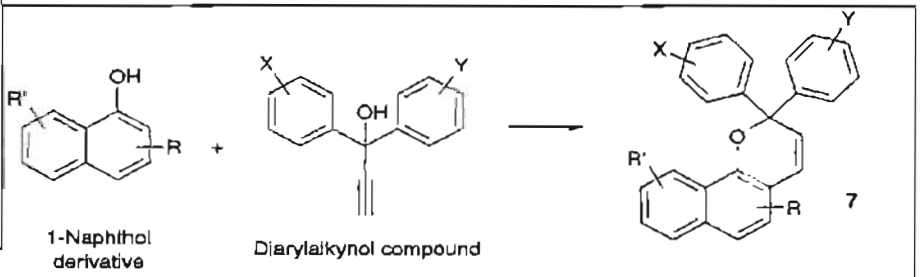


commercial synthetic route to indolinospirobenzopyrans



synthetic routes to marketed spirooxazines





commercial synthetic route to naphthopyrans (using [1,2-*b*] derivatives as an example)

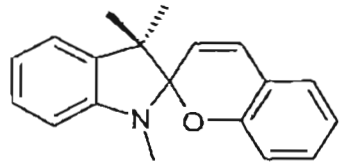
Color. Technol. **2009**, *125*, 249-261. *Chem. Brit.* **2003**, *39*, 26-29.

Factores en materiales fotocrómicos tipo T

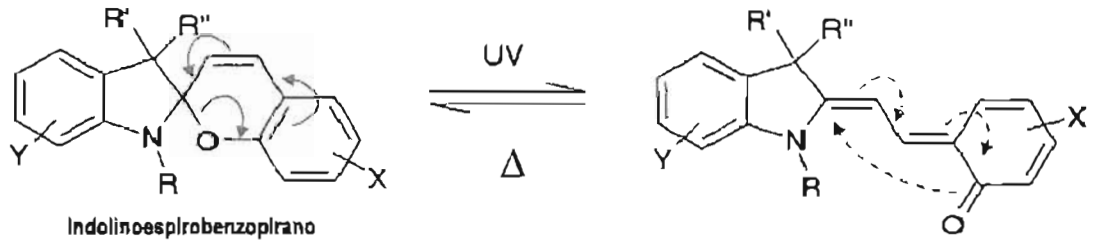
- **Colorante:**
  - activación rápida desde la forma incolora a la coloreada
  - decoloración a velocidad adecuada para la aplicación ⇒ Vida media $t_{1/2}$
  - intensa absorción de luz por la forma coloreada (cambio apreciable aun a baja concentración)
  - leve "color residual" para la forma incolora
  - fotocromismo poco dependiente de la temperatura
  - fotoestabilidad para la forma incolora y la coloreada
  - resistencia a la fatiga que conduce al debilitamiento del color. P.ej. lentes ⇒ 2 años de vida
  - buena solubilidad en la matriz polimérica (no disperso)
- **Polímero:**
  - poco rígido (más volumen disponible para los cambios de forma moleculares) influye en las cinéticas del fotocromismo (activación y decoloración)
  - polímeros de baja T_g (polietilenos, siliconas,...con cadenas flexibles)
- **Polaridad de la matriz:**
  - influye en las cinéticas del fotocromismo
  - influye en el tono de color, ya que los colorantes suelen ser solvatocrómicos
- **Capacidad de combinación de distintos colorantes:**
  - para aplicaciones que requieren mezclas de colorantes las propiedades fotocrómicas deben estar emparejadas (cinéticas, tonos de color,...)
  - uso de colorantes de la misma familia (p.ej. naftopiranos)
  - uso de colorantes con diferente patrón de sustituyentes

Colorantes comerciales de tipo T

Espiropiranos



+ Síntesis fácil
+ Colores intensos (violetas, azules,...)
+ Se decoloran a velocidad adecuada
– Fuerte dependencia de T que debilita el color
– Poca fotoestabilidad
– Débil resistencia a la fatiga
~ Sustitución de O por S permite absorción NIR (pero disminuye la fotoestabilidad)



Indolinoespirobenzopirano

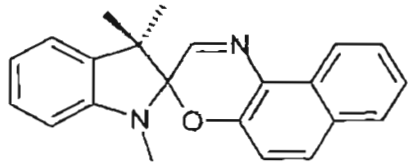
Colourless spiropyran 1

R = alkyl; R', R" = alkyl (usually both methyl)
X, Y = H, halogen, nitro, etc.

