Structure and dynamics in weakly ordered systems studied by emission and mobility probes

Weakly ordered systems

Emission probes

Mobility probes

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Geographical Situation

Buenos Aires

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INQUIMAE

My office

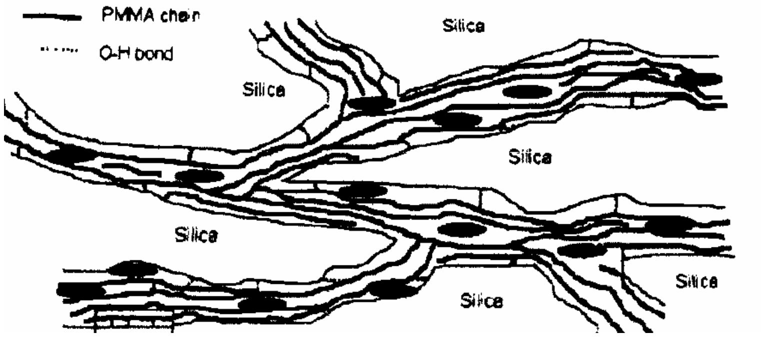
Weakly ordered systems

Polymers in films or in solution
Composite materials
Gels
Liquid crystals
Microemulsions

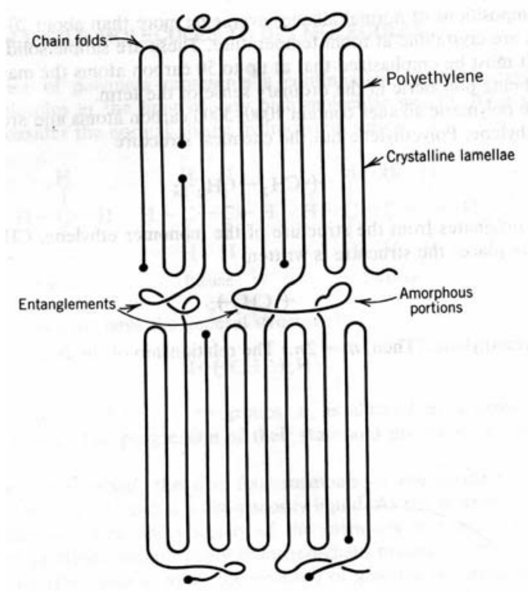
Relevant questions:
Microdomains: which is their structure? (main features)
Which is the characteristic time for their change?

Microheterogeneity ↔ relaxation dynamics
Spatial and time domains.

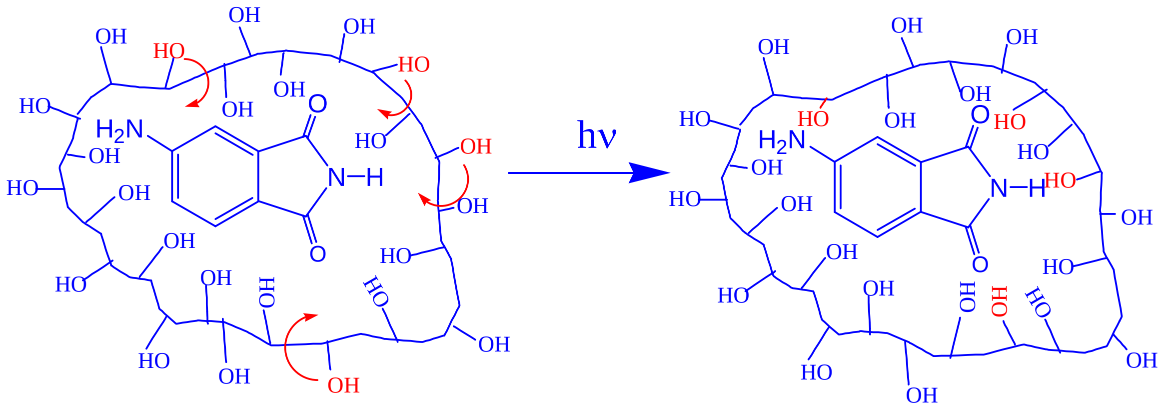
Polymers and composites



Polymer-gel composite material

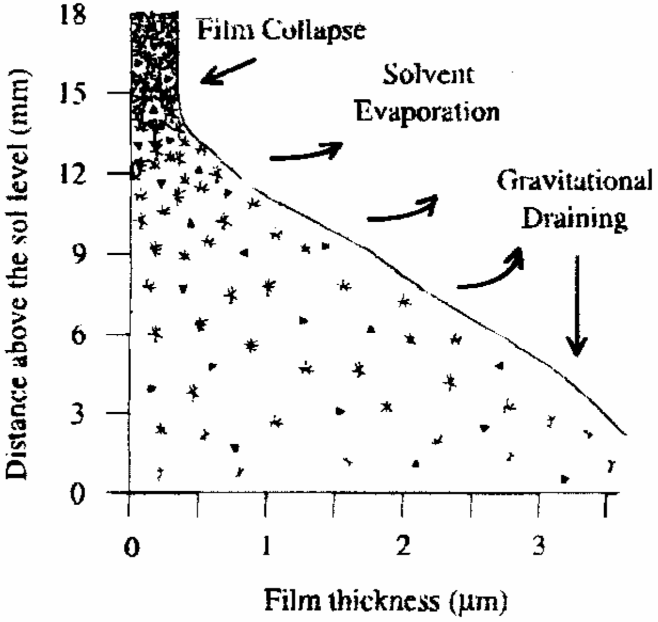


Semicrystalline Polyethylene

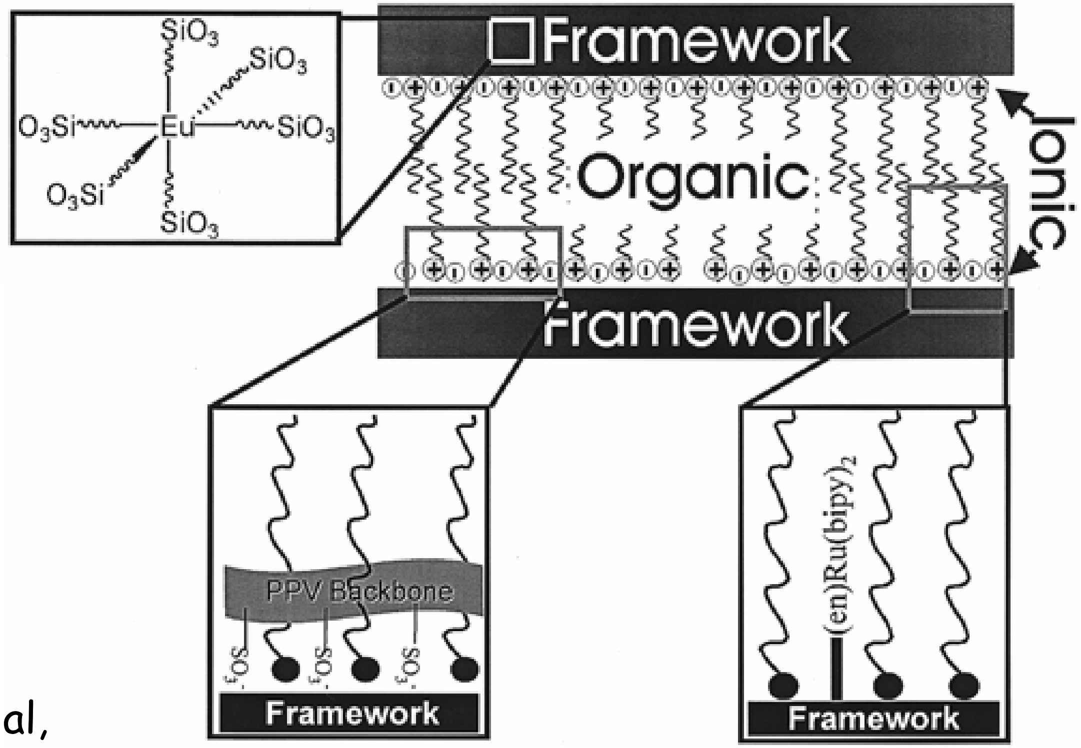


OH- pockets in Poly(vinyl alcohol)

Inorganic or hybrid sol-gel



M. Huang et al. Chem. Mater 12 (2000) 231.

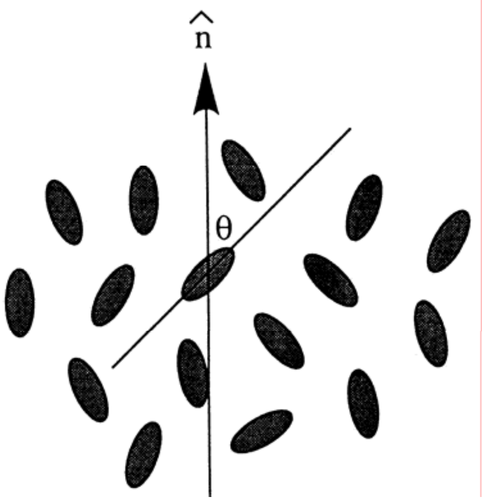


R. Hernandez, et al, JACS 123 (2001)1248.

Liquid Crystals

Nematic

Uniaxial



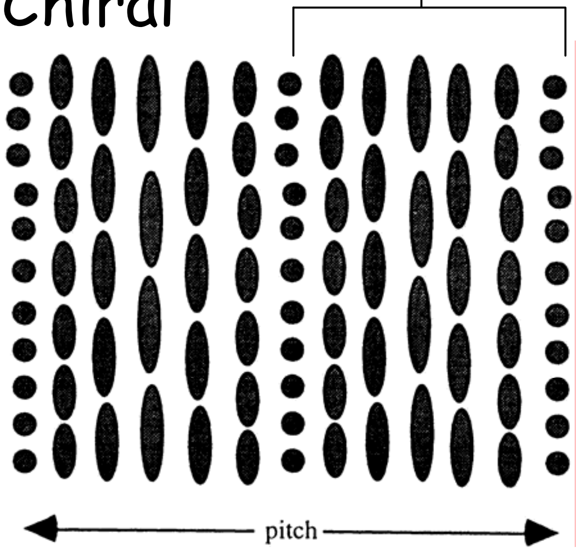
Order parameter:

$$S = 1/2\langle 3\cos^2\theta - 1\rangle$$

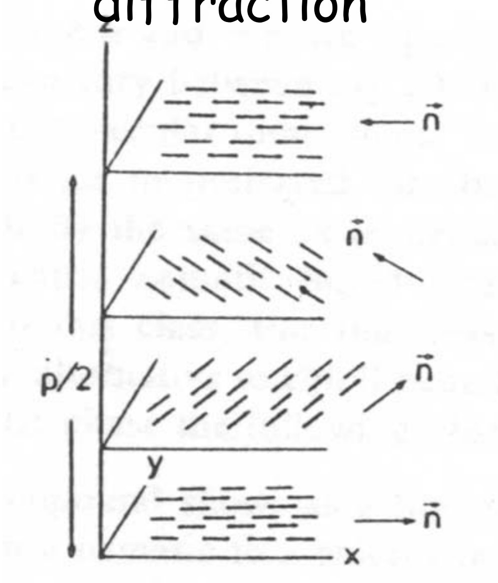
$$S \approx (1 - p[T/T_C])^q$$

Twisted nematic

Chiral



Bragg diffraction



Director:

$$n_x = \cos(q * z + \varphi)$$

$$n_y = \mathrm{sen}(q * z + \varphi)$$

$$n_z = 0$$

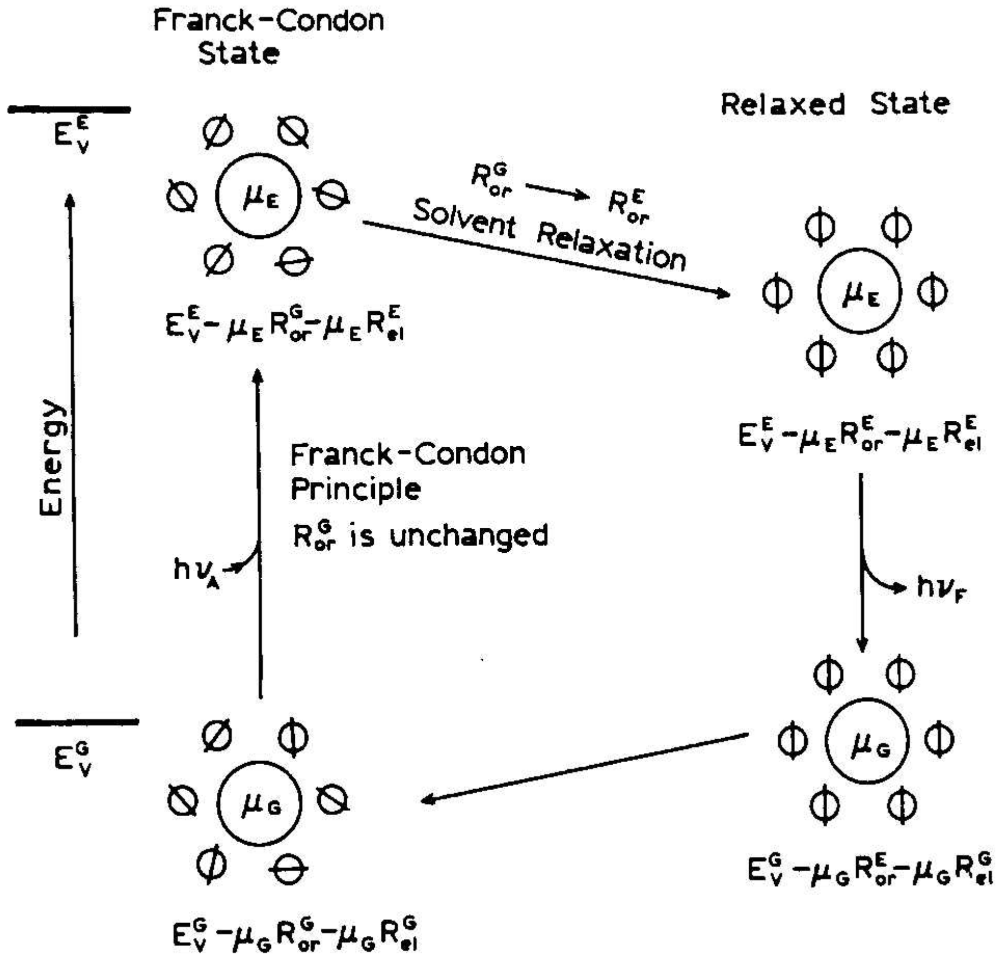
Pitch:

$$L = \pi / |q|$$

$$q = (c * \beta)^{-1}$$

Emission probes

Fluorescence. Characteristics.



