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

Examples

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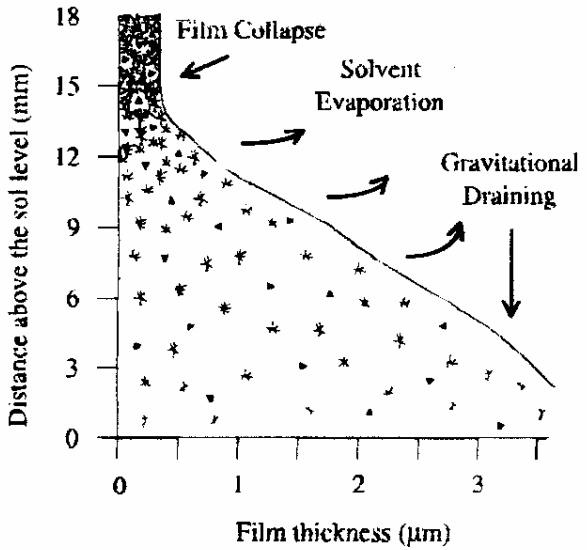
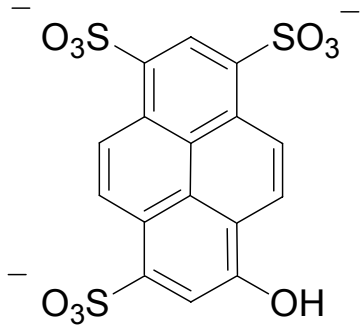
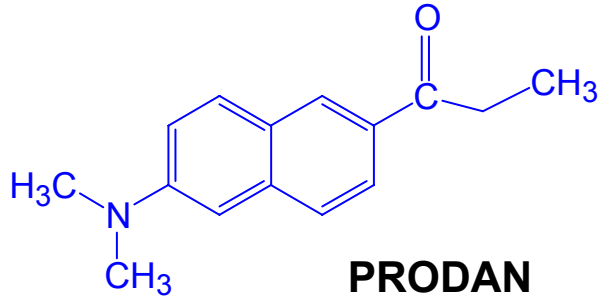
In-situ monitoring of the gelation of dip-coated films

Probes: Pyranine and Prodan
Emission polarization



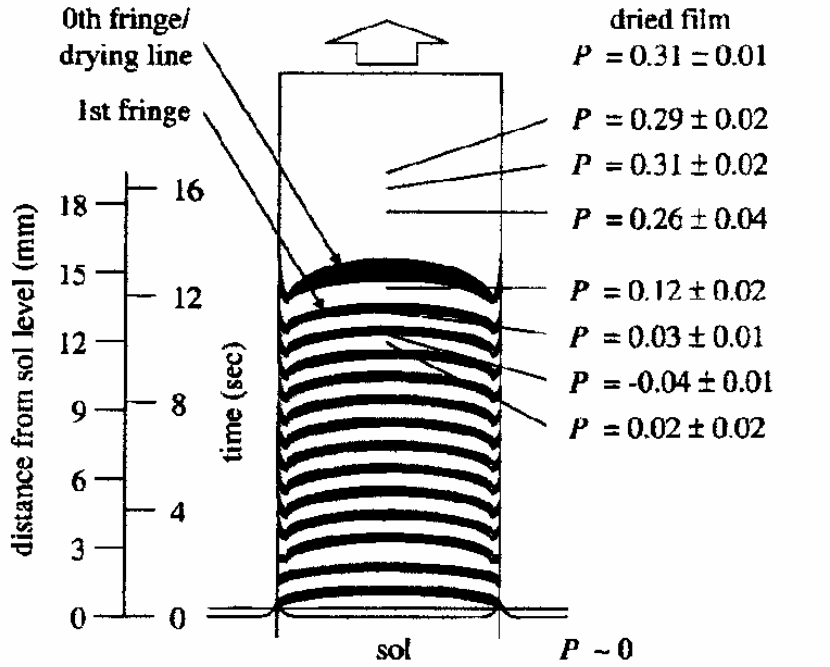


PYRANINE



PRODAN

$$\frac{1}{r} = \frac{3}{2}\left(\frac{1}{P} - \frac{1}{3}\right)$$



- Probes rotate freely until the film is ca. 500nm thick
- Aging of the sol also restricts the mobility

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

Aging of TMOS gels

$$r = \frac{r_0}{1 + \tau_f / \phi_r} \qquad \phi_r = \frac{\eta V_h}{kT}$$

Gels tested by Prodan decay lifetime and anisotropy.

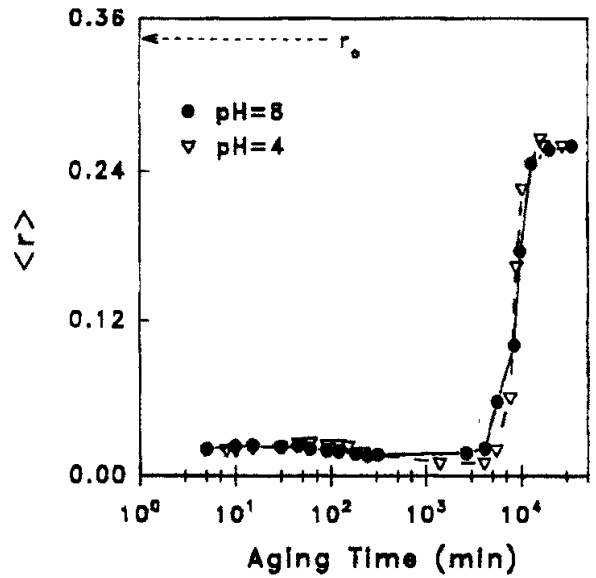


Figure 2. Steady-state anisotropy of PRODAN-doped TMOS sol–gels processed at pH 8 (●) and pH 4 (▽) as a function of aging time.

Aging time

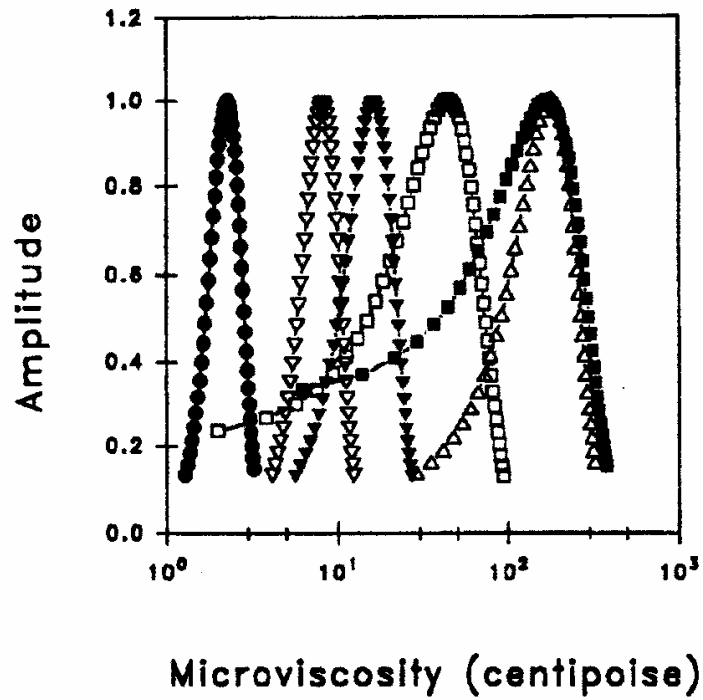
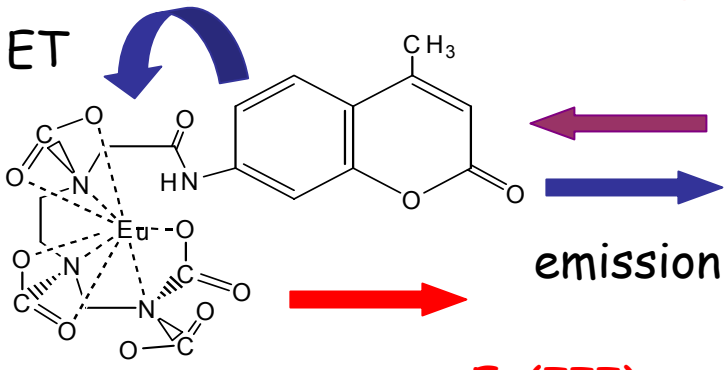


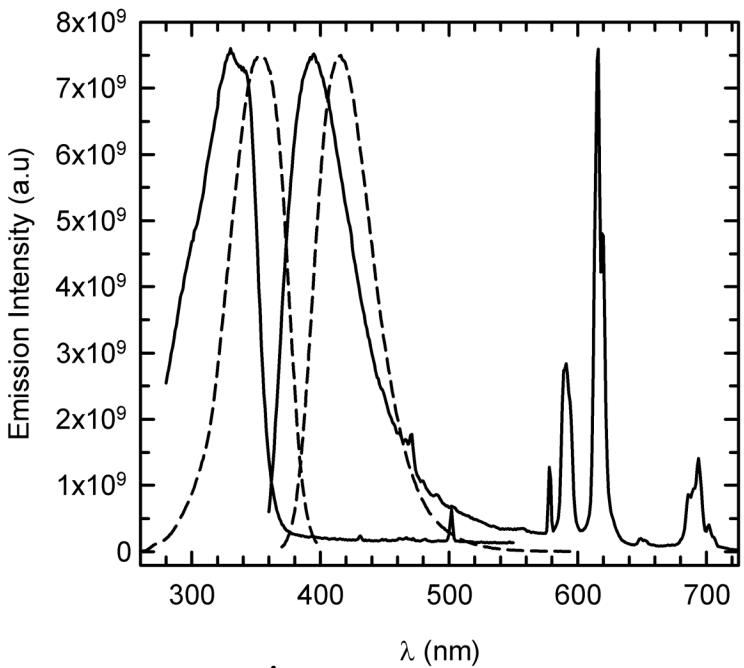
Figure 7. Recovered microviscosity distribution for a PRODAN-doped TMOS sol–gel (pH 8) after aging for 4 (●), 95 (▽), 141 (▼), 165 (□), 245 (■), and 573 h (△).

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

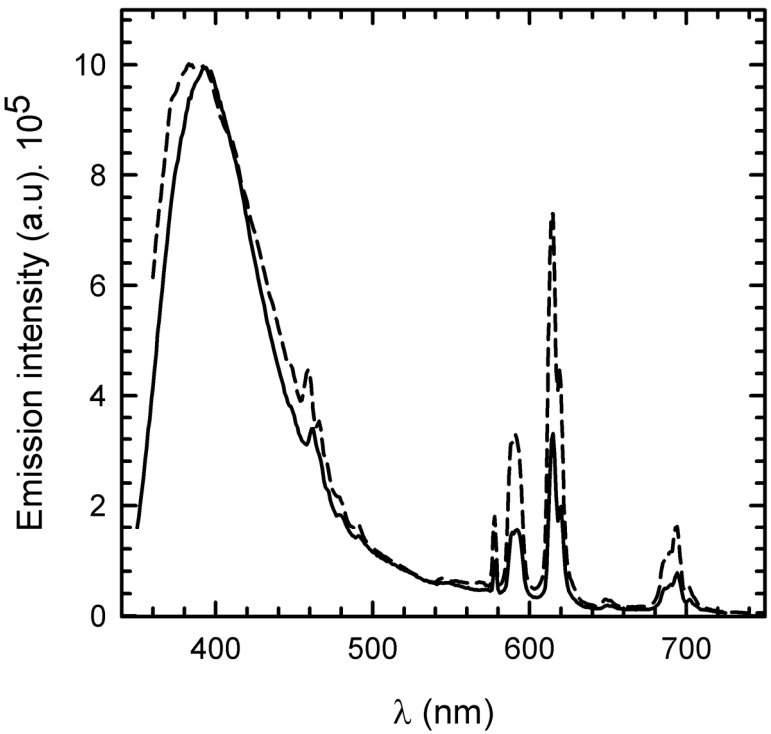
Energy transfer in Eu(III)-antenna complex in silica gels: Effect of aging

