

# Alignment of Conjugated Polymers in a Nematic Liquid-crystal Host

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# Introduction

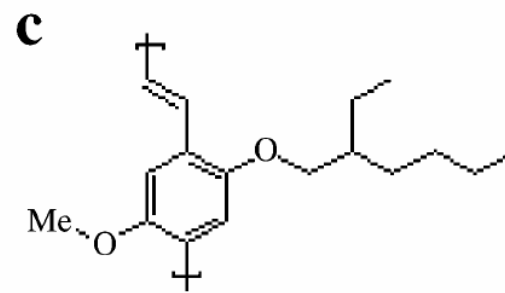
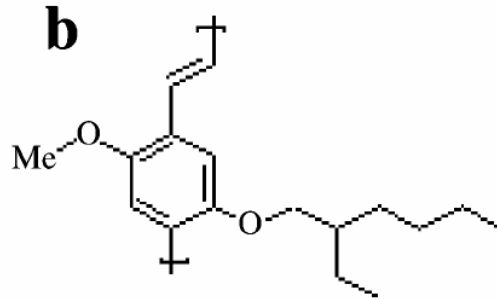
Determination of **order parameter** characterizing the alignment of the host with respect to the liquid-crystal director

: using **linear absorption dichroism** and **fluorescence anisotropy**.



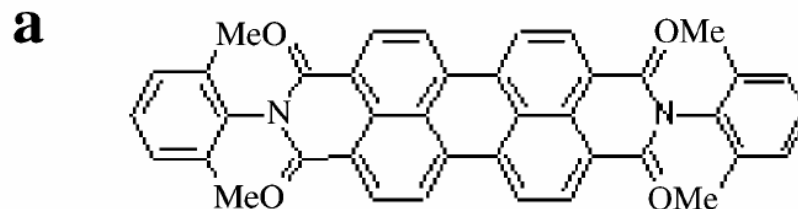
Conjugated polymer

Poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV)



dye

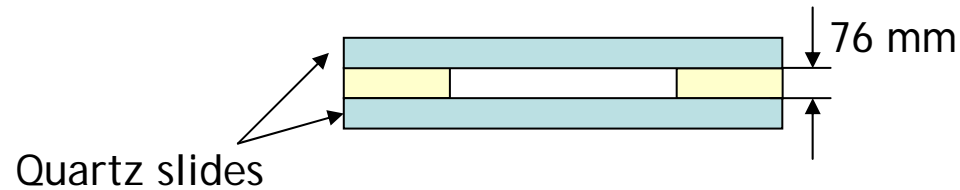
N',N'-bis(2,6-dimethylphenyl)-3,4,9,10-perylenetetracarboxylic (PERY)



# Experimental

## Sample preparation

0.2% aqueous solution of poly(vinyl alcohol) - unidirectionally rubbing



## Two different method of preparation

(1) guest-host method

: PERY was mixed with 5CB and left overnight to homogenize

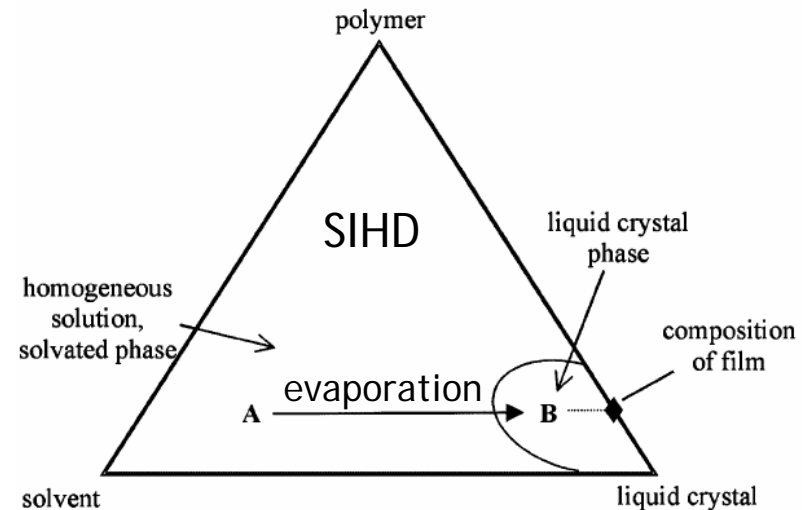
(2) solvent-induced homogeneous dispersion (SIHD)

