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Chiral Selection by Interfacial Shearing of Self-Assembled Achiral Molecules

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We report a novel phenomenon of chiral selection in self-assembled condensates of achiral amphiphiles. The handedness of chiral textures, reproducing the collective rotational component of the molecular orientation inside submillimeter circular domains, is correlated with the sign of a vortical stirring in the aqueous subphase. We propose an explanation based on the distinctive kinetics of topological defect annihilation during domain coalescence at the initial coarsening stage of a phase-separating monolayer.

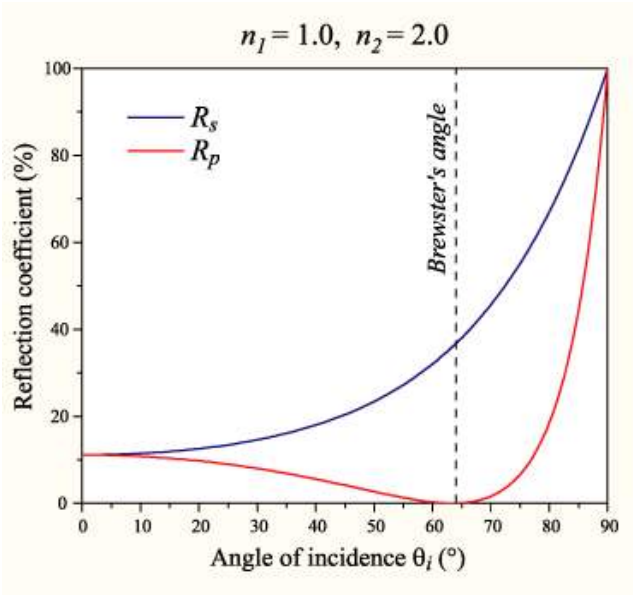
2012.07.28 Journal Club

Presenter: Woongmo Sung

Brewster Angle

$$r_s = \frac{n_1 \cos\theta_i - n_2 \cos\theta_t}{n_1 \cos\theta_i + n_2 \cos\theta_t}$$

$$r_p = \frac{n_2 \cos\theta_i - n_1 \cos\theta_t}{n_1 \cos\theta_t + n_2 \cos\theta_i}$$

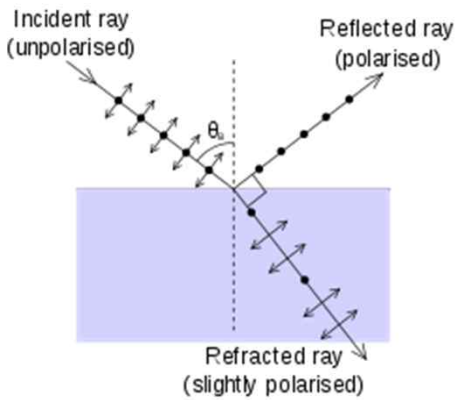


At $r_p=0$,

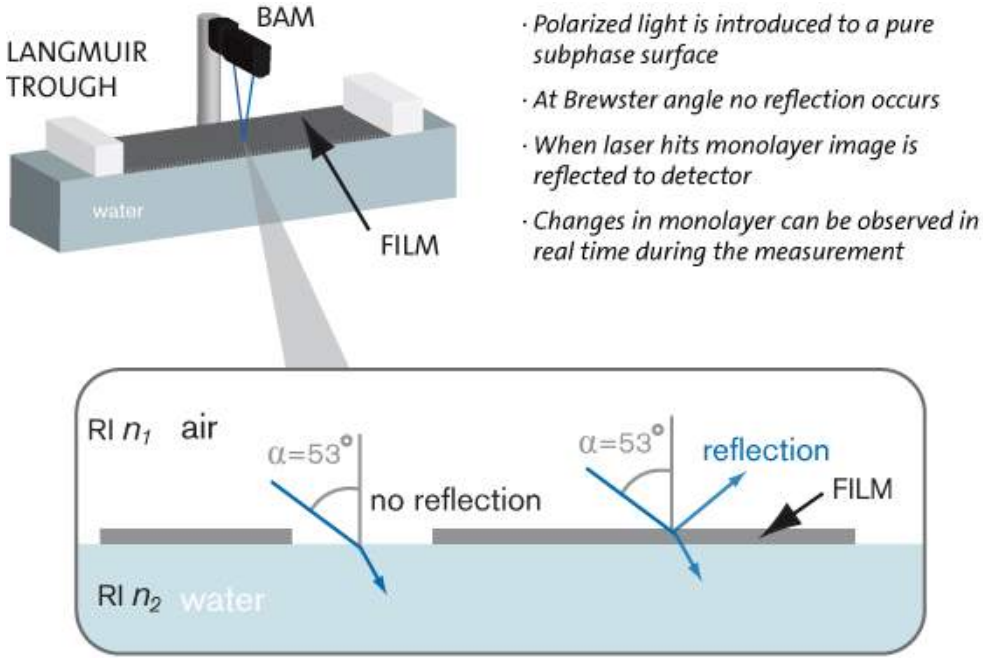
$$n_2 \cos\theta_i - n_1 \sqrt{1 - \frac{n_1}{n_2} \sin^2\theta_i} = 0$$