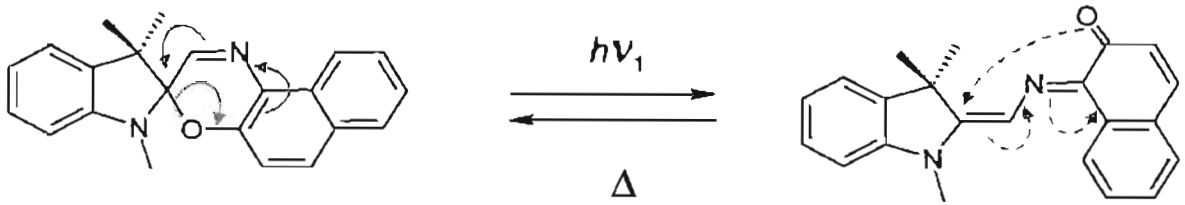
Coloured photomerocyanine dye
(mixture of isomers – others not shown)

Colorantes comerciales de tipo T

Espirooxazinas

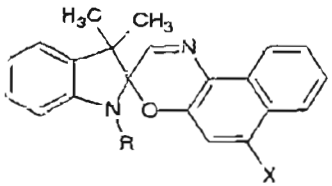


+ Síntesis fácil
+ Colores intensos (azules, rojos, púrpuras,...)
+ Muy buena resistencia a la fatiga
+ Alta fotoestabilidad (desarrollo de lentes fotocrómicas en 1980–1990)
+ Color y cinética de decoloración optimizables con sustitución adecuada



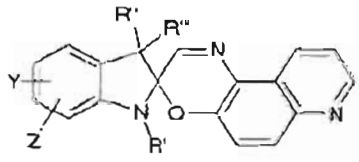
Closed Form

Open Form (Merocyanine)
(Quinonic form)



4 X = N-piperidino

Industrially useful spirooxazine types



5

Indolinoespiropiridobenzoxazinas
derivadas de 5-nitroso-6-hidroxiquinolina

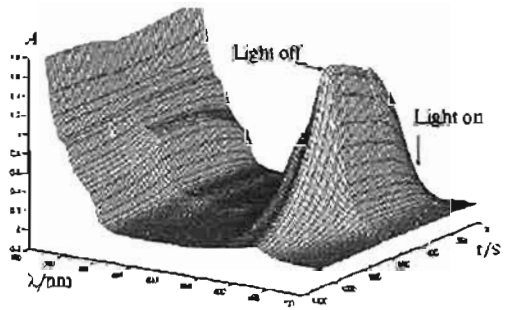
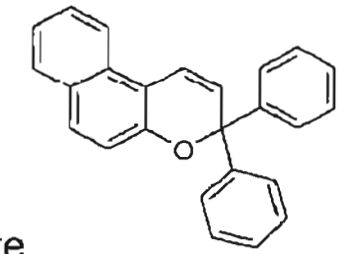


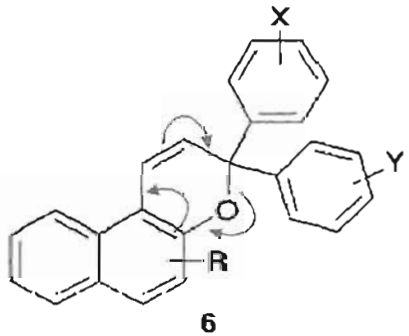
Fig. 5. Evolution of the electronic absorption spectrum of photochromic 8-cyanoindoline-spironaphthoxazine (toluene, 25 °C).

Colorantes comerciales de tipo T

Naftopiranos (cromenos)



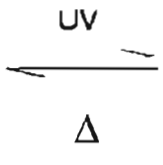
+ Alta fotoestabilidad
+ Fotocromismo poco dependiente de T
+ Síntesis económica, aun con diferentes tipos de sustituyente
+ Toda la gama de colores (amarillo, naranja, rojo, púrpura, azul)
+ Los más usados comercialmente para lentes fotocrómicas

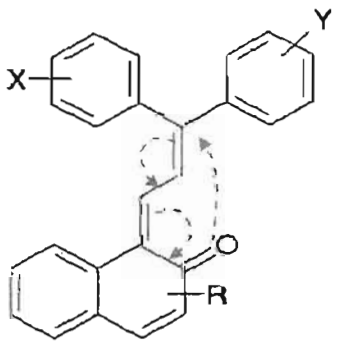


6

Colourless [2,1-*b*]naphthopyran

X, Y = H, alkoxy, amino, etc.
R = H, amino, etc.