Eu(dtpa)Coum





Aqueous solution

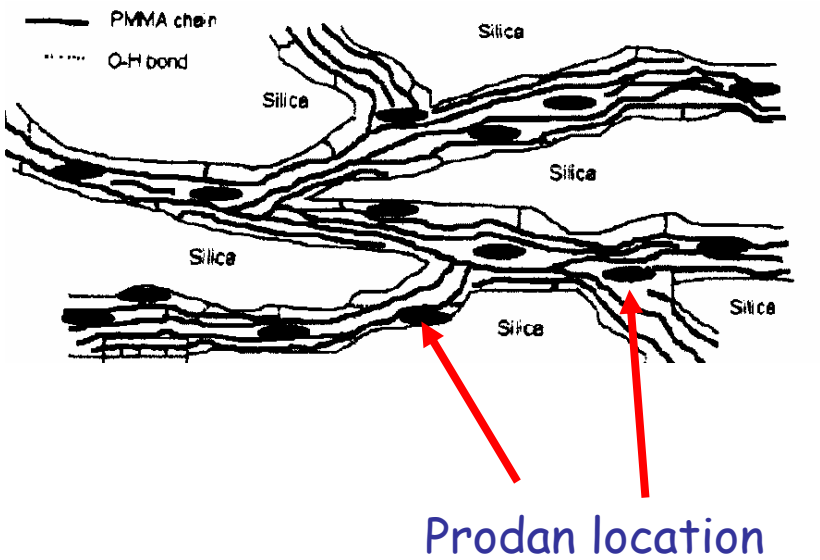


Silica gel 6 months difference

Barja, Remorino, Aramendía. Submitted

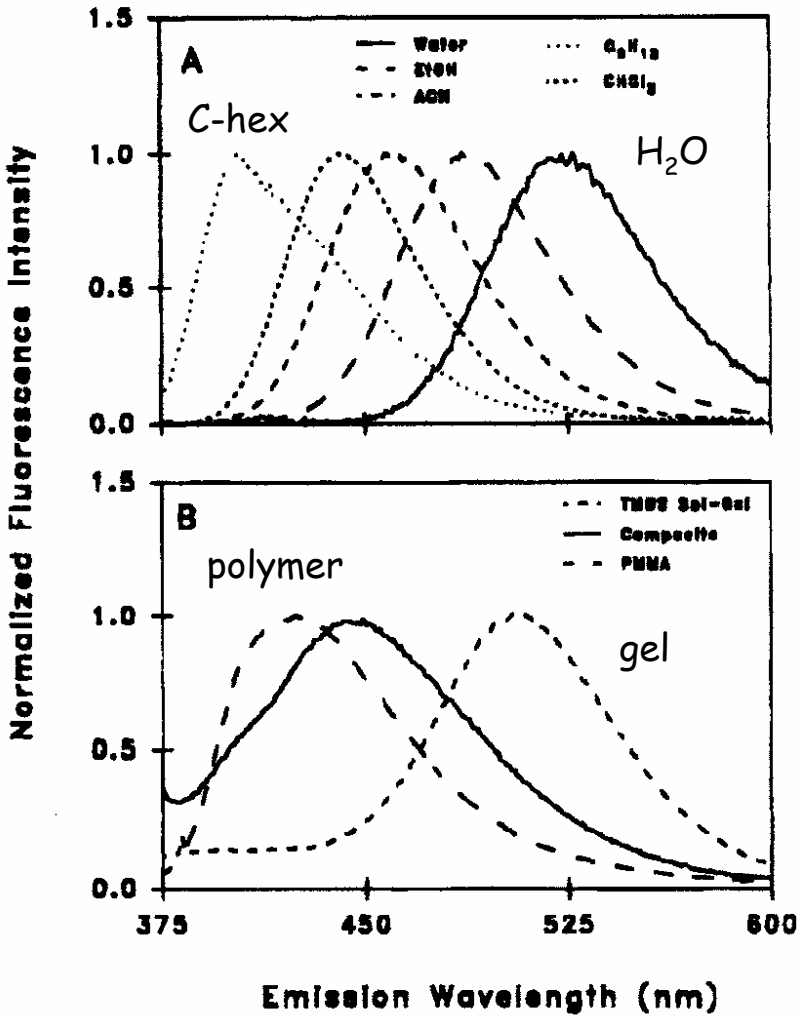
Polymer-gel composite material

- PMMA-silica-gel
- Prodan as probe
- Steady state and time-resolved spectroscopy



Prodan location

Prodan locates in PMMA and is influenced by the -OH bonds of the gel

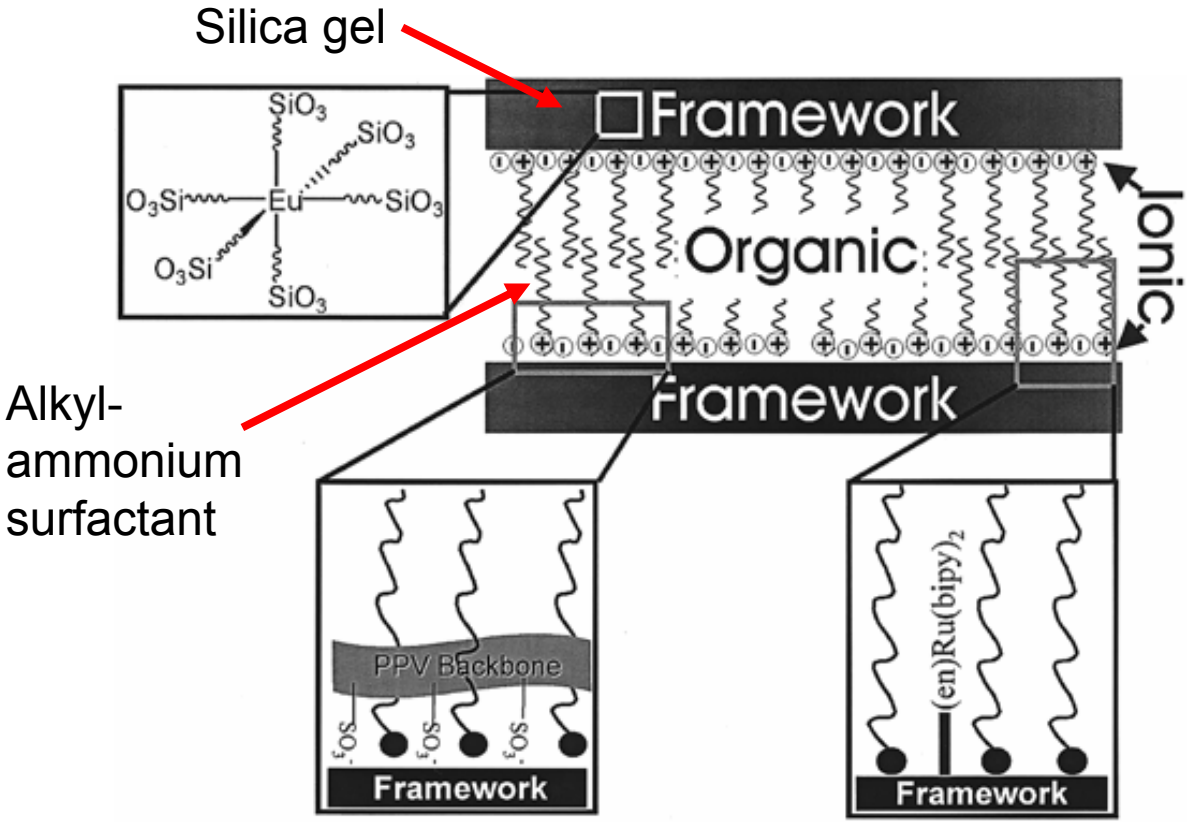


Emission spectra in different solvents and in the composite

R. Gvishi et al Chem. Mater. 7 (1995) 1703.

Controlled placement of luminescent probes in mesostructured sol-gel thin films

Probing different environments with multiple probes



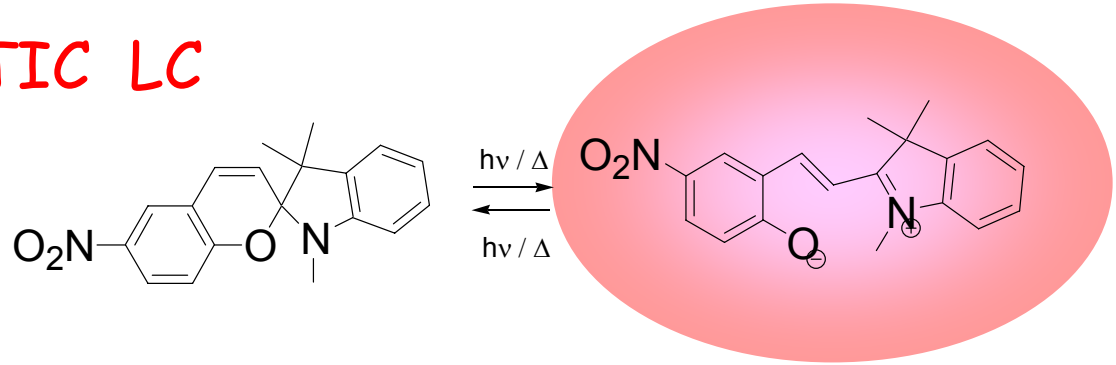
Probes:

- Eu(III) in the silica gel
- Anionic polymer in the ionic layer (Poly-2,5-methoxy,propyloxysulfonate phenylene vinylene
- $Ru(II)(bpy)_2(en)$ attached to the framework surface

Steady state,
time resolved emission
emission anisotropy

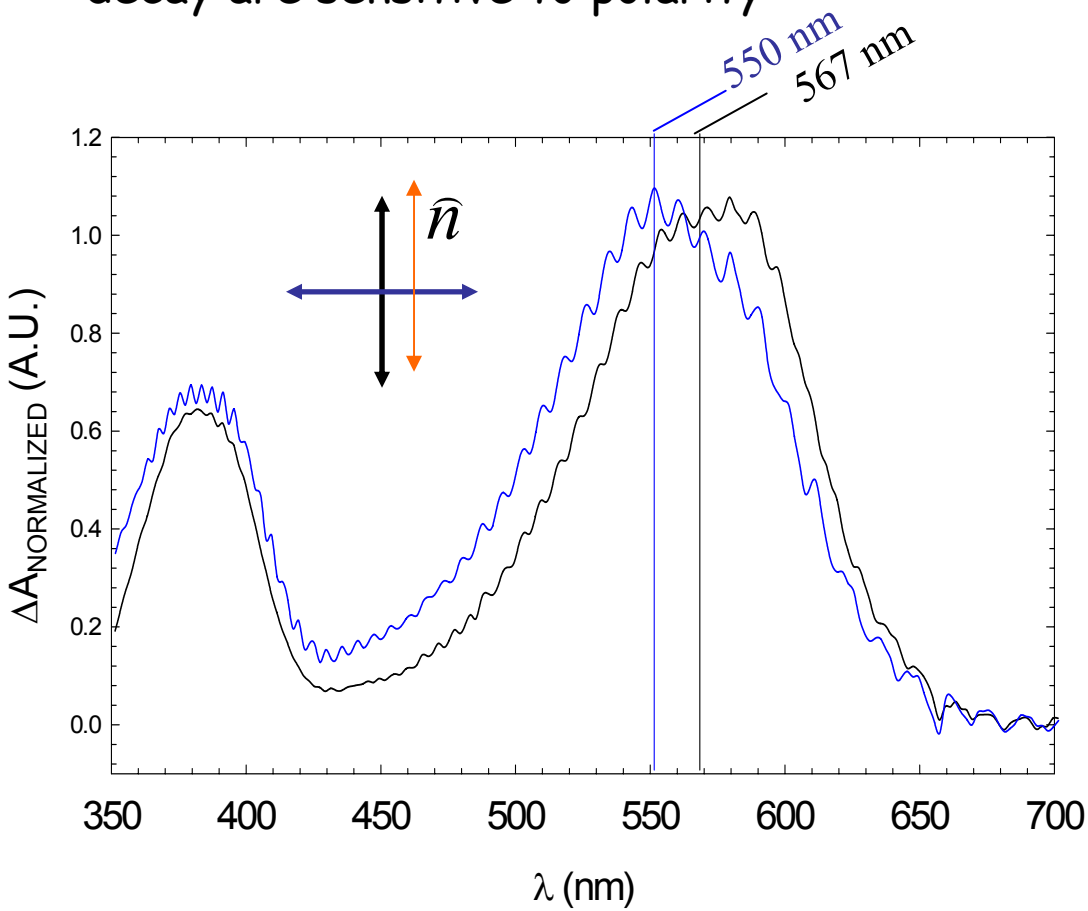
R. Hernandez, et al, JACS 123 (2001)1248.