$$\frac{n_2^2}{n_1^2} \cos\theta_i = 1 - \frac{n_1^2}{n_2^2} \sin^2\theta_i$$

$$\tan\theta_B = \frac{n_2}{n_1}$$

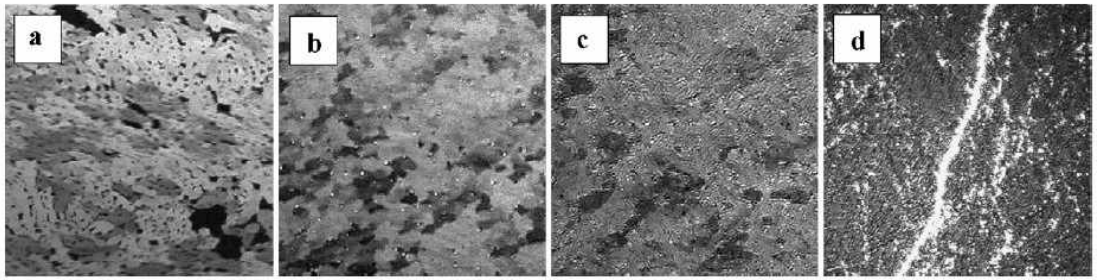


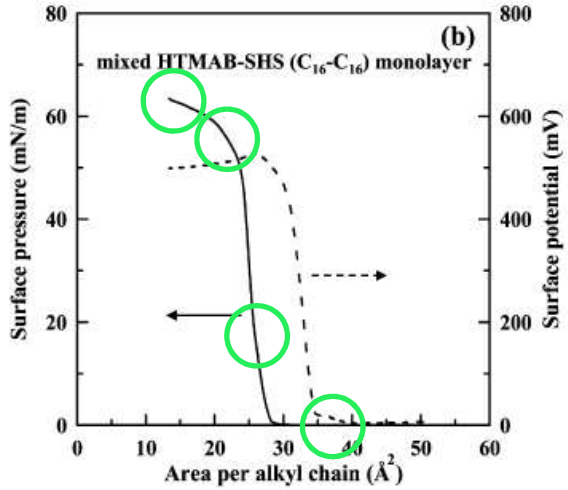
Brewster Angle Microscopy (BAM)