Spectrum and Stokes shift

Red edge effect

Polarization

Electronic energy transfer

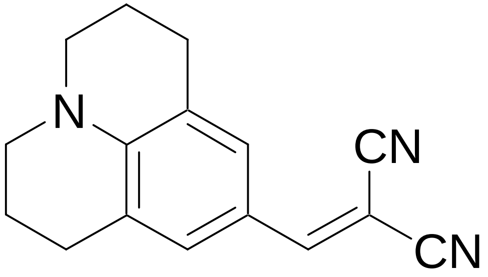
Quenching

Single molecule fluorescence

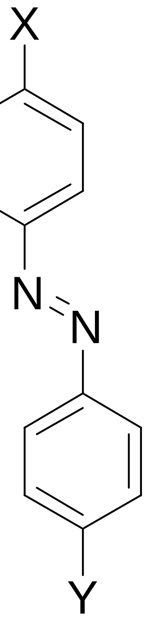
Mobility probes

Internal rotors
Photoisomerization

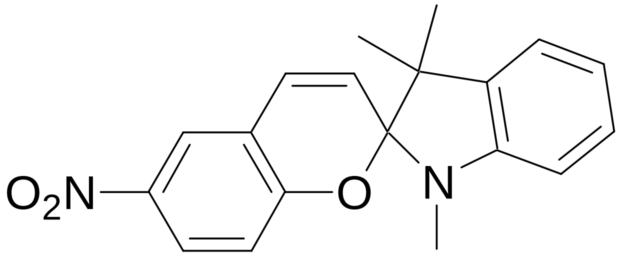
Excimers
Emission anisotropy



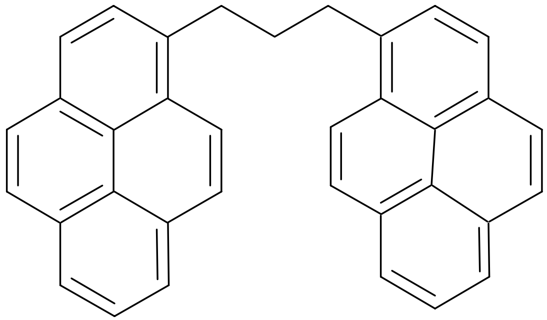
JMN



Azobenzenes



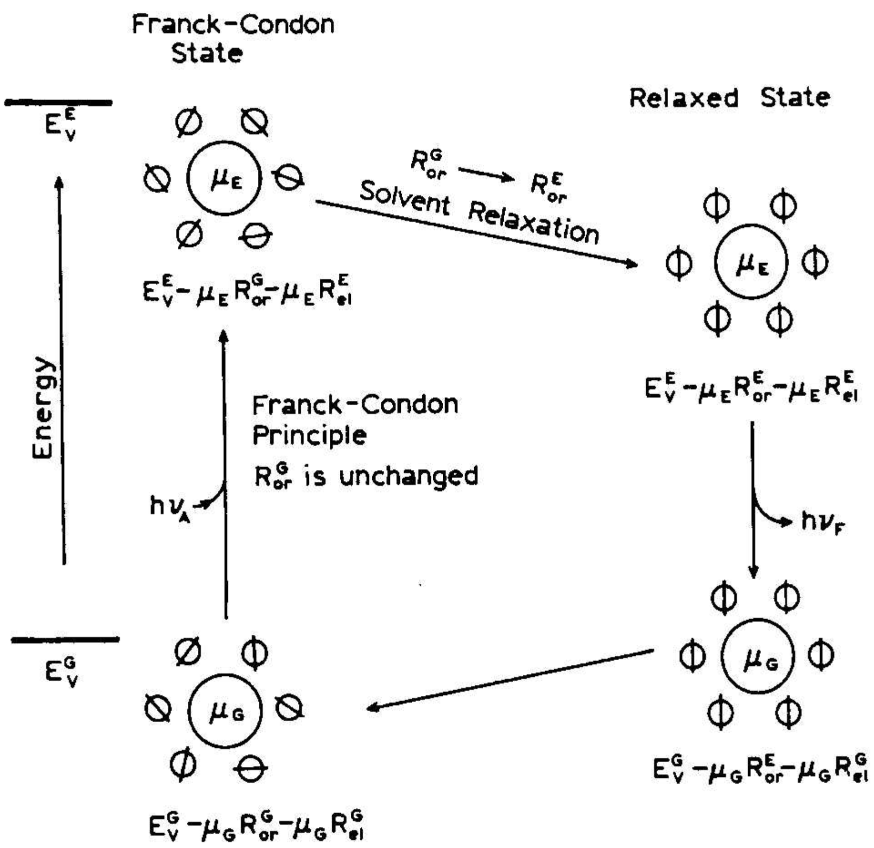
Spiropyrans



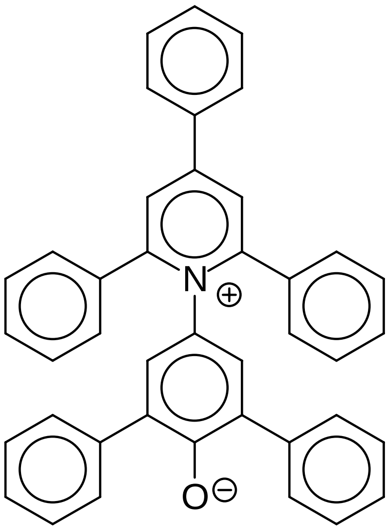
Di-pyrenyl propane

Fluorescence

Spectrum and Stokes shift
Solvatochromic scales: what do they measure?

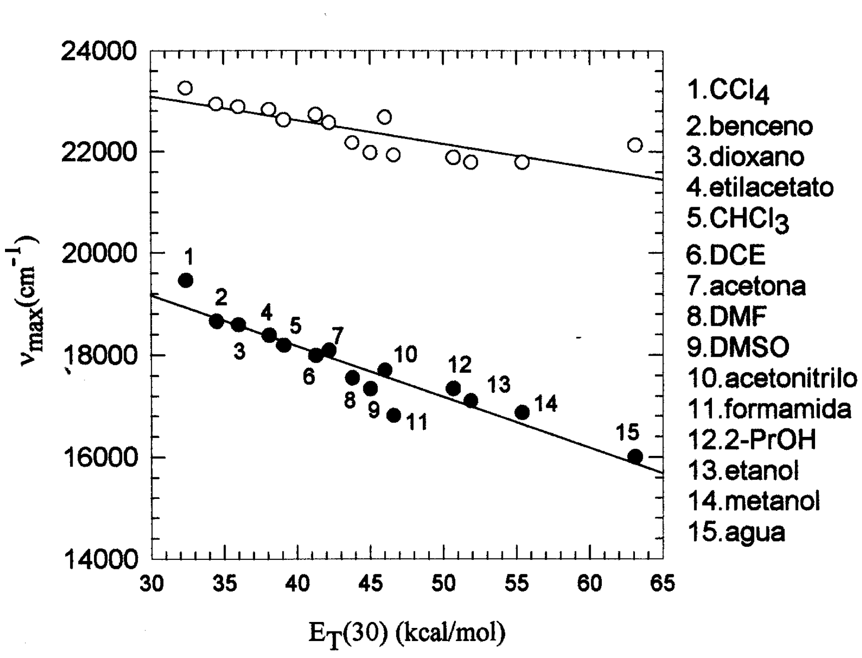


$E_T(30)$
Pyrene
Emission correlated with $E_T(30)$

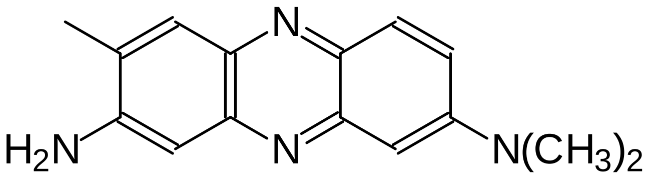


$E_T(30)$

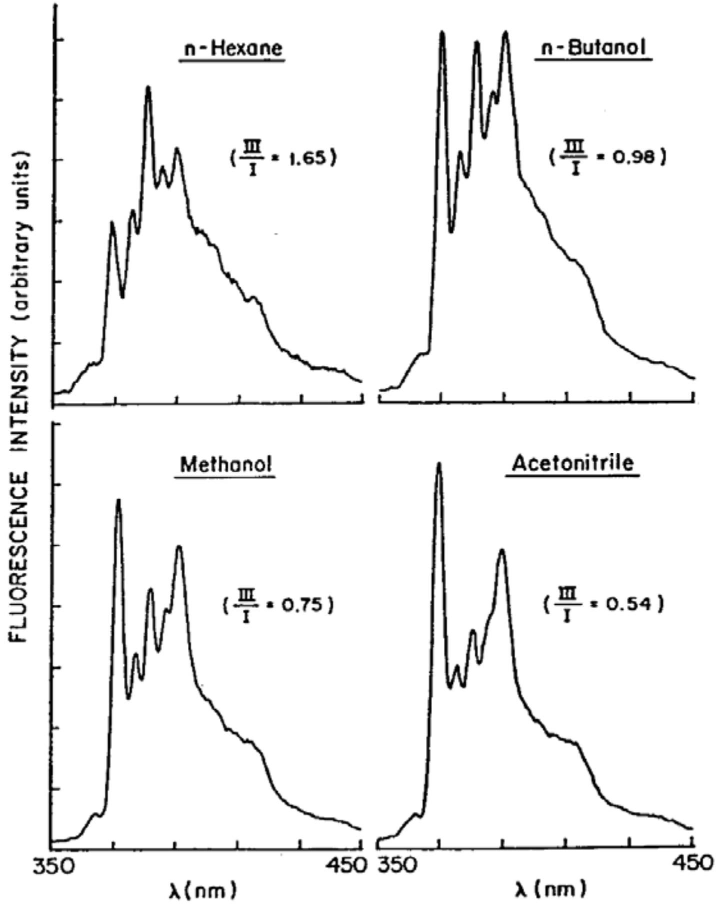
Solvatochromic scales: what do they measure?