SPIROPYRAN in NEMATIC LC



- The absorption of the merocyanine form and its decay are sensitive to polarity

→ Diference between perpendicular and parallel absorption



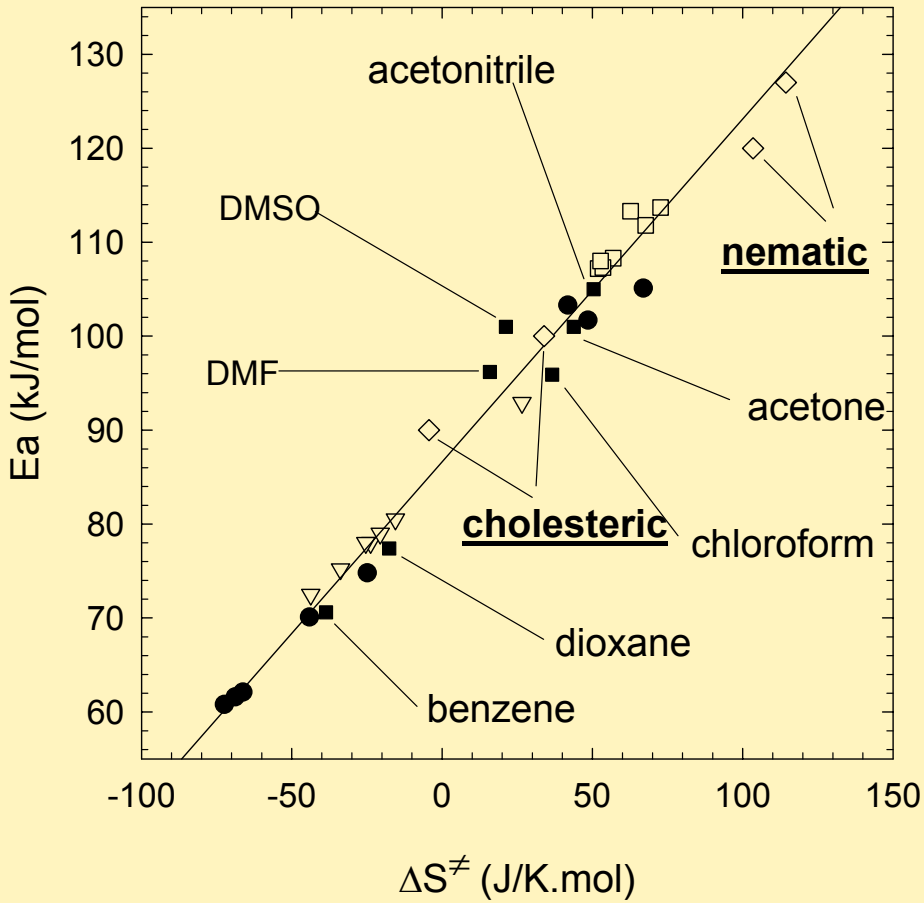
Environment similar to acetonitrile (553 nm, ⊥) or acetone (565 nm, ∥)

Biexponencial decay (∥ y ⊥)
High E_a y $\Delta S^{\neq}$.

$k^{30°}$ (s^{-1})	$6{,}7.10^{-3}$	$2{,}4.10^{-3}$
E_a (kJ/mol)	130	126
$\Delta S^{\neq}$ (J/K.mol)	134	113

Bossi, Aramendía, unpublished results

SPIROPYRAN in NEMATIC LC

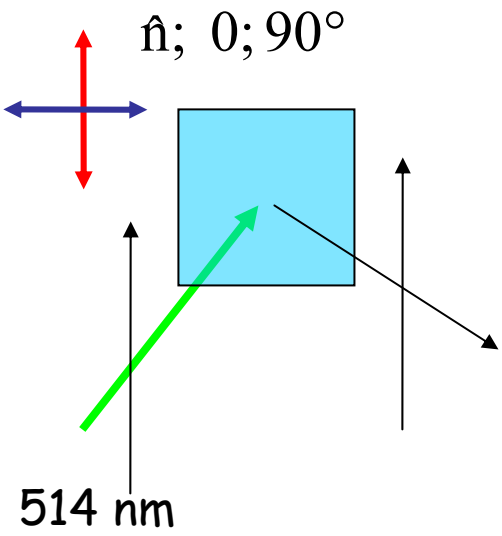


Ea y $\Delta S^{\neq}$ of MC decay are linearly related in fluids.

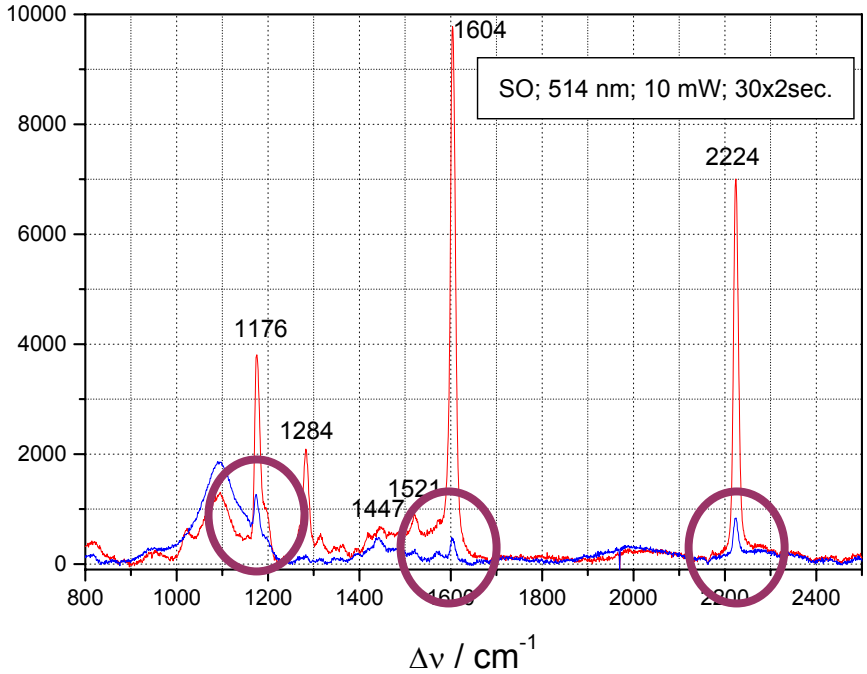
The slope: 365 K is quite apart from the average temperature: 310 K