$\theta_B \square 53^o$ for water

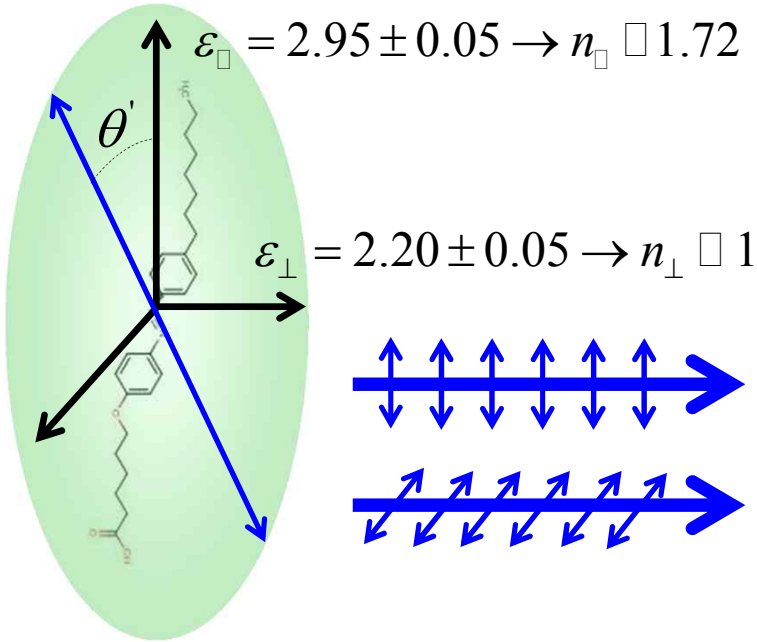
http://www.ksvnima.com/brewster-angle-microscopy





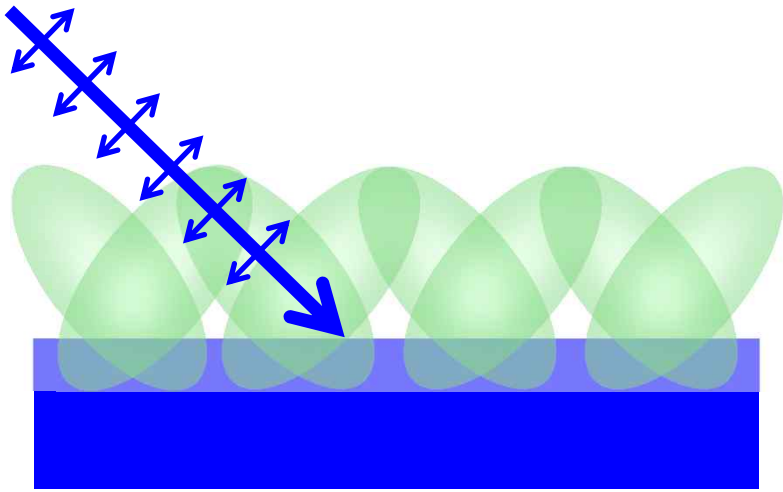
J. Colloid Interface Sci. 2008, 321, 384-392.