Neutral red



Polarity and HBD capability



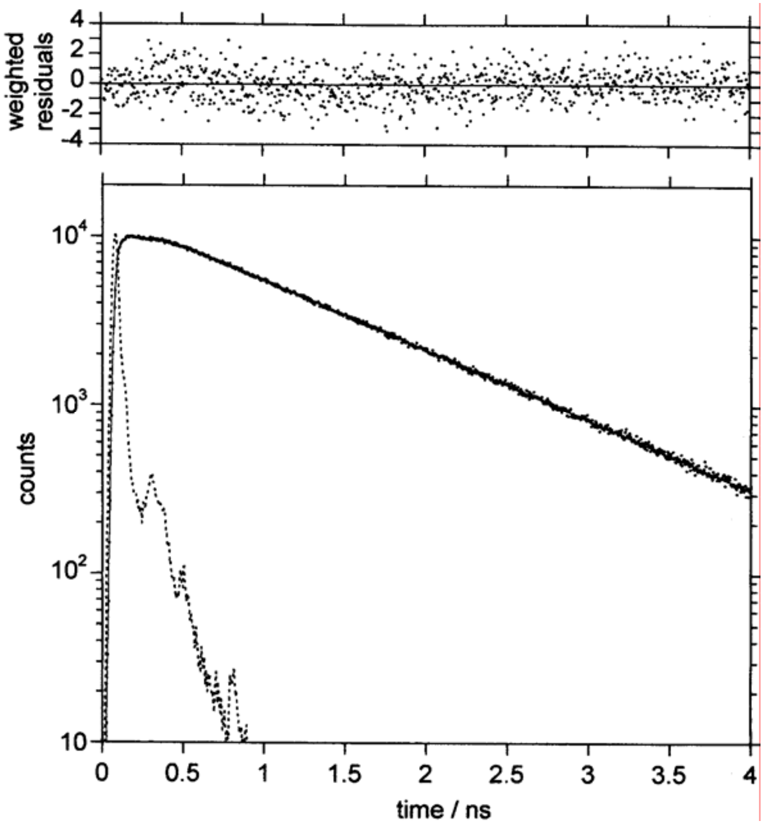
Ratio I_{III}/I_I for pyrene

Polarity

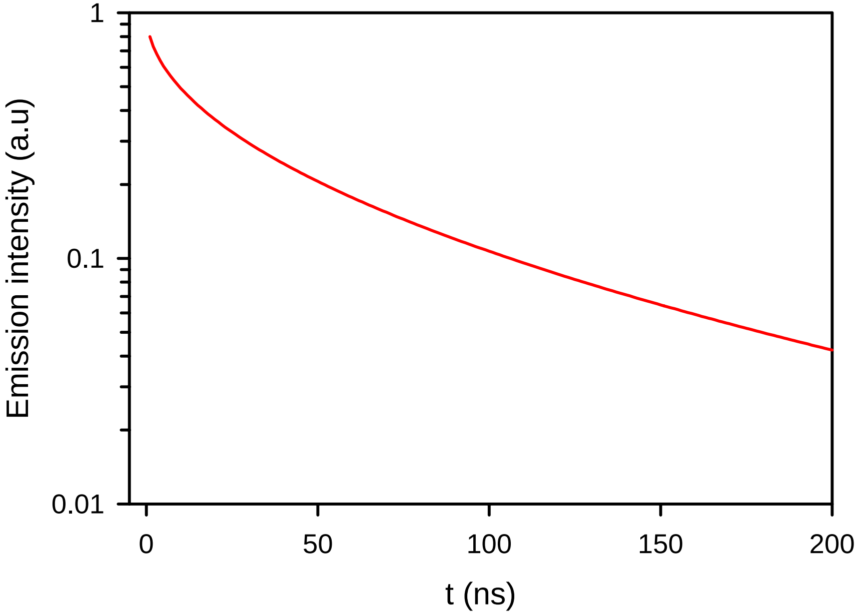
Fluorescence

Fluorescence lifetime and time-resolved emission spectroscopy

Emission decay



Decay of POPOP in cyclohexane



$$\langle t \rangle = \frac{\int t.I_f(t).dt}{\int I_f(t).dt}$$

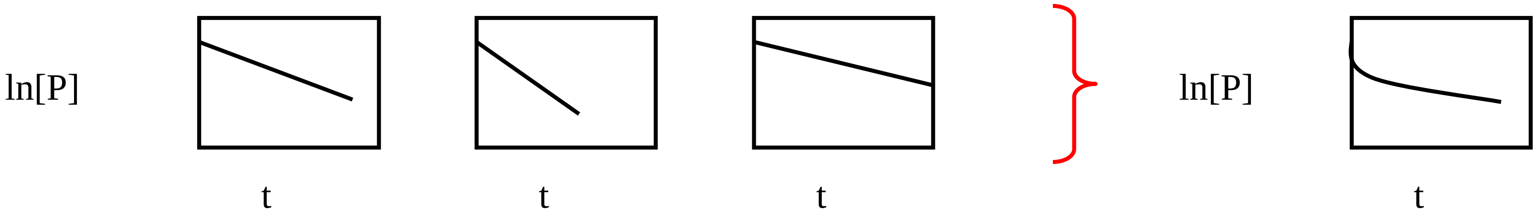
Dynamic domains for the kinetics

Comparison between the characteristic times of relaxation:

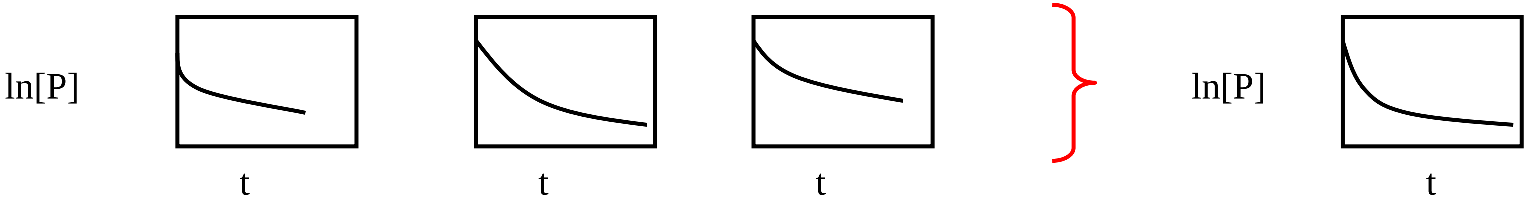
τ_P : of the metastable state

τ_M : of the environment

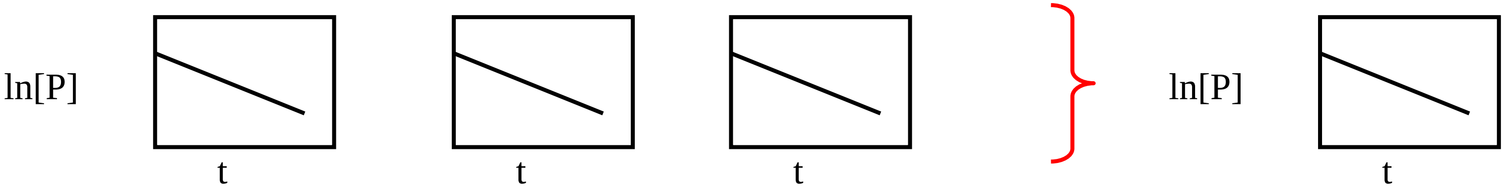
1: Distribution: $\tau_M >> \tau_P$



2: Dynamic: $\tau_M \approx \tau_P$



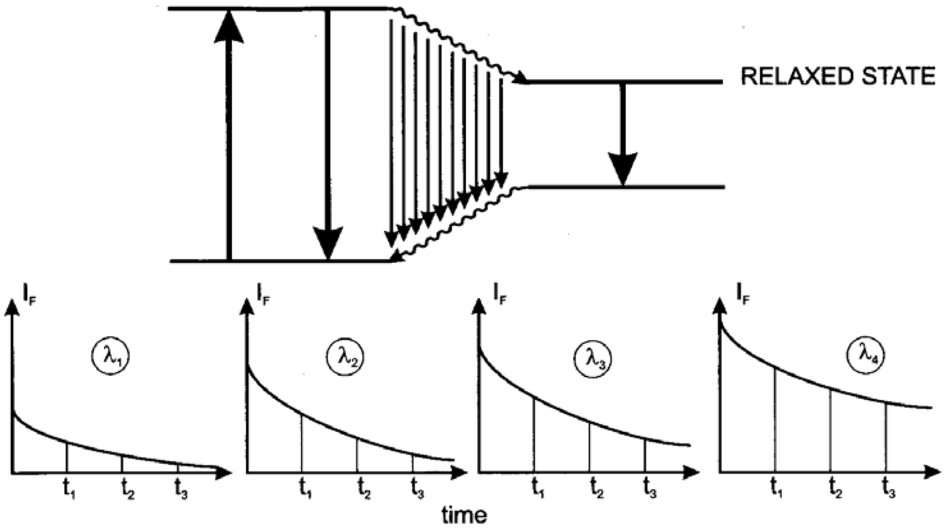
3: Equilibrium: $\tau_M << \tau_P$



Fluorescence

Fluorescence lifetime and time-resolved emission spectroscopy

TRES: time-resolved emission spectra



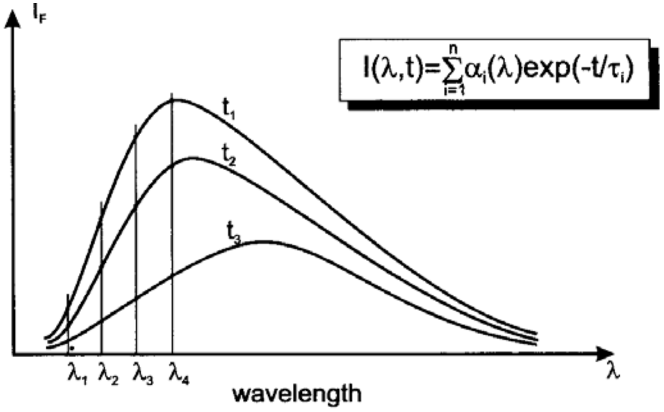
Relaxation

Excited state reaction

- excimer
- proton exchange
- energy transfer

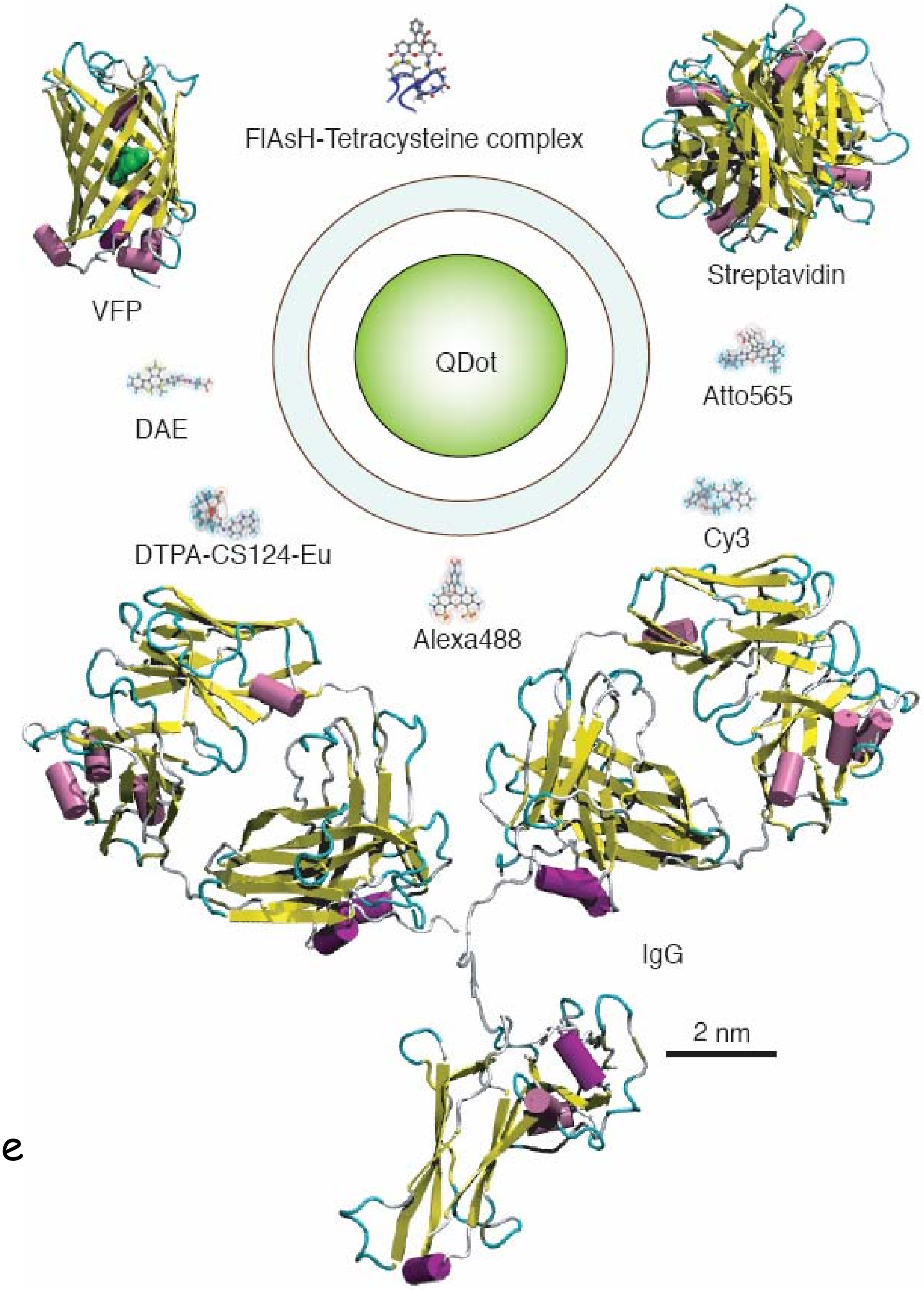
Decay registered at various emission wavelengths