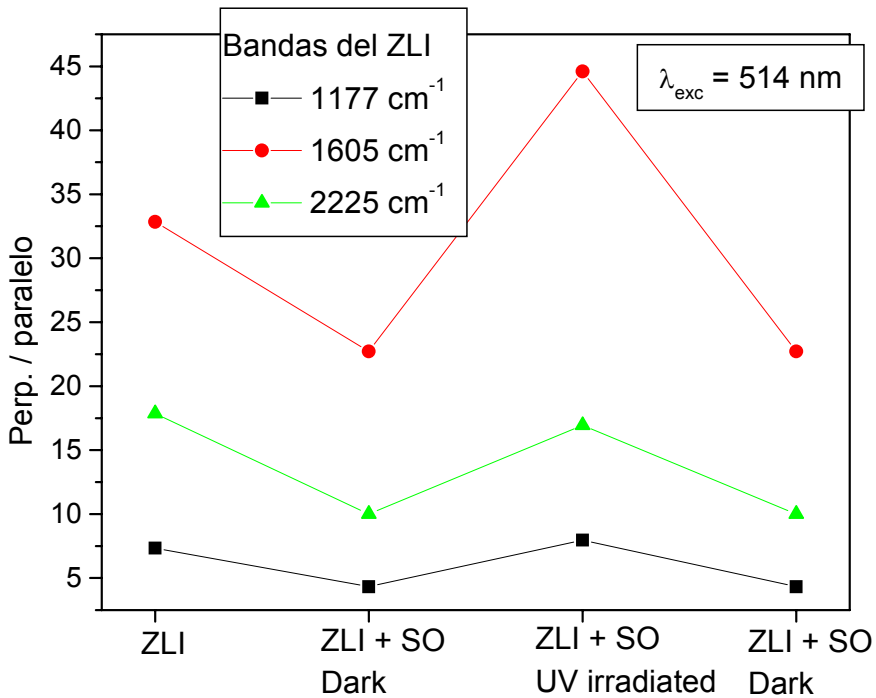
Bossi, Aramendía, unpublished results

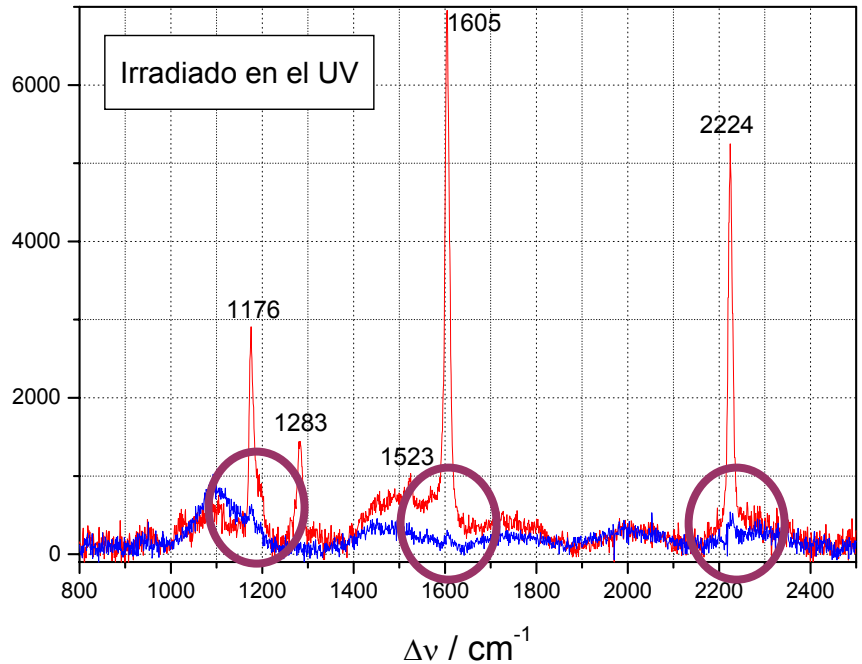
Spirooxazine in nematic LC



Polarized Raman scattering



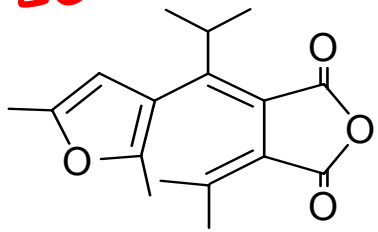


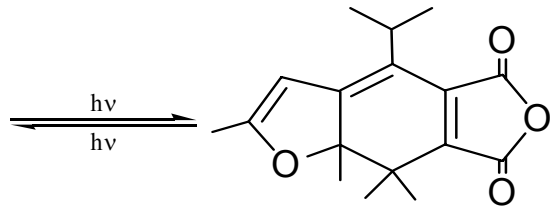


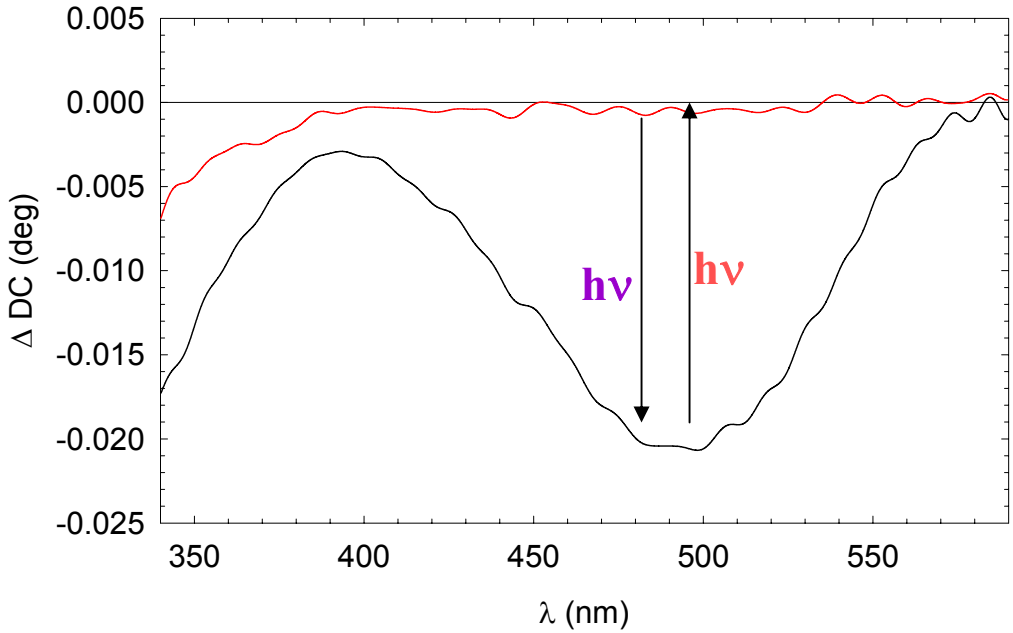
Bossi, Murgida, Aramendía, unpublished results

Fulgides in twisted nematic LC

Circular Dichroism







Cholesteric Phase Reversible Signal

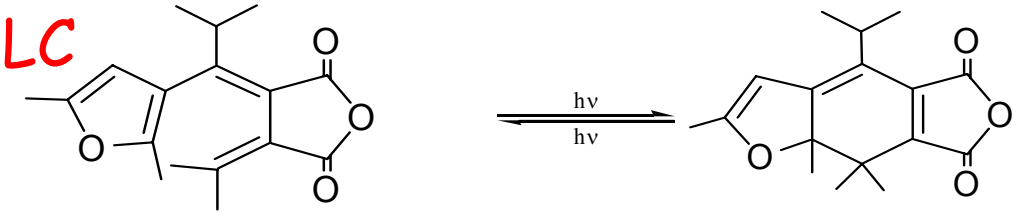
Chiral order of the mesophase

⇑

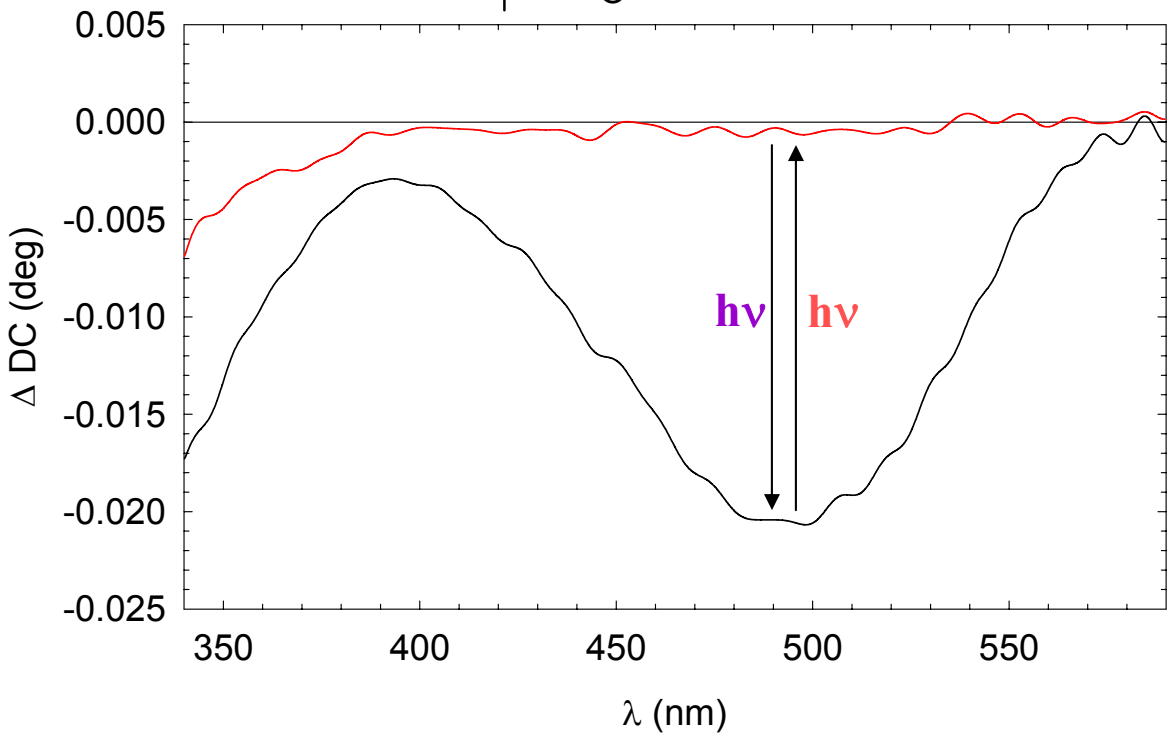
Solution → **NO SIGNAL**

Bossi et al JPPA In press

Fulgides in twisted nematic LC



Circular Dichroism



$$\theta_{CD}(\nu) = 0{,}576 lc\left[\varepsilon_L(\nu) - \varepsilon_R(\nu)\right]$$

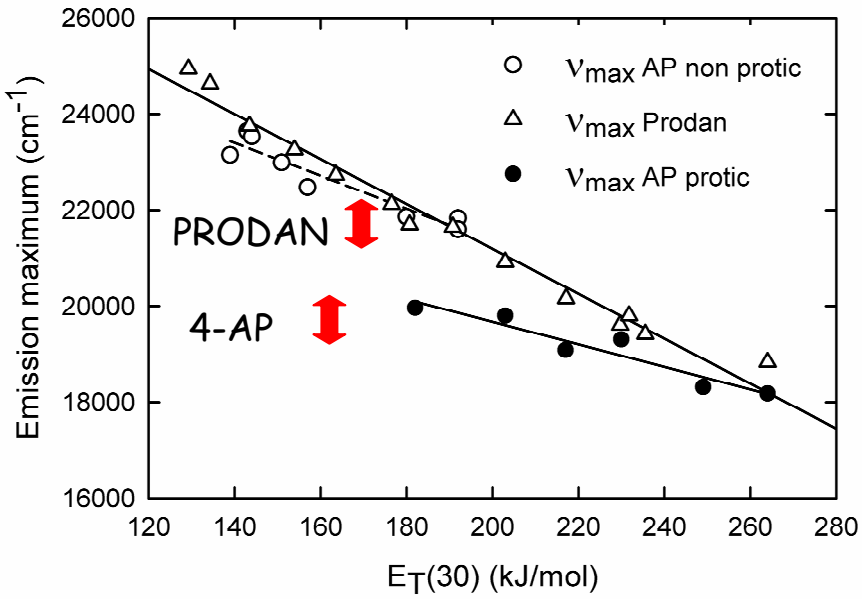
$$\Delta\varepsilon_{CD}(\lambda) = -P\Delta n\bar{\nu}\Delta\varepsilon_{LD}(\lambda)/2$$

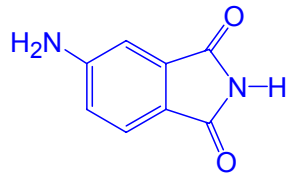
$$\Delta A_{LD} \approx 1{,}3.10^{-3}$$

Bossi et al JPPA In press

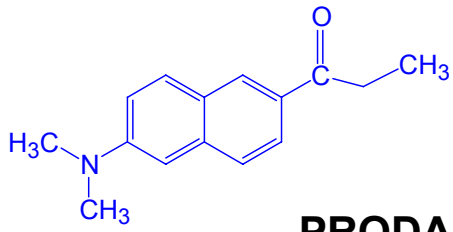
Relaxations in PVA

Solvatochromic plots for PRODAN and 4-AP



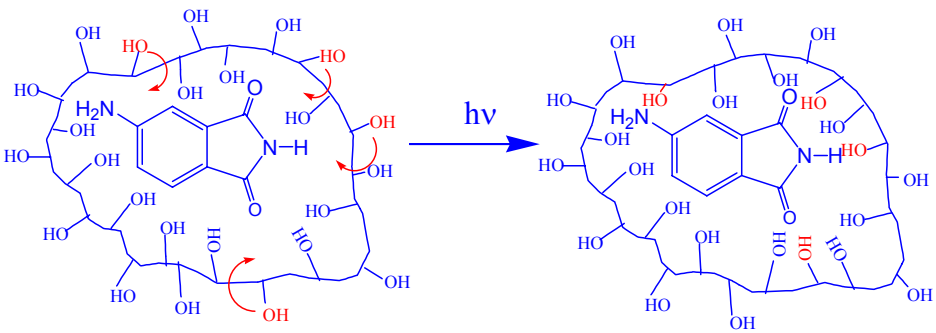


4-AP

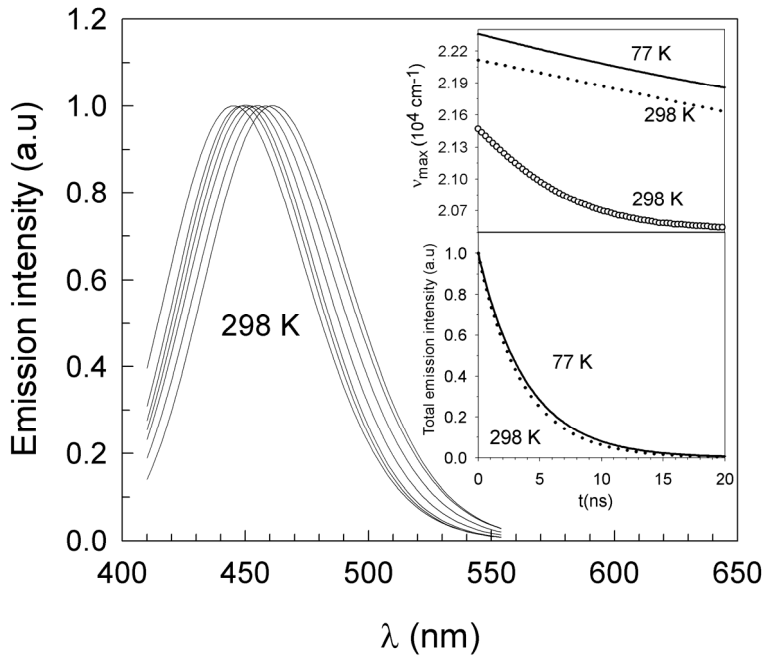


PRODAN

OH-pockets in PVA



TRES of Prodan in PVA

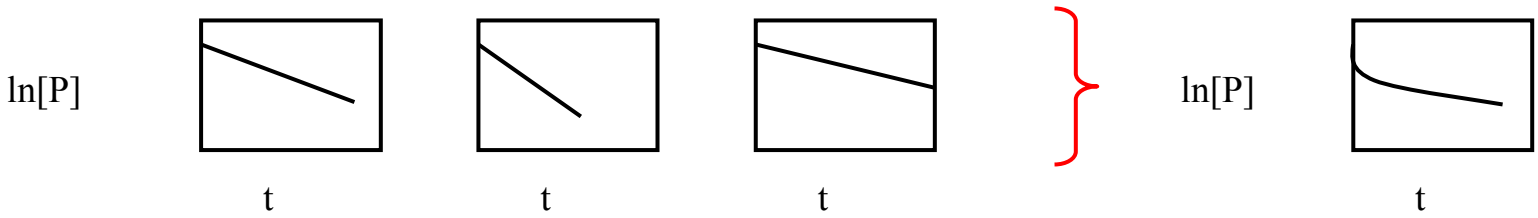


Barja et al J. Phys. Chem. B. In Press

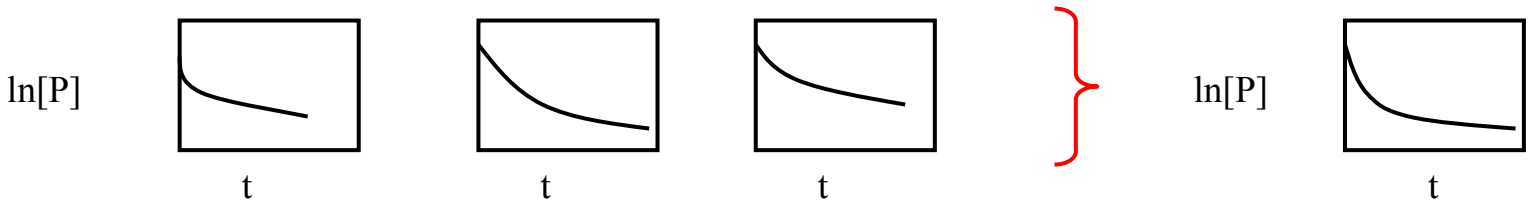
Dynamic domains for the kinetics

Comparison between the characteristic times of relaxation:
τ_P : of the metastable state
τ_M : of the environment