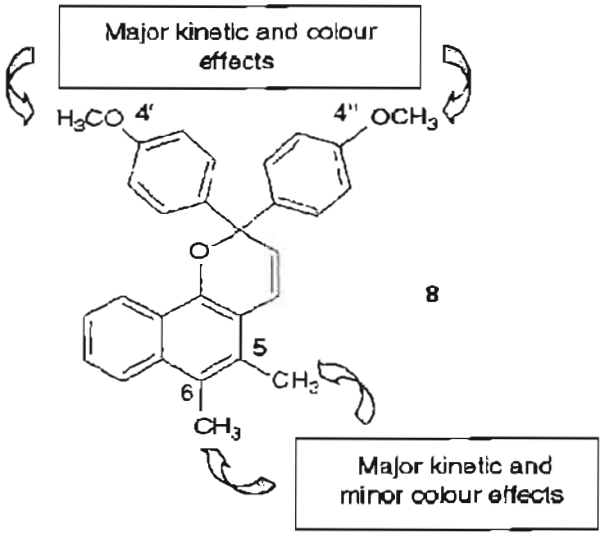




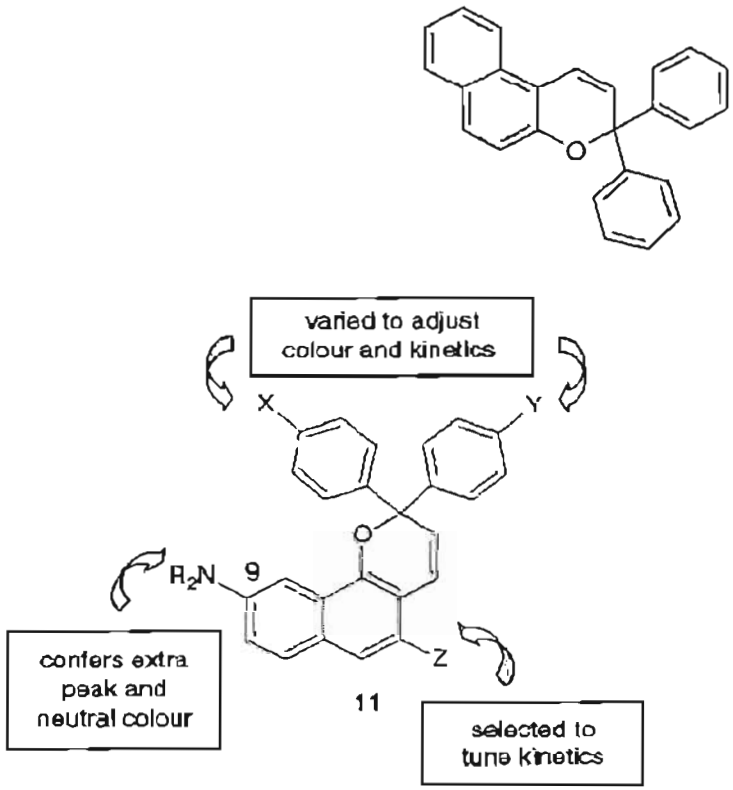
Coloured dye; typically yellow, orange or red
(mixture of isomers – others not shown)

Colorantes comerciales de tipo T

Naftopiranos (cromenos)



8



11

Substituent effects in some commercial naphthopyrans

Incorporación de colorantes fotocrómicos en polímeros

- En **masa**, disueltos en monómero o resina que se cura con calor o UV
- Por **recubrimiento superficial** mediante **inmersión** o **centrifugación** (*spin-/dip- coating*)
- Por **imbibición** (adsorción + difusión facia el interior del polímero ~ 0.2 μm)
- **Laminación** (incorporación de un film de material fotocrómico a modo de *sandwich* entre dos láminas de polímero)

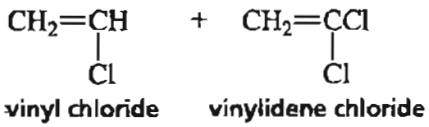
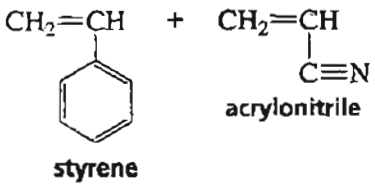
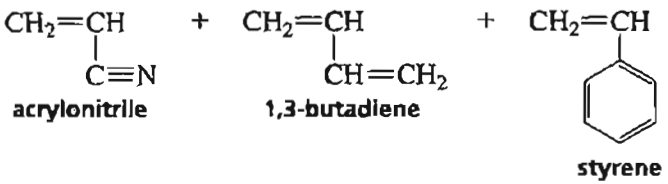
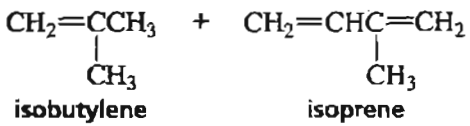
En principio, ***no todos los polímeros sirven*** para la incorporación de moléculas fotocrómicas (*han de permitirlas adoptar la conformación plana*).
Son mejores los de estructura menos rígida:

+ polietileno
+ polipropileno
+ poliuretano
+ cloruro de polivinilo

Unos fundamentos sobre polímeros ...