Film having anisotropic domain



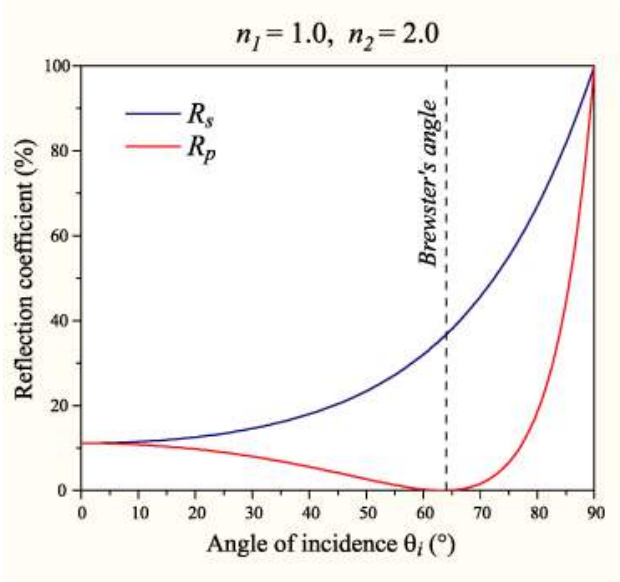
<Azobenzene molecule>

http://hyperphysics.phy-astr.gsu.edu/hbase/phyopt/freseq.html#c1



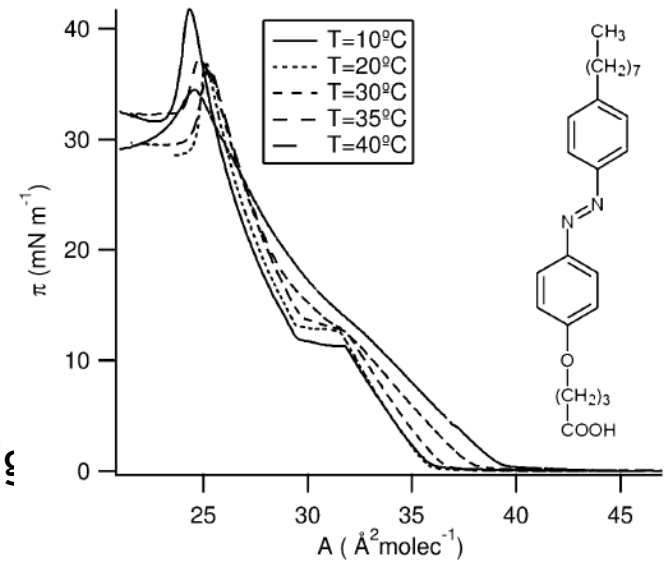
Uniaxial anisotropy

$$\frac{\cos^2\theta'}{n_{\parallel}^2} + \frac{\sin^2\theta'}{n_{\perp}^2} = \frac{1}{n_e^2}$$



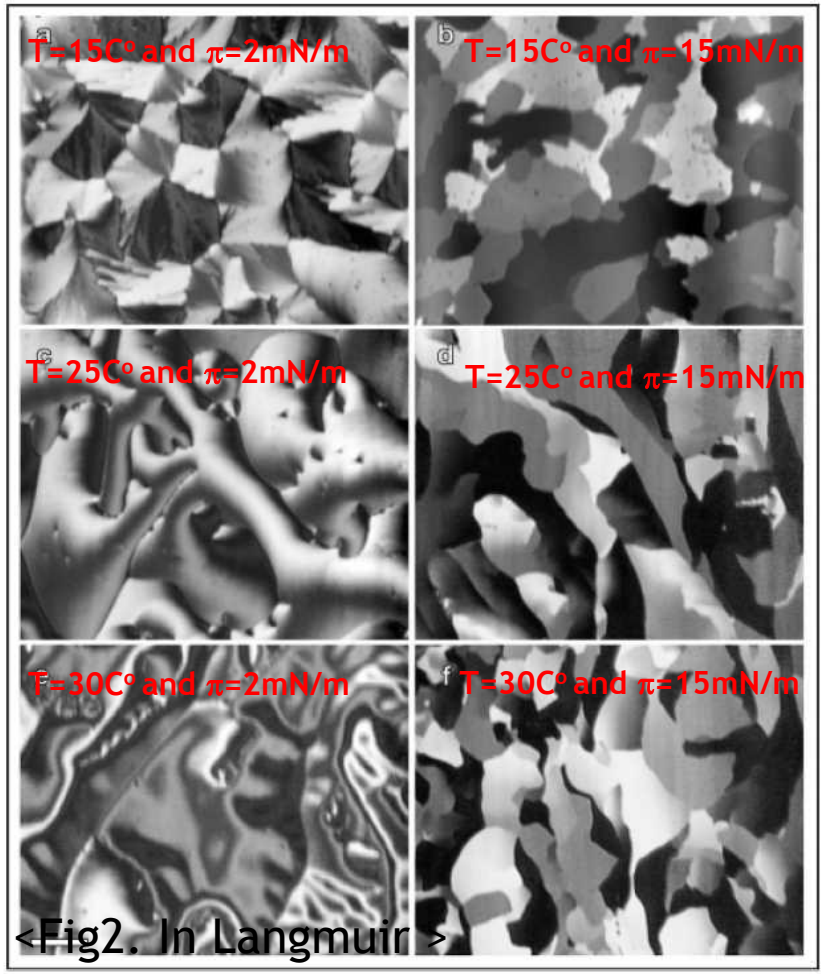
Observation of domain anisotropy by BAM

By setting $\theta_i = \theta_B \square 60^o$ for $\varepsilon_{\square}$,



<Fig

- Sharp domain boundary of tilted condensed phase of azobenzene was observed.
- In low surface pressure, monolayer turns to fluidic phase as temperature increases.