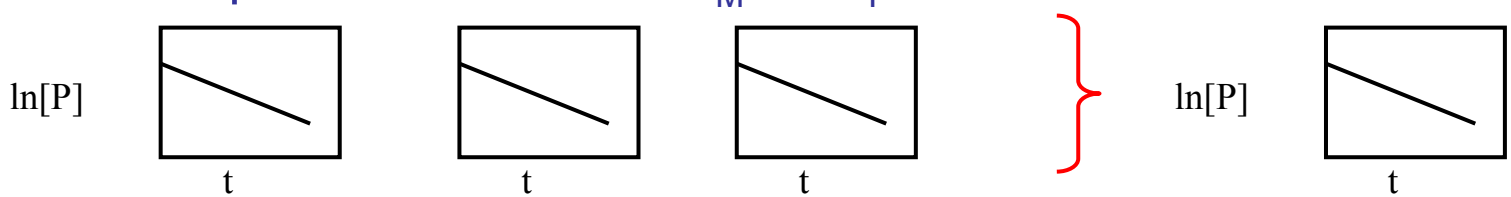
1: Distribution: $\tau_M >> \tau_P$



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

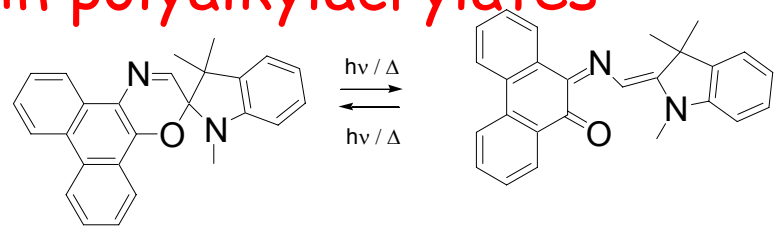


3: Equilibrium: $\tau_M << \tau_P$



Isomerization of spirooxazines in polyalkylacrylates

Testing: Decay of metastable open form



Systems

- Three polyalkylacrylates of different side chain length
- Different rigidity,decreasing: PMMA > PEMA > PiBMA
- Four naphtho- and phenanthrospirooxazines

Relaxation based decay

$$k = (k_0 - k_\infty).\exp(-t/\tau_m) + k_\infty$$

k_0 and k_∞: initial and relaxed decay rate constants

τ_m: relaxation time of the medium controlling the isomerization

Average activation energies; 4 probes

Polymers	**PMMA**	**PEMA**	**PiBMA**
Ea(k_0)	64±2	65±4	61±2
Ea(k_∞)	72±9	78±8	78±4
Ea($1/\tau_m$)	62±5	60±6	56±4
E rel= Ea(k_∞)- Ea(k_0)	8±7	14±4	18±3

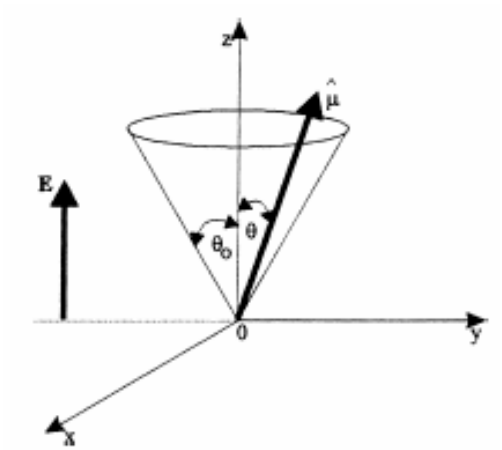
The softest polymer stabilizes more the extended open form

Levitus et al. J. Phys. Chem B 101(1997) 7680, 103(1999)1864, Völker et al . Helv. Chim. Acta 84(2001) 2751

Emission anisotropy of dyes embedded in polystyrene-co-2%-divinylbenzene

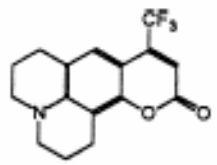
The probes rotate freely in a restricted volume

Wobbling in cone model

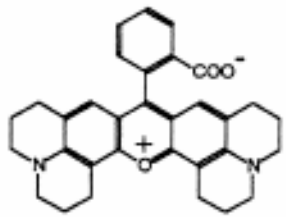


Levitus et al. JPPA (1997)

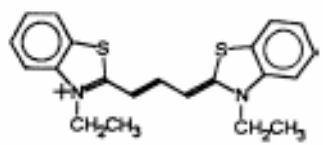
	τ_f (ns)	$\langle r \rangle$	r_0	S^a	$\theta_0{}^b$
Coumarin	~5[c]	0.018 ± 0.003	0.375[d]	0.22 ± 0.02	71° ± 1°
DTCI	0.3[e]	0.033 ± 0.003	0.370[f]	0.30 ± 0.01	65° ± 1°
Rhodamine 101	5.2[g]	0.044 ± 0.003	0.365	0.35 ± 0.01	62° ± 1°



Coumarin 153

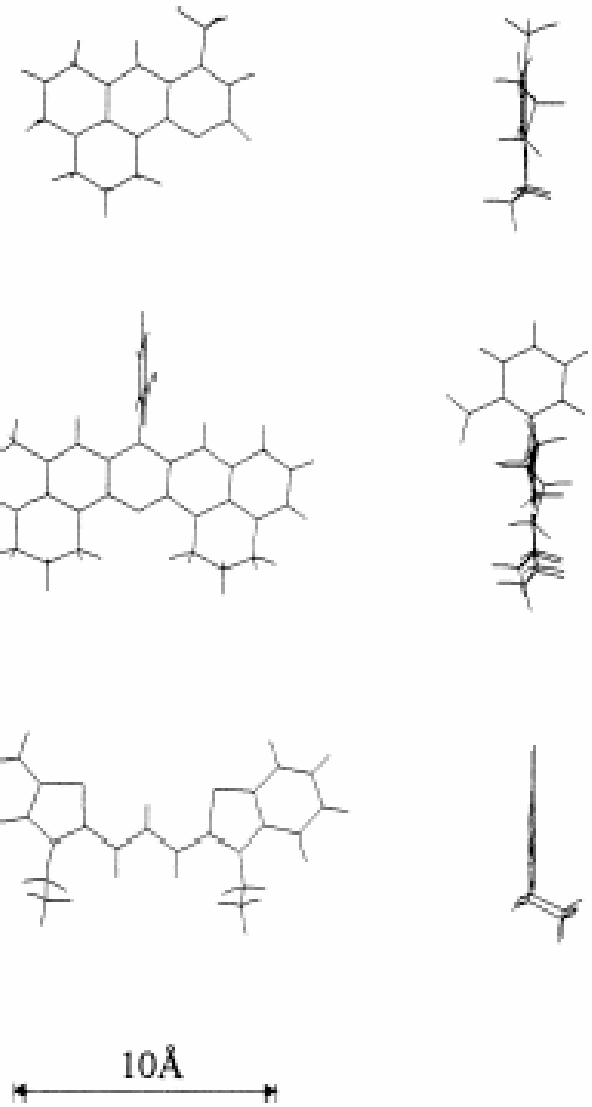


Rhodamine 101



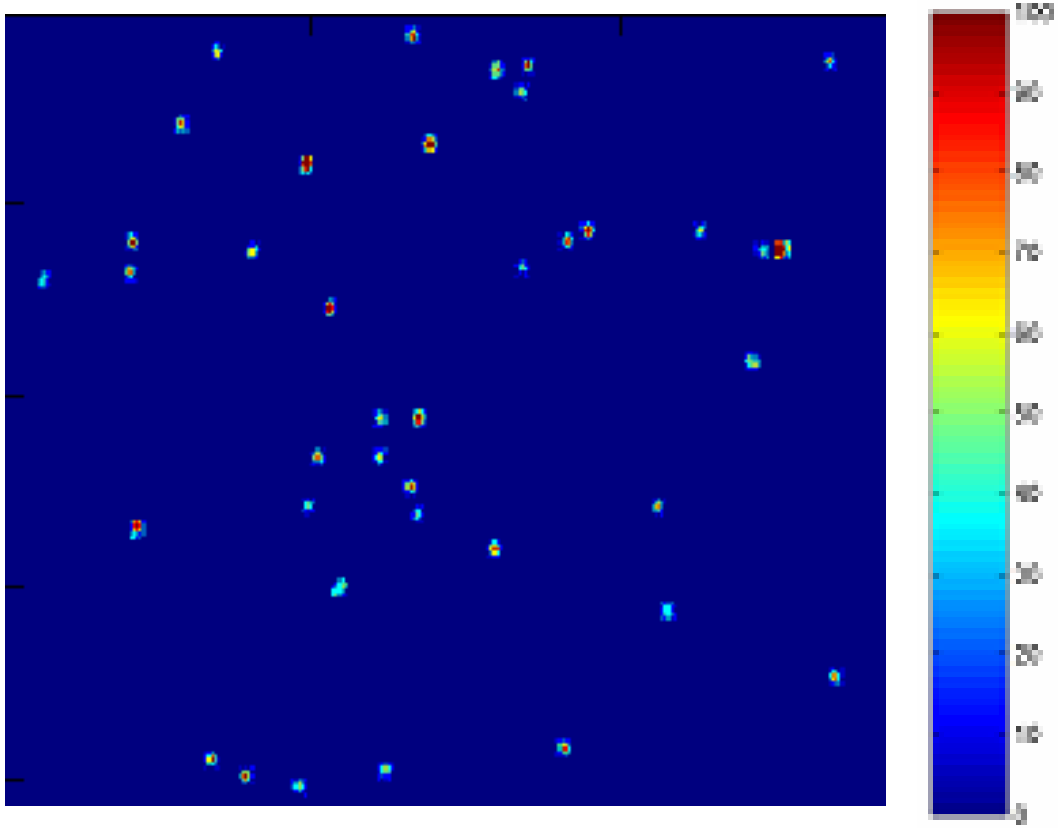
DTCI

Fig. 1. Structures of the dye molecules



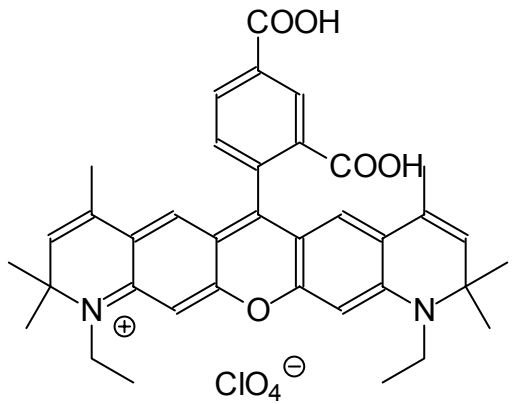
Single molecule blinking of Atto dyes in PVA