Build emission spectra at different times



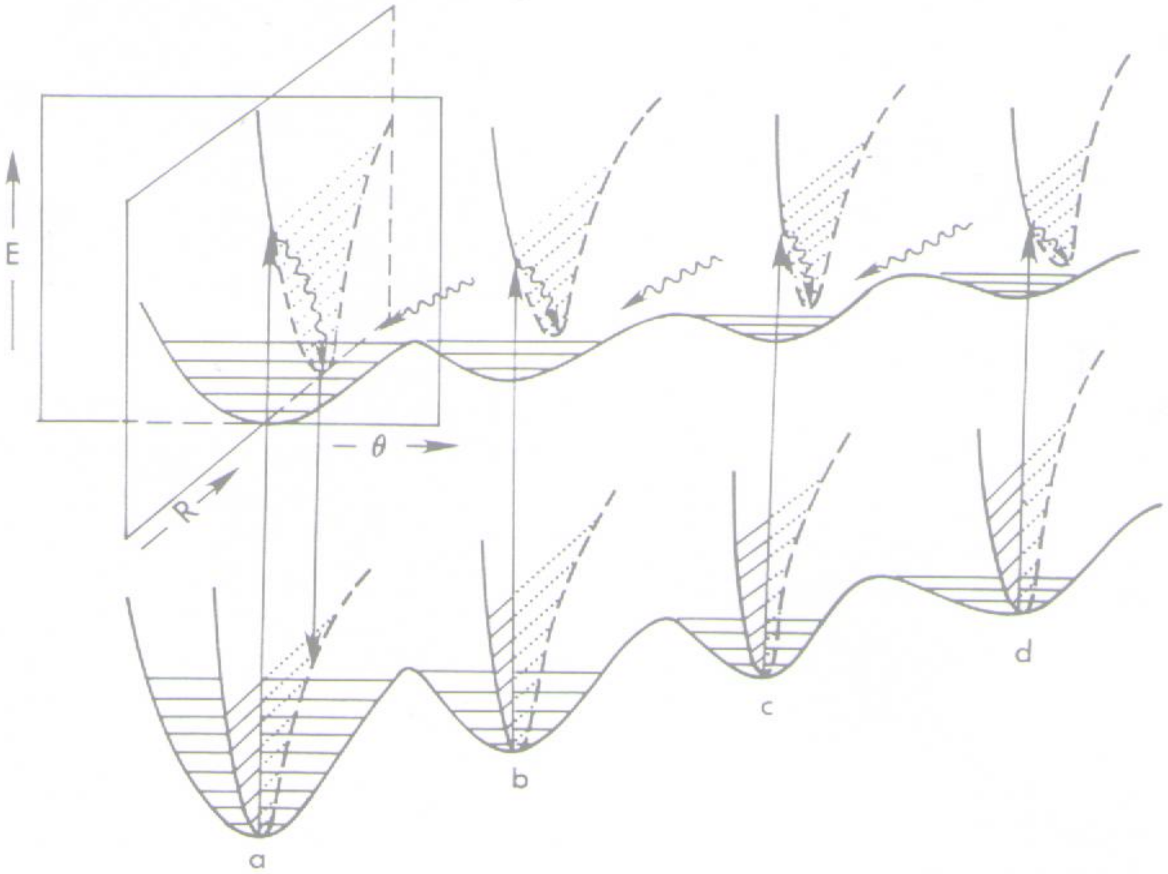
Emission probes

Relative size



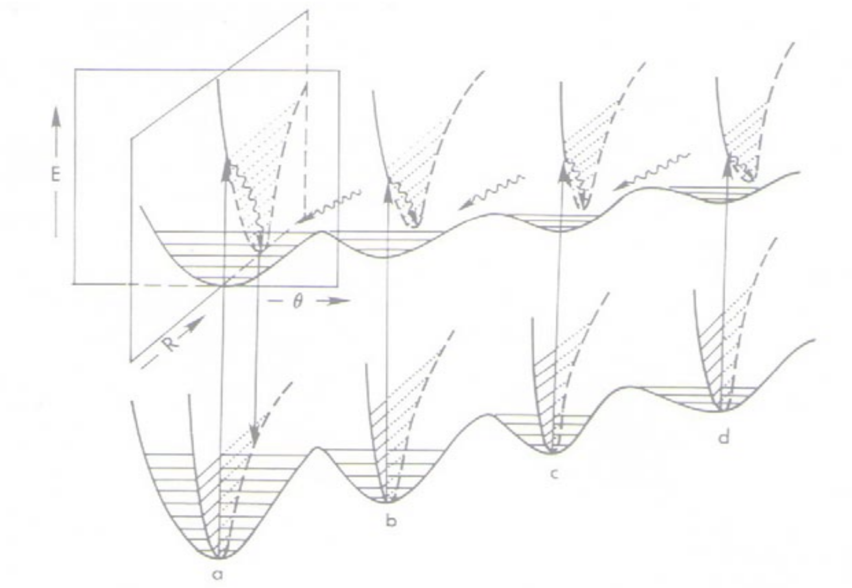
E. Jares-Erijman, T. Jovin. Nature Struct. Biology. 2004

Red Edge Excitation Shift (REES)



Ground and excited-state potential curves for different sites *a*, *b*, *c* and *d* differing in the orientation of surrounding molecules, θ, but having the same intermolecular separation R. Site *a* represents the most stable conformation with the largest interaction energy while site *d* represents the least favorable situation.

Red edge excitation shift (REES)



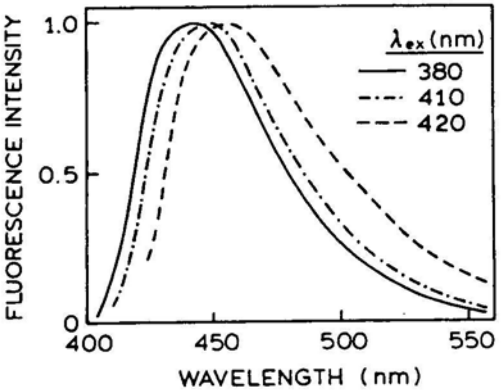
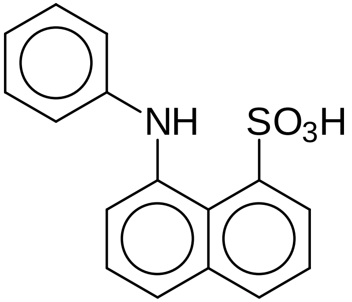


Figure 7.36. Fluorescence emission spectra of 1,8-ANS in 1-propanol at 77 K for various excitation wavelengths. The excitation and the emission bandpass are both 5 nm. Revised from Ref. 74.



ANS

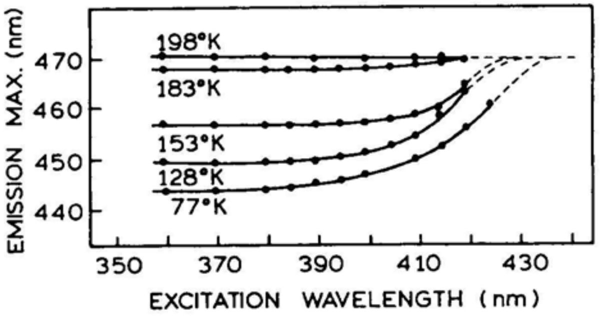
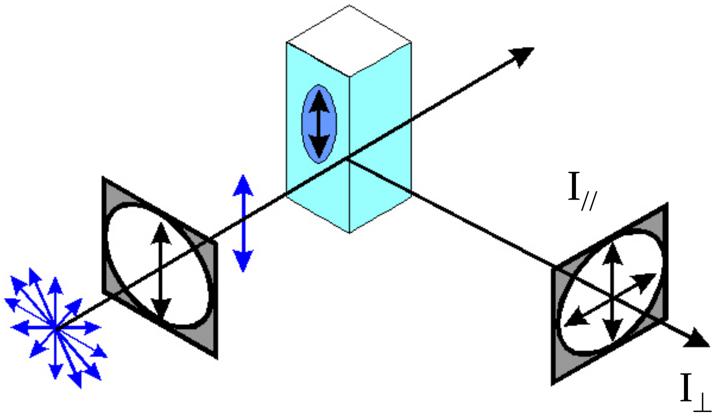


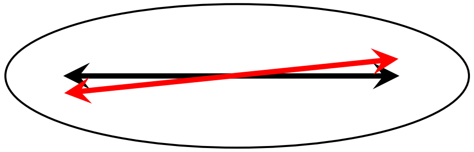
Figure 7.37. Temperature dependence of fluorescence excitation red shift for 1,8-ANS in 1-propanol. Revised from Ref. 74.

Fluorescence anisotropy



excitation polarizer

emission polarizer



Absorption moment

Emission moment

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

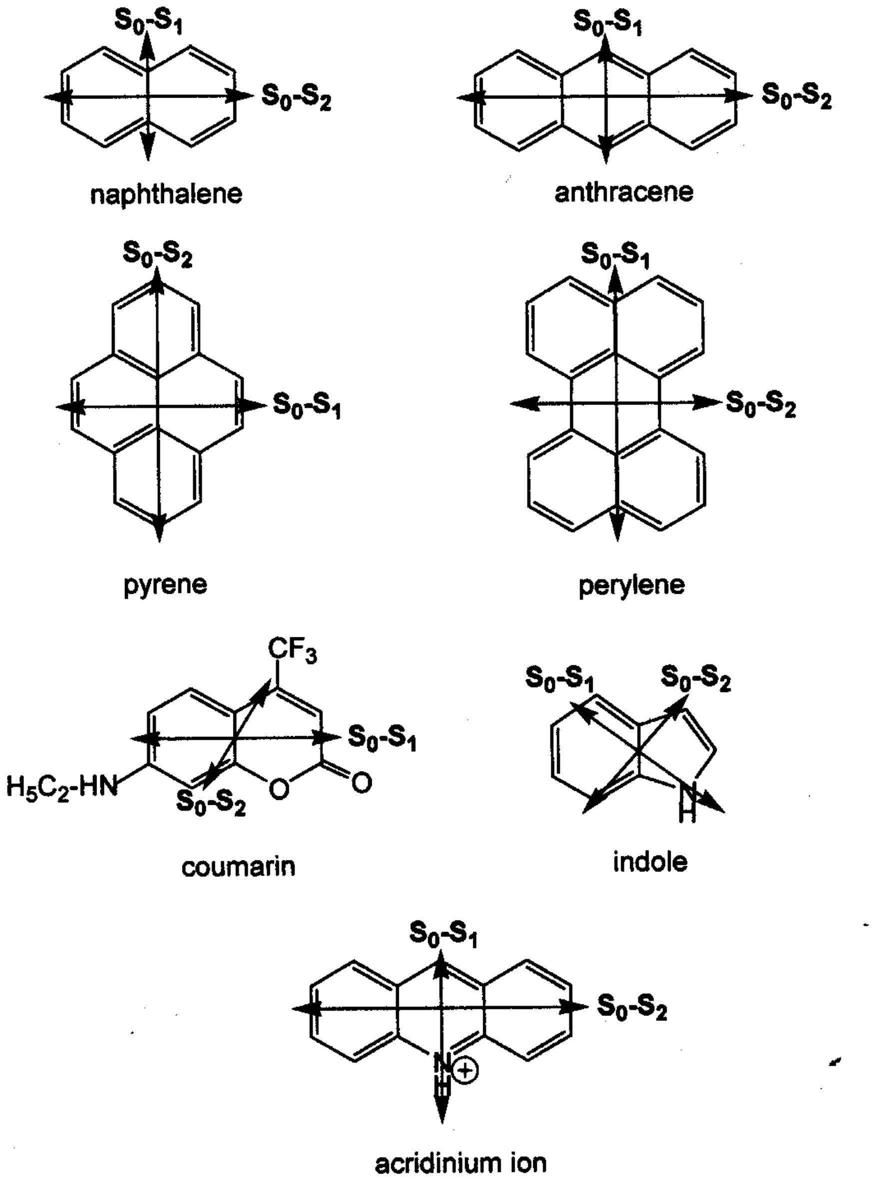
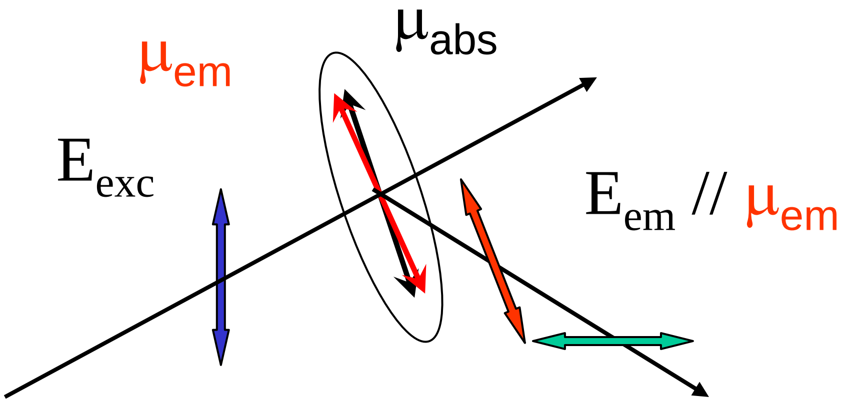


Fig. 2.3. Examples of molecules with their absorption transition moments.

