Optical effects based on dye-doped liquid crystal films*

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Outline

1. Introduction
   - Liquid crystals
   - Azo dye: Photoisomerization effect
2. Experiments: results and discussion
   - Lasing in dye-doped Cholesteric LC : Optically tunable
   - Photo-tunable cholesteric gratings
   - Biphotonic self-phase modulation
3. Conclusions

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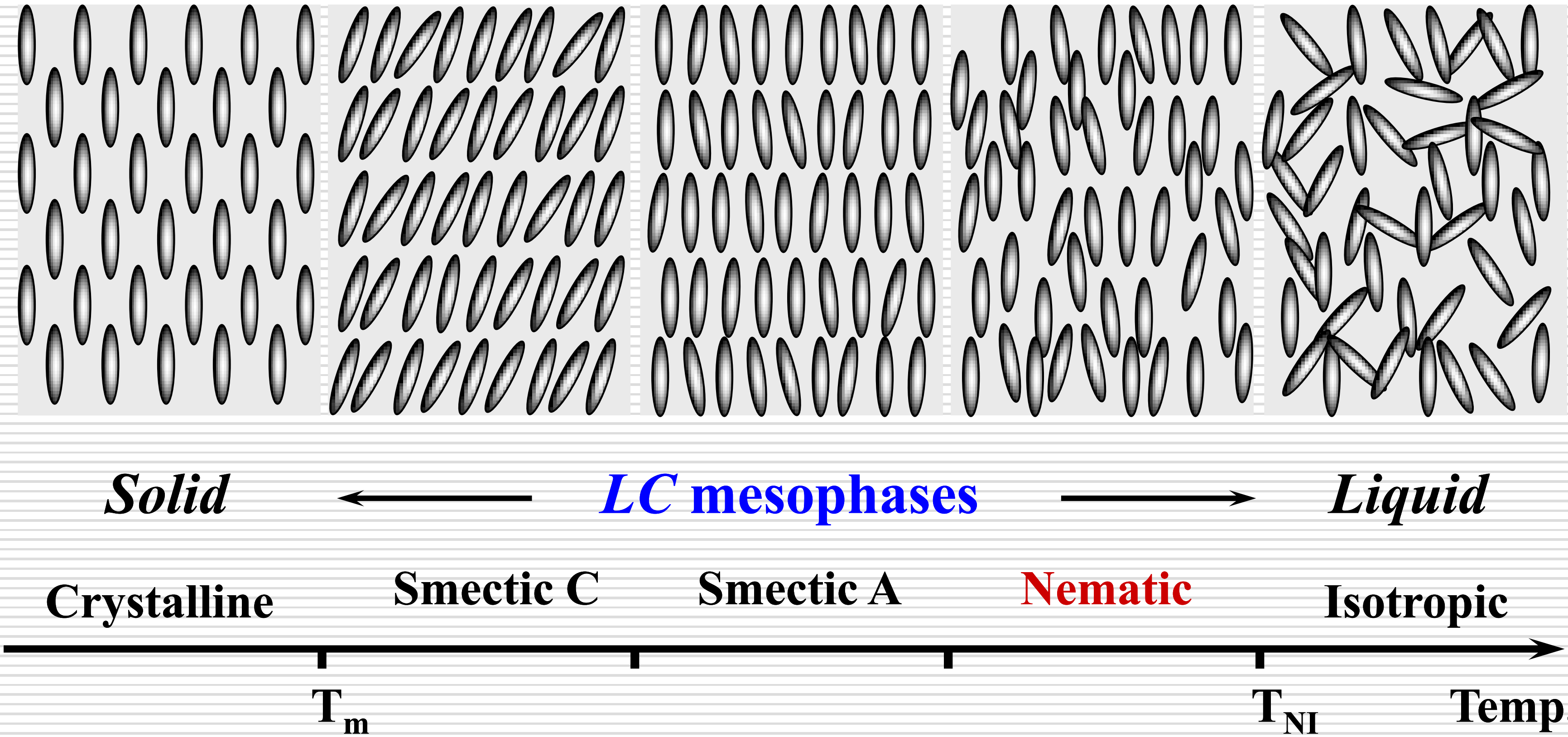
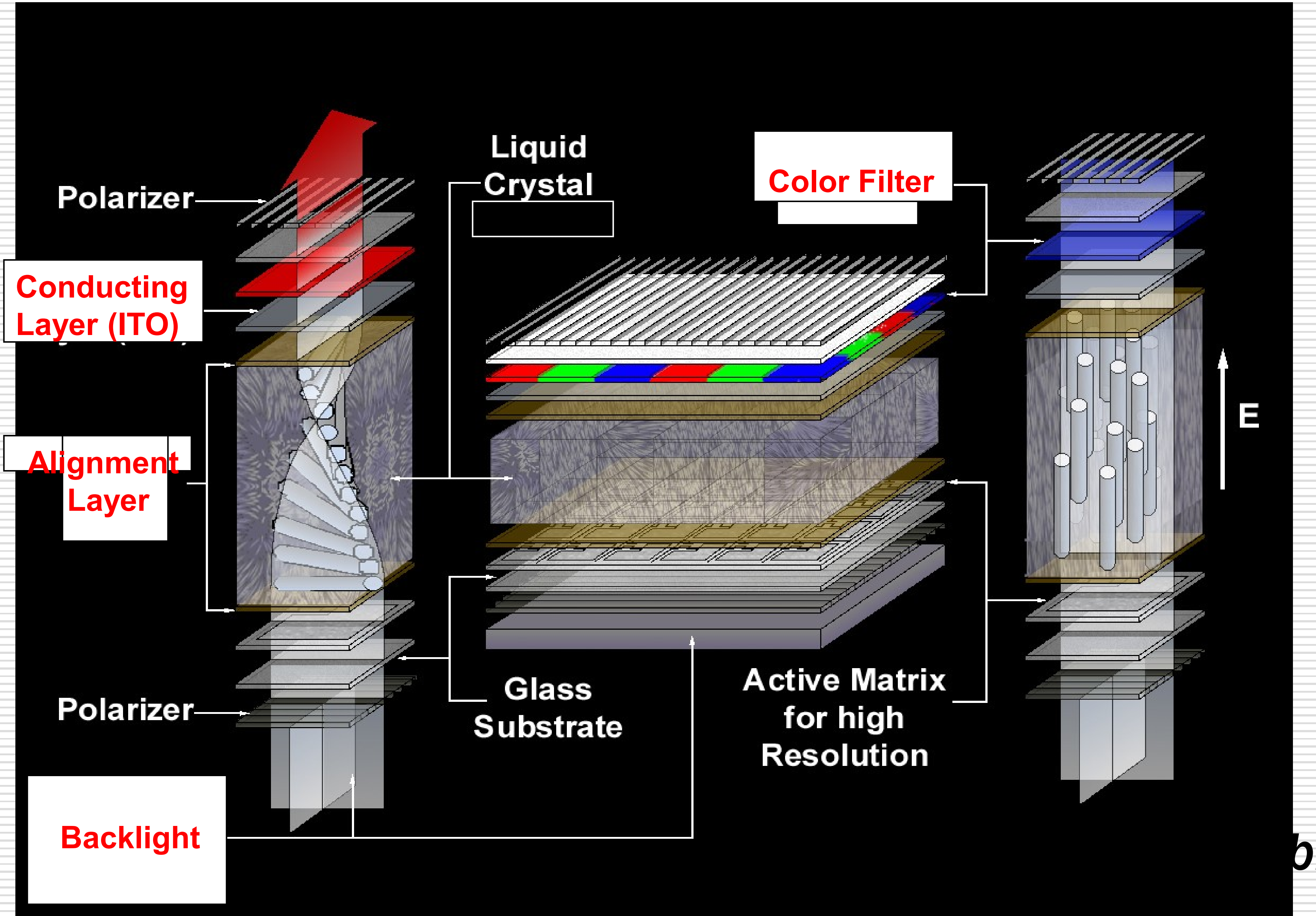
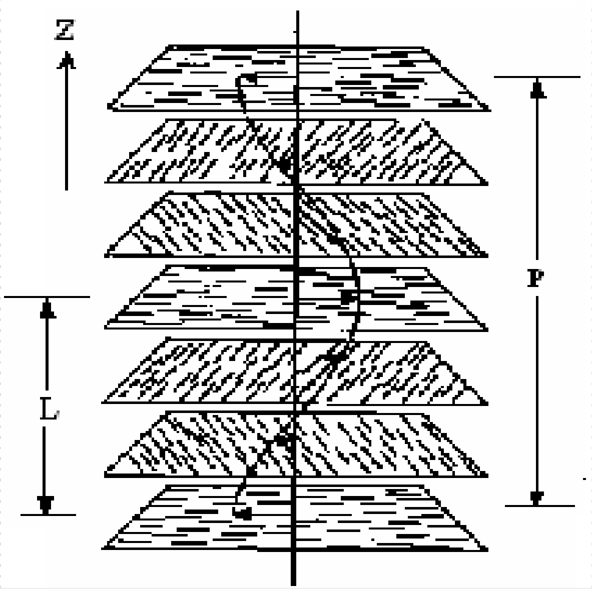
Liquid Crystals (LCs)



Twisted Nematic Liquid Crystal Displays



Cholesteric Liquid Crystal (CLC)



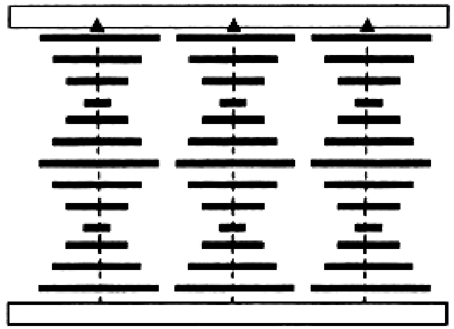
- Cholesteric / Nematic + chiral
- $$\frac{1}{p \cdot c} = H.T.P \text{ (Helical Twisting Power)}$$

  p: pitch (um), L=P/2,

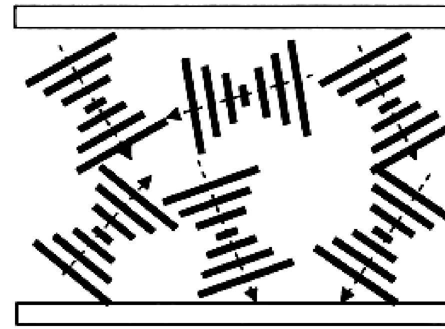
  c: chiral concentration (wt%)

The structures of Cholesteric liquid crystals

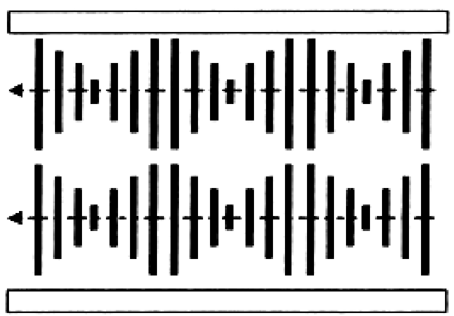
(1-D Photonic crystal)-
laser



planar texture

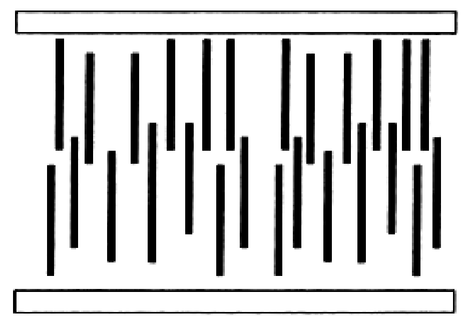


focal conic texture



fingerprint texture

grating



homeotropic texture

ıb.

Cholesteric Liquid Crystals

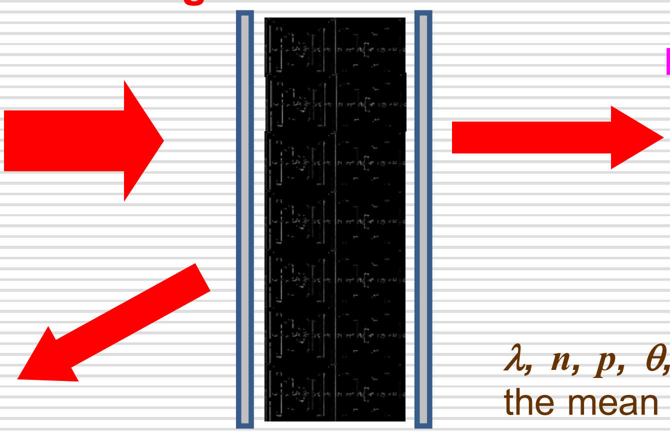
Focal conic texture   Fingerprint texture   Homeotropic texture

Selective Reflection

Planar texture

Right-handed CLC

unpolarized light



Left-handed circular polarized light 50%

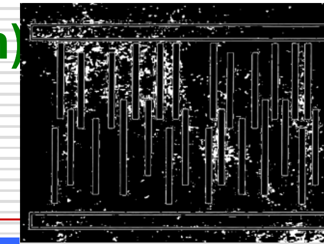
Right-handed circular polarized light 50%

$$\lambda = np\cos\theta$$

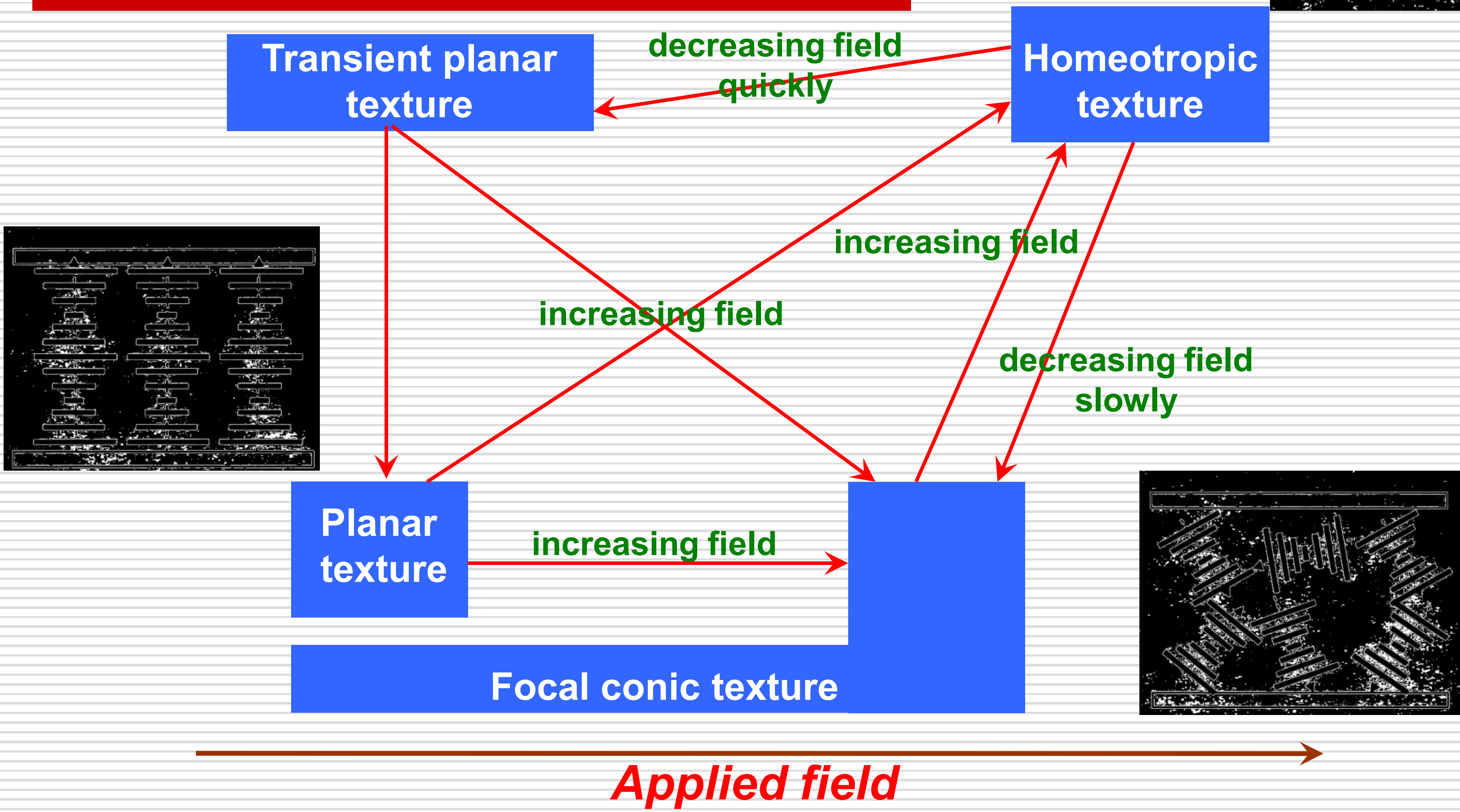
$$\Delta\lambda = \Delta np\cos\theta$$

λ, n, p, θ, $\Delta\lambda$, Δn are the reflected wavelength, the mean refractive index of LC, the pitch length, the angle of incidence, the reflection band and the birefringence, respectively.