Wide field CCD camera detection of hundreds of single molecules simultaneously



Counts per pixel

Atto590

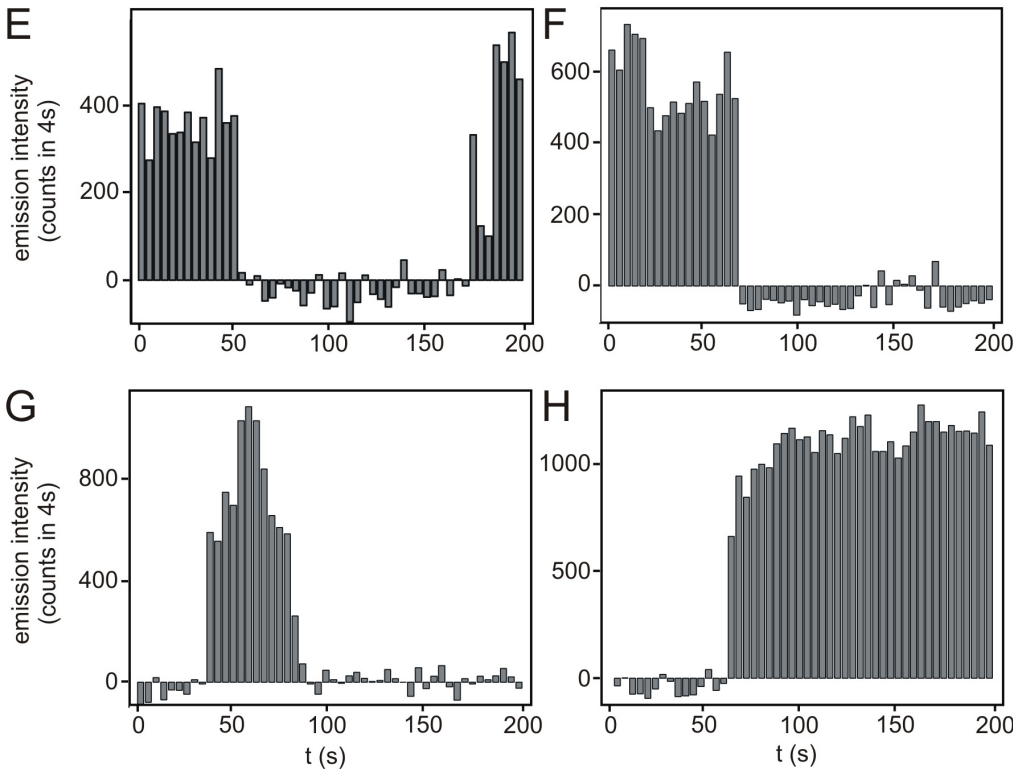


Time evolution followed by picture sequence

Gensch, Böhmer, Aramendía. J. Phys. Chem. A. (2005) In press

Single molecule blinking of Atto dyes in PVA

Time traces of selected single molecules

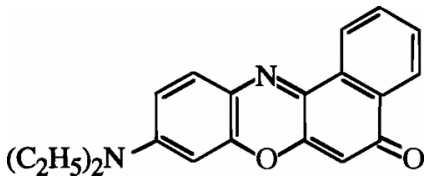


Frame 1 (Status)	Frame 4 (Status)	Frame 20 (Status)	Emission intensity on frame 20 (Nr of molecules)	Standard deviation[a]
ON	--	ON	747 (77)	500
OFF	--	ON	583 (50)	270
--	ON	ON	750 (79)	492
--	OFF	ON	570 (48)	271

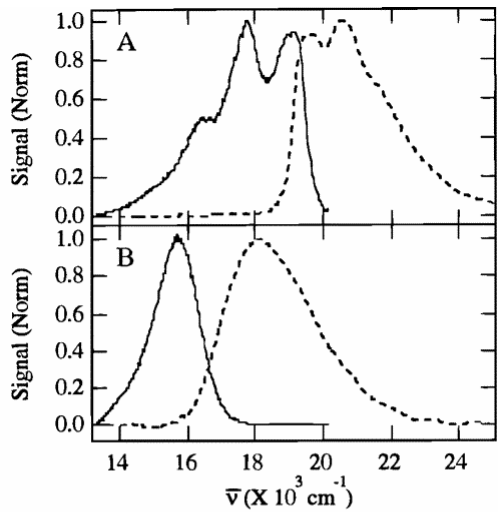
Blinking molecules locate in different environments than bright ones