: a. MEH-PPV dissolved in chlorobenzene

b. 1mL of that solution was mixed with a small amount of 5CB

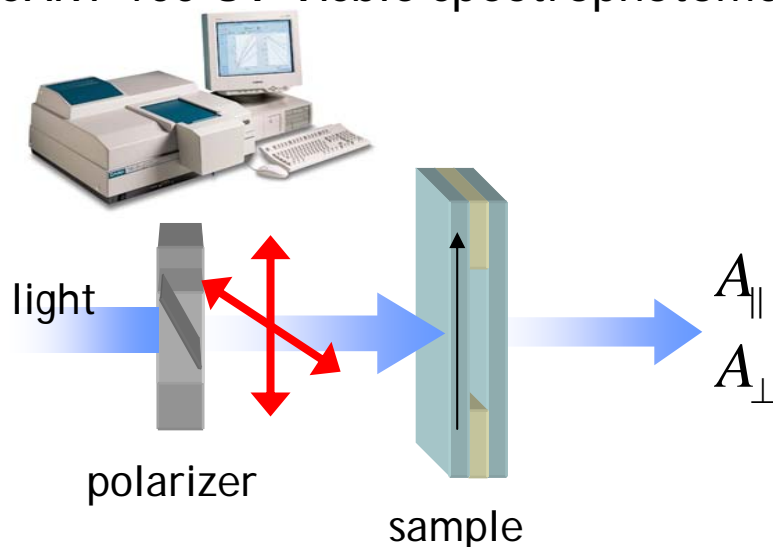
c. nitrogen flow for about 20min to evaporate the solvent

d. nitrogen flow was stopped once the phase transition occurred, thereby leaving a homogeneous mixture of MEH-PPV and 5CB.



# Experimental

## CARY 100 UV-Visible spectrophotometer



◆ Dichroic ratio (D)

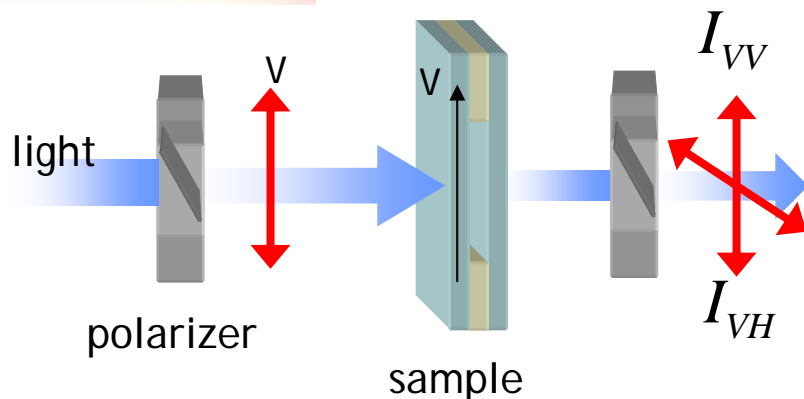
$$D = \frac{A_{\parallel}}{A_{\perp}}$$

◆ Linear dichroism (LD) spectrum

$$LD = A_{\parallel} - A_{\perp}$$

LD : positive - polarization of the light is **parallel** to the orientation of axis of the sample.  
 negative - polarization of the light is **perpendicular** to the orientation of axis of the sample.

## Spex Fluorolog 3-22 fluorometer

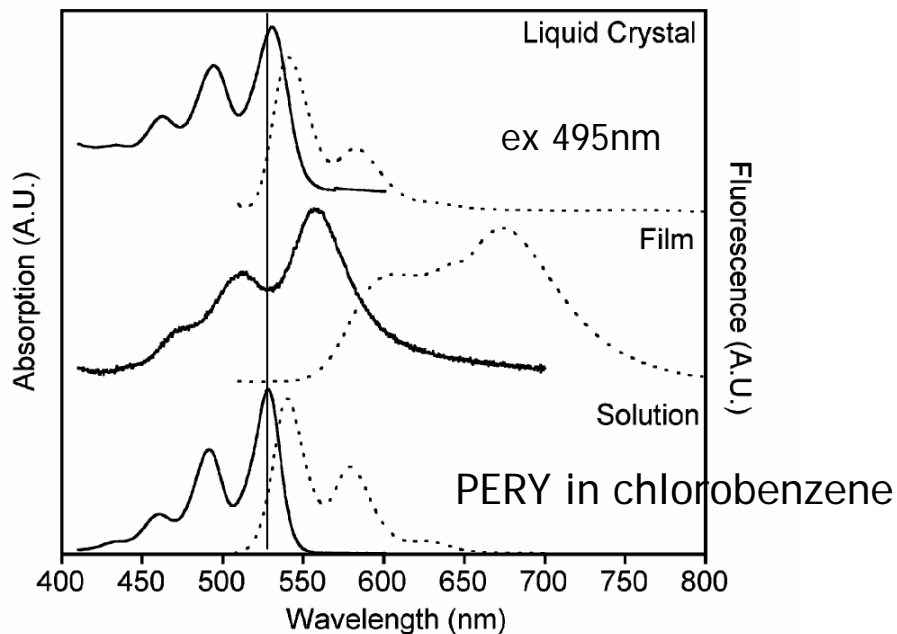


◆ Fluorescence anisotropy (r)