Fluorescence anisotropy



$$I_{abs} \propto E_{exc}^2\, \mu_{abs}^2 \cos^2\theta_{abs}$$

$$I_{em} \propto I_{abs}\, \phi_f \cos^2\theta_{em}$$

If the molecule rotates during the excited state lifetime, the polarization of the emission changes.

Thus, emission anisotropy measures the molecular rotation during the excited state time window

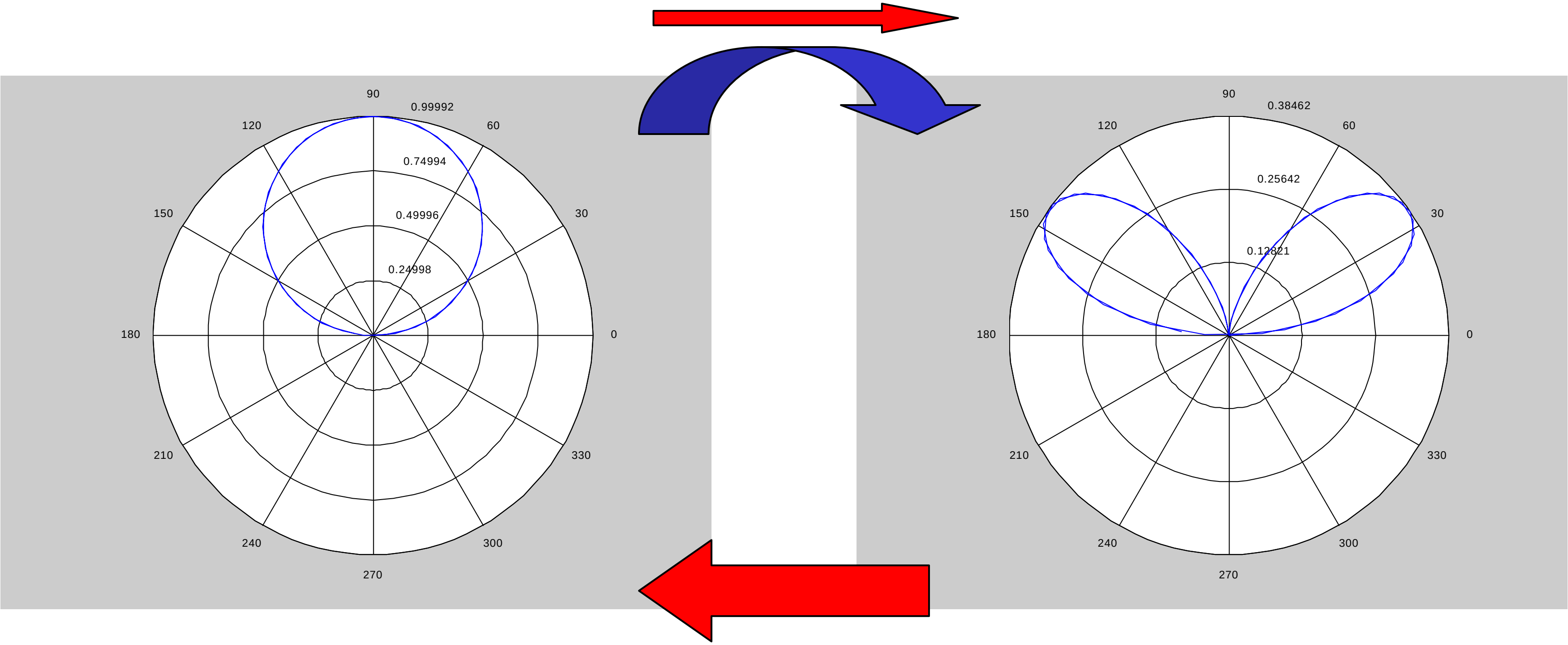
Fluorescence anisotropy

Photoselection

Before: random orientation

After: preferential orientation in the polarization direction

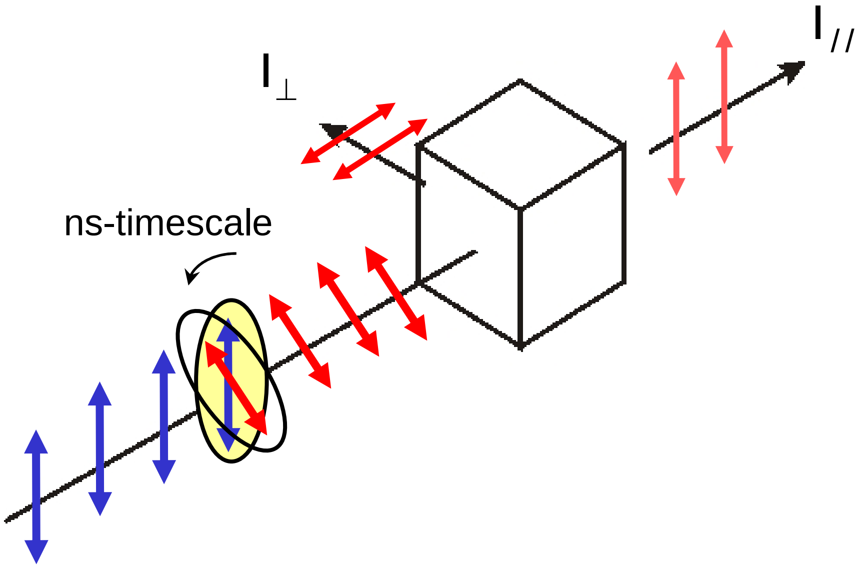
Polarization of the absorbed light



Rotational diffusion

Fluorescence anisotropy

Effect of rotational diffusion



Fluorescence anisotropy

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

Depends on viscosity (η), temperature, specific interactions with the environment (C), shape and volume of fluorophore (V_h).

ϕ_r : Rotational correlation time

$$\phi_r = \frac{C.\eta.V_h}{kT}$$

Fluorescence: Energy transfer

Förster type:

- Electrical interaction between the donor (D) emission transition dipole and the acceptor (A) absorption transition dipole (Resonance effect).
- Distance and orientation dependent

$$k_{ET}(r) = \frac{1}{\tau_D^0} . \left(\frac{R_0}{R} \right)^6$$

$$\Phi_{ET} = \frac{k_{ET}}{1/\tau_D^0 + k_{ET}} = \frac{1}{1 + \left(R/R_0 \right)^6}$$

k_{ET}:energy transfer rate constant

R_0: Förster distance

τ_D^0 : Fluorescence lifetime of the energy donor

Spectral overlap integral

$$R_0^{\,6} = \phi_D.\kappa^2.\left(\frac{9000.\ln 10}{128\pi^5 N_A n^4}\right).J(\lambda)$$

J(λ): spectral overlap
F_D (λ): Donor emission
ε_A (λ): Acceptor absorption

$$J(\lambda) = \int_0^{\infty} F_D(\lambda).\varepsilon_A(\lambda).\lambda^4.d\lambda$$

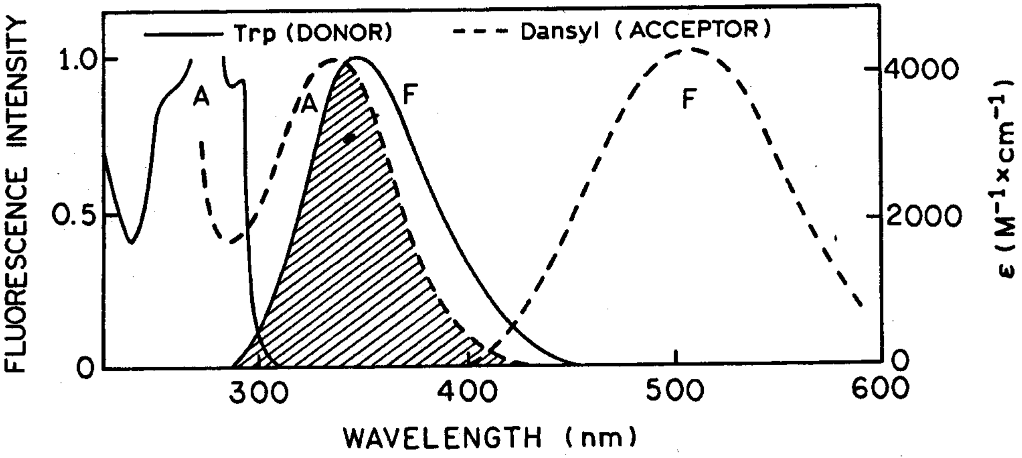
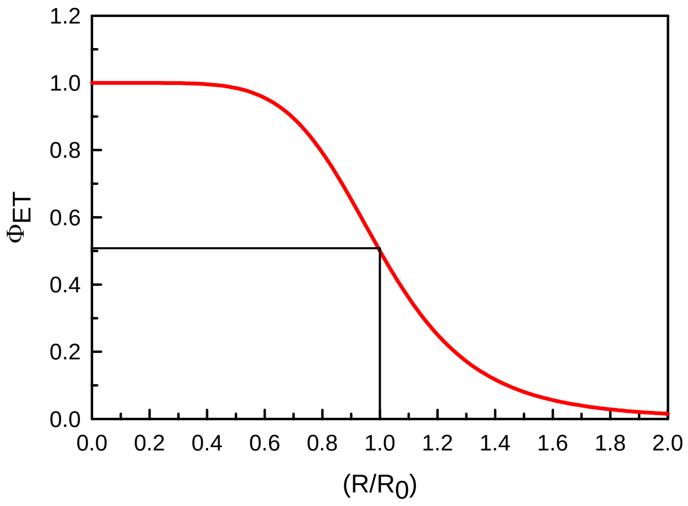


Figure 13.8. Overlap integral (shaded area) for energy transfer from a tryptophan donor to a dansyl acceptor on melittin. $R_0 = 23.6$ Å. Data from Ref. 24.

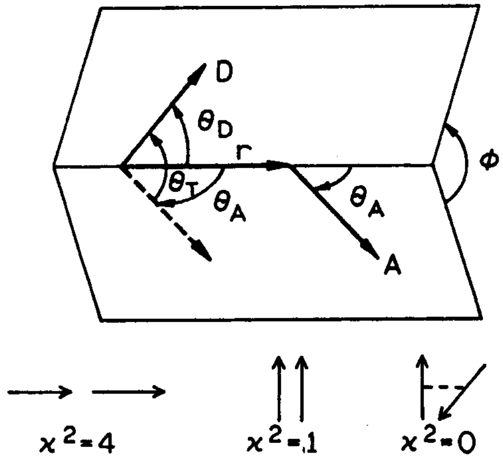
Förster energy transfer

Distance dependence



Useful range 1 - 10 nm

Orientation dependence



$$\kappa^2 = (\cos\theta_T - 3\cos\theta_D\cos\theta_A)^2$$

$$\kappa^2 = (\sin\theta_D\sin\theta_A\cos\phi - 2\cos\theta_D\cos\theta_A)$$

Förster energy transfer
Donor emission decay

The decay is heterogeneous and depends on the acceptor distribution

$$I_{fD}(t) = I_{fD}(0).\exp\left[-t/\tau_D^o - 2\gamma.(t/\tau_D^o)^{1/2}\right]$$

$$\gamma = \frac{\sqrt{\pi}}{2}.[A].\frac{4}{3}\pi R_0{}^3$$

Random distribution

Förster energy transfer

Distance distribution

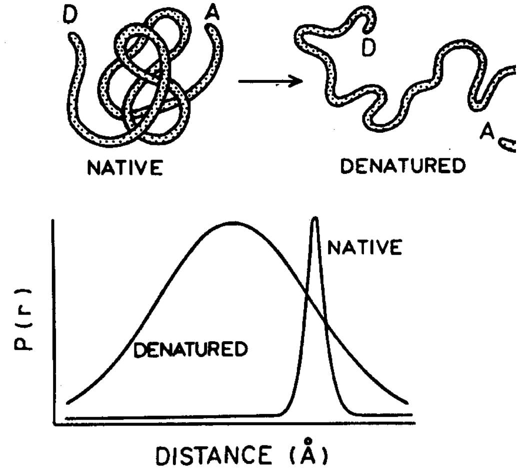


Figure 14.1. Distribution of donor–acceptor distances for a nati
a denatured protein. The probability functions $P(r)$ are peak norma