Gensch, Böhmer, Aramendía. J. Phys. Chem. A. (2005) In press

Microheterogeneity by single molecule emission spectra

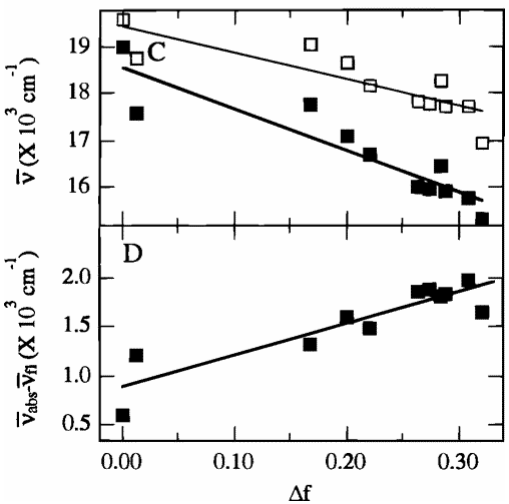


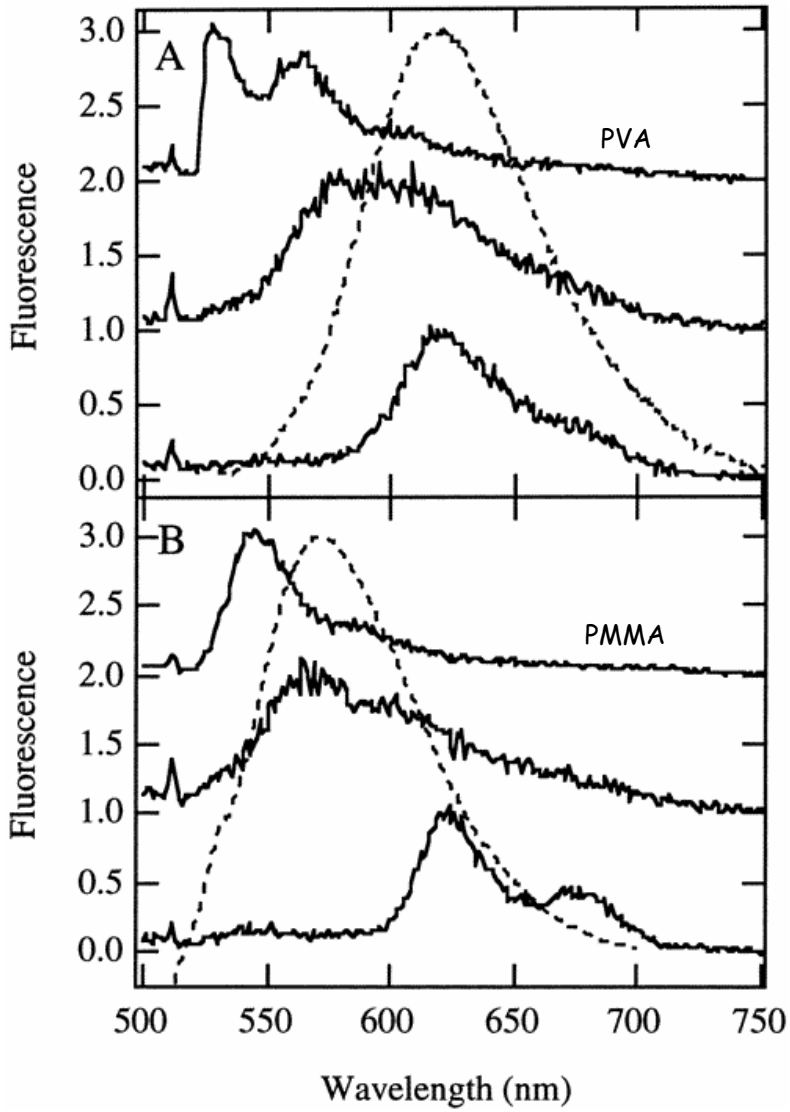
Nile red



hexane

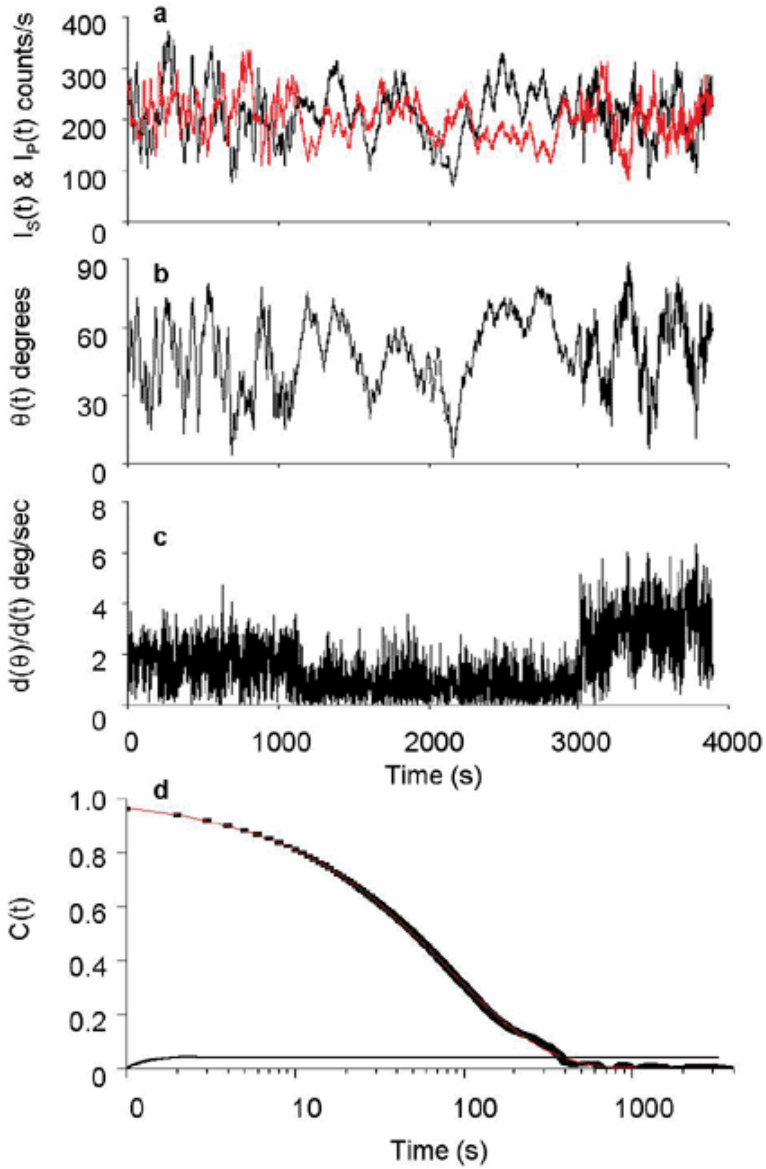
methanol

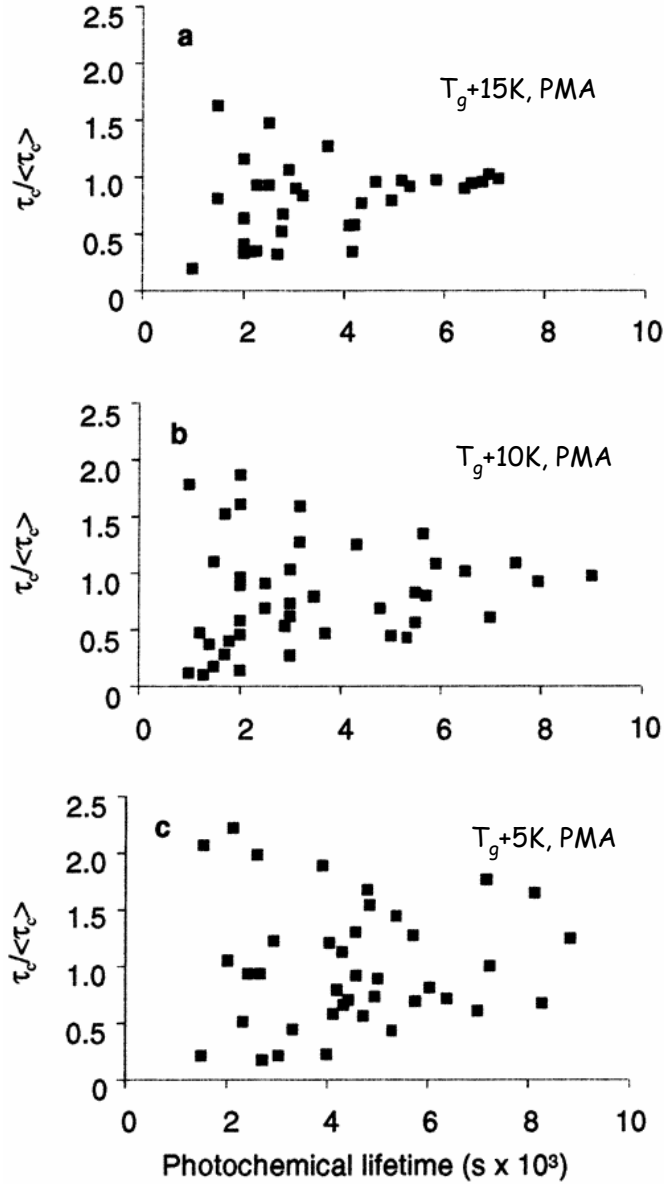




D. Higgins. *J. Phys. Chem. B,* 104 (2000) 212.

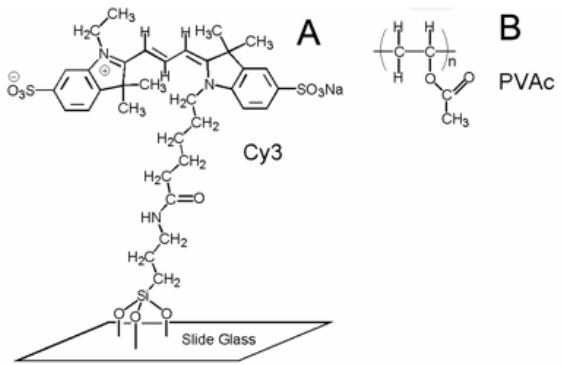
Local orientational fluctuations of Rh6G in PMA and PnBMA

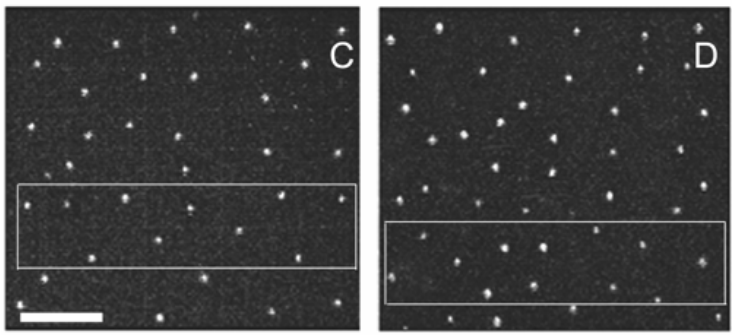


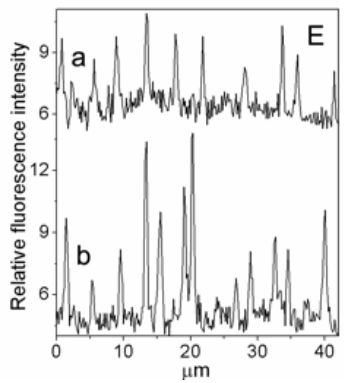


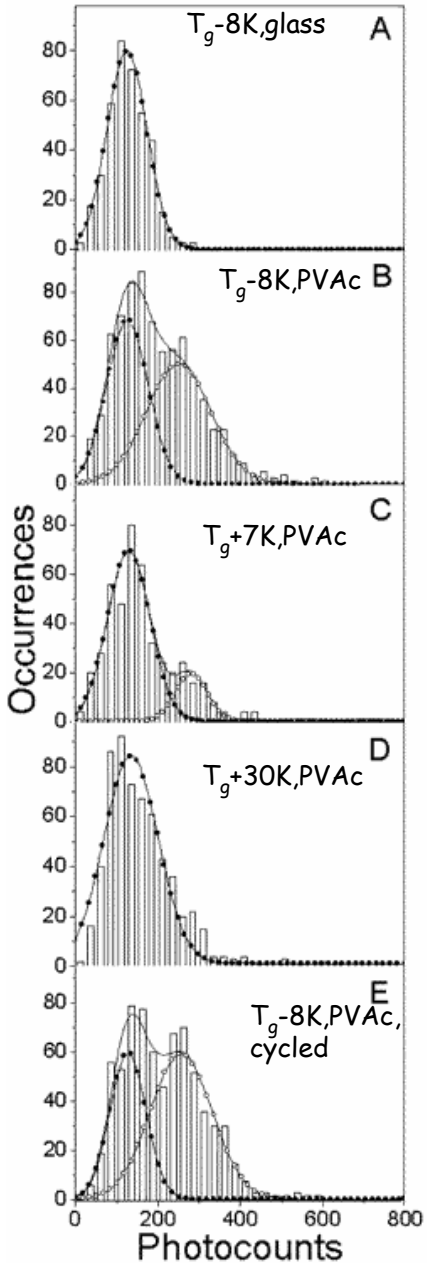
D. Vanden Bout *J. Phys. Chem. B* 105 (2001) 11978

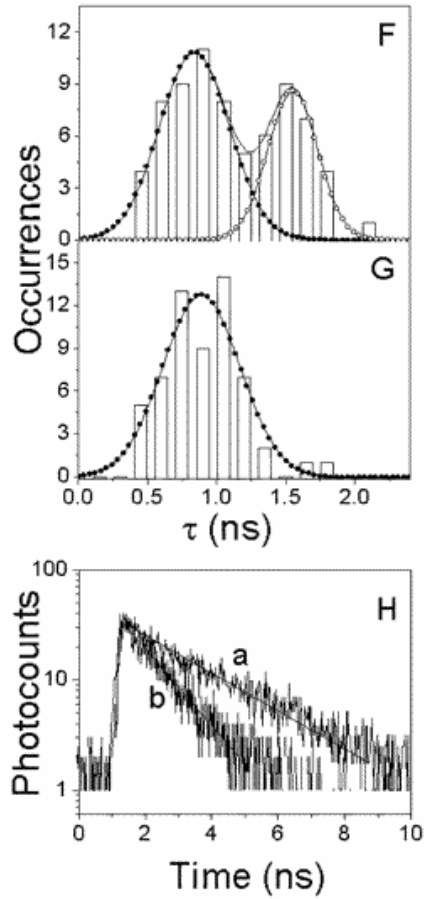
Spatial heterogeneity in PVAc thin films









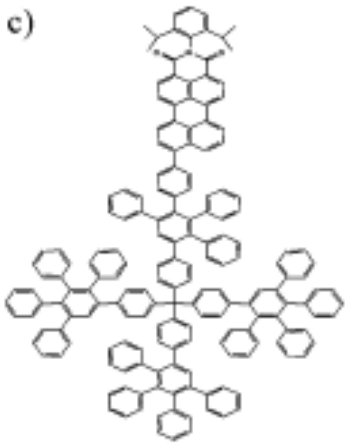


Biju, V. P.; Ye, J. Y.; Ishikawa, M. *J. Phys. Chem. B.* 107 (2003) 10729

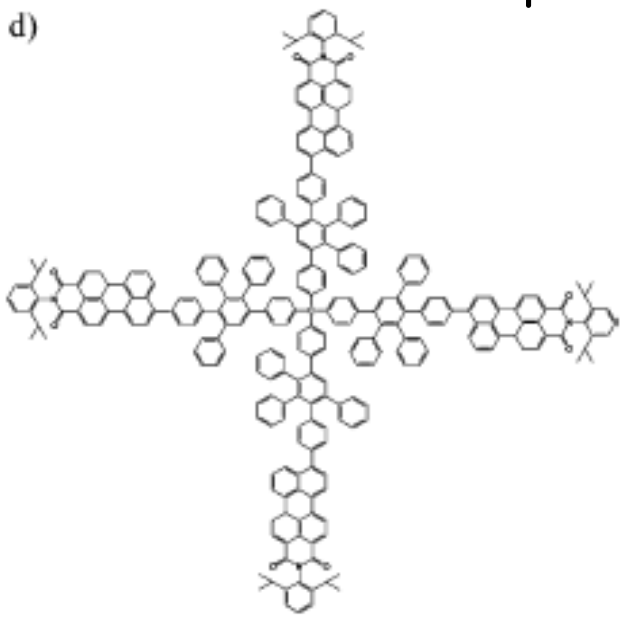
Electronic energy transfer in multichromophoric systems

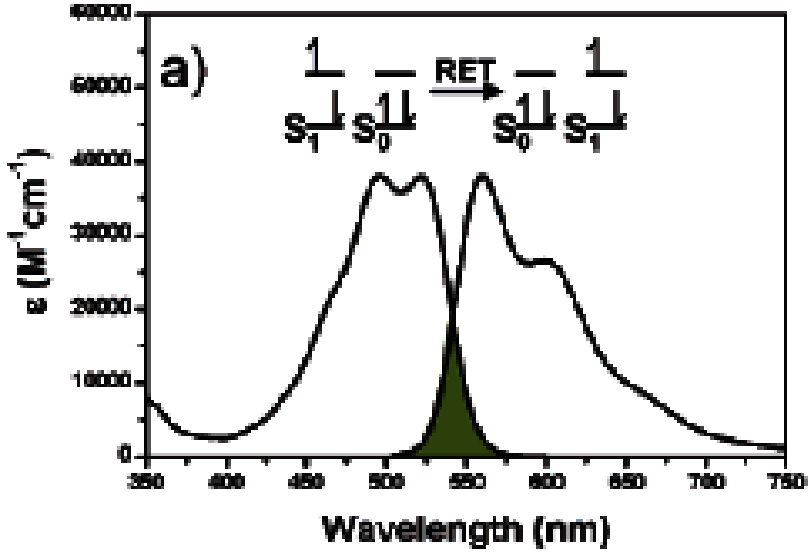
Dendrimers with peryleneimide chromophores

C1P1p



C1P4p





Absorption and emission of C1P1p and C1P4p in toluene. Spectral overlap is shadowed

C1P1p and C1P4p
ϕ_f = 0.98
τ_f = 4 ns
Anisotropy decay
ϕ_r = 0.05 ns and 1.7 ns

De Schryver et al. Acc Chem. Res. 380 (2005) 514.