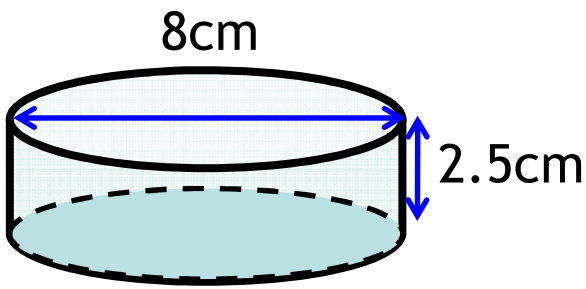


<Fig2. In Langmuir >

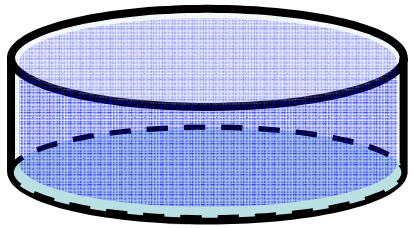
Langmuir, Vol. 20, No. 20, 2004

Vortex formation of monolayer by stirring

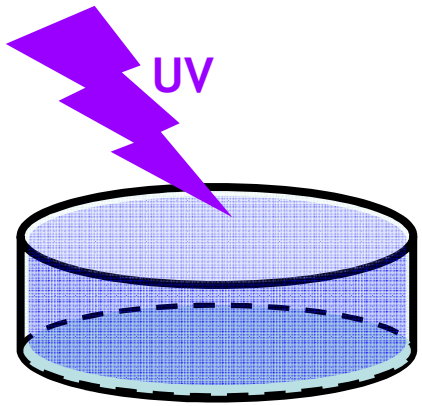
⊙ Sample preparation



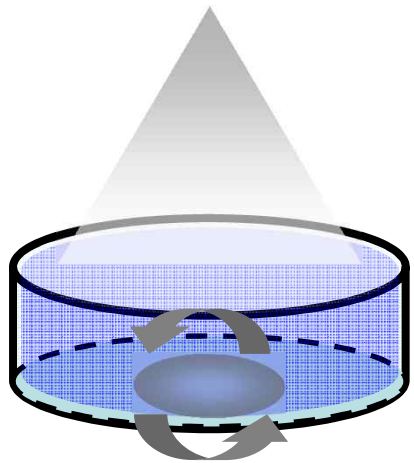
(1) Pour 40ml water and deposit Azobenzene molecules on the water surface.



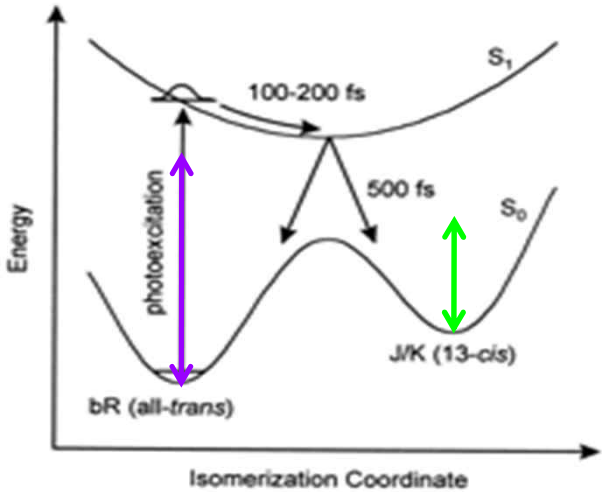
(2) Irradiate UV light for 10minute to make maximum presence of *cis*-isomer.

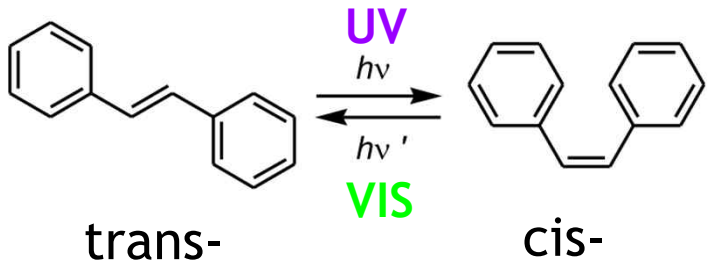


(3) Irradiate white light during stirring (0~1600rpm, 5 min)