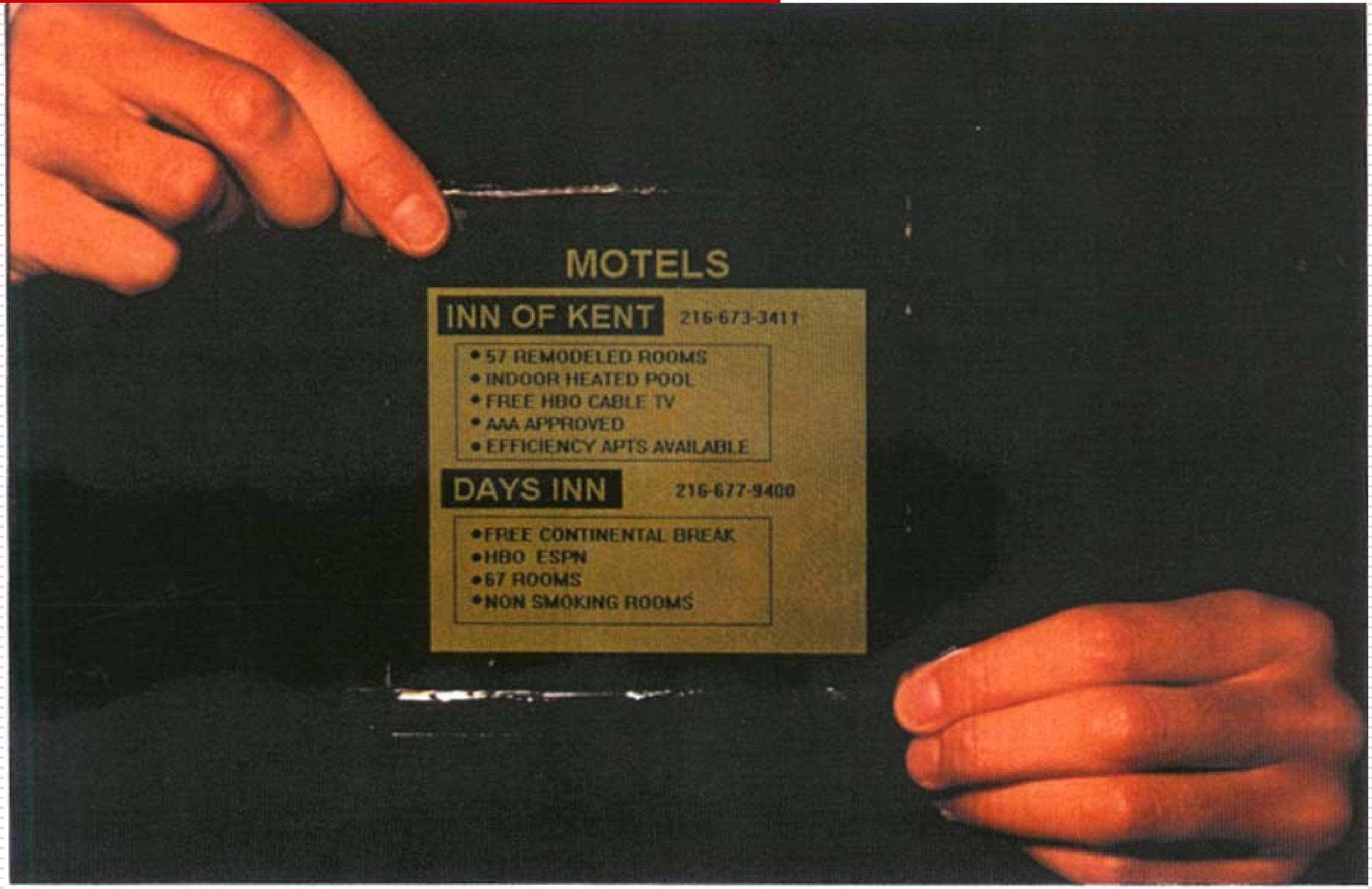
Electrical Field Effect of CLC (pitch~ visible light wavelength)



$\Delta\varepsilon > 0$

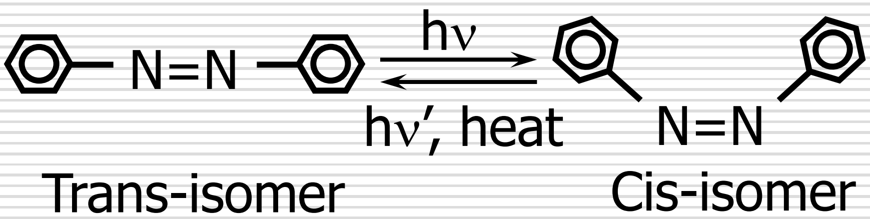


PSCT (SSCT) reflective bistable display

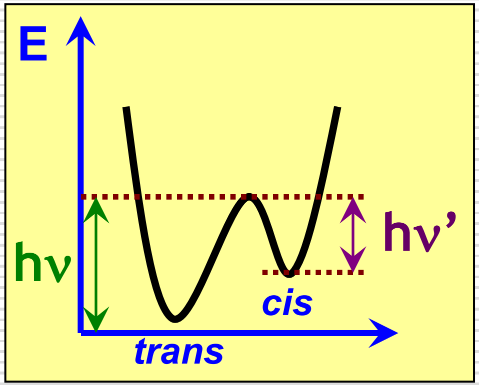


Azo dye
Photoisomerization effect

Upon absorbing light, azo-dye molecules may undergo a photo-induced conformational change, which is called photoisomerization effect.

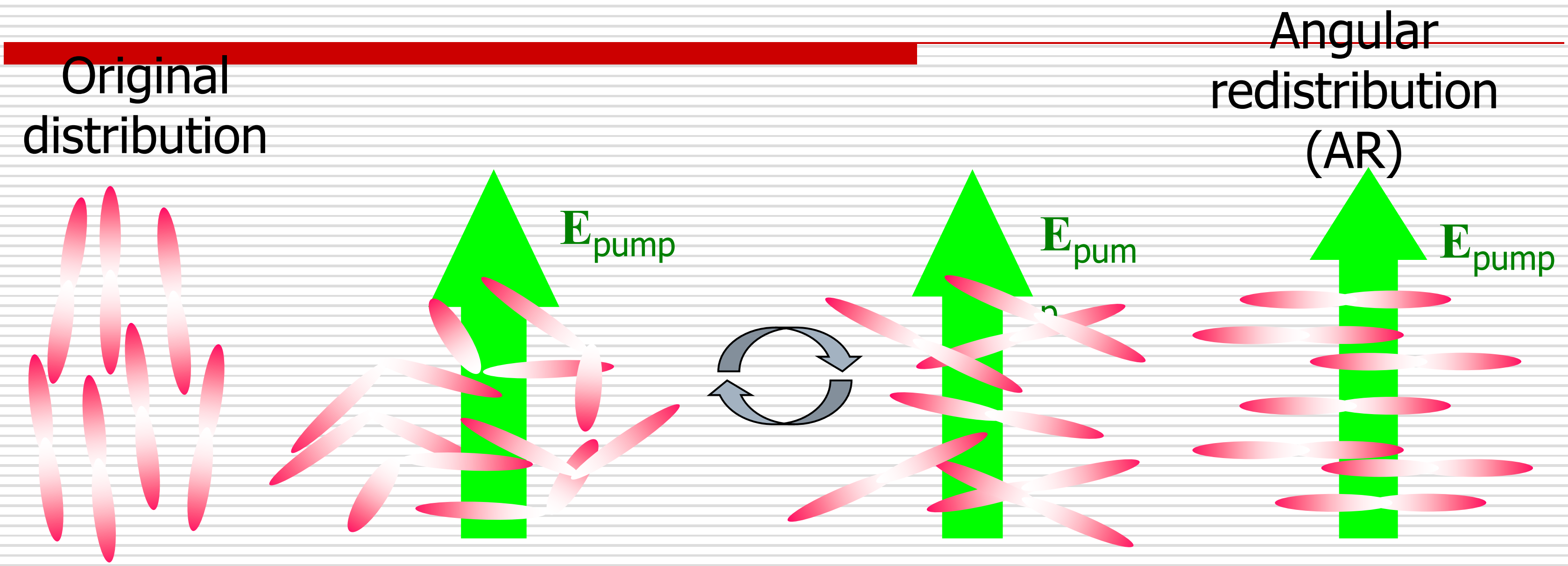


$h\nu > h\nu'$



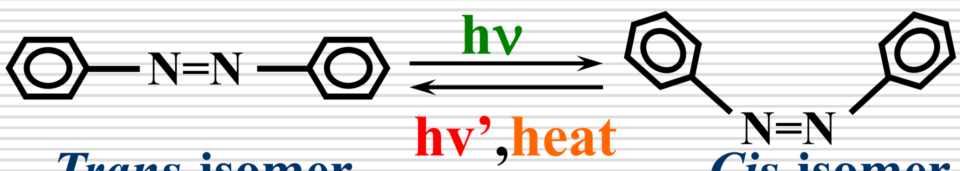
T. V. Galstyan, B. Saad and M. M. Denariez-Roberge, J. Chem. Phys. **107**, 9319 (1997).

Photoisomerization effect
Light-induced LC Reorientation



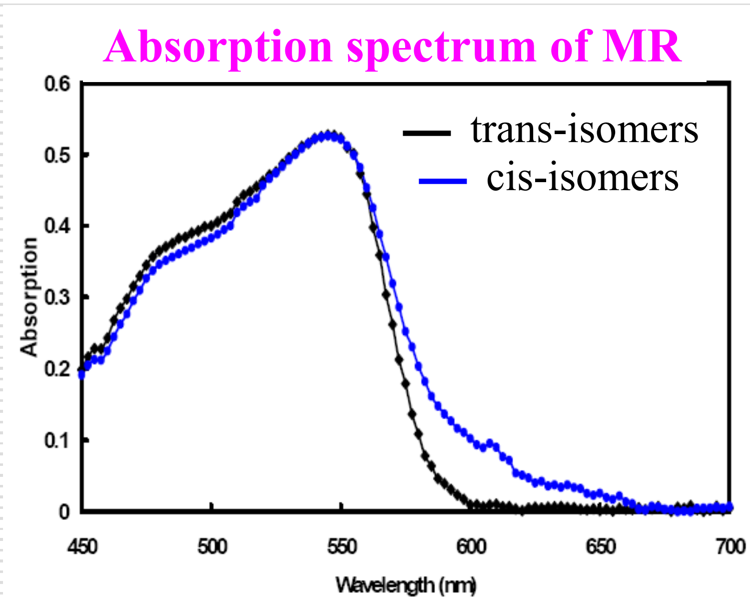
The trans molecules are photoexcited and then transform to cis-isomers initially. After a long-term period, multiple trans-cis isomerization cycles undergo and finally the trans molecules leave the direction parallel to $\mathbf{E}_{pump}$ and eventually align perpendicular to $\mathbf{E}_{pump}$ with a lowest excitation probability.

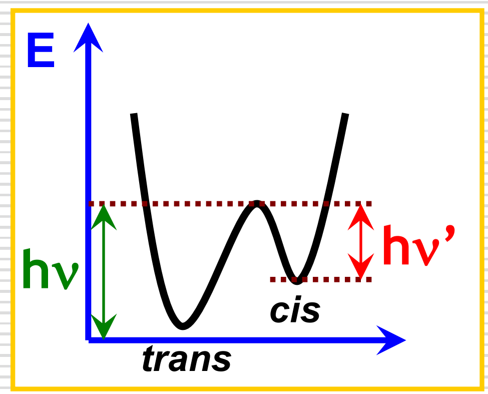
Absorption spectrum of Methyl Red



Trans-isomer *Cis*-isomer

hν > hν’





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CLC laser

Appl. Phys. Lett., **86**, 161120 (2005)-Optically tuning
Appl. Phys. Lett., **88**, 061122 (2006)-Electrically tuning
Opt. Express **17**, 12910-12921 (2009)- Cone lasing

Cholesteric LC (CLC) **Lasing**

-CLC:1-D Photonic crystals ⇒ Lasing

V. I. Kopp et al. Opt. Lett.**23**, 1707(1998)

-Lyotropic CLCs lasing;

P.V. Shibaev et al., Macromolecules **35**, 3022-3025 (2002)

-Ferroelectric LCs lasing;

M. Ozaki et al., Adv. Mater., **14**, 306-309 (2002)

-Cholesteric Network Polymer lasing;

J. Shmidike et al., Adv. Mater., **14**, 746-749 (2002)

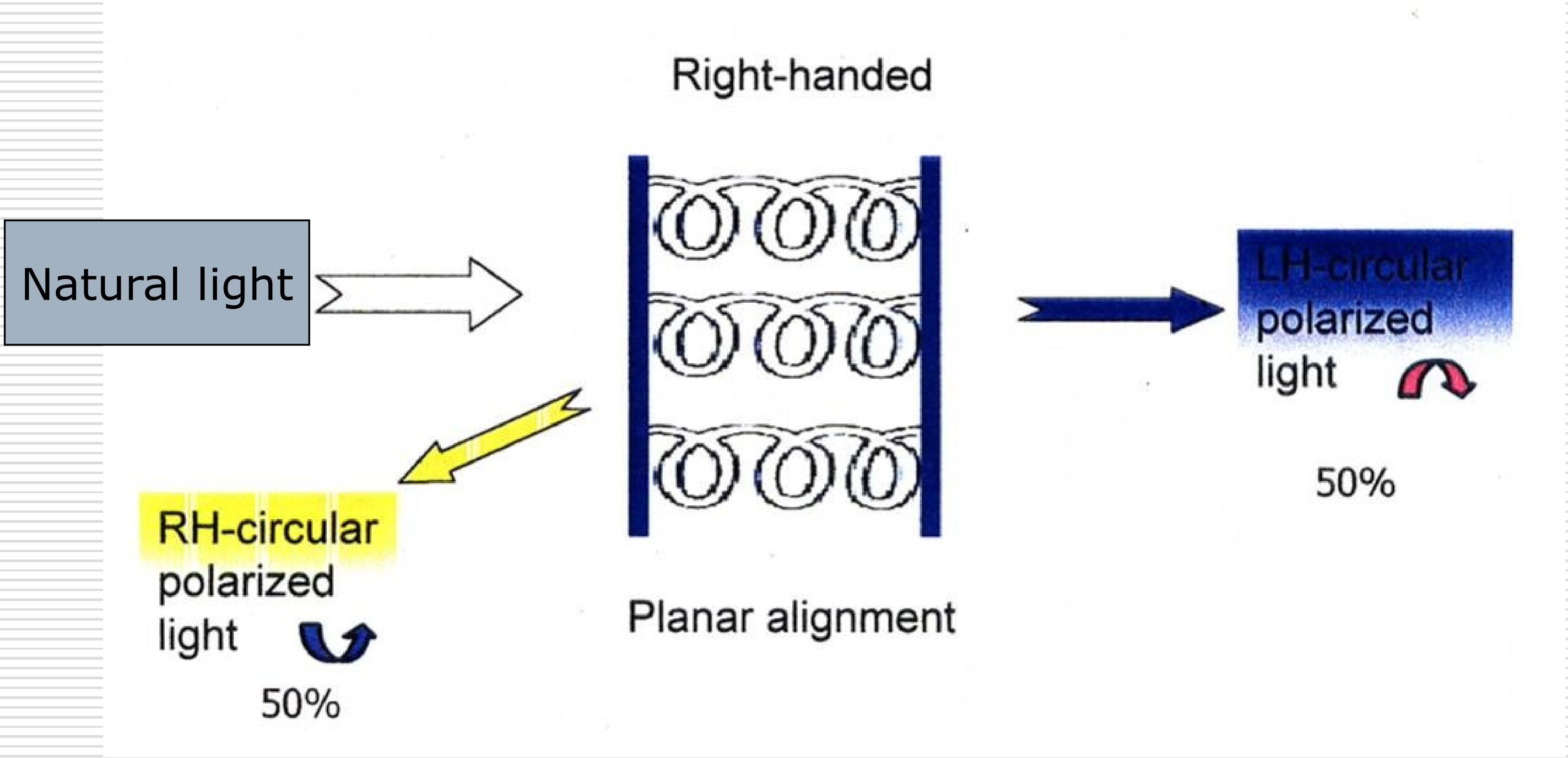
-CLC Elastomers;

H. Finkelmann et al., Mater., **13**, 1069-1072(2001)

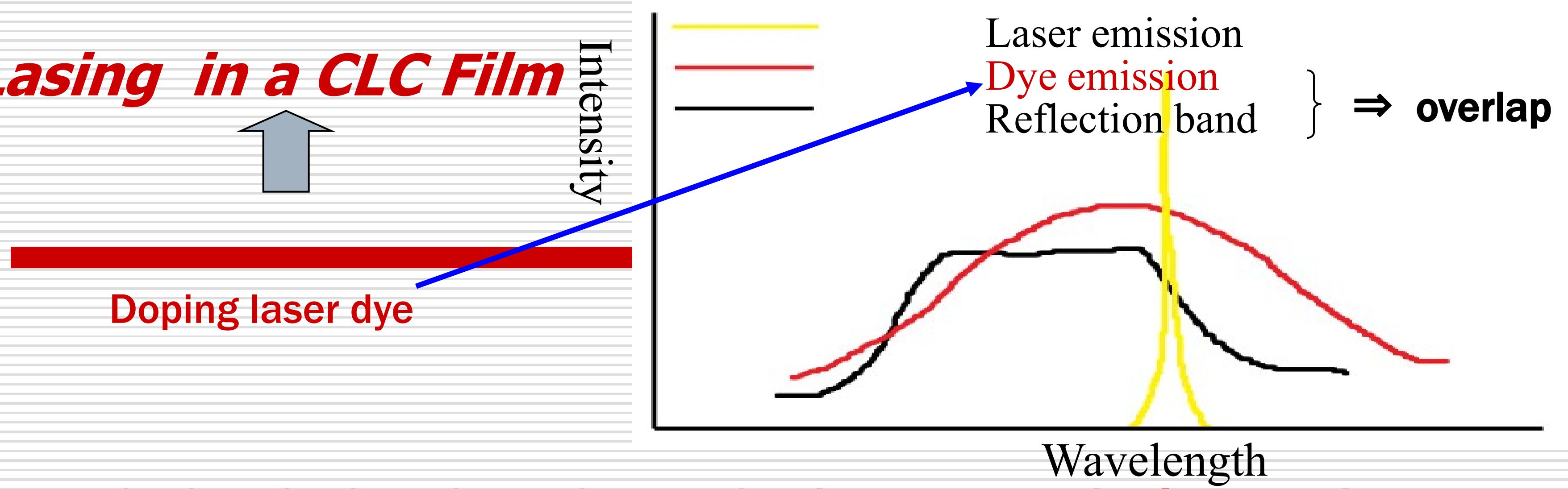
-LC Blue Phase (3D)