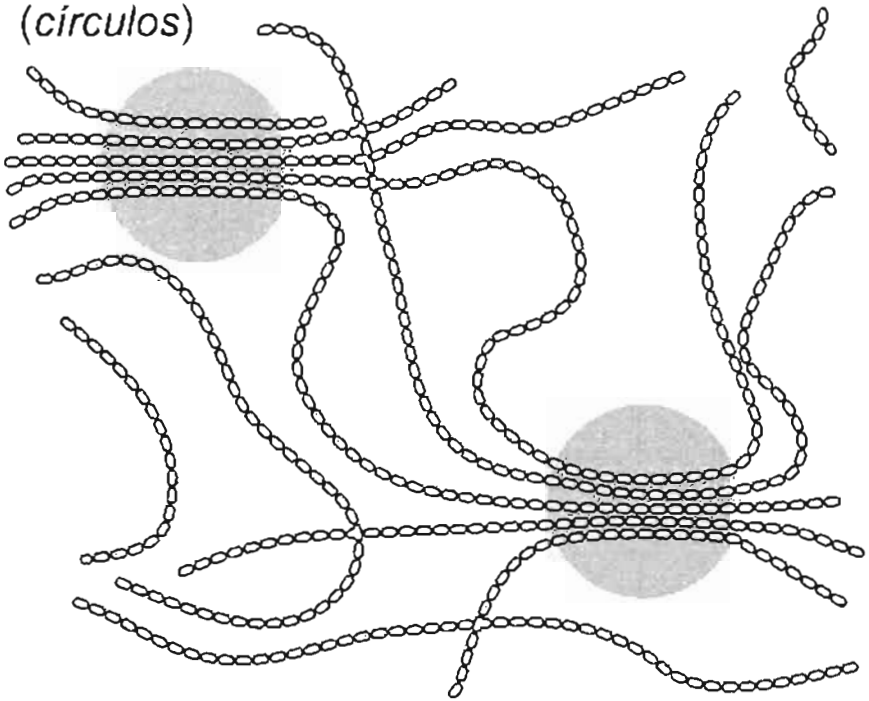
Monomer	Repeating unit	Polymer name	Uses
$CH_2=CH_2$	$-CH_2-CH_2-$	polyethylene	film, toys, bottles, plastic bags
$CH_2=CH(Cl)$	$-CH_2-CH(Cl)-$	poly(vinyl chloride)	"squeeze" bottles, pipe, siding, flooring
$CH_2=CH-CH_3$	$-CH_2-CH(CH_3)-$	polypropylene	molded caps, margarine tubs, indoor/outdoor carpeting, upholstery
$CH_2=CH(C_6H_5)$	$-CH_2-CH(C_6H_5)-$	polystyrene	packaging, toys, clear cups, egg cartons, hot drink cups
$CF_2=CF_2$	$-CF_2-CF_2-$	poly(tetrafluoroethylene) Teflon®	nonsticking surfaces, liners, cable insulation
$CH_2=CH(C\equiv N)$	$-CH_2-CH(C\equiv N)-$	poly(acrylonitrile) Orlon®, Acrilan®	rugs, blankets, yarn, apparel, simulated fur
$CH_2=C(CH_3)(COCH_3)$	$-CH_2-C(CH_3)(COCH_3)-$	poly(methyl methacrylate) Plexiglas®, Lucite®	lighting fixtures, signs, solar panels, skylights
$CH_2=CH(OCCH_3{=}O)$	$-CH_2-CH(OCCH_3{=}O)-$	poly(vinyl acetate)	latex paints, adhesives

Unos fundamentos sobre polímeros ...

Monomer	Copolymer name	Uses
 vinyl chloride + vinylidene chloride	Saran	film for wrapping food
 styrene + acrylonitrile	SAN	dishwasher-safe objects, vaccum cleaner parts
 acrylonitrile + 1,3-butadiene + styrene	ABS	bumpers, crash helmets, telephones, luggage
 isobutylene + isoprene	butyl rubber	inner tubes, balls, inflatable sporting goods

Unos fundamentos sobre polímeros ...