Electronic energy transfer in multichromophoric systems

Single molecule emission anisotropy of C1P4p immobilized in a polymer matrix

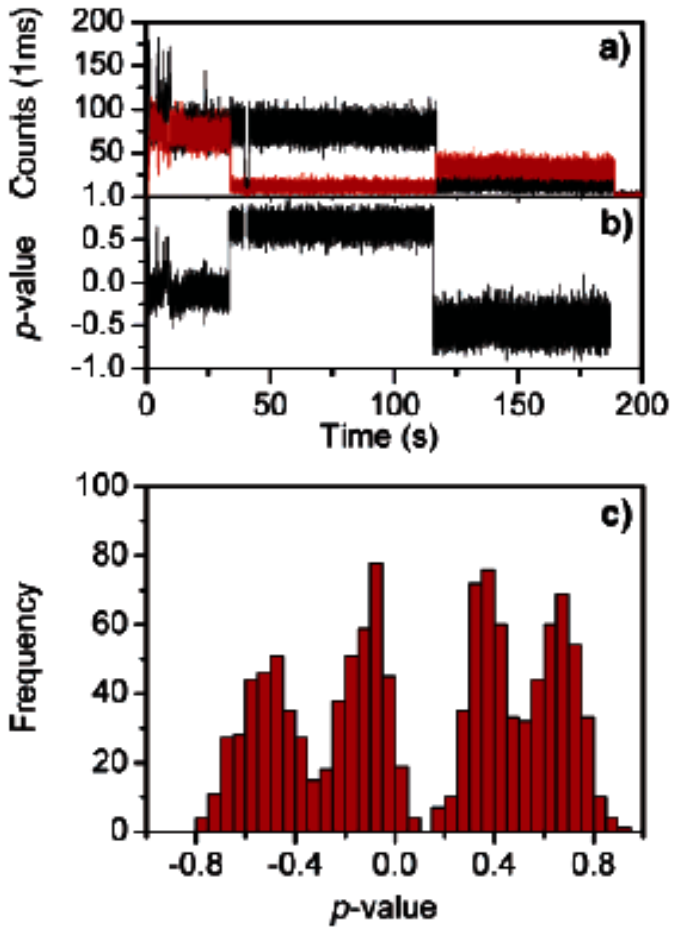


FIGURE 4. Example of (a) a transient of C1P4p where the parallel and perpendicular component where detected separately, (b) the polarization value of the trace in panel a, and (c) a histogram of the four *p* levels of the trace in panel b.

Electronic energy migration in a single molecule

Three dimensional orientation of the emission dipole of a single C1P4p molecule immobilized in a polymer matrix

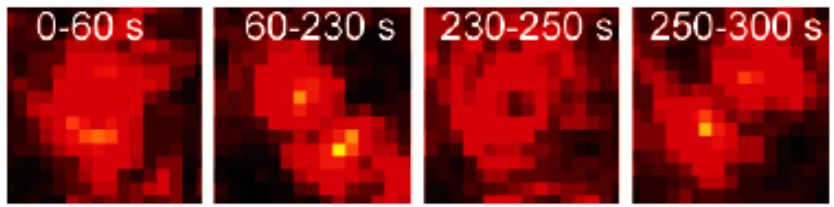


FIGURE 5. Emission patterns taken from a series of consecutive defocused images recorded for a single C1P4p in a 100 nm Zeonex film. Images were recorded at 1 μm defocusing to the glass surface. Time intervals, during which successive patterns have been observed, are listed underneath the images. The emission pattern of a single C1P4p molecule changes as function of time. The patterns provide direct evidence that different chromophores of the C1P4p emit in time as different dipole orientations.

De Schryver et al. Acc Chem. Res. 380 (2005) 514.

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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

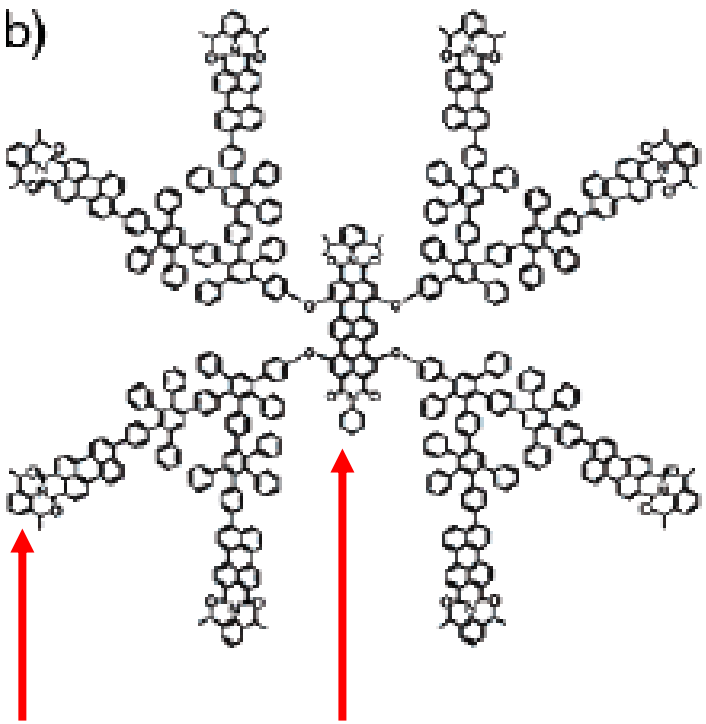
Processes

- ✓ Gel aging
- ✓ Spatial and time heterogeneity in polymer films
- ✓ Free volume in polymers
- ✓ Photoinduced CD in liquid crystals

Electronic energy transfer in multichromophoric systems

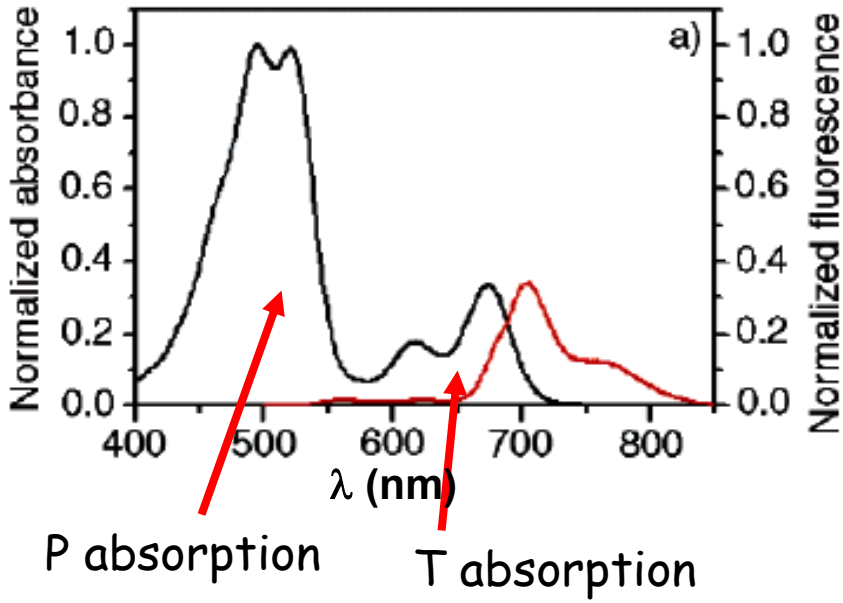
Dendrimer with different chromophores

T2P8



Peryleneimide (P) Terrylenediimide (T)

Absorption and emission of T2P8 in toluene.



Antenna effect is expected

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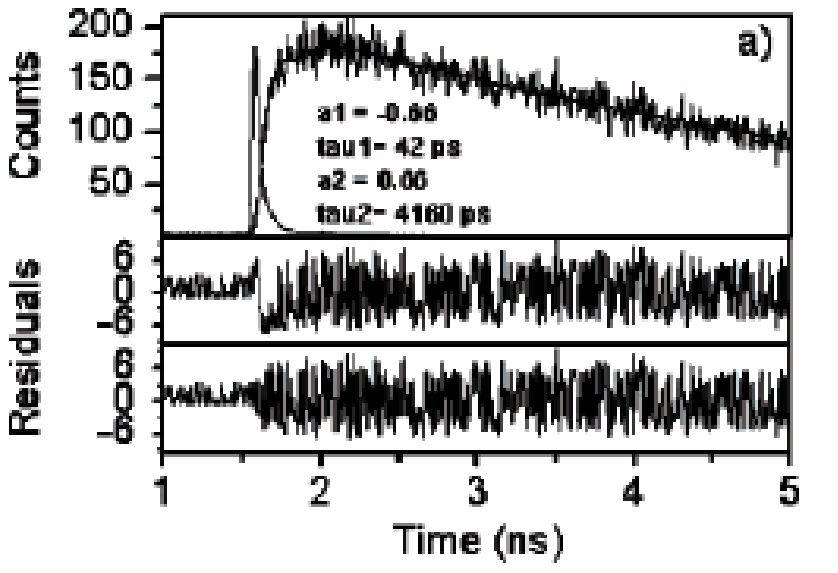
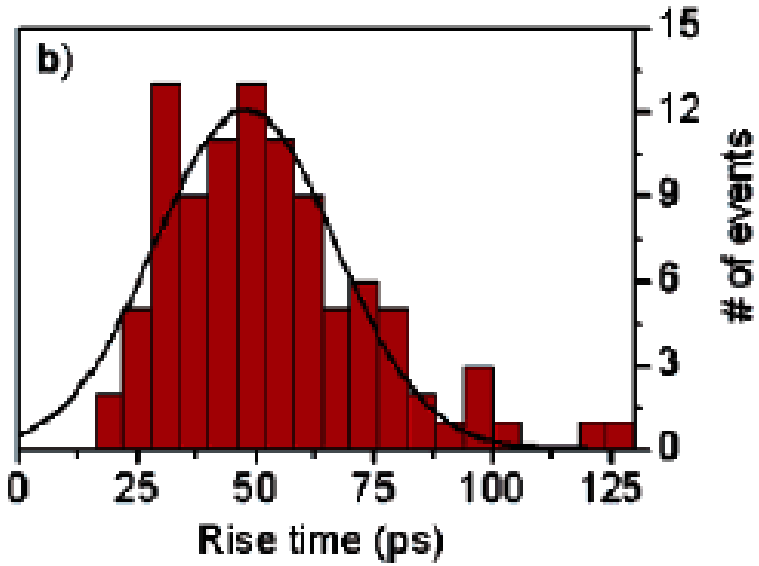
Electronic energy transfer in multichromophoric systems

$$D \xrightarrow{h\upsilon(488nm)} D^* \xrightarrow{ET} A^* \longrightarrow A + h\upsilon_f(A)$$



Time resolved emission of a single molecule of T2P8 monitored at the T emission

Histogram of the emission risetime of 100 T2P8 molecules.
Broad distribution of conformations



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Excimer formation of pyrene in PDMS.

Steady state emission and fluorescence lifetime of pyrene

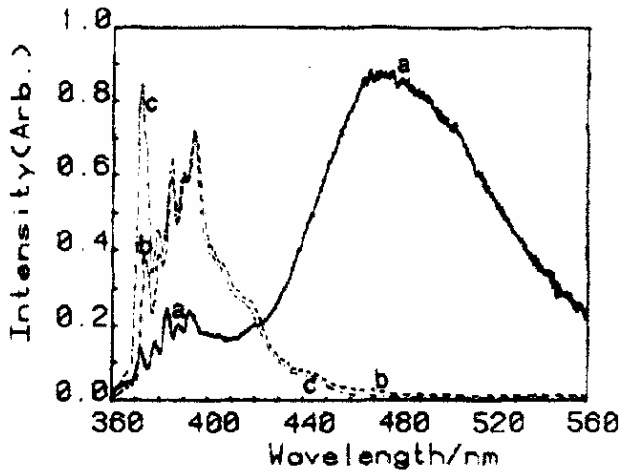
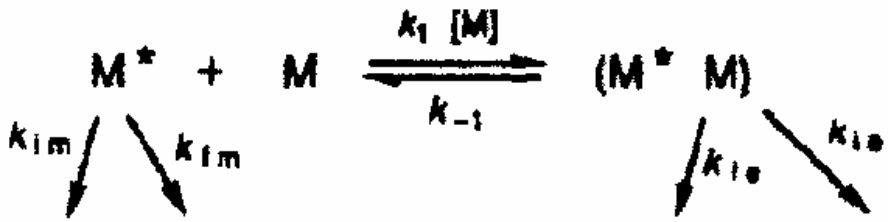


Figure 1. Emission spectra of 0.01 M pyrene fluorescence (a) in poly(dimethylsiloxane) (PDMS; 50 cP) (—), (b) in polystyrene (- - -), and (c) in epoxy film (– · –).



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

Free volume evidence in polymers

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