W. Y. Cao et al., Nat. Mater **1**, 111-113(2002)

CLC 1D Photonic Crystal: Reflection



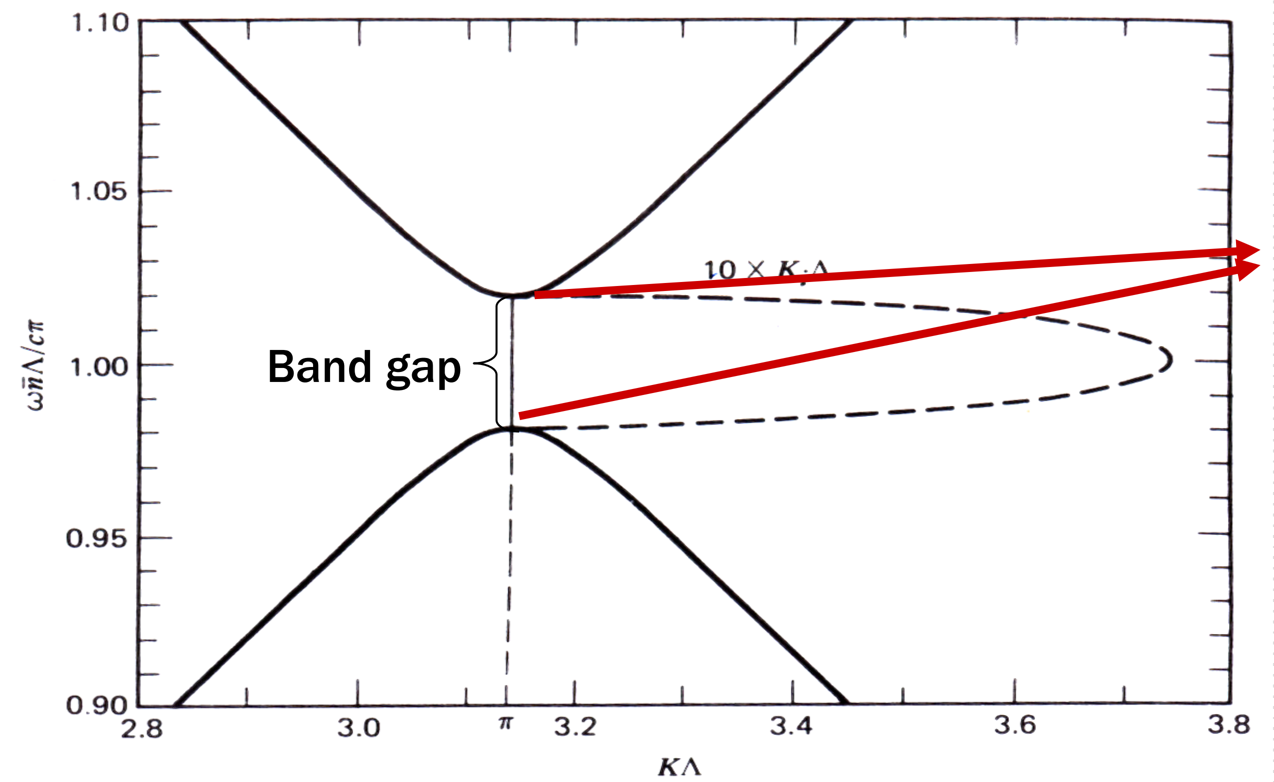
Lasing in a CLC Film



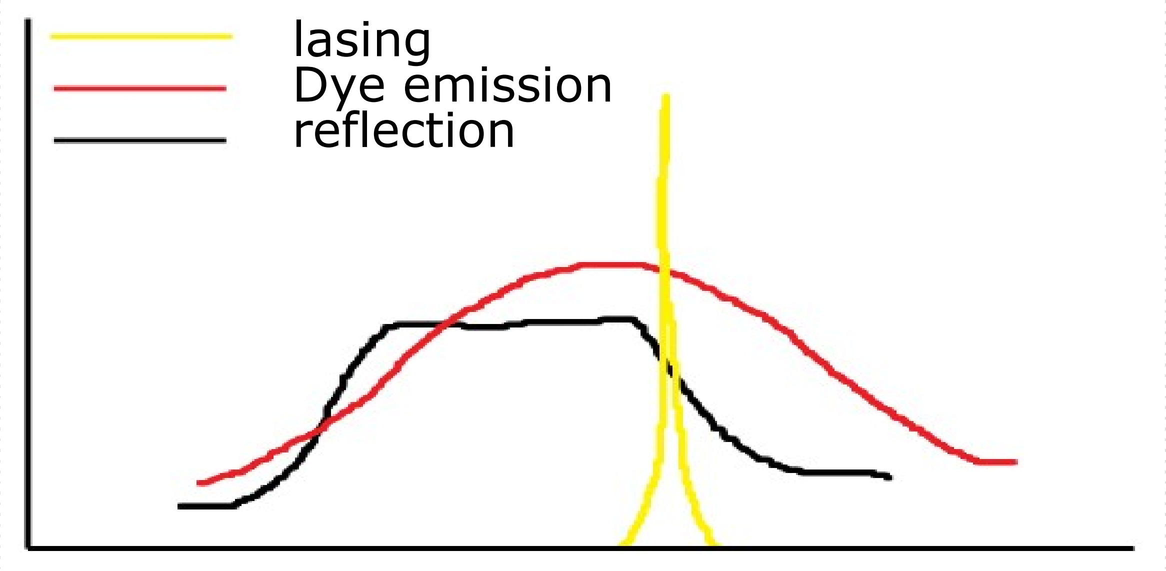
near the band edge : it can be used to **improve cavity laser gain**

- The ***group velocity (v$_g$)*** of the fluorescence light approaches ***zero*** at the band edges.
  (Density of photonic state (ρ) for light that is reflected in the stop band centre shows a narrow singularity.) $\rho \propto 1/v_g$
- This effect implies an exceedingly ***long optical path length*** in the structure.