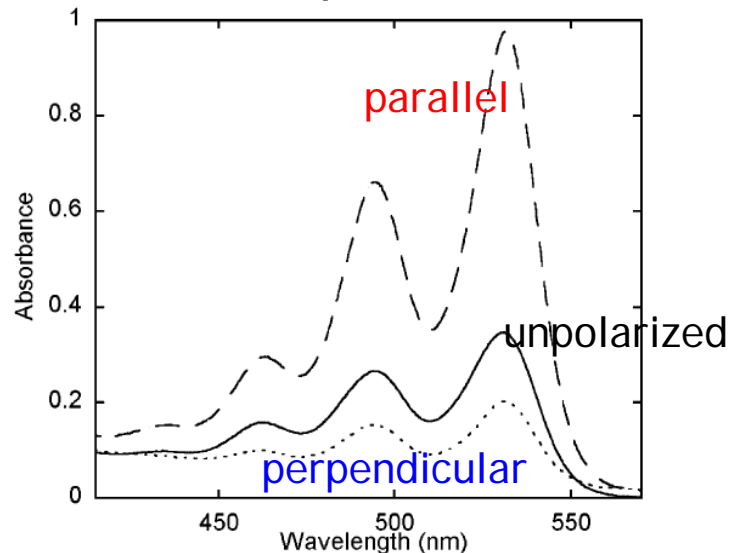
$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}}, G = \frac{I_{VH}}{I_{HH}}$$

# Results & discussion

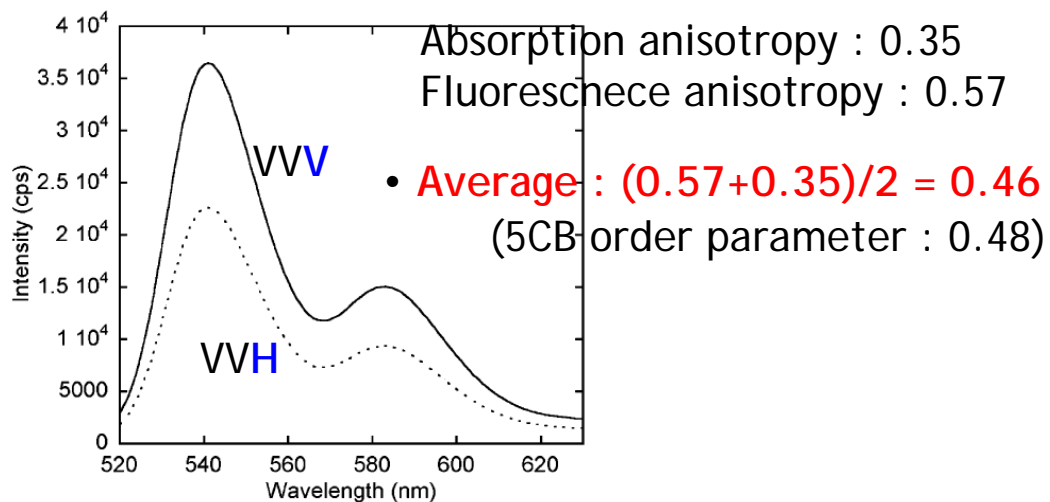
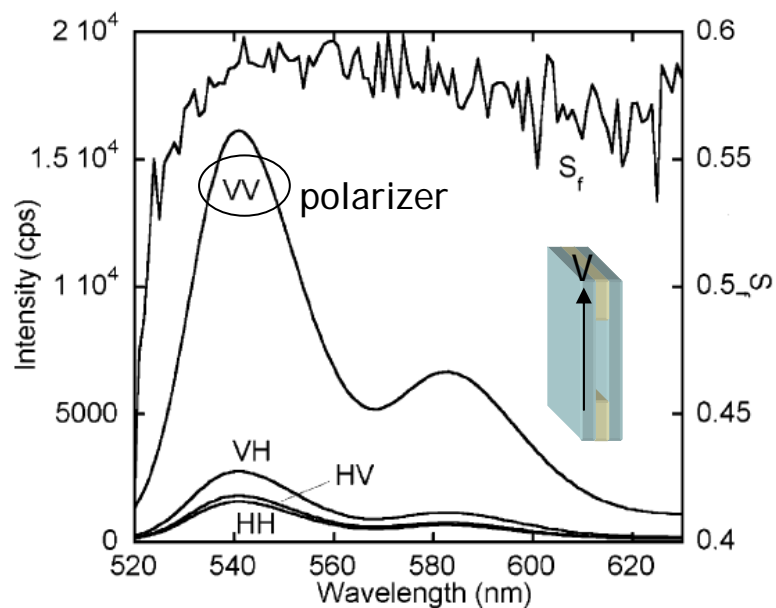
## PERY doped liquid crystal