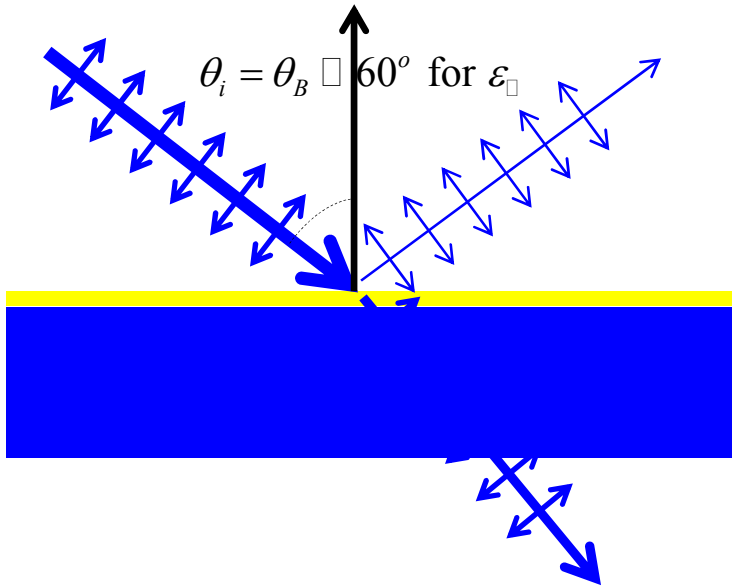
Vortex formation of monolayer by stirring





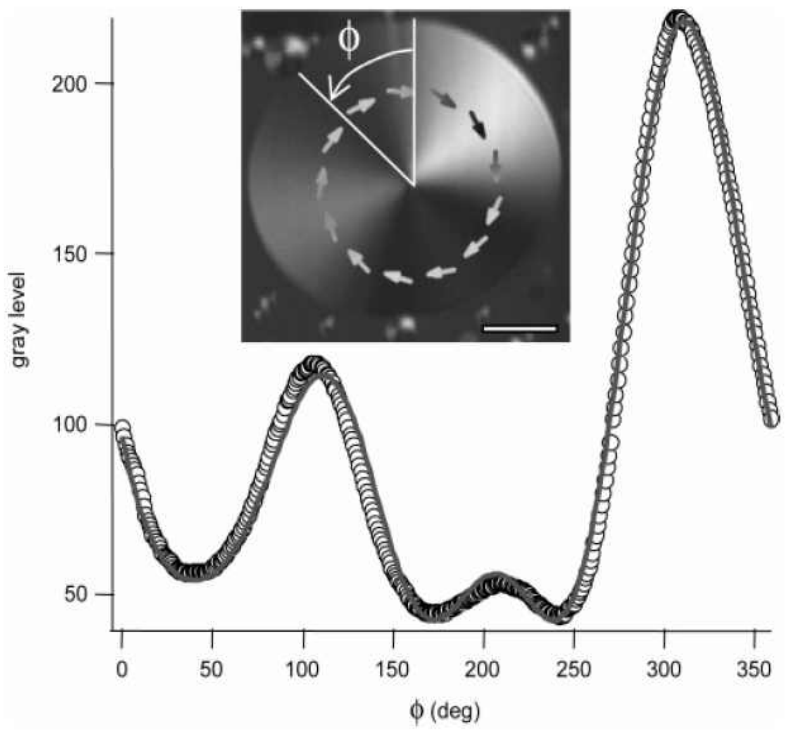
<Photoisomerization>

(4) After stopping stirring and irradiation, BAM was performed within 30minutes.