Dispersion Relation



Tuning Methods

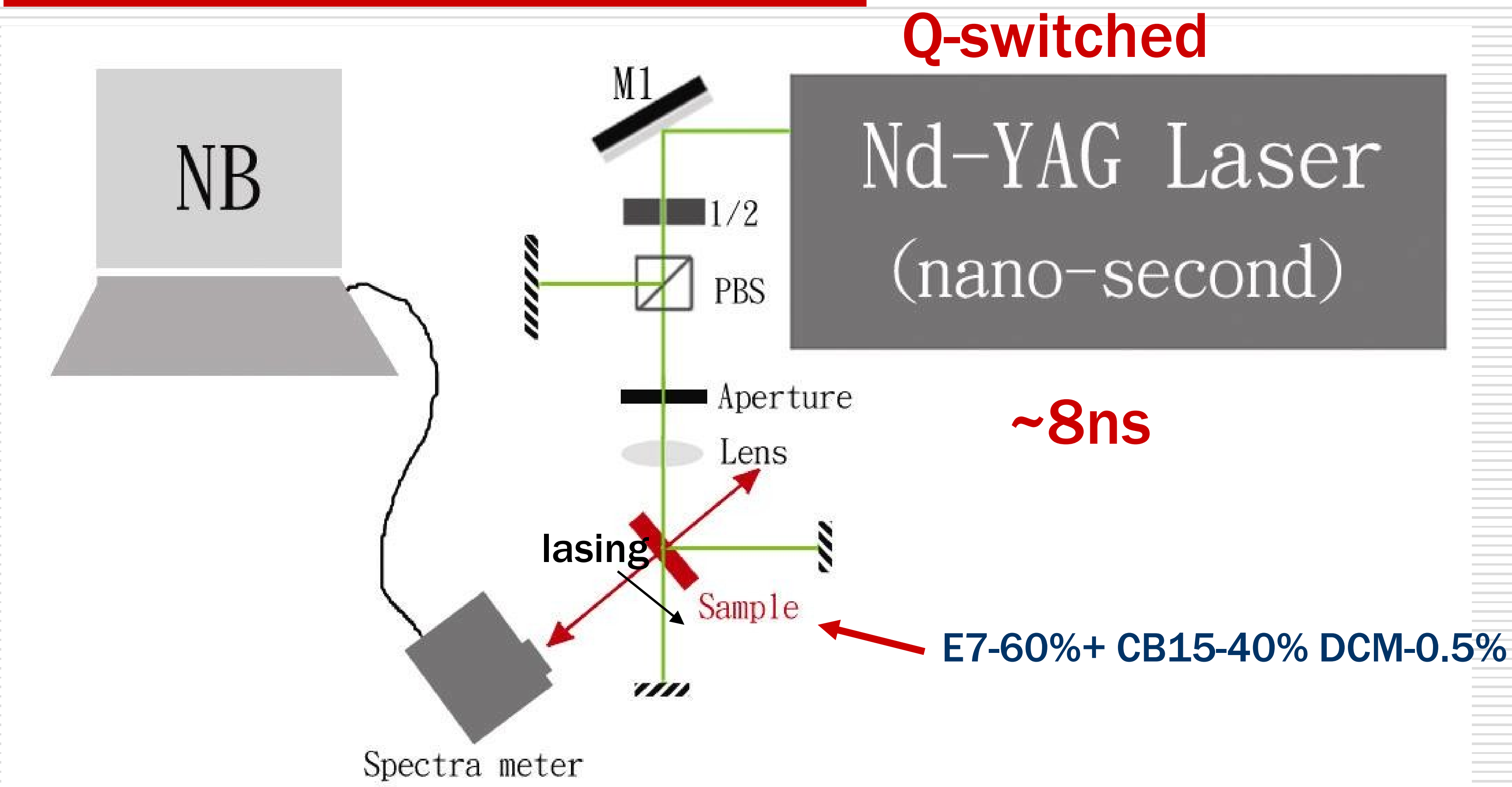


1). Shift CLC reflection band (change pitch length),

OR

2). Change the bandwidth

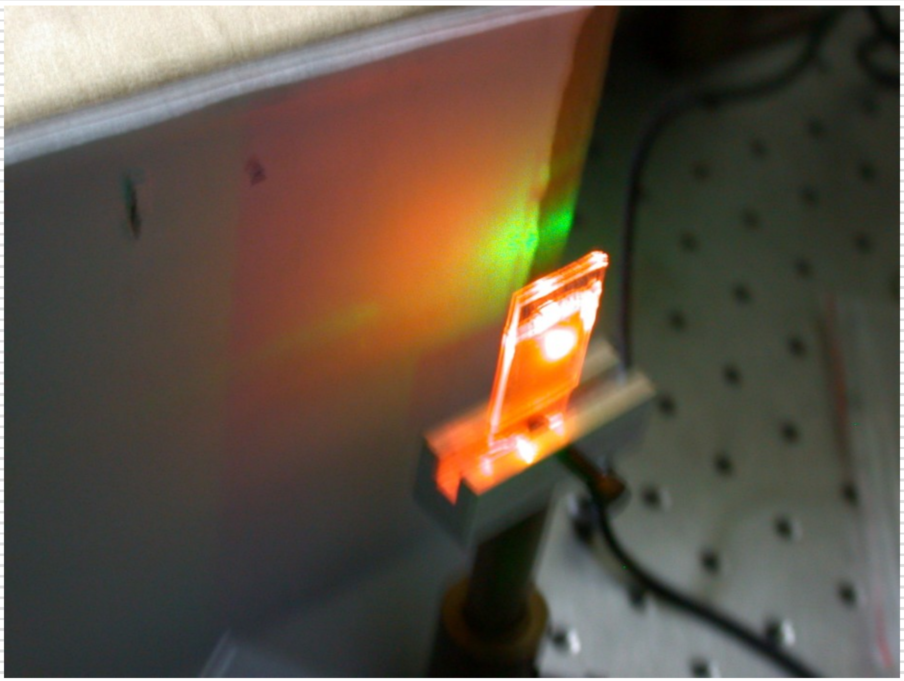
Setup for CLC lasing



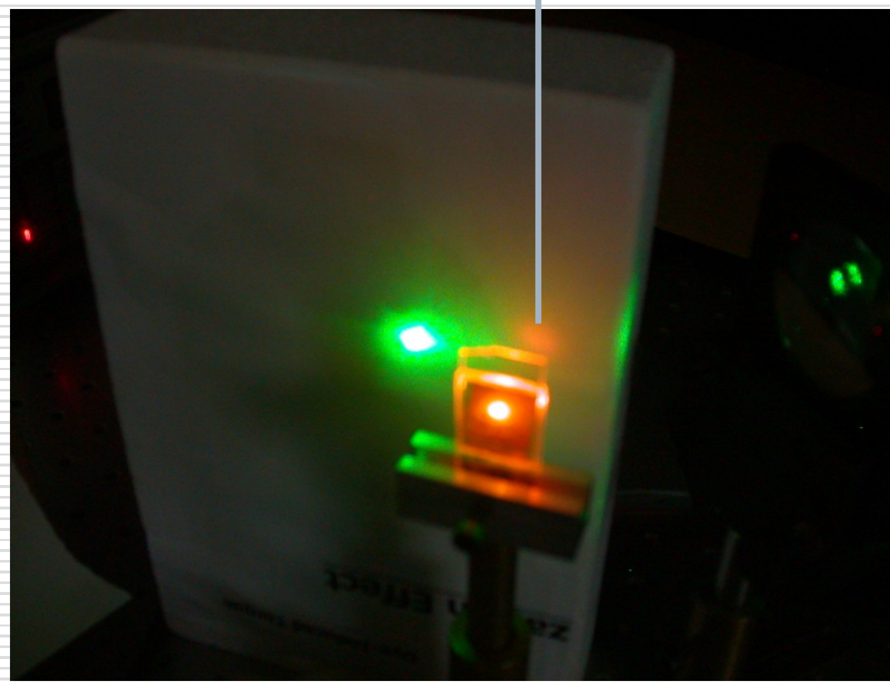
Character of CLC lasing

- Low lasing threshold~1uJ

lasing



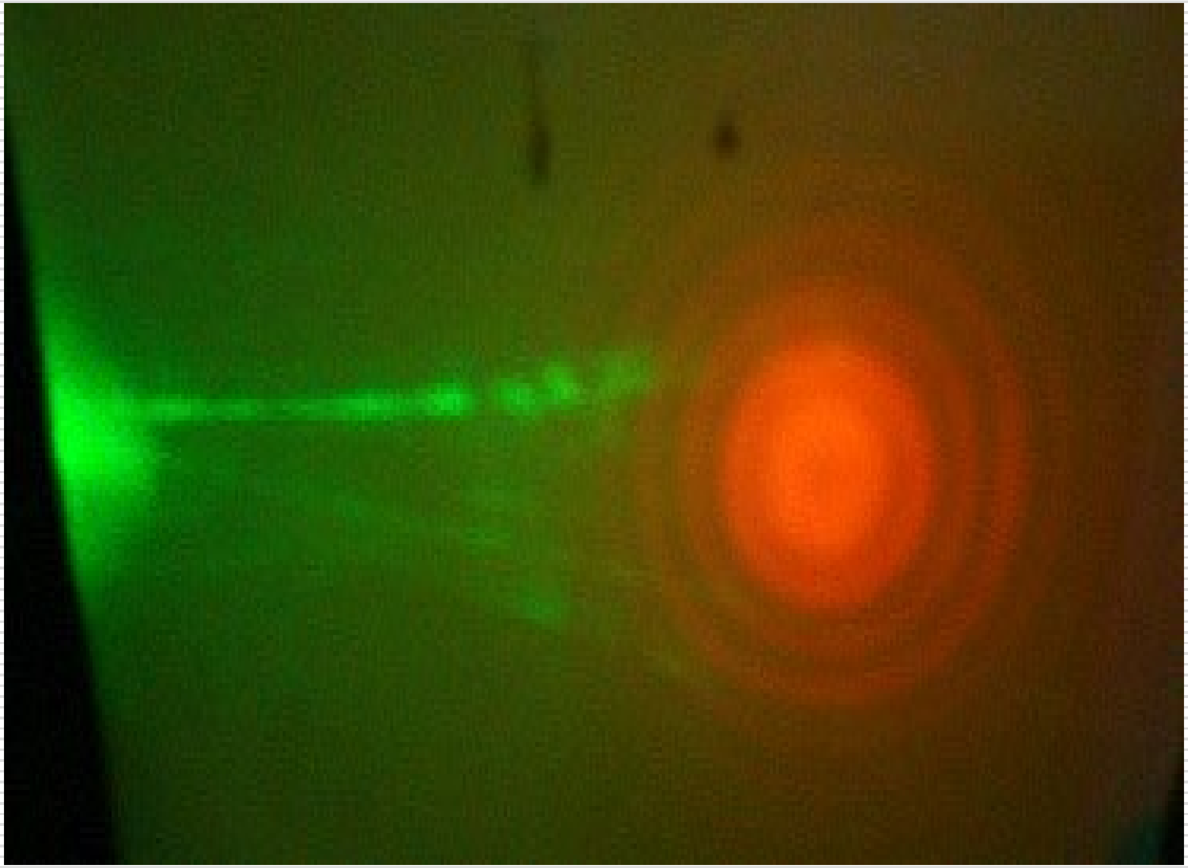
Non-lasing



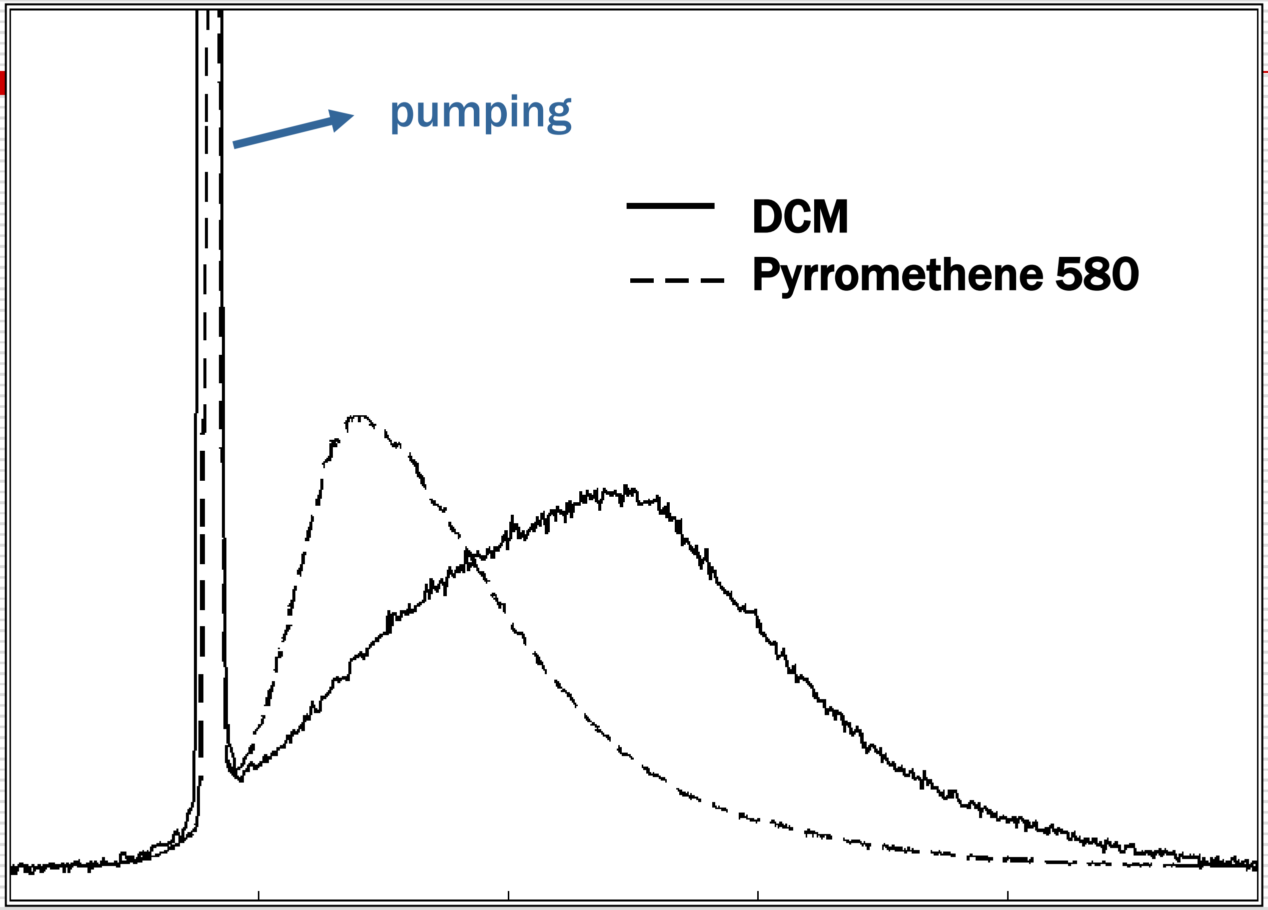
lasing

Far Field of CLC Lasing

Ring pattern ⇒high coherence



Wide Tuning Cholesteric Laser: doped two laser dyes



Tunable chiral material (TCM)

Sample: ZLI 2293 (62.2wt %), S811 (31.1wt %) and TCM (AzoB) (6.7wt %)

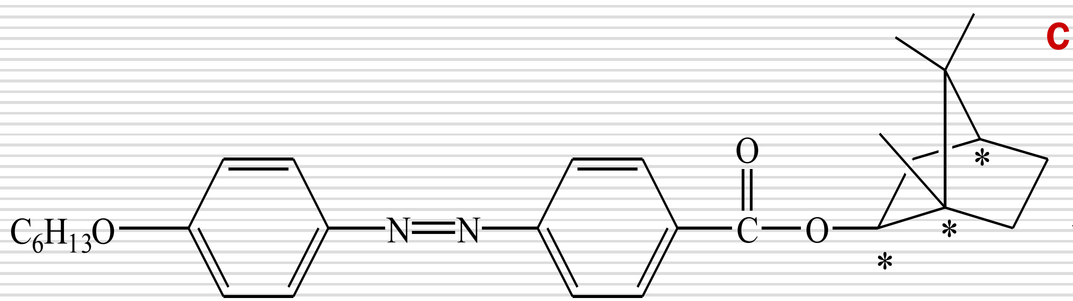
$\Delta\varepsilon>0$

λ_r~520 nm.

Add AzoB➔

λ_r~ 670 nm.

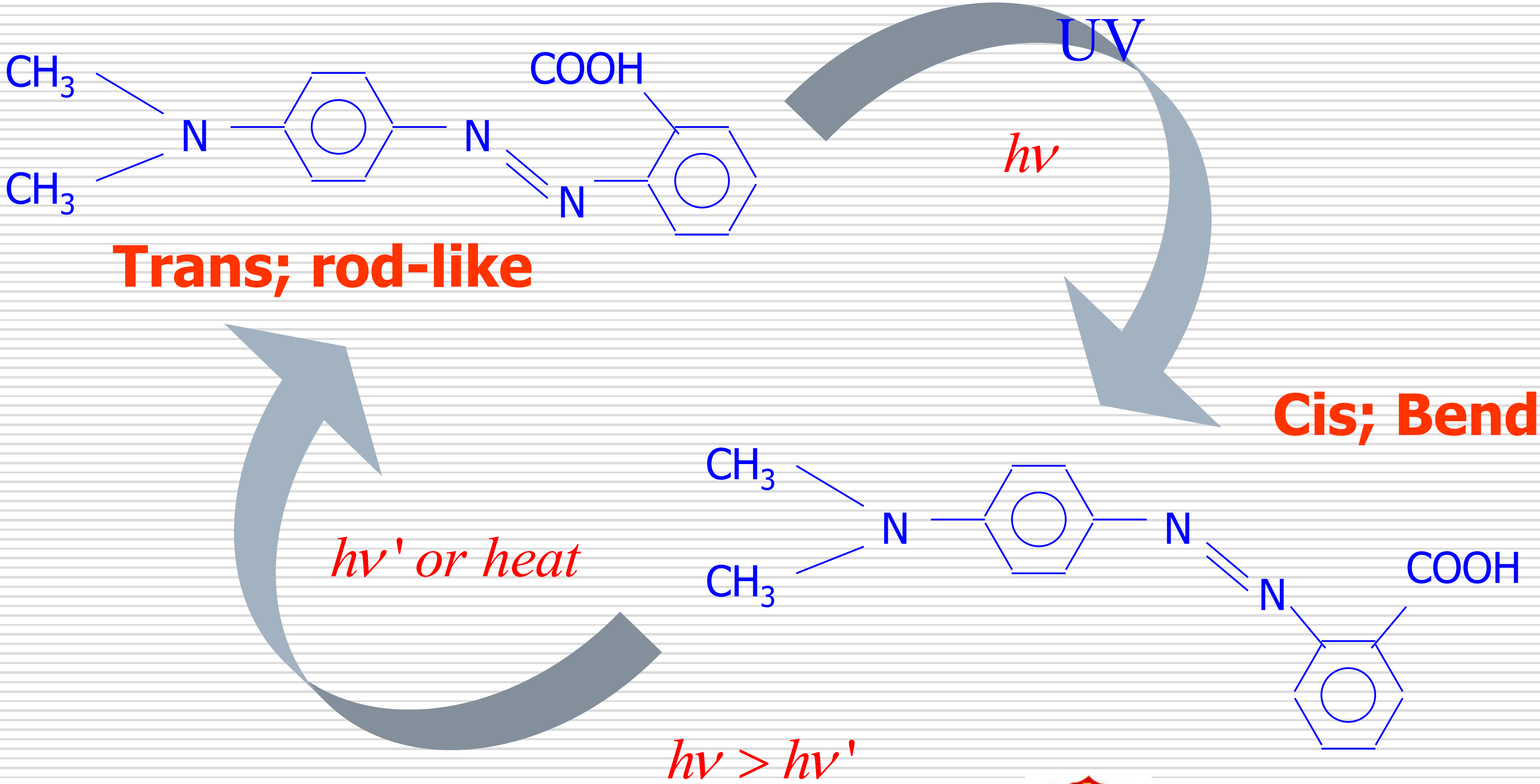
Due to Conformation change



AZOB

Azo Benzene（provided by prof. J.-H. Liu, Chem. Eng. Dept., NCKU)

AzoB- Photoisomerization



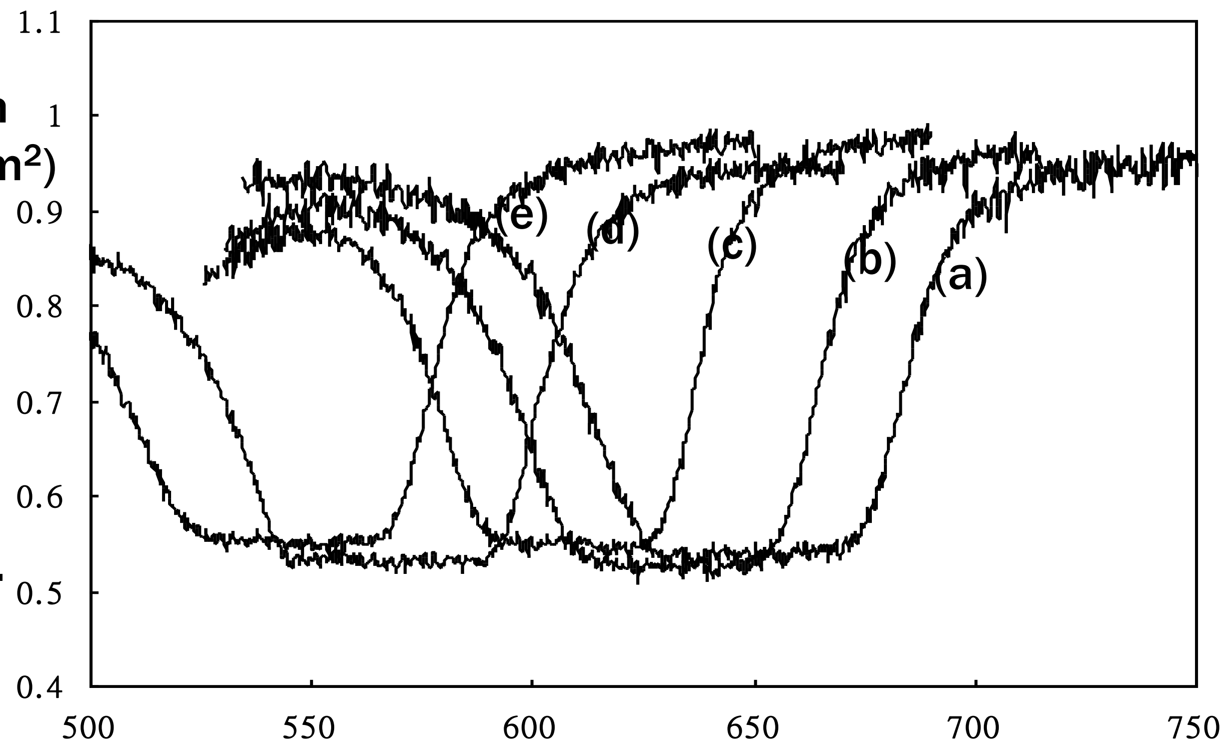
Conformation change of AZOB

- The **rod-like** trans-azobenzene molecule promotes the stabilization of the cholesteric phase. However,the **bend** cis-azobenzene molecule tends to disorganize the molecular orientations of the host liquid crystal phase, changing the geometrical structure rather than the chirality of the AzoB derivatives.

Doping tunable chiral material (TCM)
⇒ shift the reflection band

UV ~350 nm
($7.74\ mW/cm^2$)
radiation

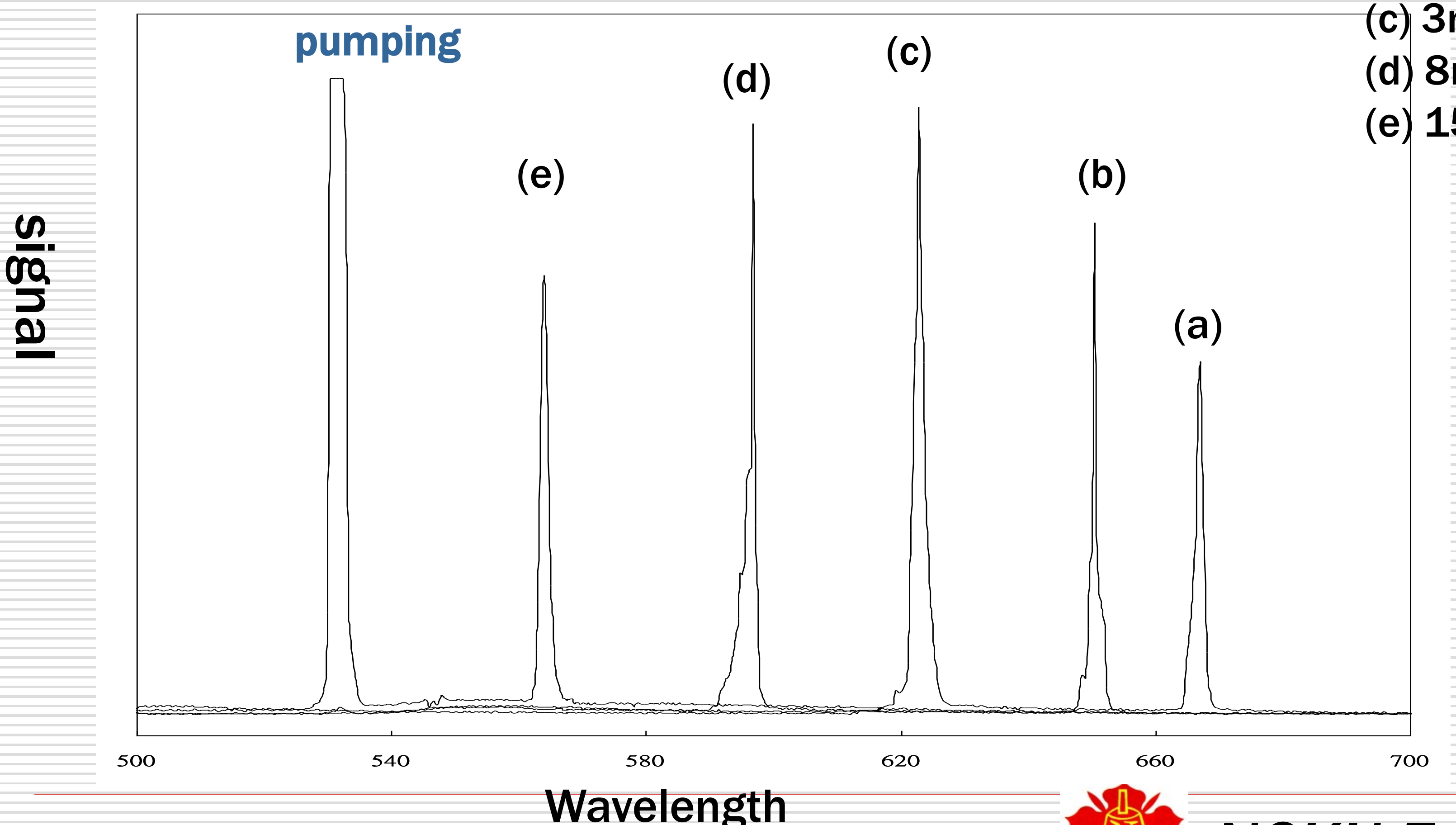
(a) 0min,
(b) 1min,
(c) 3min,
(d) 8min,
(e) 15min.