## Dichroic absorption of PERY in 5CB

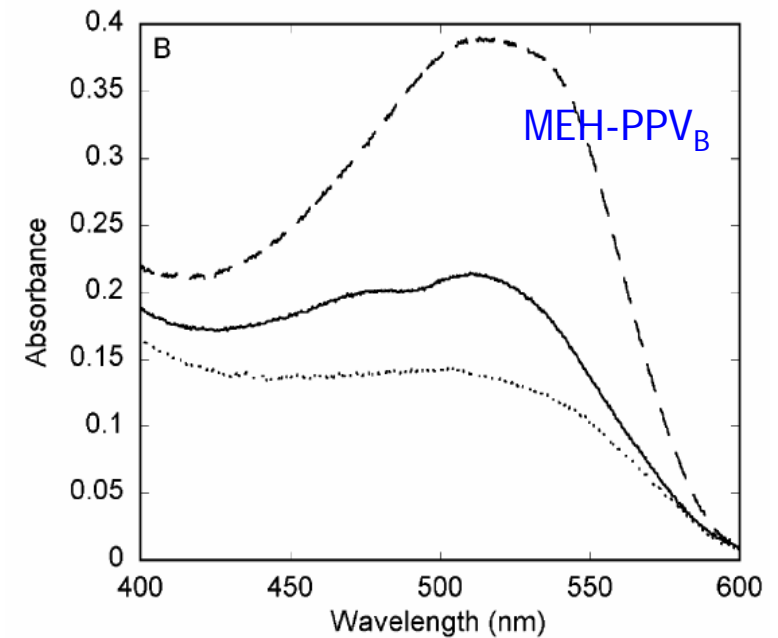
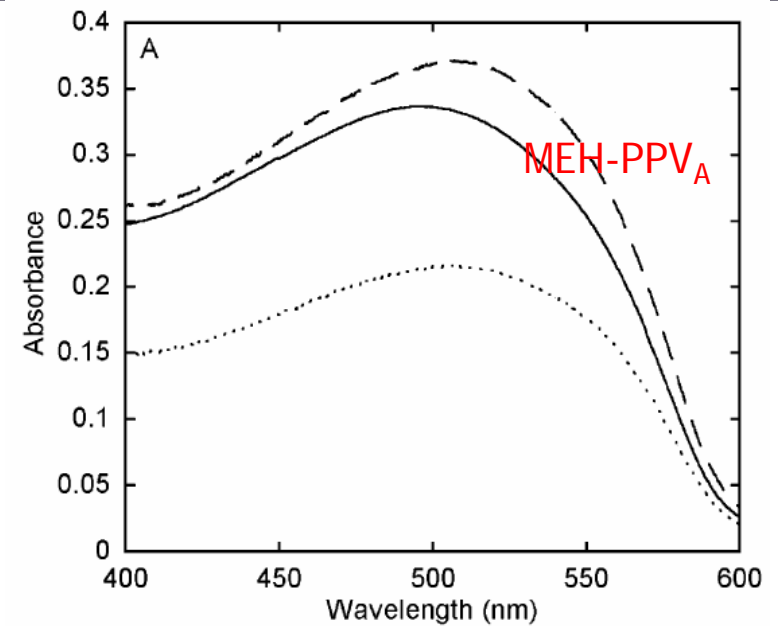
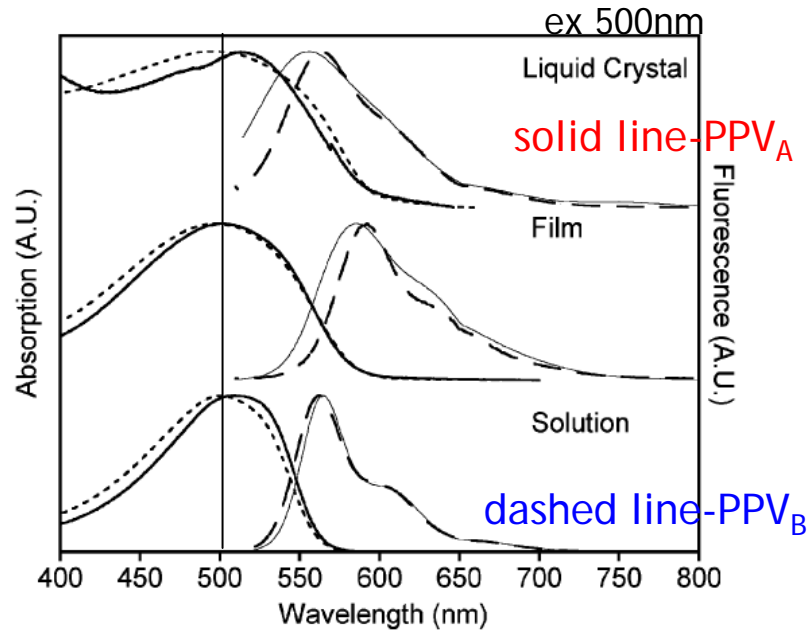