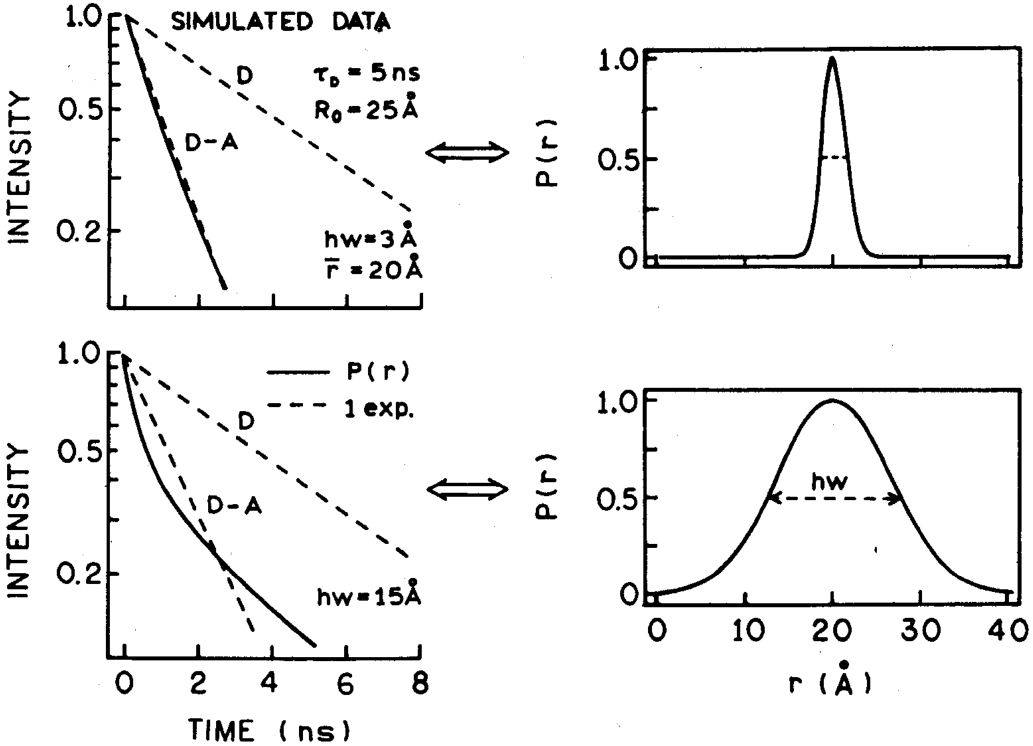
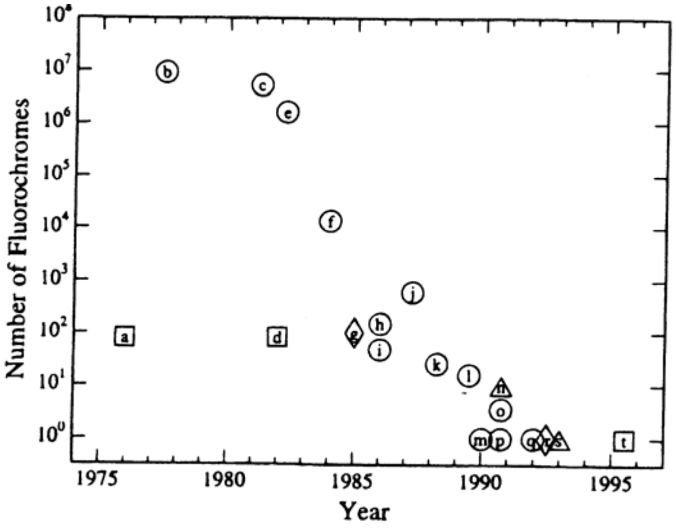


Figure 14.2. Simulated data illustrating the effect of D–A distance distributions of different half-widths (hw) (*right*) on the TD intensity decay of the donor (*left*): ———, Donor intensity decay in the presence of acceptor; – – –, single-exponential fits to the donor intensity decay in the presence (D–A) and absence (D) of acceptor.

Single molecule fluorescence

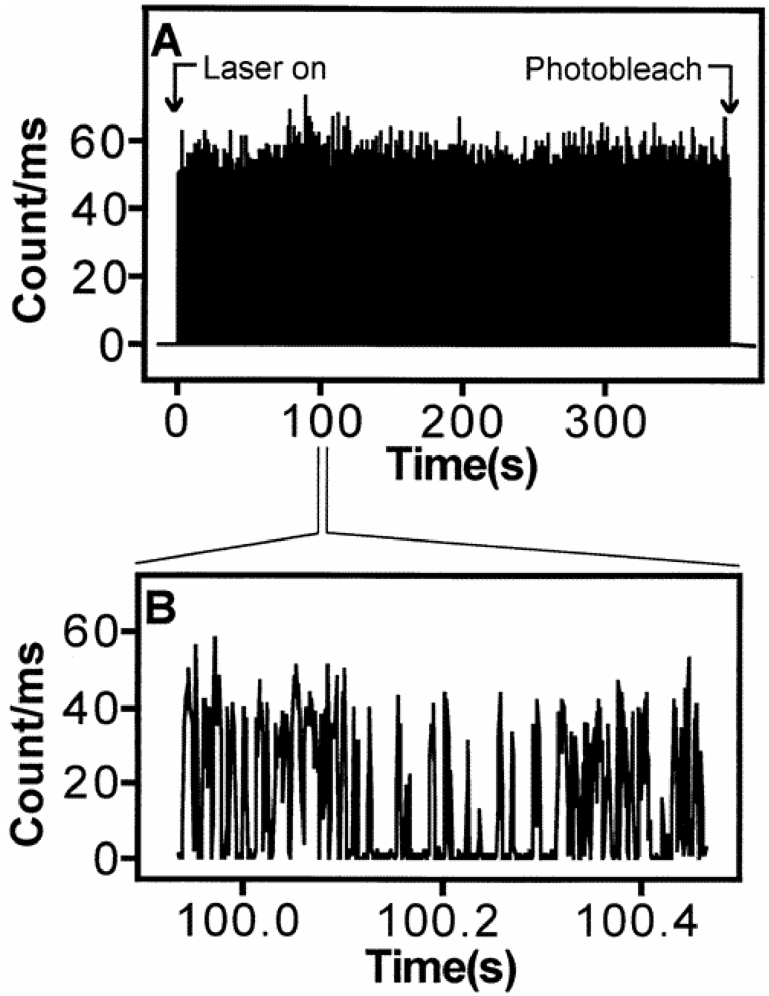


R. Keller et al. *Chem. Rev.* 99 (1999) 2929

Distinctive features

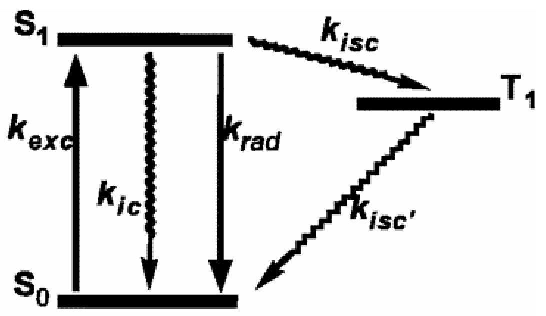
- Individual behavior
- Distribution of values instead of average in bulk measurements
- Spatial resolution (scanning microscopy)
- Single molecule photochemistry:
  - Blinking
  - One sptep photobleaching

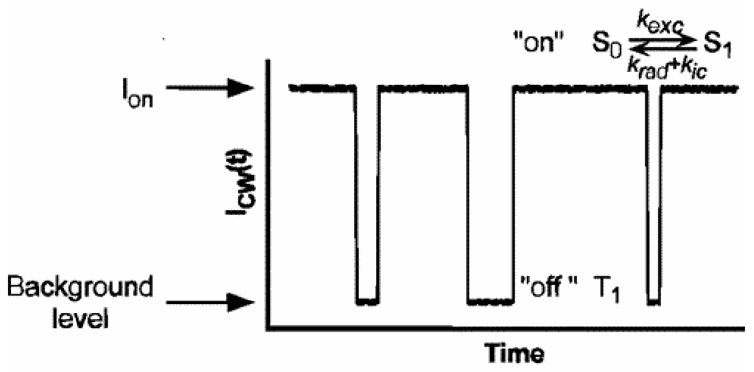
Single molecule fluorescence



P. Barbara et al. *J. Phys. Chem. A,* 102 (1998) 7564

Blinking





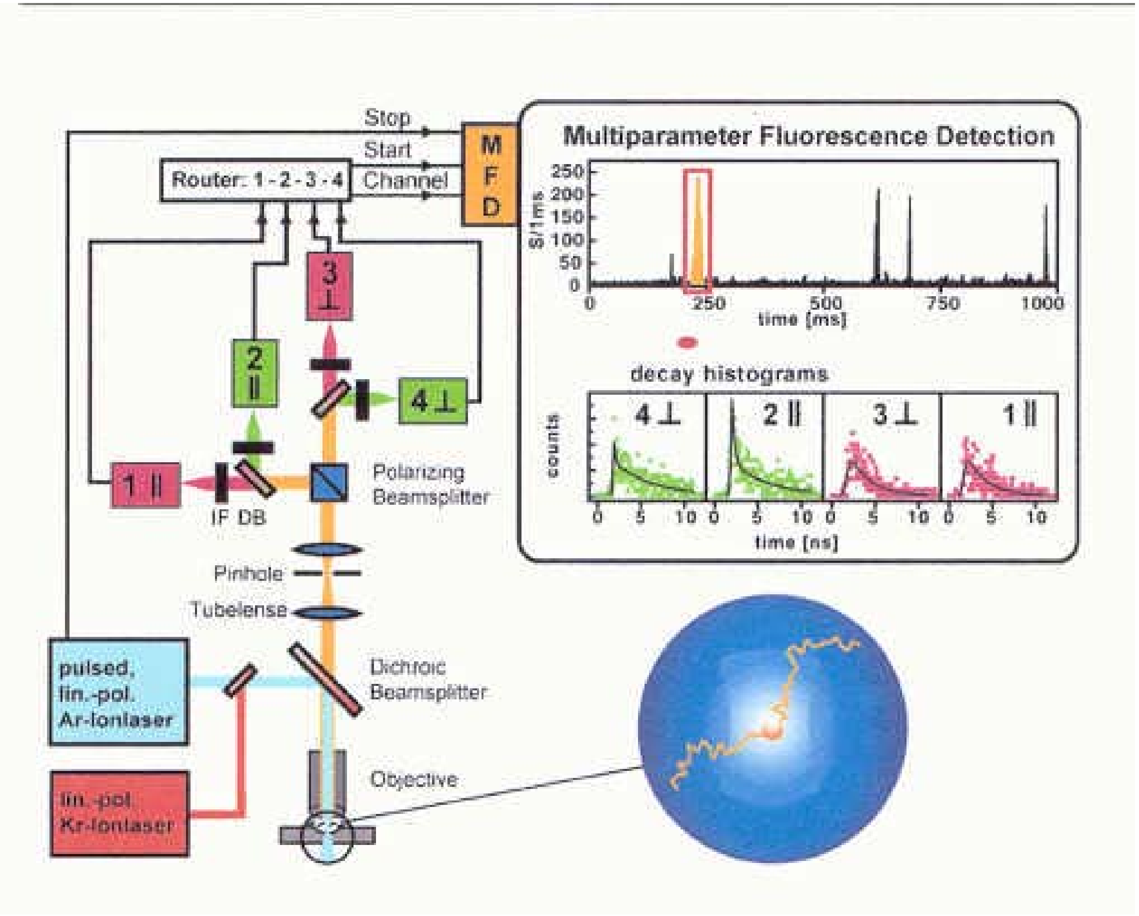
$$I_{on} = k_{exc} \frac{k_{rad}}{k_{rad} + k_{ic} + k_{isc}} E_{det}$$

$$\frac{1}{\tau_{on}} = k_{exc} \frac{k_{isc}}{k_{rad} + k_{ic} + k_{isc}}$$

$$\frac{1}{\tau_{off}} = k_{isc'}$$

Single molecule fluorescence

Single Molecule Multiparameter Fluorescence Spectroscopy



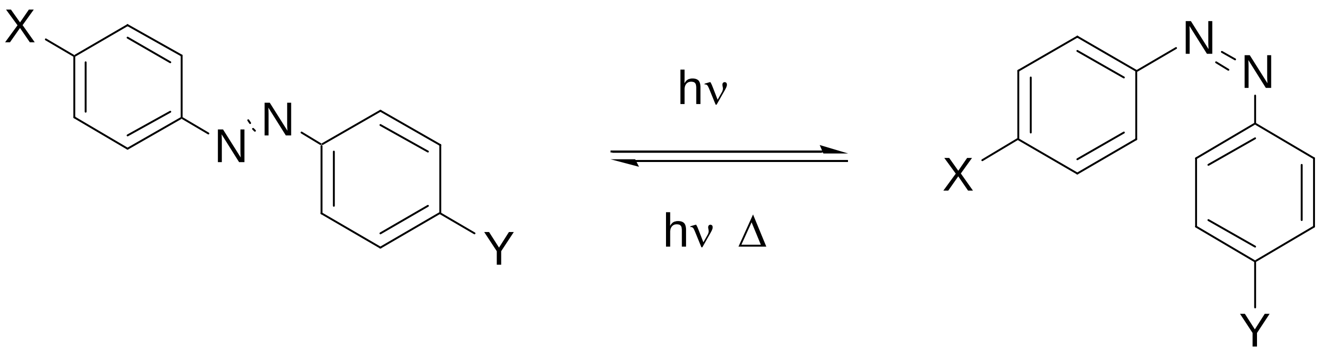
- ✓Two time bases
- ✓Two channels: donor and acceptor
- ✓Two polarization directions in each channel
- ✓Simultaneous measure of I_{fD}; I_{fA}; τ; r