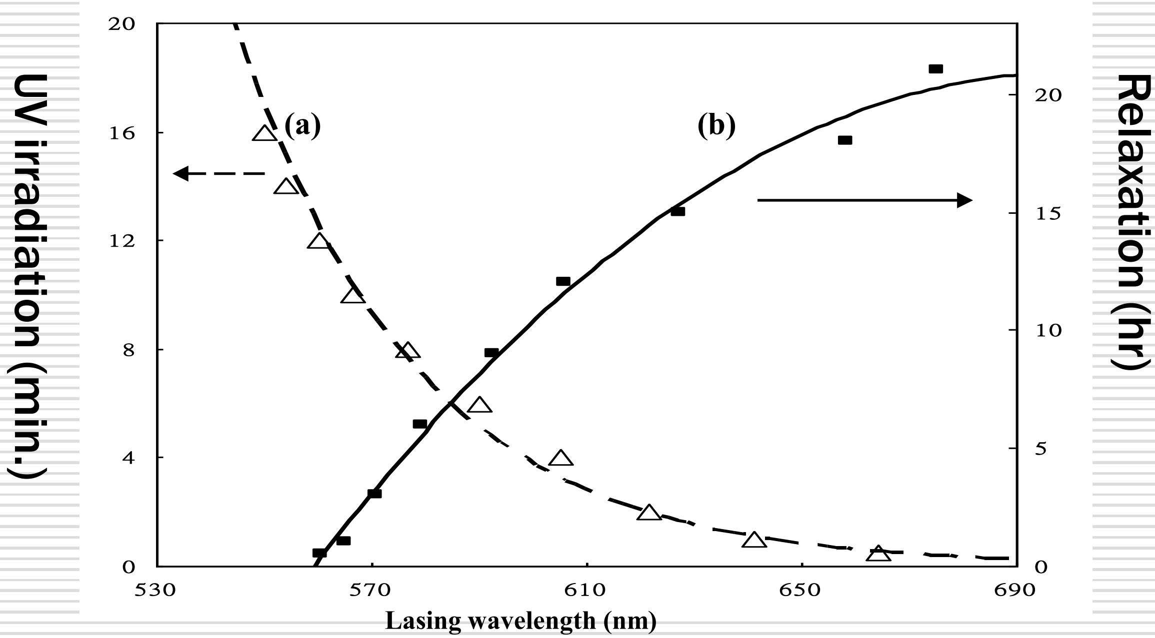
Lasing → Tuning range~ 110nm

UV Radiation

(a) 0min,
(b) 1min,
(c) 3min,
(d) 8min,
(e) 15min



Reversable



Variations of lasing wavelength of an AzoB-doped CLC cell (a) with irradiation under UV light and (b) relaxing after lasing at 563nm,

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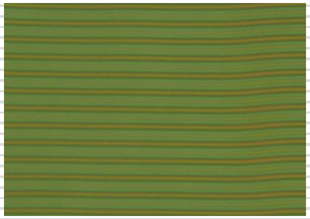
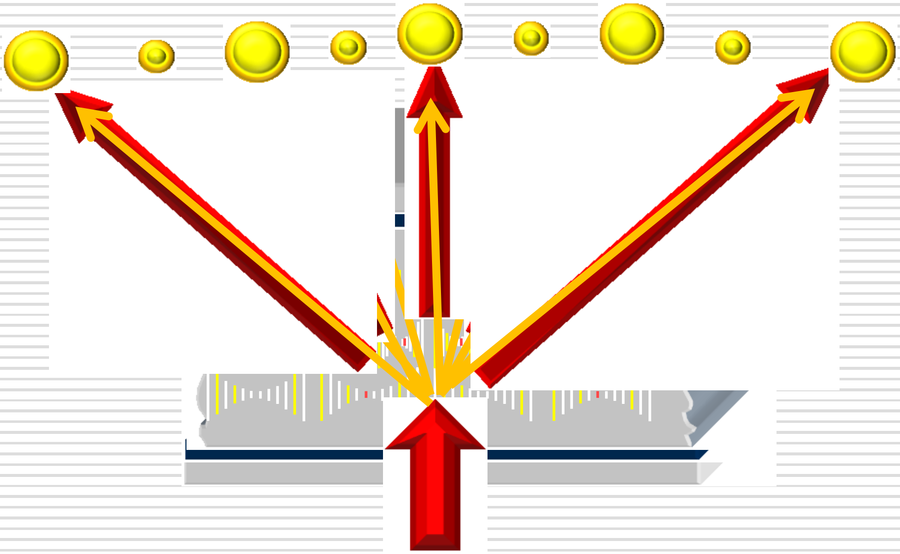
Phto-tunable cholesteric grating: fingerprint structure*

- Self assembly



- Tunable period by varying CLC pitch.



*Opt Exp. **18,** 17499-17503 (2010)

Cholesteric gratings
with field-controlled period (dp/dE›0)

- C= 8.1 %
- P= 1.7 μm
- d= 2.5 μm
- d/p = 1.47
- Tuning range = 15º

Appl. Phys. Lett., **71**, 8 (1997)

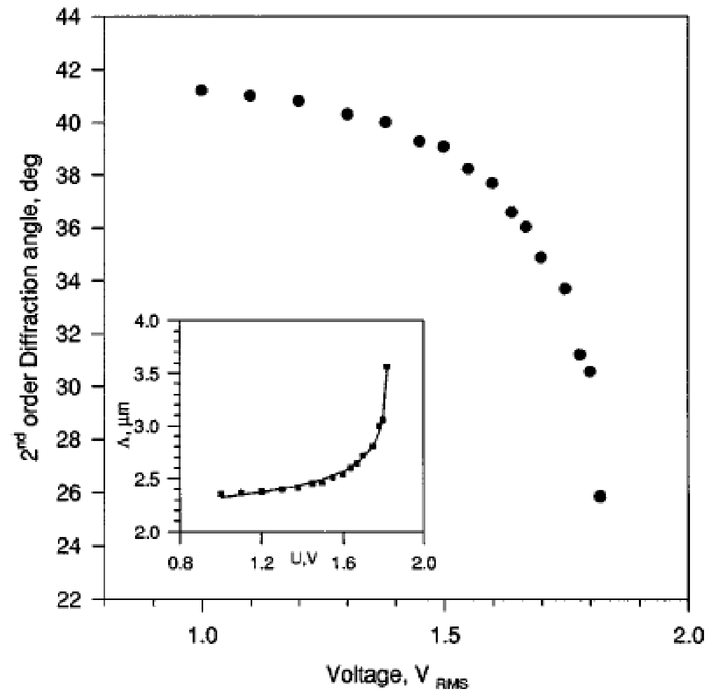


FIG. 3. Direction of the second diffraction maximum and the grating period Λ [calculated from Eq. (2)] as the function of the voltage applied to the cell No. 2. Experimental data $\Lambda(U)$ are fitted by Eq. (3) with $U_C = 1.85$ V ($U_C = E_C \cdot d$) and equilibrium pitch $p = 1.95$ μm.

Phto-tunable cholesteric grating
Experimental setup

- Homogeneous alignment (PVA,180^o rubbing)
- Cell gap = 3.7 μm
- E7+S811(p_o=1.7 μm)
- Azo-C5 : 5%

Setup

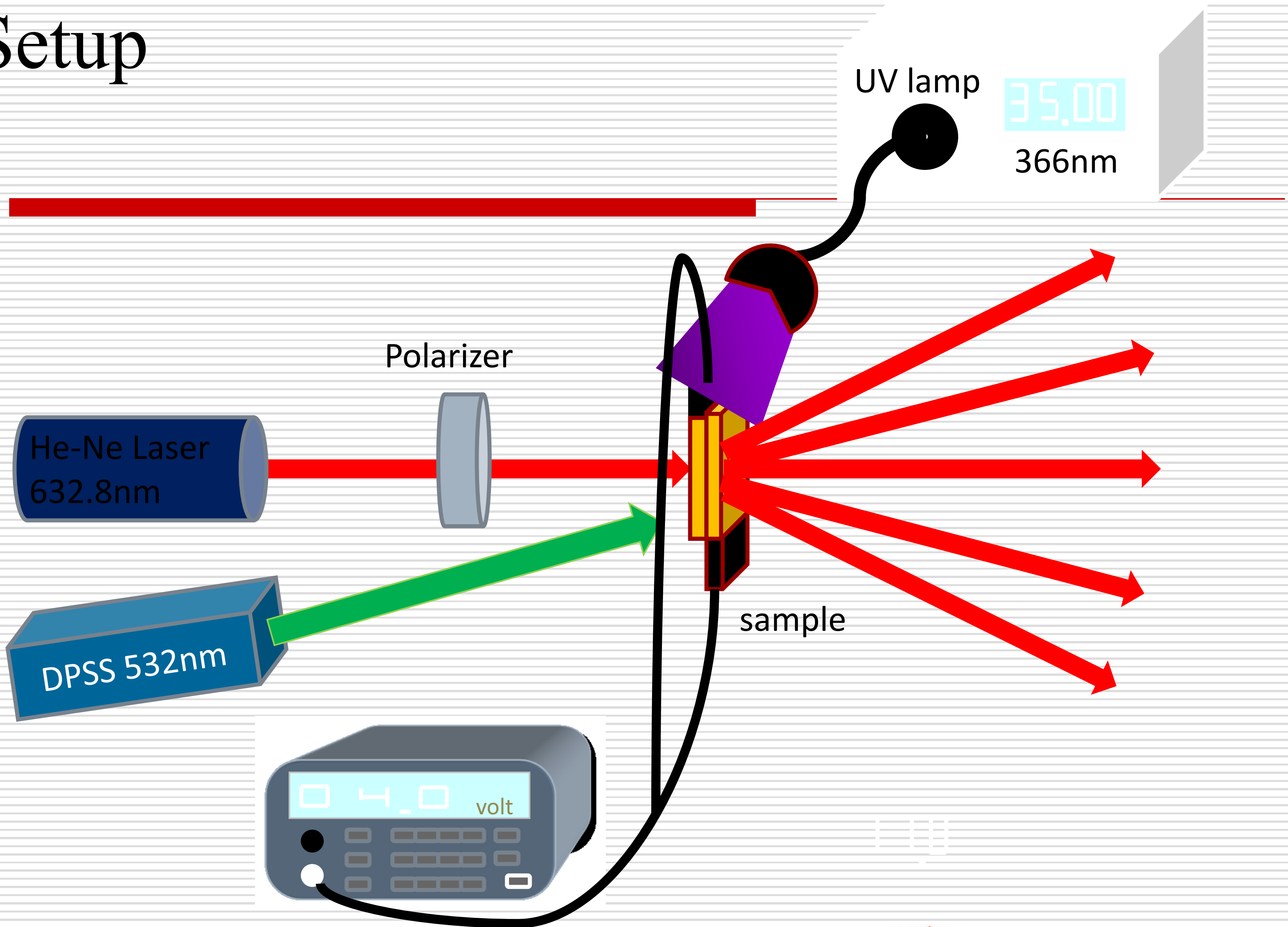
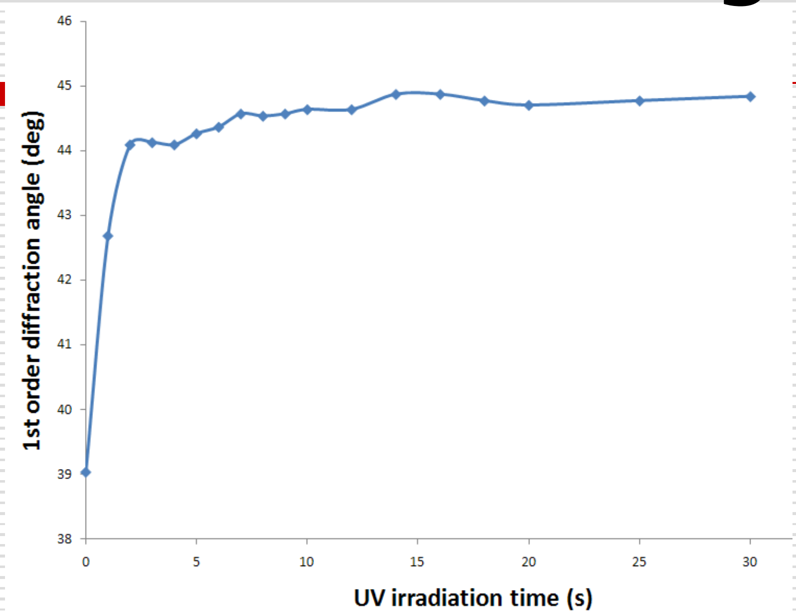
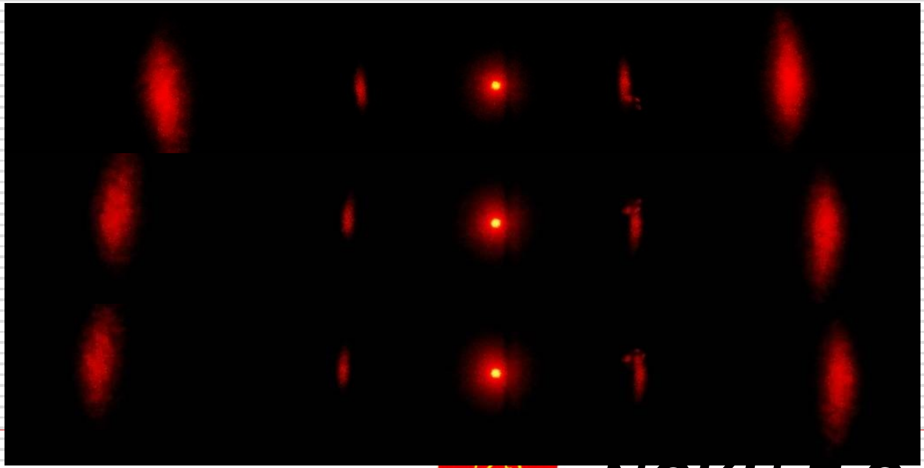

UV lamp
35.00
366nm
Polarizer
He-Ne Laser
632.8nm
DPSS 532nm
sample
volt

Photo-tunable diffraction angle

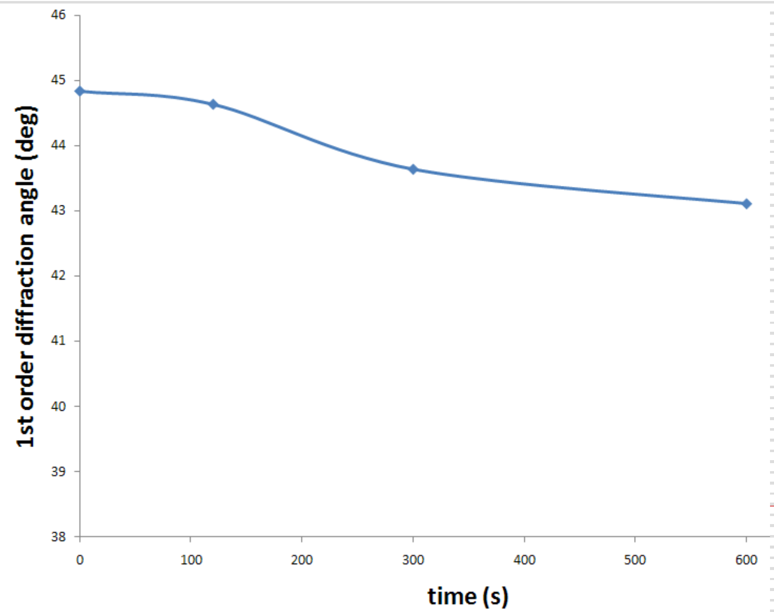
- V=1.5V (finger-print)
- UV strength= 34 mW/cm^2
- Tuning range ~ 6^o
- Equilibrium pitch
  p=2*λ/sinθ
  Before UV: 2.00 μm
  After UV : 1.79 μm

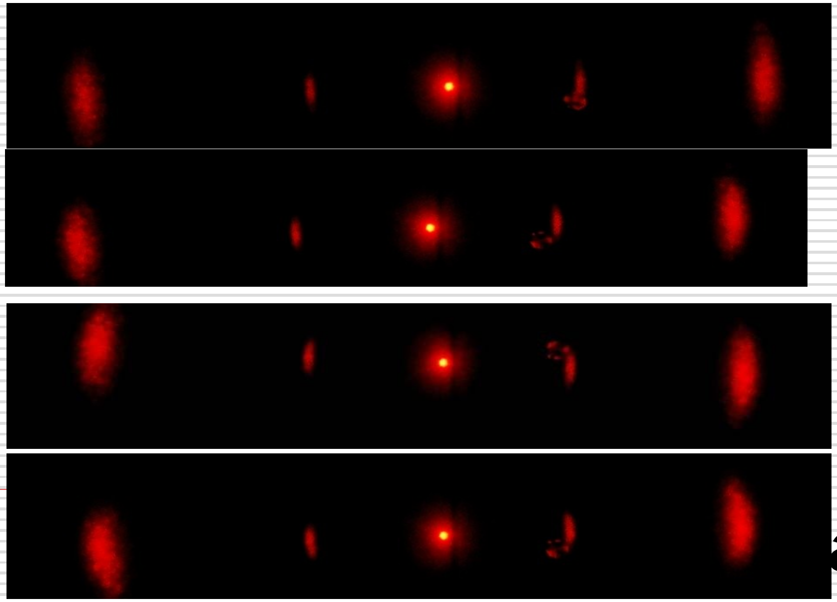




Stability (After UV removed)

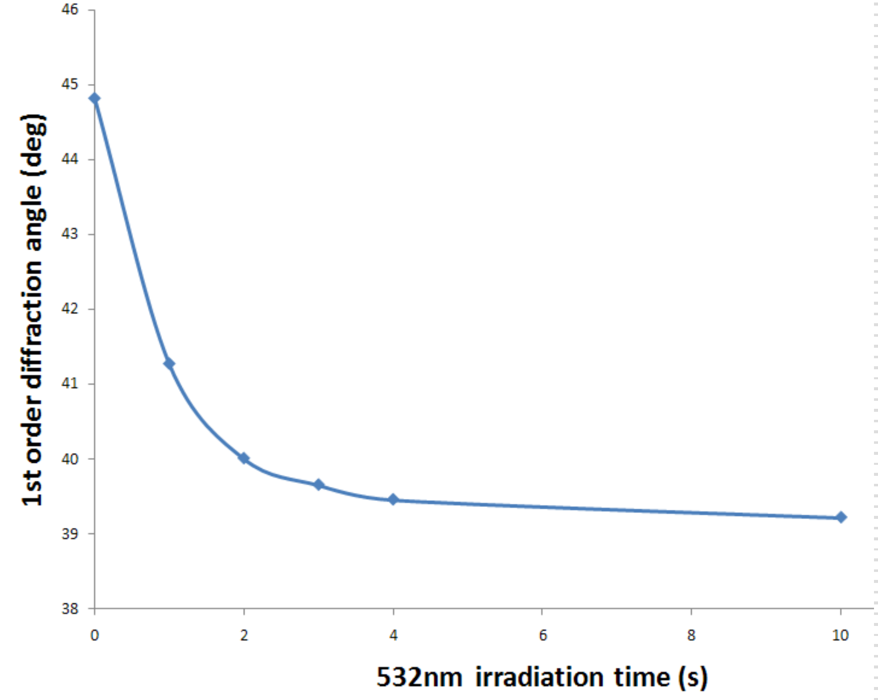
- Can fix the tuning angle within 120s.
- After 600s, the tuning angle decreases ~25%.
- Much more stable than the thermal effect .