## Fluorescence anisotropy of PERY in 5CB



# Results & discussion

## MEH-PPV doped liquid crystal



### Dichroic ratio & LD

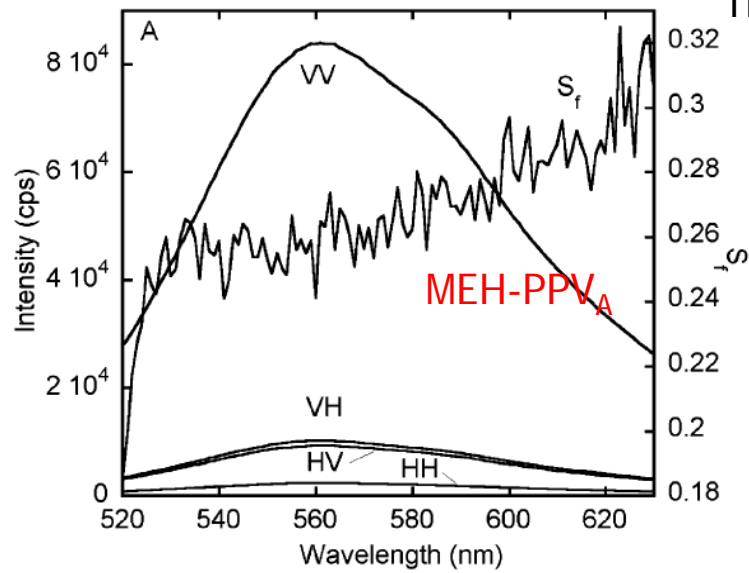
- MEH-PPV<sub>A</sub> : 1.7 & 0.14
- MEH-PPV<sub>B</sub> : 0.29 & 0.14

### Absorption anisotropy

- MEH-PPV<sub>A</sub> : 0.20
- MEH-PPV<sub>B</sub> : 0.29

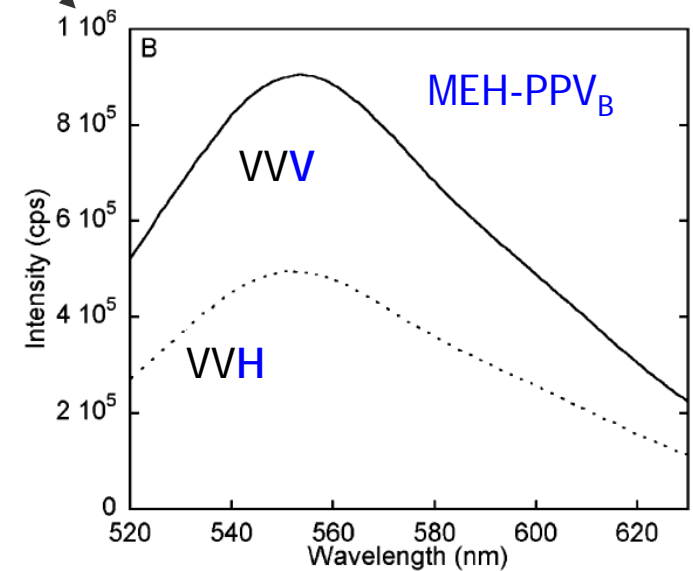
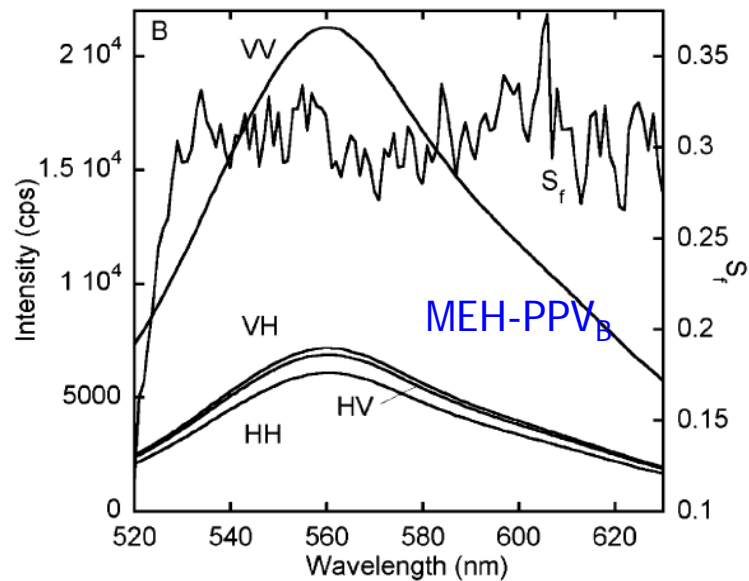
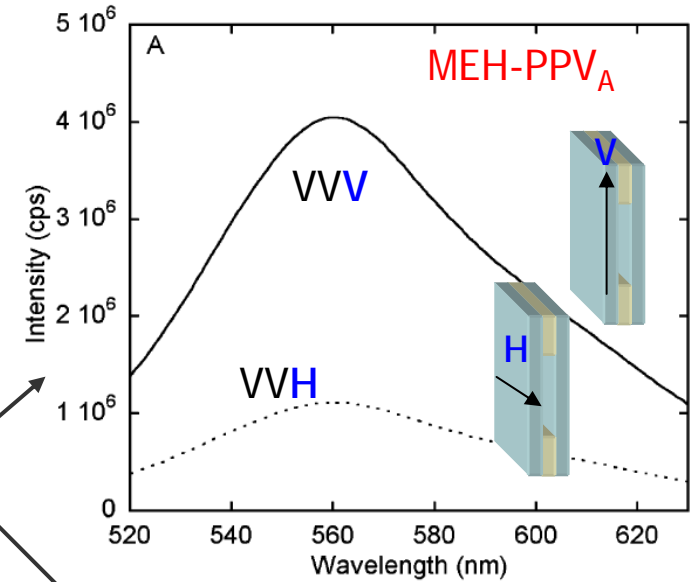
# Results & discussion