C. Seidel et al. Single Molec 2 (2001): 251 PNAS 100 (2003) 1655

Mobility probes

Photoisomerization

a) E ↔ Z



E/Z ratio at the photostationary state

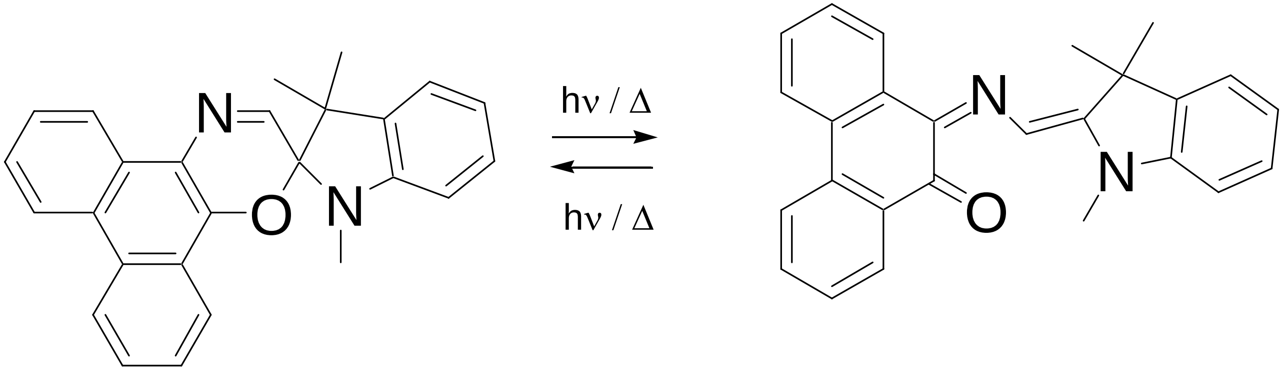
Structure	Compound	Group	τ (s)	Bands
X = Y = H	Azobenzene	Azobenzene	> 10^3	(n-π*)<(π -π*)
X = $N(CH_3)_2$ Y = H	4-(Dimethylamino)-azobenzene	Aminoazobenzene	~10	(n-π*)~(π -π*)
X = $N(CH_3)_2$ Y = NO_2	4-(Dimethylamino)-4'-nitroazobenzene	Pseudostilbene ***"push-pull"***	~10^{-3}	(n-π*)>(π -π*)

Mobility probes

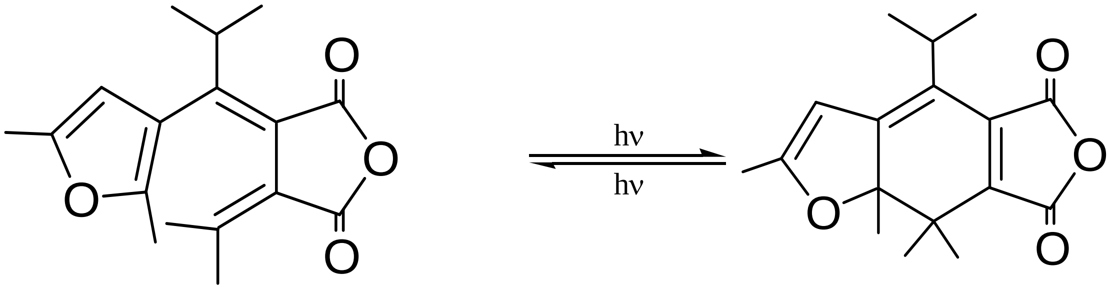
Photoisomerization

b) Cyclization ↔ ring opening

Spirooxazines

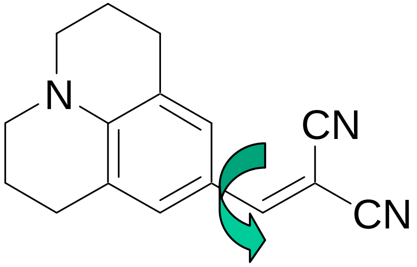


Furylfulgides



Mobility probes

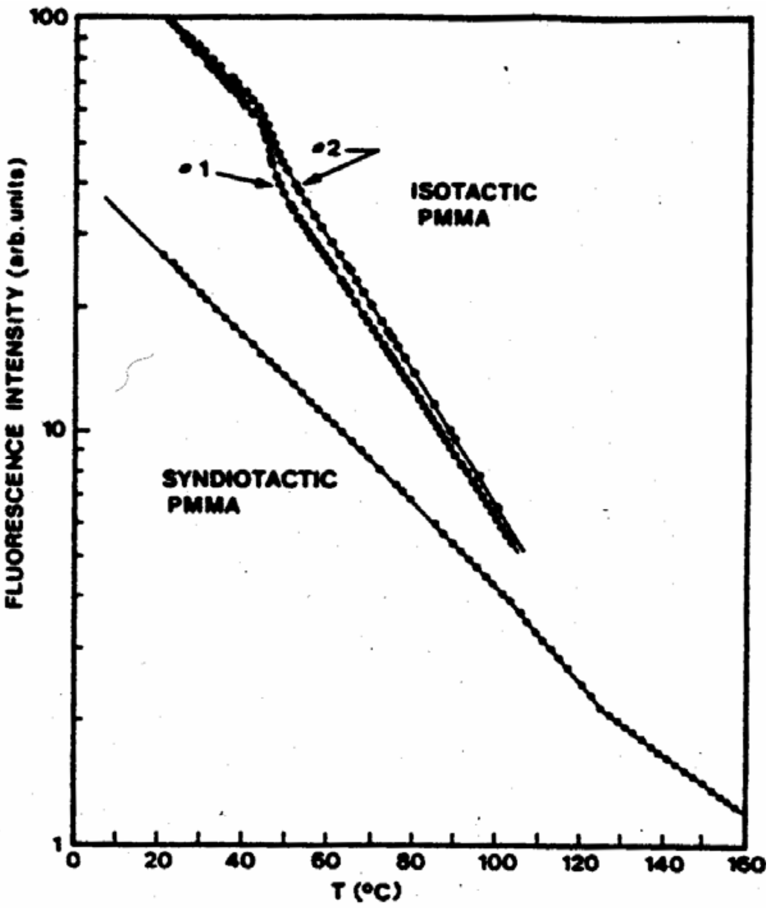
Internal rotations



JMN

Internal rotation competes with emission

Temperature dependent (viscosity) or free volume dependent emission intensity



R. O. Loutfy. Photophysical and photochemical tools in polymer science. 1986. Reidel Publ. Co.

Mobility probes

Emission decay dynamics and spectroscopy

Excimer formation

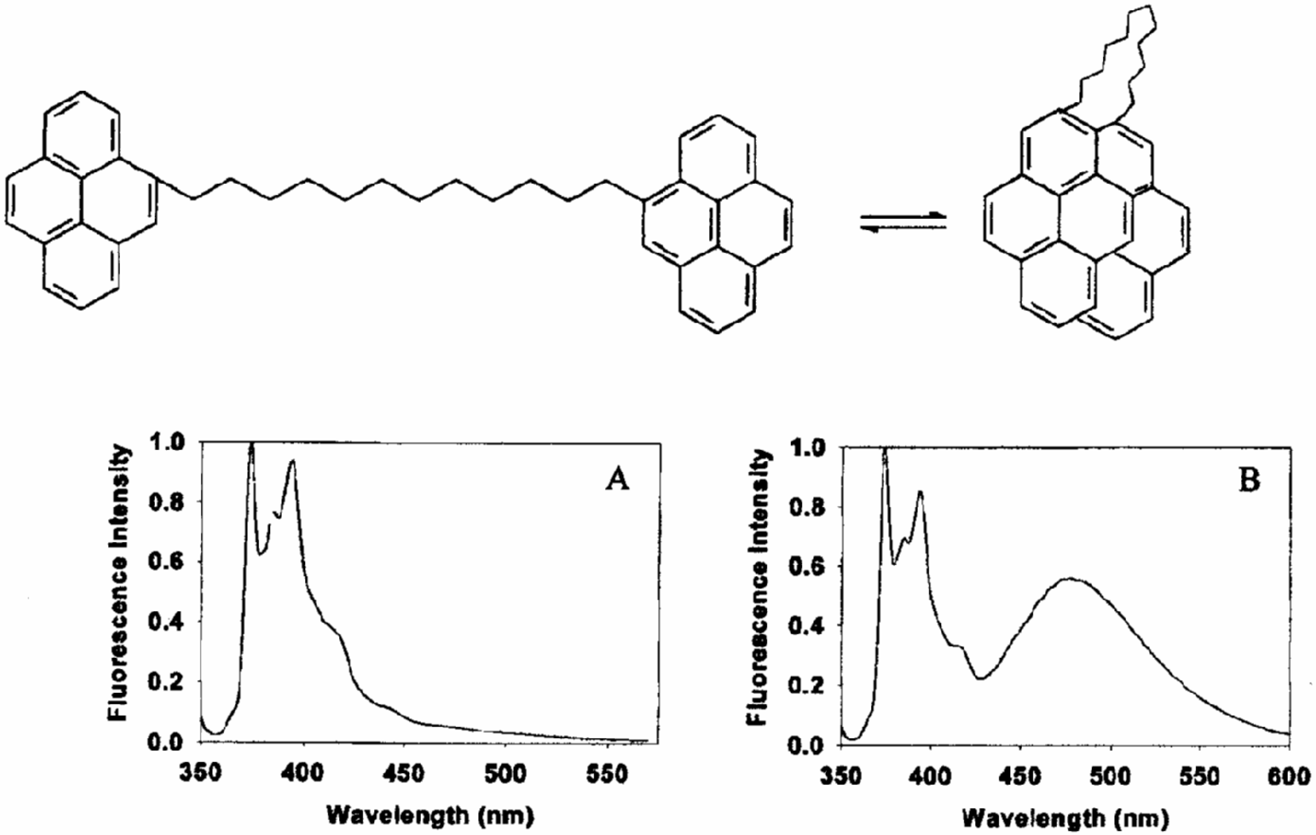


Figure 5. Open and closed forms of 1,12(bispyrenyl)dodecane and the corresponding emission profiles of (A) the extended form (monomer emission) and (B) the compact form (excimer emission) (adapted from ref 14).

Dunn & Zink. Chem. Mater. 9 (1997) 2280. Narang, U.; Bright, F. V. *Chem. Mater.* 1996, *8*, 1410

Mobility probes

Free volume evidences in polymers and in gels

Excimer formation of pyrene in PDMS.

D.Y.Chu & J.K.Thomas. Macromolecules 230 (1990) 2217

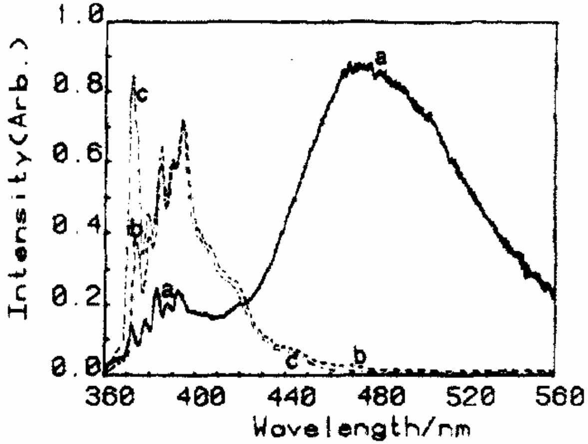
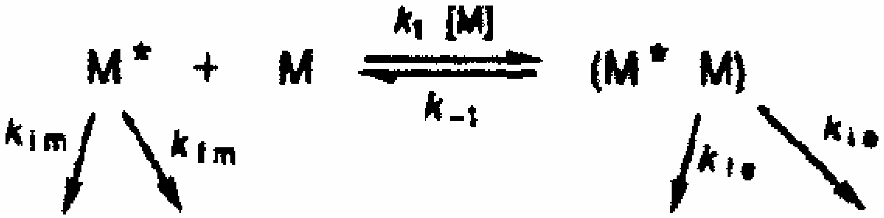


Figure 1. Emission spectra of 0.01 M pyrene fluorescence (a) in poly(dimethylsiloxane) (PDMS; 50 cP) (—), (b) in polystyrene (- - -), and (c) in epoxy film (– · –).