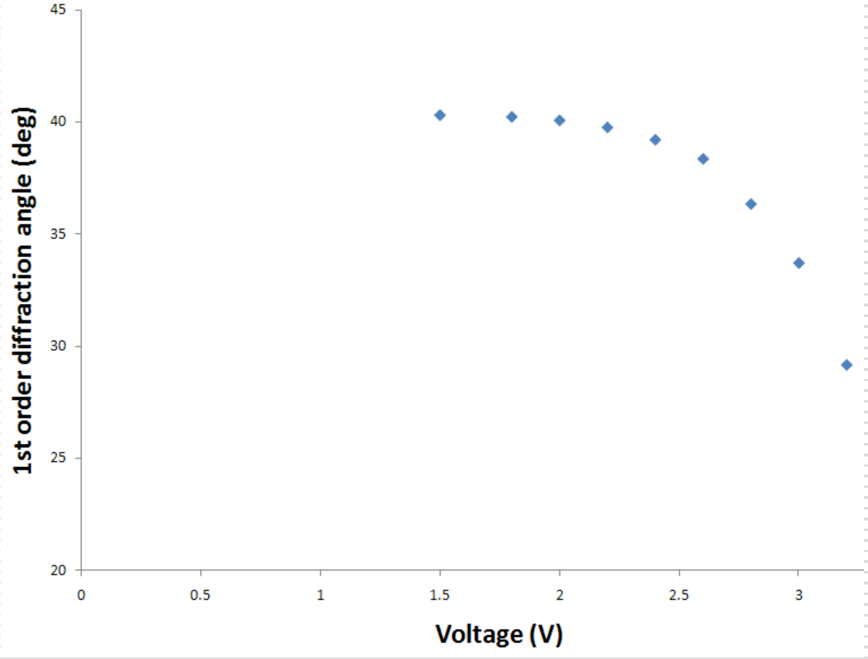
Reverse tuning (cis to trans)

- 532 nm DPSS laser 93mW/cm^2
- Reverse tuning time: within 4s



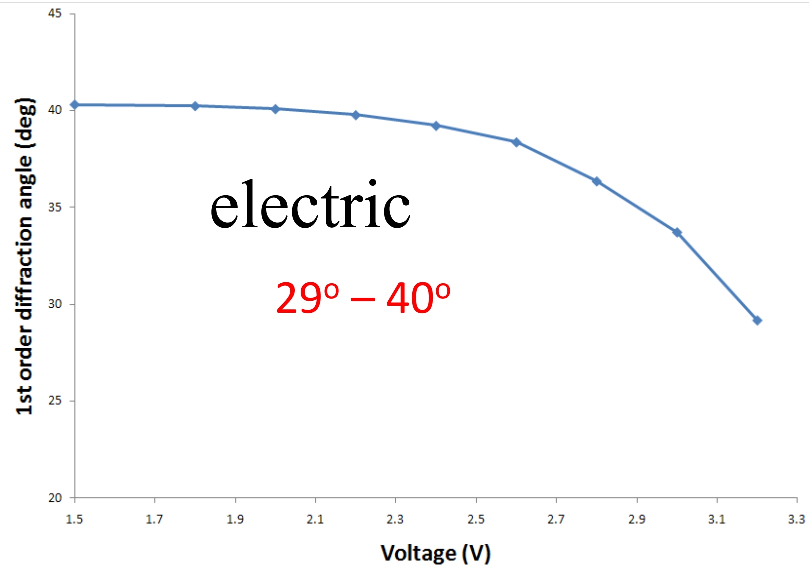
Electrical tuning

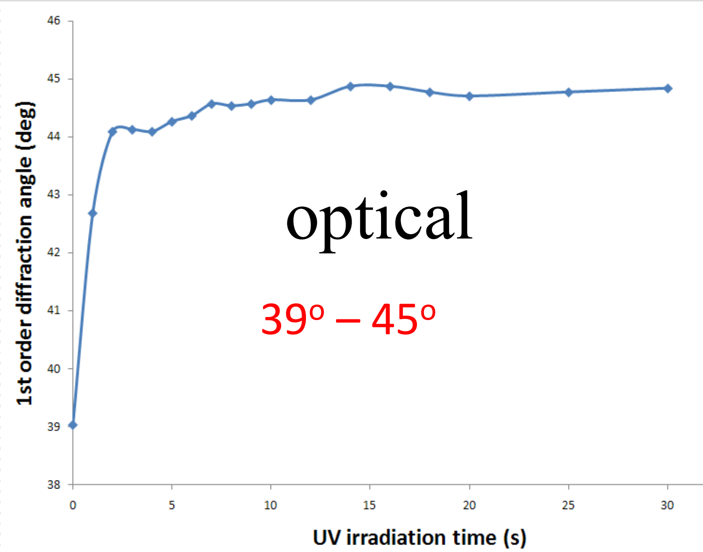
- Tuning range ~ 11°
- V> 3.2V or V<1.5V =>structure collapse

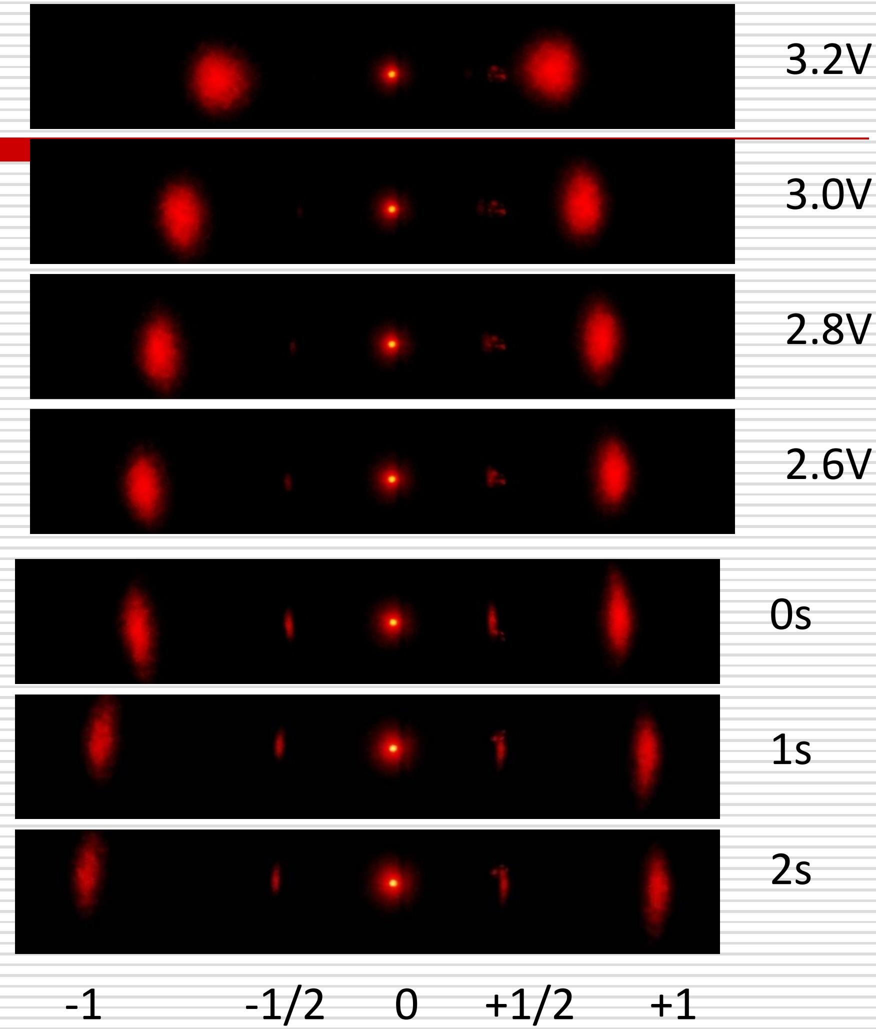


Optical + Electrical tuning: 16°

Total tuning range: 29° – 45°







NCKU E-O Lab.

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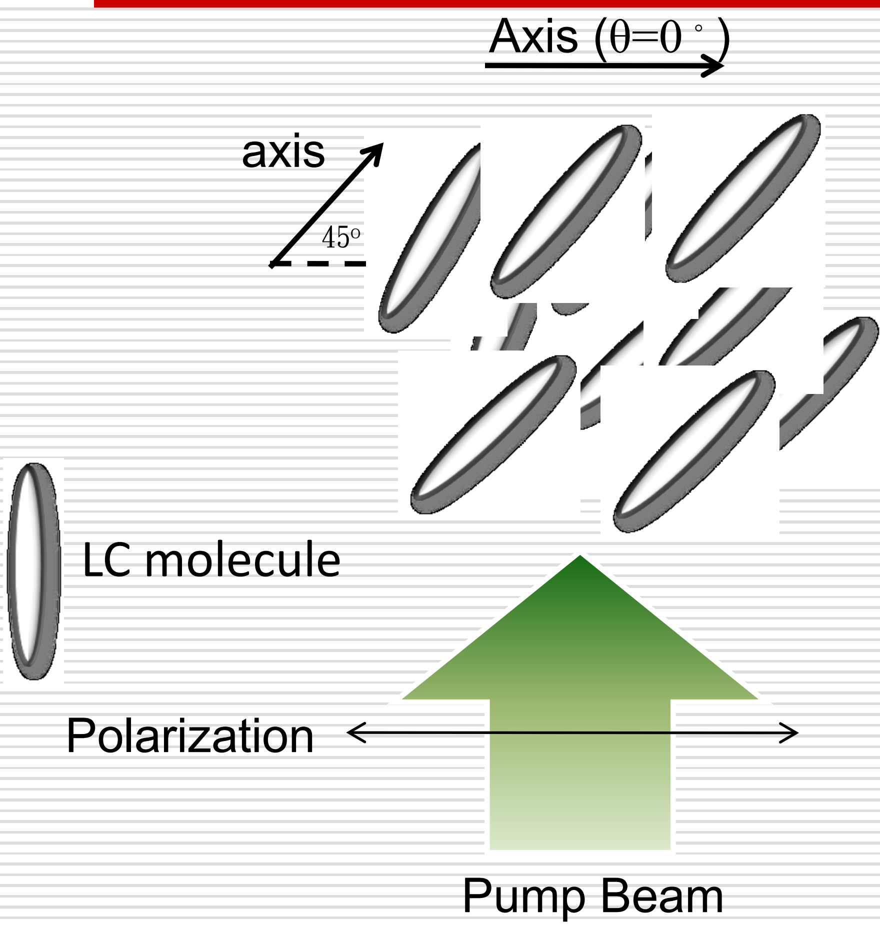
Self-phase modulation
Torque Induced by Optical Field

Opt. Exp. (submitted)



Optical Torque :

$$\vec{\Gamma}_{opt} = \varepsilon_0 \varepsilon_a (\hat{n} \bullet \vec{E})(\hat{n} \times \vec{E}) \propto \sin 2\theta$$

θ=45°, Γ_{opt} is maximum

$$-\frac{1}{4\pi}\int \vec{D} \bullet d\vec{E} = -\frac{\varepsilon_{\perp}}{8\pi}E^2 - \frac{\Delta\varepsilon}{8\pi}(n \bullet E)^2$$

$\Delta\varepsilon = \varepsilon_{//} - \varepsilon_{\perp} > 0$,
then $\hat{n}$ // $\hat{E}$ gives minimum energy => $\hat{n}//\hat{E}$

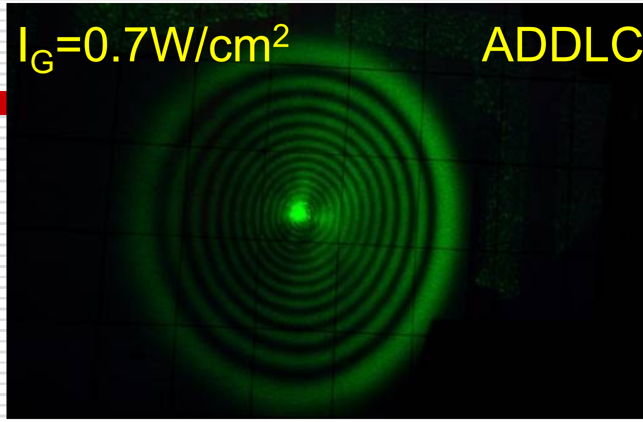
Positive Γ

Phase Shift:

Reorientation

$$\Delta\varphi(\rho) = \frac{2\pi}{\lambda}\int \Delta n(\rho, z)\, dz$$

Self-phase modulation



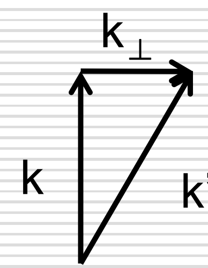
Phase Shift：

$$\Delta\varphi(\rho)=\frac{2\pi}{\lambda}\int \Delta n(\rho,z)dz$$

Gaussian Distribution：

$$\Delta\varphi(\rho)=\varphi_0 \exp(-2\rho^2/a^2)$$

$$\frac{d\Delta\varphi(\rho)}{d\rho}=\boxed{k_\perp}$$

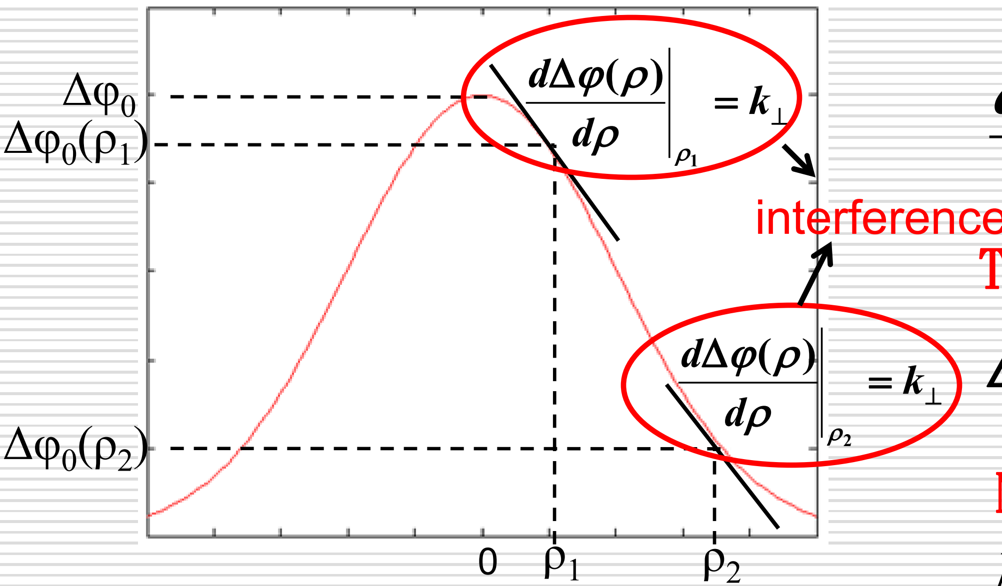


The direction of propagation

$$\Delta\varphi_0 >> 2\pi$$

Number of ring：

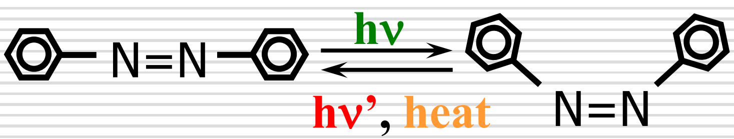
$$N \cong \Delta\varphi_0 / 2\pi$$



Distribution of Phase Shift

Biphotonic Effect and Dye Induced Torque

Chemical Structure of Azo-Dye



Trans-isomer *Cis*-isomer

Opt. Comm. **281**, 3183 (2008)