## MEH-PPV doped liquid crystal



fluorescence anisotropy  
- MEH-PPV<sub>A</sub> : 0.27  
- MEH-PPV<sub>B</sub> : 0.30

Samples are aligned parallel to the director of the LC



# Discussion & Conclusion

**TABLE 1: Summary of All the Measured Alignment Data for the Three Samples, PERY, MEH-PPV<sub>A</sub>, and MEH-PPV<sub>B</sub>**

guest in LC	LD	D	$S_A$	$S_F$
PERY	0.22	2.9	0.35	$0.57 \pm 0.09$
MEH-PPV <sub>A</sub>	0.14	1.7	0.20	$0.27 \pm 0.03$
MEH-PPV <sub>B</sub>	0.14	2.6	0.29	$0.30 \pm 0.02$

Chain-chain interaction between polymer Or chain folding back on itself.

- Absorption

$$A = -\log_{10}[T]$$

~~$$S_A = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + A_{\perp}} \cdot \frac{2}{3 \cos^2 \beta - 1}$$~~

- Order parameter (absorption anisotropy)

$$S = \frac{1}{2}(3 \cos^2 \theta - 1)$$

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}}$$

$$T_{\parallel} = \exp[-(2S + 1)\alpha_0 D]$$

$$T_{\perp} = \exp[-(1 - S)\alpha_0 D], \quad T_{\perp} = 1, T_{\parallel} = \exp(3\alpha_0 D) \text{ when } S=1$$

$\alpha_0$  : attenuation constant

D : cell of thickness

$$T_{\perp} = T_{\parallel} = \exp(\alpha_0 D) \text{ when } S=0$$

$$S = \frac{\log T_{\parallel} - \log T_{\perp}}{\log T_{\parallel} + 2 \log T_{\perp}} = \frac{(2S + 1) - (1 - S)}{(2S + 1) + 2(1 - S)}$$

$$= \frac{3S}{3} = S$$

Actual order parameter of the polymer may be higher than that by our measurement

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} \cdot \frac{2}{3 \cos^2 \beta - 1}$$

$\beta$  : angle between the transition moment and the long molecular axis



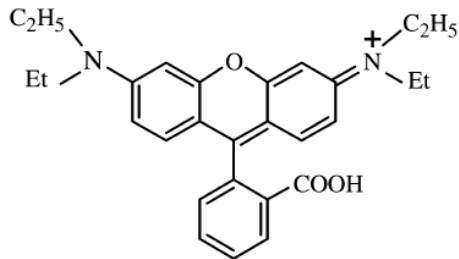
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# Absorption anisotropy and molecular association of some ionic dyes in liquid crystalline solution