Segmento de un polímero lineal que se pliega varias veces sobre sí mismo en dos **regiones cristalinas** (*círculos*)



Los **polímeros cristalinos** (polímeros con muchas regiones cristalinas) son:

- duros
- rígidos
- quebradizos

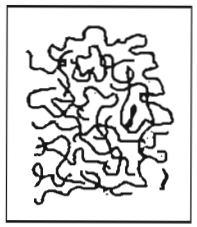
Los **polímeros con cadenas orientadas al azar** son:

- blandos
- flexibles

Table 28.7 Properties of Polyethylene as a Function of Crystallinity

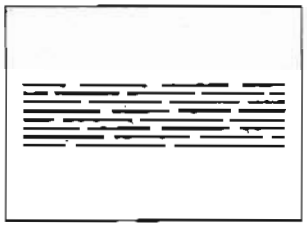
Crystallinity (%)	55	62	70	77	85
Density (g/cm^3)	0.92	0.93	0.94	0.95	0.96
Melting point (°C)	109	116	125	130	133

Unos fundamentos sobre polímeros ...



cadenas orientadas al azar

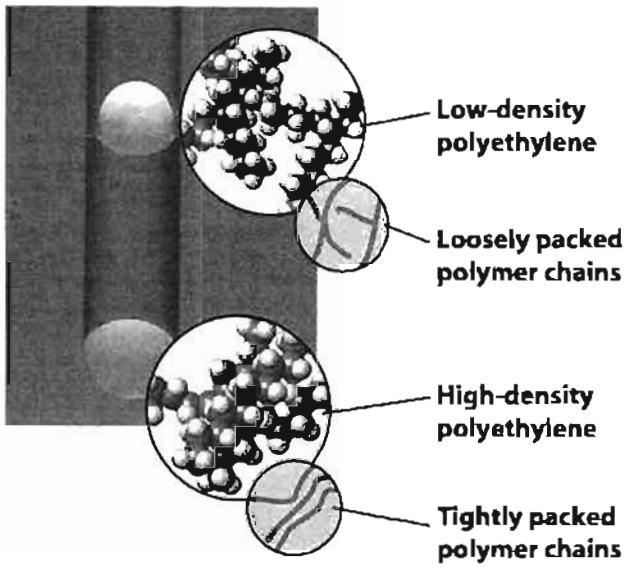
conventional polymer

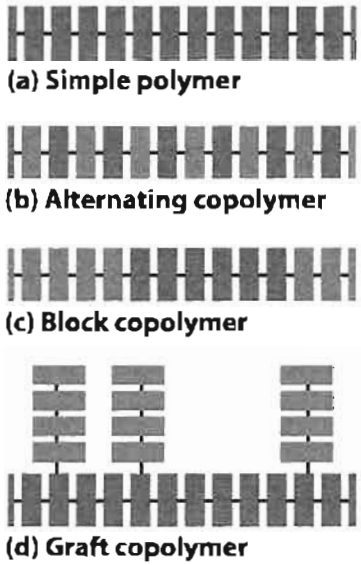


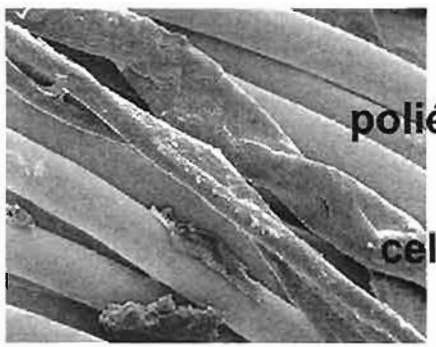
oriented polymer

más duros

pueden conducir e⁻



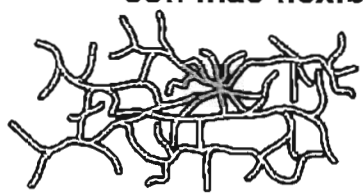




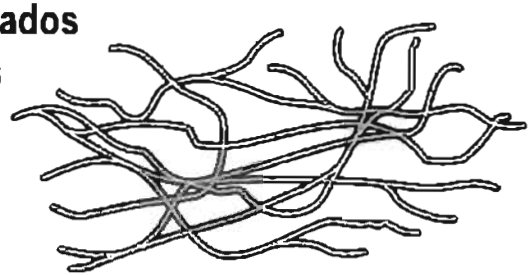
poliéster

celulosa

Los polímeros ramificados son más flexibles



chain with short branches



chain with long branches

Unos fundamentos sobre polímeros ...

Termoplásticos

Son polímeros que tienen **regiones amorfas** no cristalinas y **regiones cristalinas** bien ordenadas

Elastómeros

Polímeros que son **elásticos**, se pueden estirar y luego retornan a su forma original

Plastificante

Es un compuesto orgánico que se añade al polímero para hacerlo más flexible