1. **Reversible**
2. **Occur Simultaneously**

⇒ **Biphotonic Effect**

Dye Induced Torque： $\vec{\Gamma}_{dye} = \eta \vec{\Gamma}_{opt}$

trans-isomer cis-isomer

$\eta_t \langle 0, \quad \eta_c \rangle 0$

$$\eta = \eta_t (1 - X) + \eta_c X$$

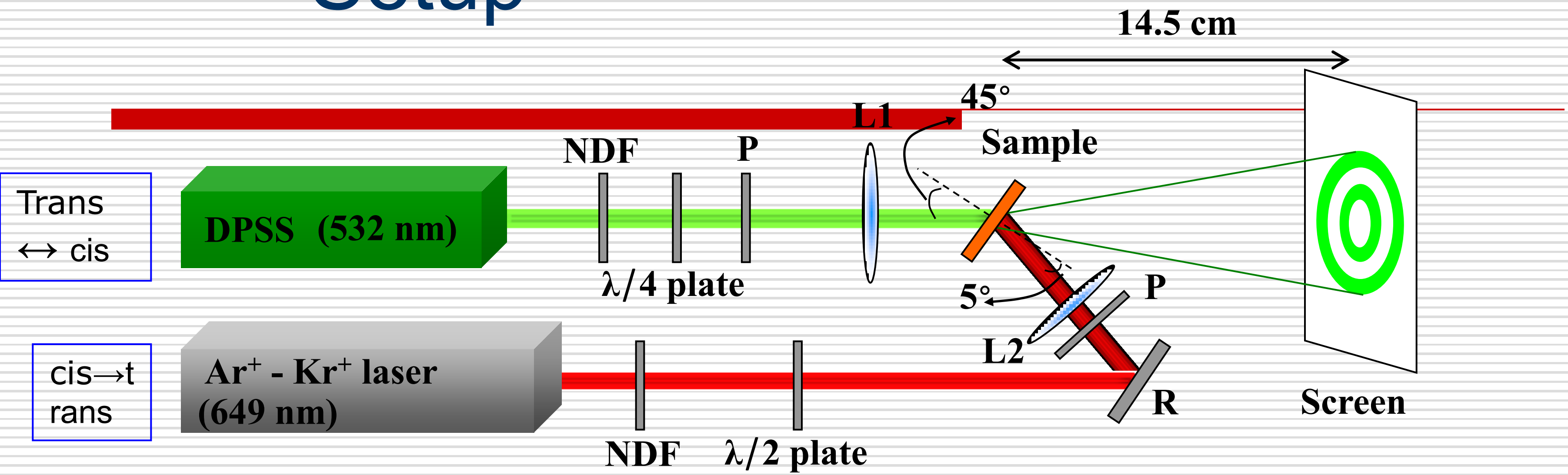
η : enhance factor

PRE **75**, 021703 (2007)

X : concentration of cis isomer

For ADDLC： $\vec{\Gamma}_{total} = \vec{\Gamma}_{opt} + \eta \vec{\Gamma}_{opt}$

Setup



Sample : BL009 (nematics) +0.5%D2 (azo dye)

Cell gap : 50μm

Alignment : Homeotropic alignment

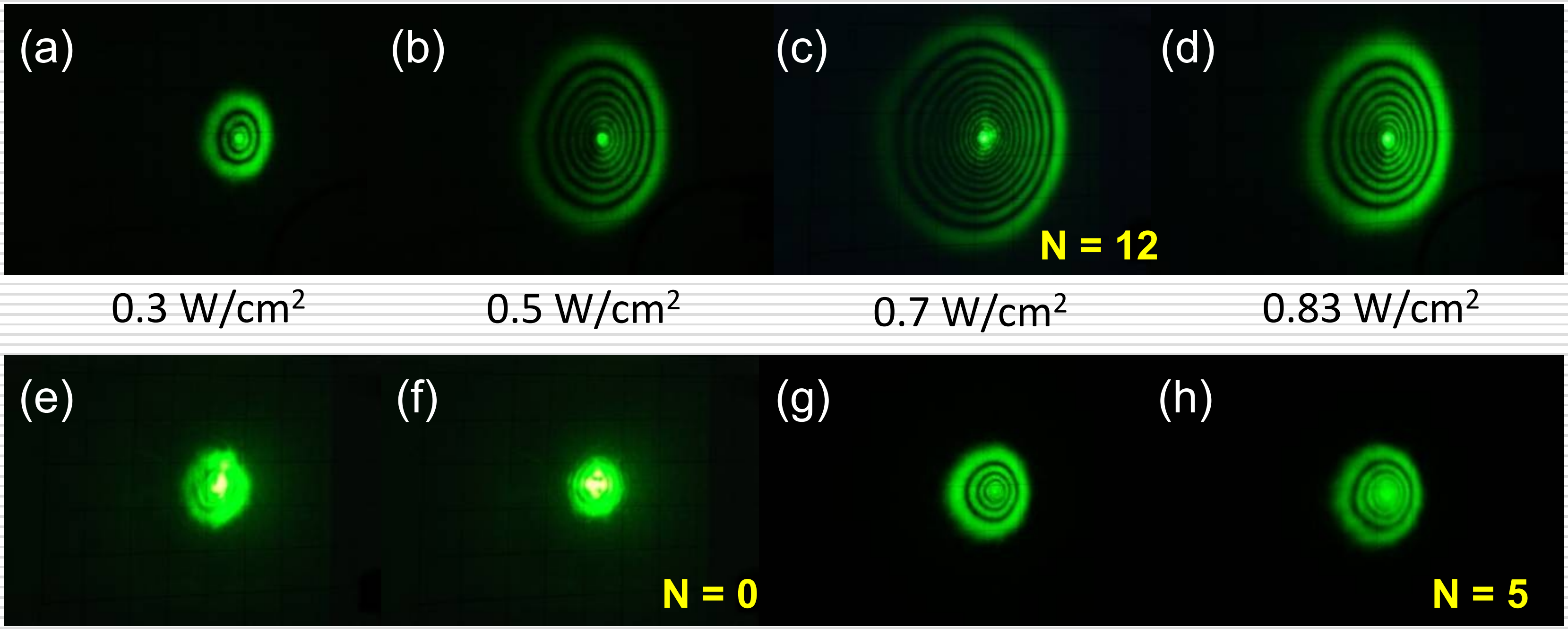
L1: 5-cm convex lens, L2: 3-cm convex lens

DPSS (532nm): 0.1 ~ 1.8 W/cm^2 (p-polarized)

Ar^+-Kr^+ laser (649nm) : 0 ~ 10.8 W/cm^2 (p-polarized)

Results and Discussions

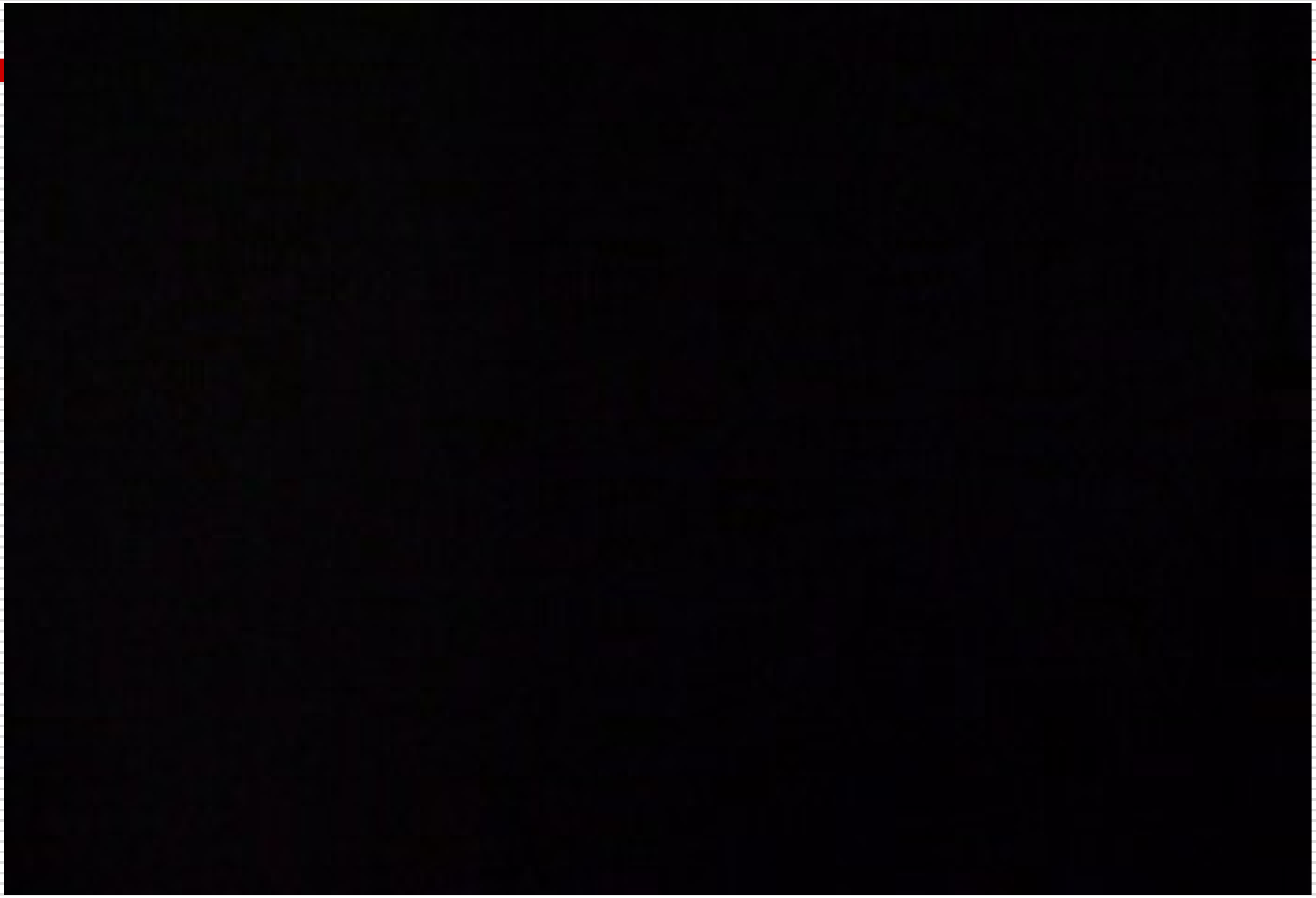
- With pump green light only



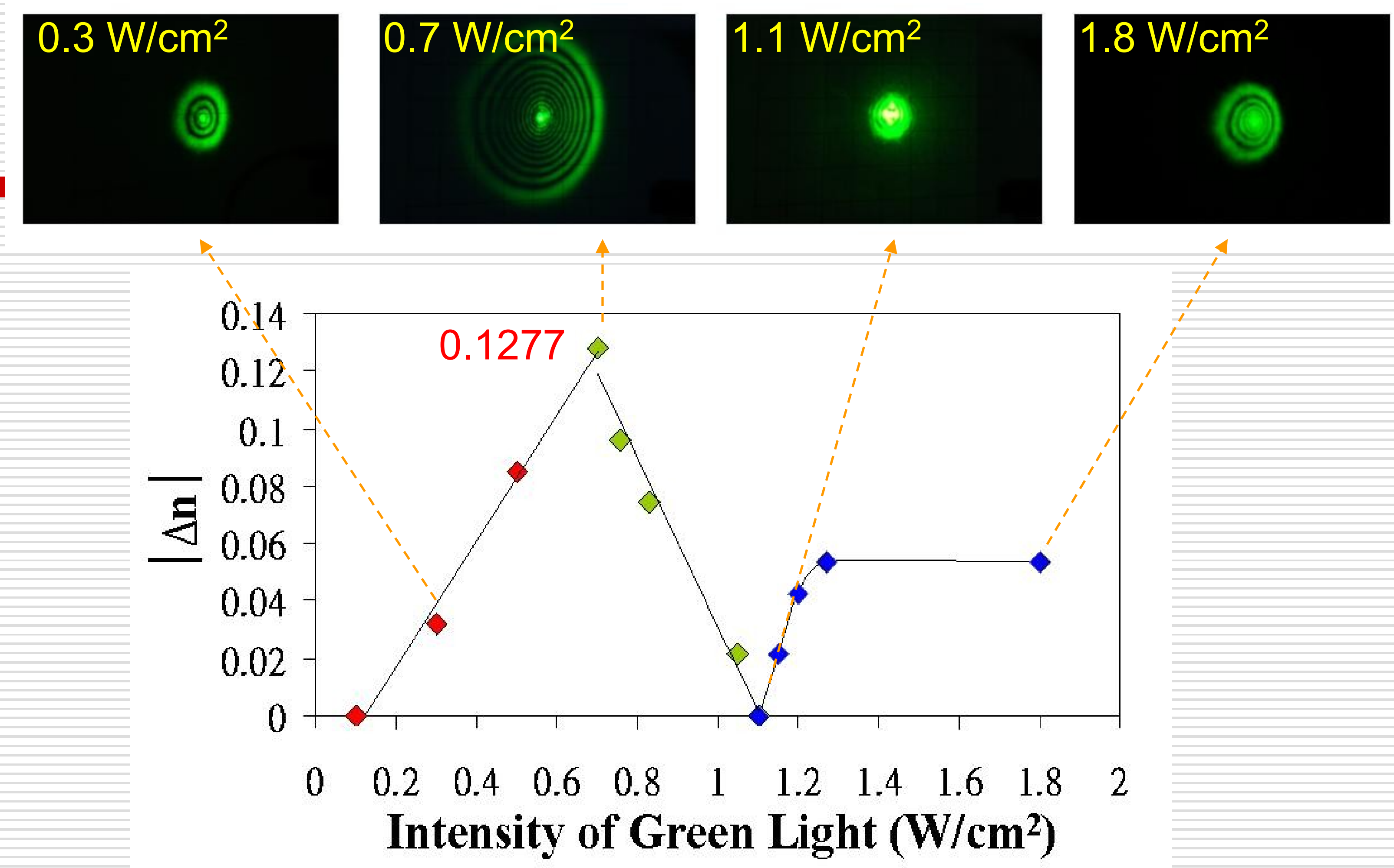
1.0 W/cm^2 | 1.1 W/cm^2 | 1.3 W/cm^2 | 1.8 W/cm^2

N : the number of SPM diffraction rings

The video of ring pattern with increasing I_G



Increase the intensity gradually I_G=0 W/cm^2~1.8 W/cm^2



$$N = \frac{\Delta\phi_0}{2\pi} = \frac{1}{\lambda}\int_{-d/2}^{d/2} \Delta n(z)dz,$$

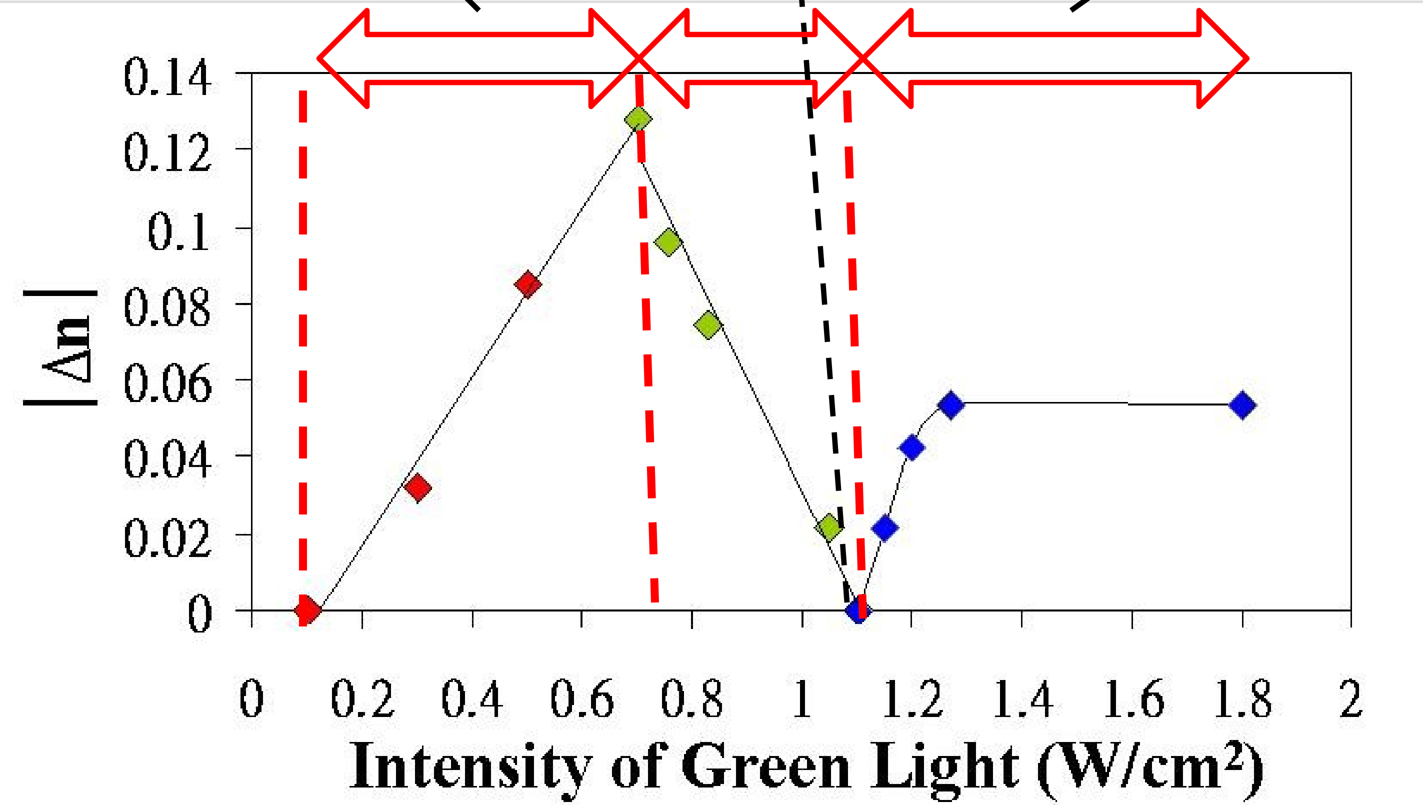
X: cis conc. $\eta = \eta_t(1 - X) + \eta_c X$, $\eta_t < 0$, $\eta_c > 0$, $|\eta_c| > |\eta_t|$