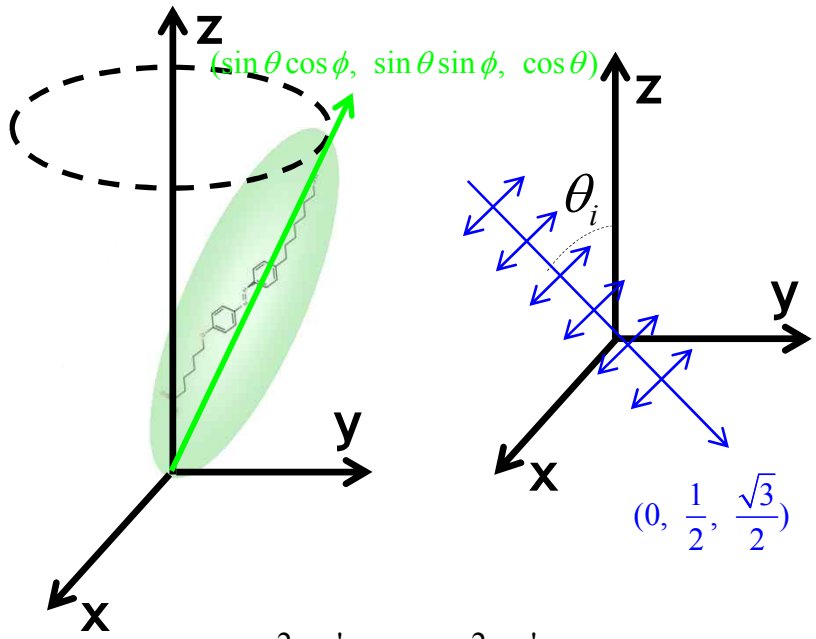
Vortex formation of monolayer by stirring

⊙ Analysis of image



<Fig3. In Langmuir >

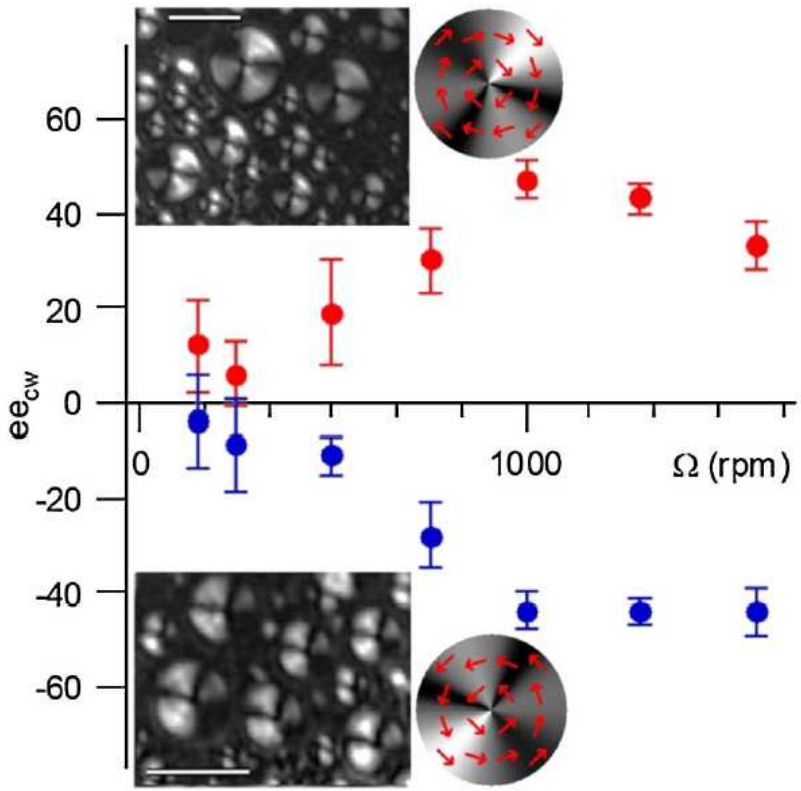
By setting polar tilt angle as θ=40~50°, intensity of reflected light was fitted with azimuth tilt angle ϕ.



$$\frac{\cos^2\theta'}{n_{\square}^{\ 2}} + \frac{\sin^2\theta'}{n_{\perp}^{\ 2}} = \frac{1}{n_e^2}$$