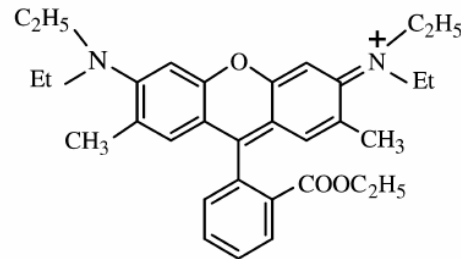
A. Ghanadzadeh, M. S. Zakerhamidi

Journal of molecular liquids 109, 149 (2004)

# introduction



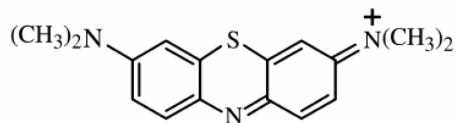
Rhodamine B (RB)



Rhodamine 6G (R6G)

◆ Dichroic ratio (D)

$$D = \frac{A_{\parallel}}{A_{\perp}}$$



Methylene blue (MB)

◆ Order parameter of dye in the nematic LC

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} \cdot \frac{2}{3\cos^2 \beta - 1}$$

$$= \frac{R - 1}{R + 2} \cdot \frac{2}{3\cos^2 \beta - 1}$$

$$S = \frac{R - 1}{R + 2}$$

$\beta$ : angle between the transition moment and the long molecular axis

transition moment vector of the dyes may be consider to be parallel to long molecular axis.

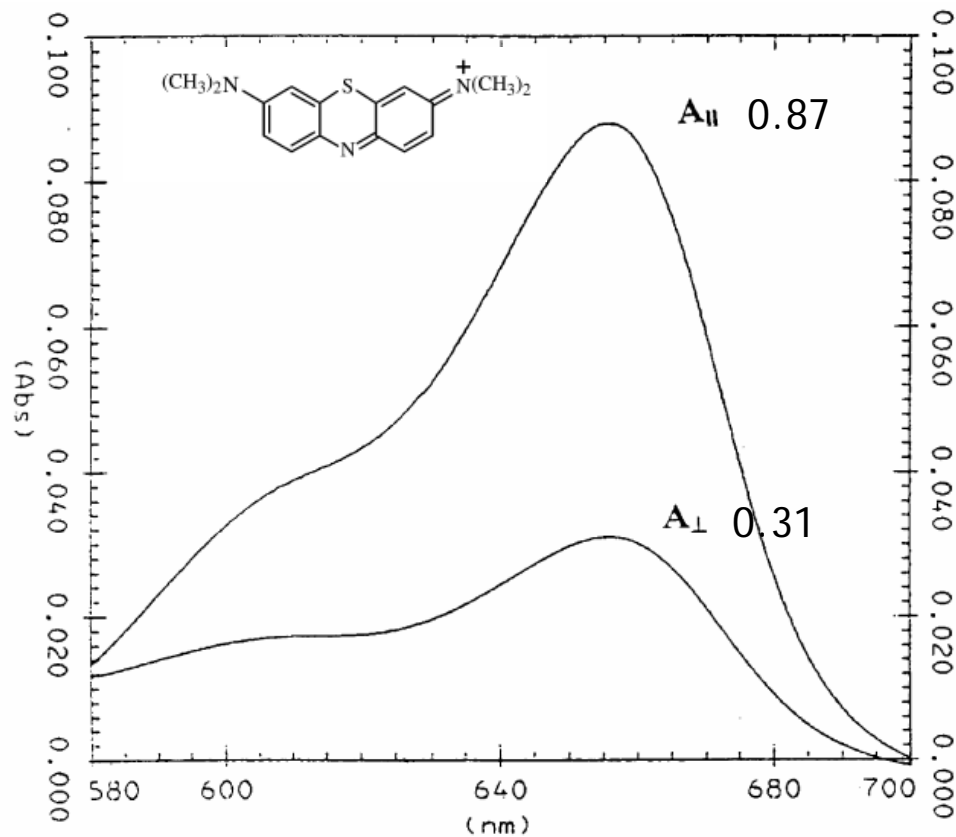


Fig. 2. Polarized absorption spectra of MB in the nematic solvent (MBBA). In the top spectrum the electric vector of light is parallel ( $A_{||}$ ) and in the bottom spectrum perpendicular ( $A_{\perp}$ ) to the nematic director (rubbing direction).