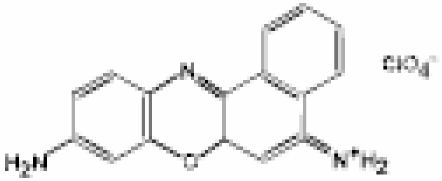


Excimer formation is twice faster in PDMS of 10^4 to 10^6 cP than in squalane (HC) of 35 cP

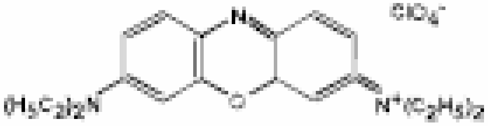
Mobility probes

Free volume evidences in polymers and in gels

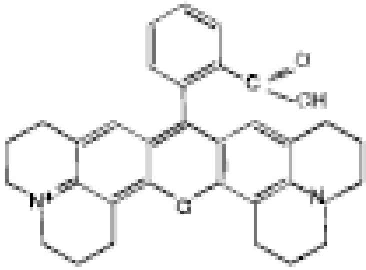
Emission anisotropy



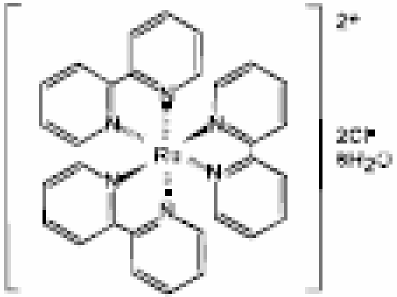
Cresyl Violet



Oxazine 1



Rhodamine101



Rbpy

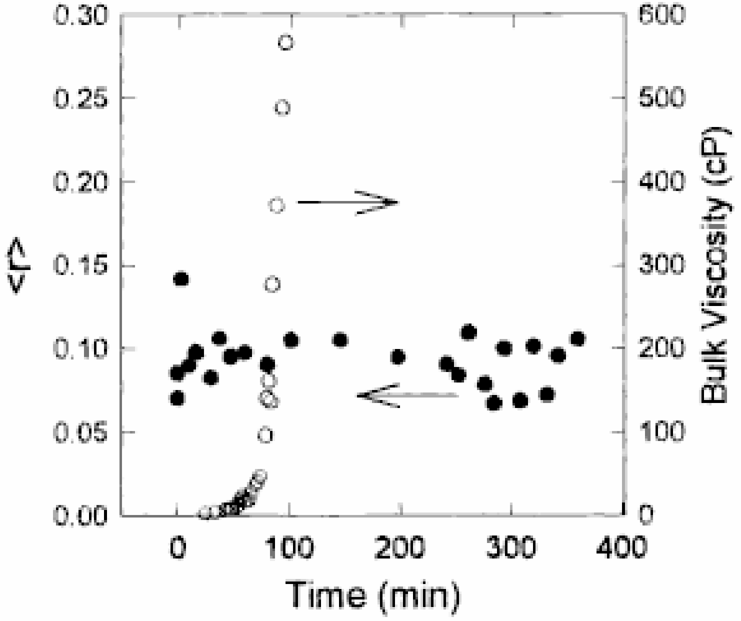


Figure 9. Steady-state anisotropy, ⟨r⟩, of Ox1 in gel A (●) and the gel bulk viscosity (○) as a function of time at 65 °C.

Marchi et al. Langmuir. 13 (1997) 3665

Mobility probes

Gels tested by PRODAN decay lifetime and anisotropy.

Aging of gels and polymers

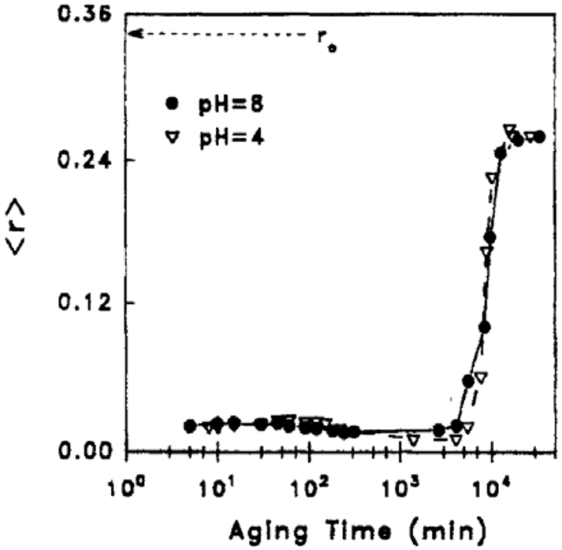


Figure 2. Steady-state anisotropy of PRODAN-doped TMOS sol–gels processed at pH 8 (●) and pH 4 (▽) as a function of aging time.

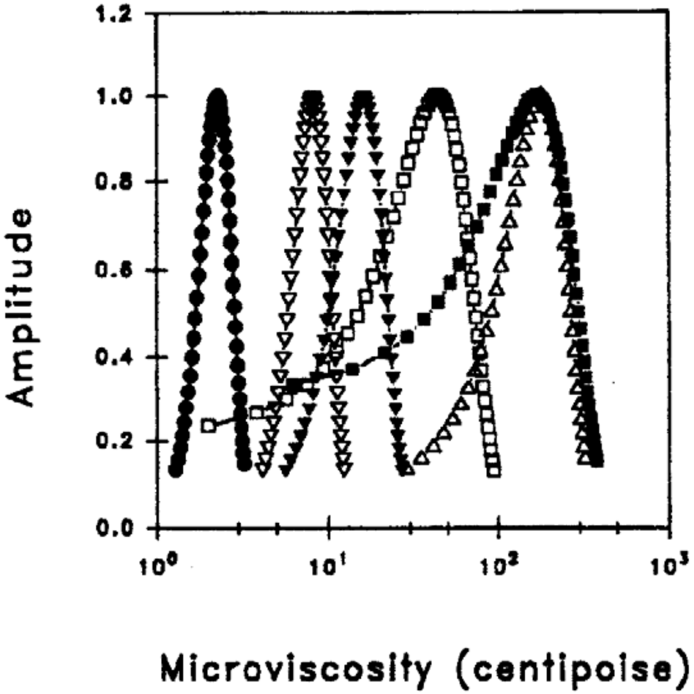
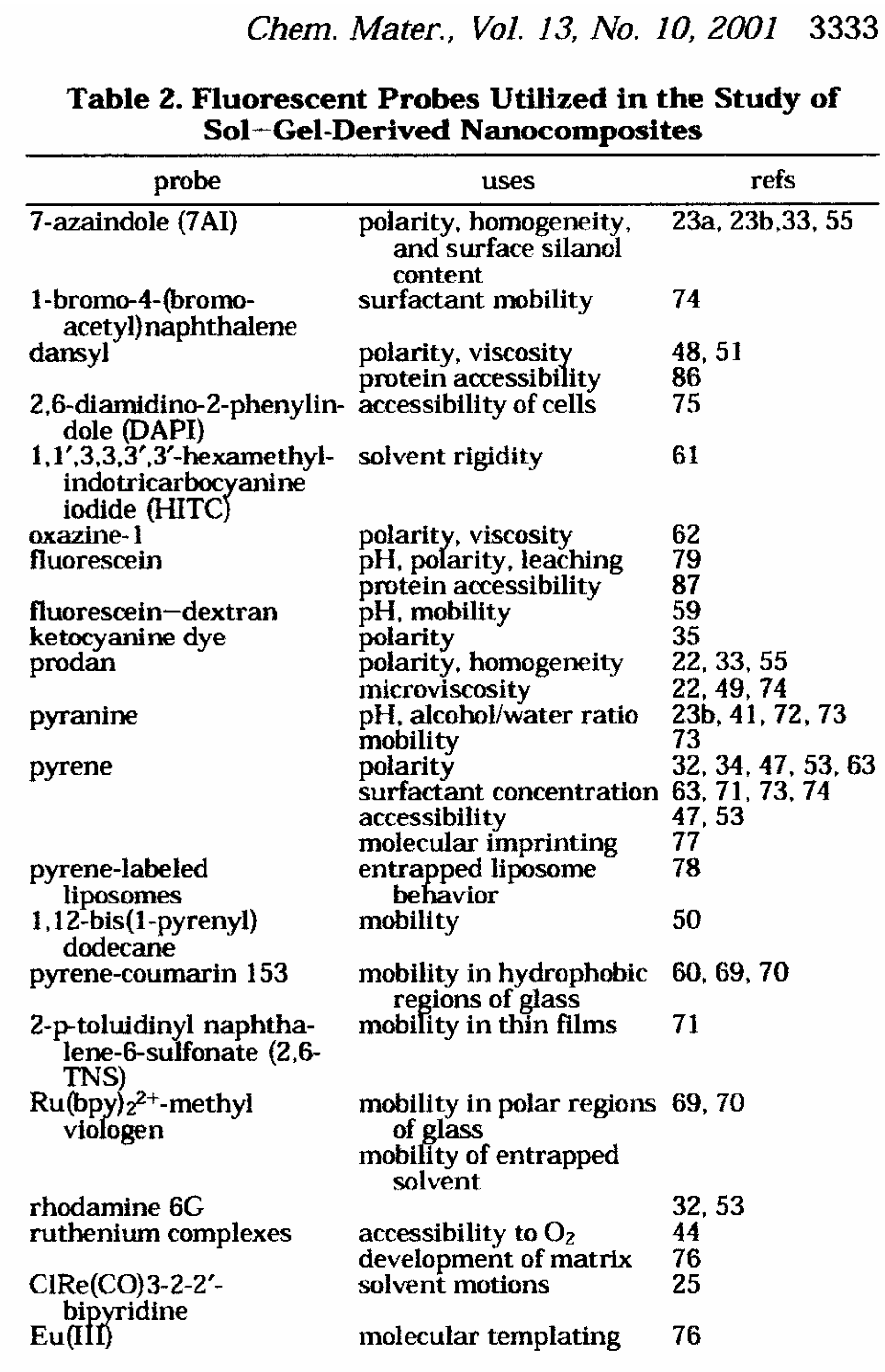


Figure 7. Recovered microviscosity distribution for a PRODAN-doped TMOS sol–gel (pH 8) after aging for 4 (●), 95 (▽), 141 (▼), 165 (□), 245 (■), and 573 h (△).

U. Narang et al. J. Phys. Chem. 98 (1994) 8101.



Chem. Mater., Vol. 13, No. 10, 2001 3333

Table 2. Fluorescent Probes Utilized in the Study of Sol–Gel-Derived Nanocomposites

probe	uses	refs
7-azaindole (7AI)	polarity, homogeneity, and surface silanol content	23a, 23b,33, 55
1-bromo-4-(bromoacetyl)naphthalene	surfactant mobility	74
dansyl	polarity, viscosity	48, 51
	protein accessibility	86
2,6-diamidino-2-phenylindole (DAPI)	accessibility of cells	75
1,1′,3,3,3′,3′-hexamethylindotricarbocyanine iodide (HITC)	solvent rigidity	61
oxazine-1	polarity, viscosity	62
fluorescein	pH, polarity, leaching	79
	protein accessibility	87
fluorescein–dextran	pH, mobility	59
ketocyanine dye	polarity	35
prodan	polarity, homogeneity	22, 33, 55
	microviscosity	22, 49, 74
pyranine	pH, alcohol/water ratio	23b, 41, 72, 73
	mobility	73
pyrene	polarity	32, 34, 47, 53, 63
	surfactant concentration	63, 71, 73, 74
	accessibility	47, 53
	molecular imprinting	77
pyrene-labeled liposomes	entrapped liposome behavior	78
1,12-bis(1-pyrenyl) dodecane	mobility	50
pyrene-coumarin 153	mobility in hydrophobic regions of glass	60, 69, 70
2-p-toluidinyl naphthalene-6-sulfonate (2,6-TNS)	mobility in thin films	71
$Ru(bpy)_2^{2+}$-methyl viologen	mobility in polar regions of glass	69, 70
	mobility of entrapped solvent	
rhodamine 6G		32, 53
ruthenium complexes	accessibility to O_2	44
	development of matrix	76
ClRe(CO)3-2-2′-bipyridine	solvent motions	25
Eu(III)	molecular templating	76

Review on fluorescent probes for nanocomposite materials.

Two classes of materials are analyzed:

Class I: Sol-gels with dispersed organic additives.

Class II. Sol-gels with attached organic functionalities.

Keeling-Tucker & Brennan. Chem. Mater. 13 (2001) 3331

Examples to work out next time:

✓ HBD probes in PVA	SS & TR Fluorescence
✓ Eu(III) complexes in silica gels	Electronic energy transfer
✓ Spiropyrans and fulgides in LC	Photoisomer absorption
✓ Coumarins & rhodamines in crosslinked polystyrene	Fluorescence anisotropy
✓ Spiropyrans and spirooxazines in poly(alkylacrylates)	Photoisomer absorption
✓ Rhodamine in PVA	Single molecule blinking

Processes

✓ Gelation & gel ageing

✓ Spatial and time heterogeneity in polymer films

✓ Free volume in polymers

✓ Photoinduced CD in liquid crystals