Vortex formation of monolayer by stirring

⊙ Enantimeric excess of CW domains



<Fig1. In PRL >

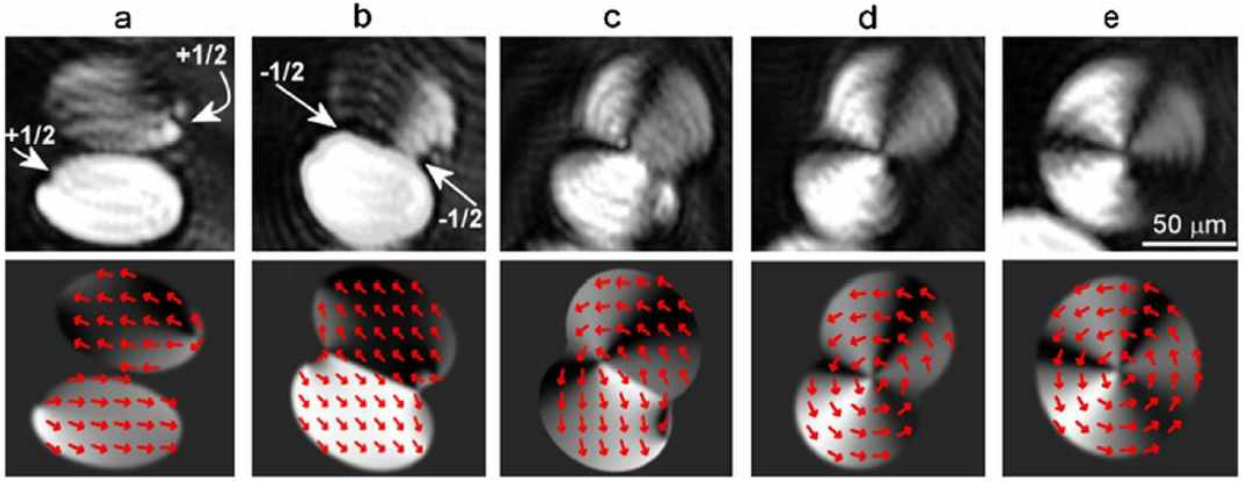
$$ee_{CW} = \frac{(2n_{CW} - n_T)}{n_T}$$

n_T □ 700 ~ 800 in entire scan image

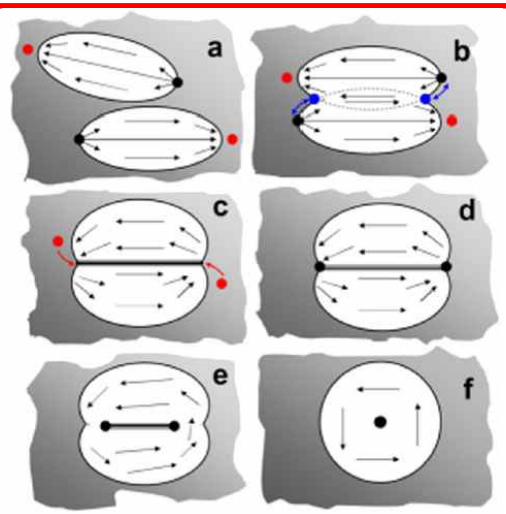
As stirring performed to the CW direction (CCW direction), enantiomeric excess in CW direction was positively (negatively) increased.

Vortex formation of monolayer by stirring

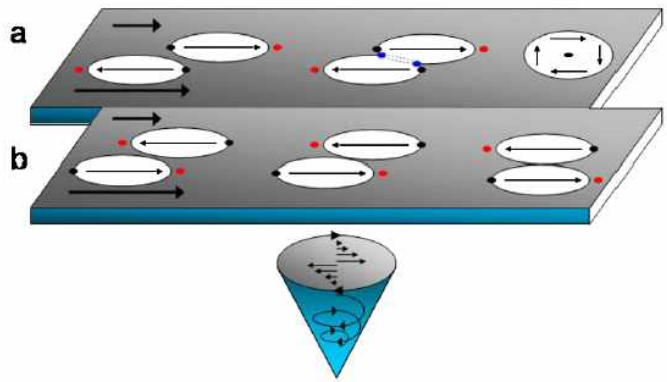
⊙ Sequence of BAM image (elapse time ~ 74s)



<Fig2. I



<Fig3.



<Fig4. In PRL >

Conclusion

- Forming macroscopic chiral domains of achiral azobenzene molecules are observed by BAM.

- Enantiomeric excess of domains depends on stirring rpm and direction.

- Mechanism of vortex forming is merging of two +1/2 and -1/2 domains.