- Dichroic ratio of MB in MBBA

$$D = \frac{A_{||}}{A_{\perp}} = 2.8$$

- Linear dichroism (LD) spectrum

$$LD = A_{||} - A_{\perp}$$

is positive for absorption bands the dyes, provided that the dye molecules have the orientation along the long axis

- Order parameter of dye in MBBA

$$S = \frac{R-1}{R+2} = 0.38$$

# Fluorescence of Ionic Liquids

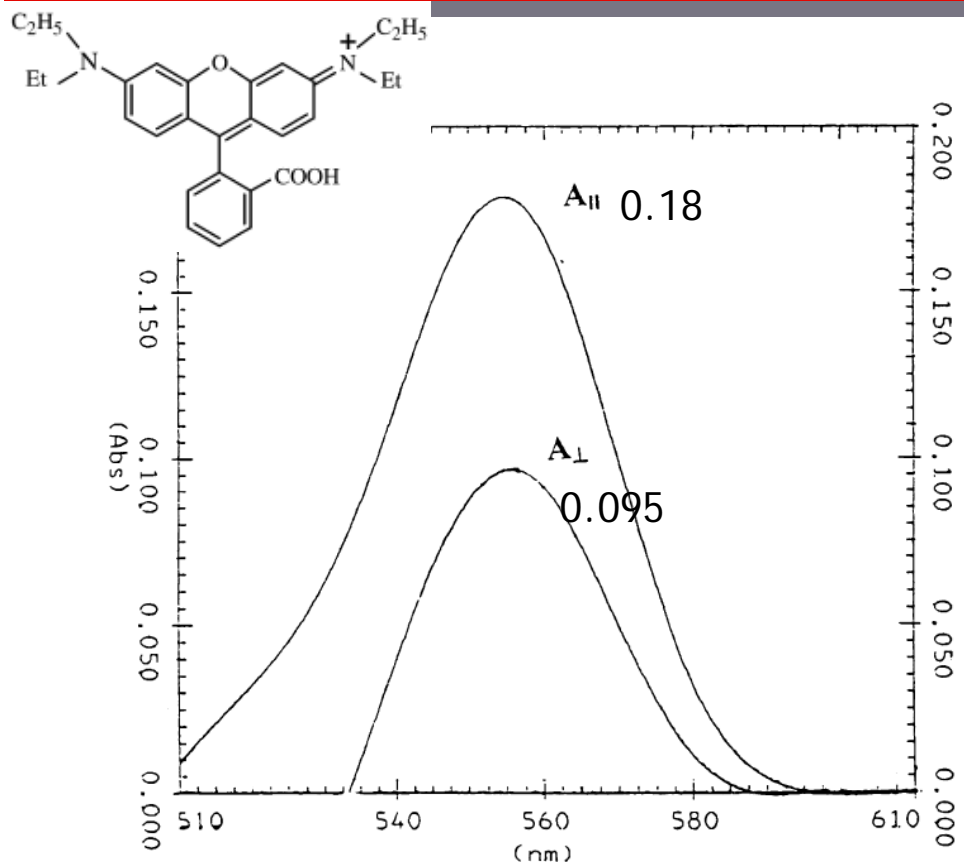


Fig. 3. Polarized absorption spectra of RB in the nematic solvent (MBBA).

Lateral groups (-Ph-COOH) attached to the xanthene group

- Dichroic ratio of MB in MBBA

$$D = \frac{A_{\parallel}}{A_{\perp}} = 1.9$$

- Linear dichroism (LD) spectrum

$$LD = A_{\parallel} - A_{\perp}$$

is positive for absorption bands the dyes

- Order parameter of dye in MBBA

$$S = \frac{R-1}{R+2} = 0.23$$

S is a function of the difference between the principal solute polarizabilities ( $\Delta\alpha = 2\alpha_{zz} - \alpha_{xx} - \alpha_{yy}$ ).

Lateral group in the dye molecules increases the polarizability

of the molecules in the x- or y-axis.

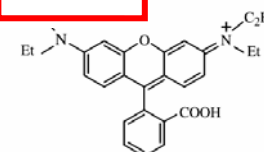
Therefore,  $\Delta\alpha$  (and hence  $S_{zz}$ ) decreases

# conclusion

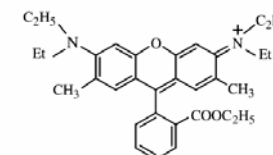
Table 1

Dichroic ratios  $R$  and order parameters  $S$  measured for the ionic dyes in MBBA solvent used in the guest–host experiments

Guest	$\lambda_{\max}$ (nm)	$R = A_{\parallel}/A_{\perp}$	$S_{\text{dye}}^a$
R6G	535	1.9	0.23
RB	555	1.9	0.23
MB	655	2.8	0.38

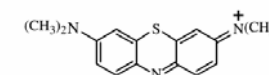


Rhodamine B (RB)



Rhodamine 6G (R6G)

lateral groups attached to the xanthene group for rhodamine dyes



Methylene blue (MB)



causes the direction of the transition moment to deviate from the long molecular axis.

MB has a higher dichroic ratio and order parameter with respect to rhodamine dyes.