$\vec{\Gamma} \propto \eta I$

X is low
η<0
I_G↑ ➡ | Δn | ↑ ,Γ<0

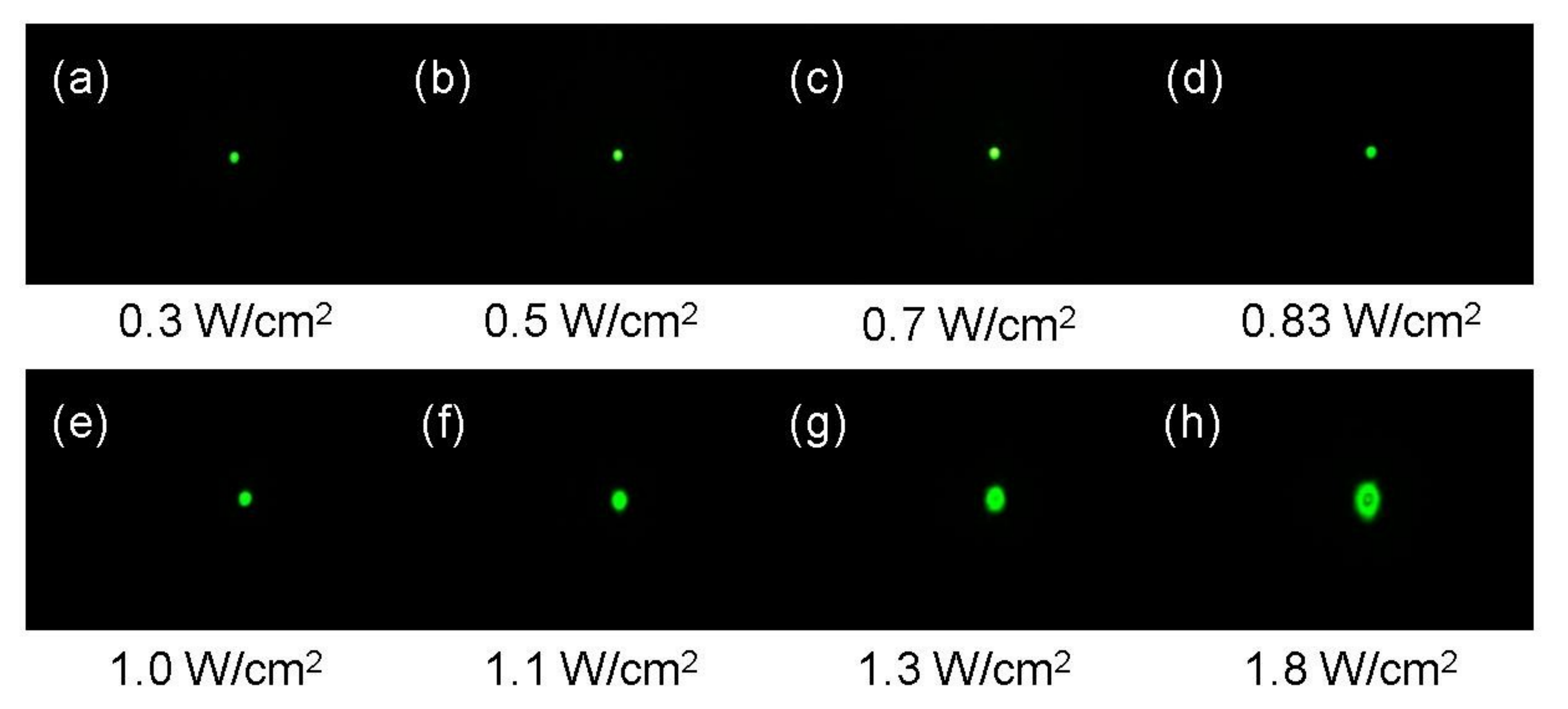
η=0
| Δn | =0, Γ=0

X is high enough
η>0
I_G↑ ➡ | Δn | ↑,Γ>0



Thermal Effect?

- With pump green light only
- under the application of an external AC voltage **~30V**



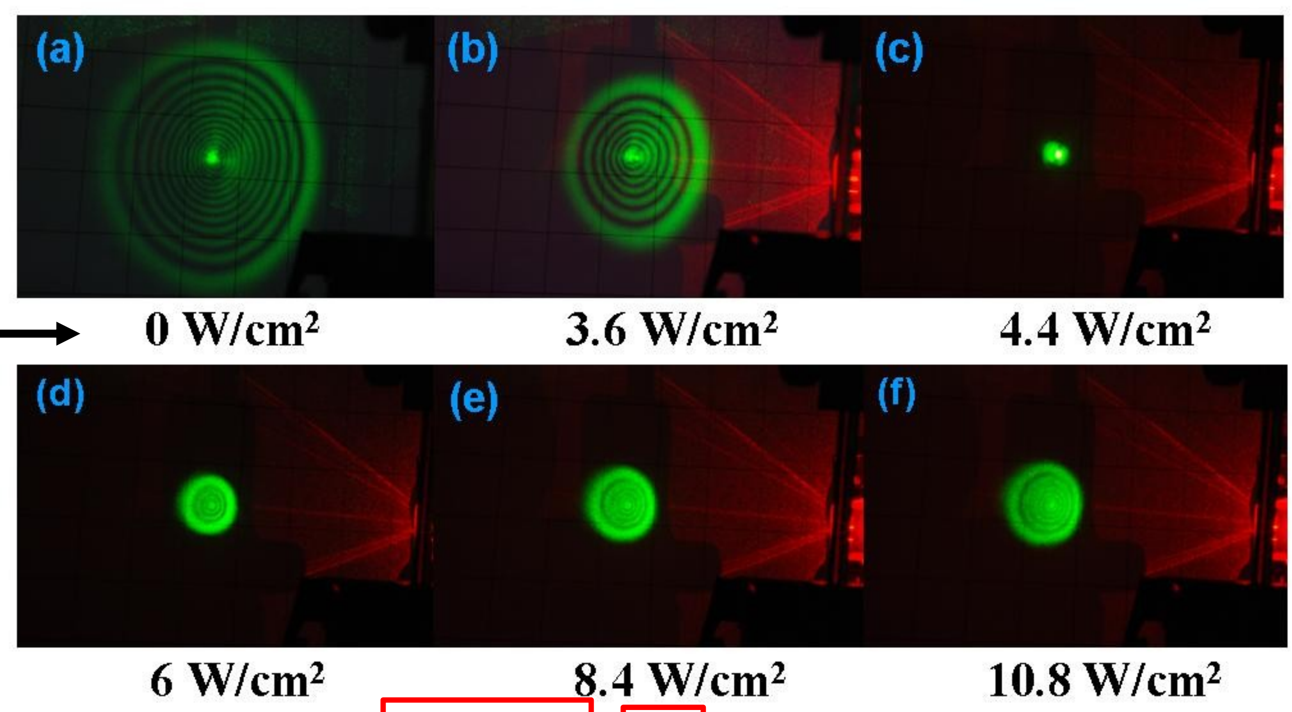
1. No significant thermal effect

2. Reorientation dominated

Biphotonic Effect ($I_G = 0.7\ W/cm^2$)

- fixed $I_G = 0.7\ W/cm^2$ and various I_R

I_R →



$$\vec{\Gamma}_{dye} = \eta \vec{\Gamma}_{opt} + \vec{\Gamma}'$$

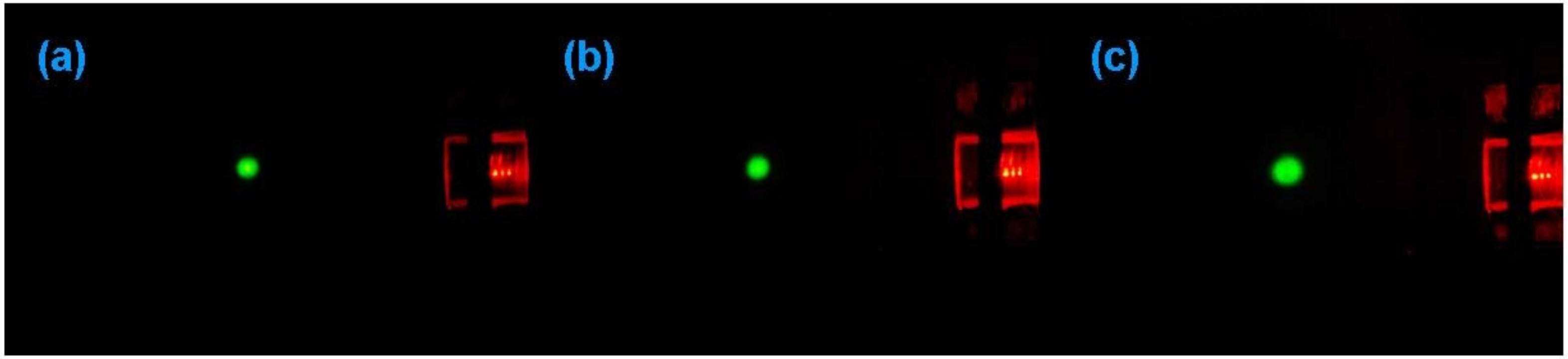
Suppress!!

1. Original, only green light
2. Negative torque

1. Cis-isomer absorb red light
2. Positive torque

Thermal Effect?

- fixed I_G = 0.7 W/cm^2 and various I_R
- under the application of an external AC voltage **~30V**



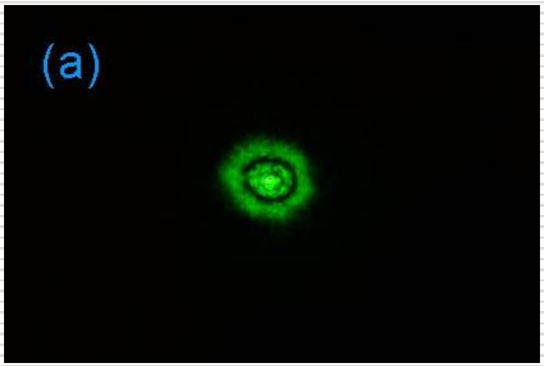
2.4 W/cm^2 + 30 V | 6 W/cm^2 + 30 V | 10.8 W/cm^2 + 30 V

1. No significant thermal effect

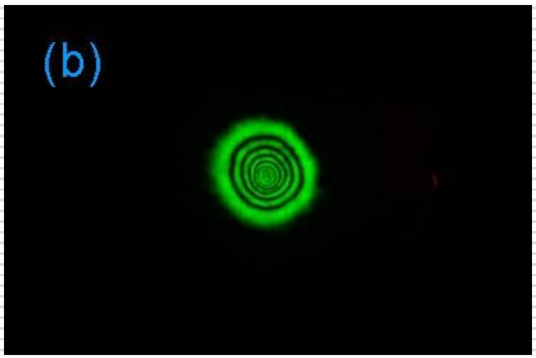
2. Reorientation dominated

Biphotonic Effect (I_G = 1.15 W/cm^2)

- **Γ_{total} > 0 (with I_G = 1.15 W/cm^2 only)**



with I_G = 1.15 W/cm^2 only



with I_G = 1.15 W/cm^2 and I_R = 3 W/cm^2

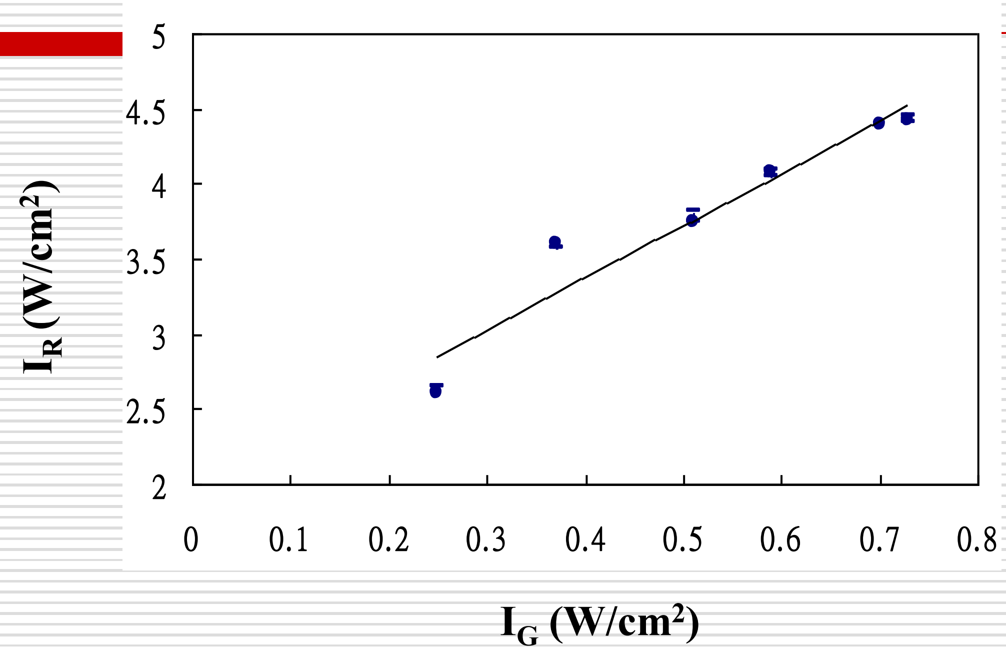
Positive

$$\vec{\Gamma}_{dye} = \eta\vec{\Gamma}_{opt} + \vec{\Gamma}'$$

Enhance!!

1. Original, only green light 2. Positive torque	1. Cis-isomer absorb red light 2. Positive torque	

I_R required to offset totally the torque resulted from I_G (give no diffraction ring)



- At low intensity of green light, the torque resulted from green light and red light are opposite.
- The value of positive torque is linearly to I_R

Conclusions

- CLC lasing is demonstrated.
  Optically tunable: ~110nm
- Optically tunable CLC grating is demonstrated. the tuning range ~16^{o} (it could be larger by usinging higher azo dye concentration).
- The photo-induced reorientation in ADDLC films is studied by observing the diffraction patterns resulting from self-phase modulation.

Co-workers

- CLC laser: Tsung-Hsien Lin, Hung-Chang Jau
- CLC tunable grating: Hung-Chang Jau, Tsung-Hsien Lin, Ri-Xin Fung, San-Yi Huang
- Self-phase modulation: H.-C. Lin, C.-W. Chu,

Thank you for your attention!!

Electrically-controllable laser based on cholesteric liquid crystal with negative dielectric anisotropy (Appl.Phys. Lett., **88**, 061122(2006))

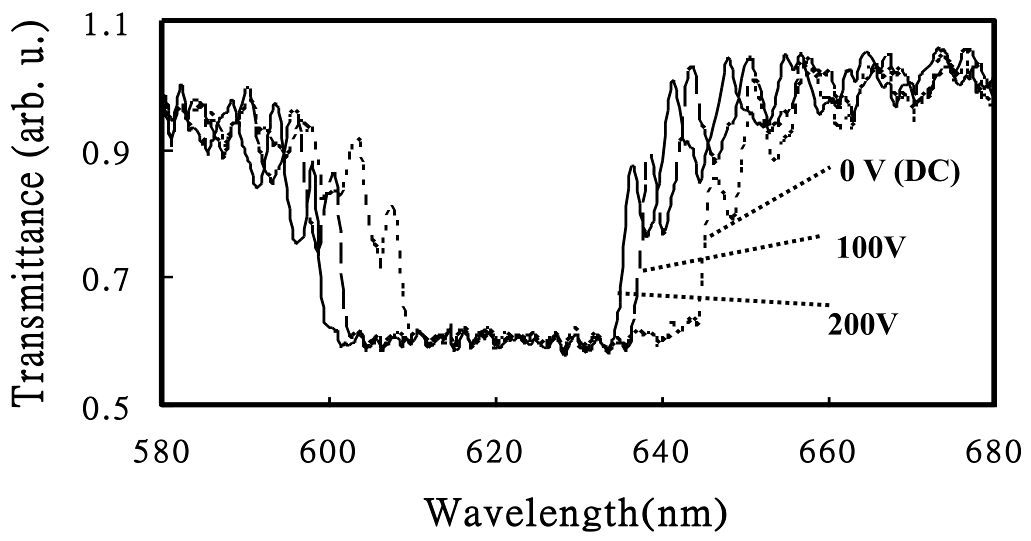
Sample Fabrication

- nematic liquid crystals* (95% MLC6608 and 5% ZLI2293, Merck): chiral material (S811, Merck) in an appropriate ratio (~67:33)
- Laser dye: DCM (Exciton)~0.5 wt%
- Cell gap: 15μm.

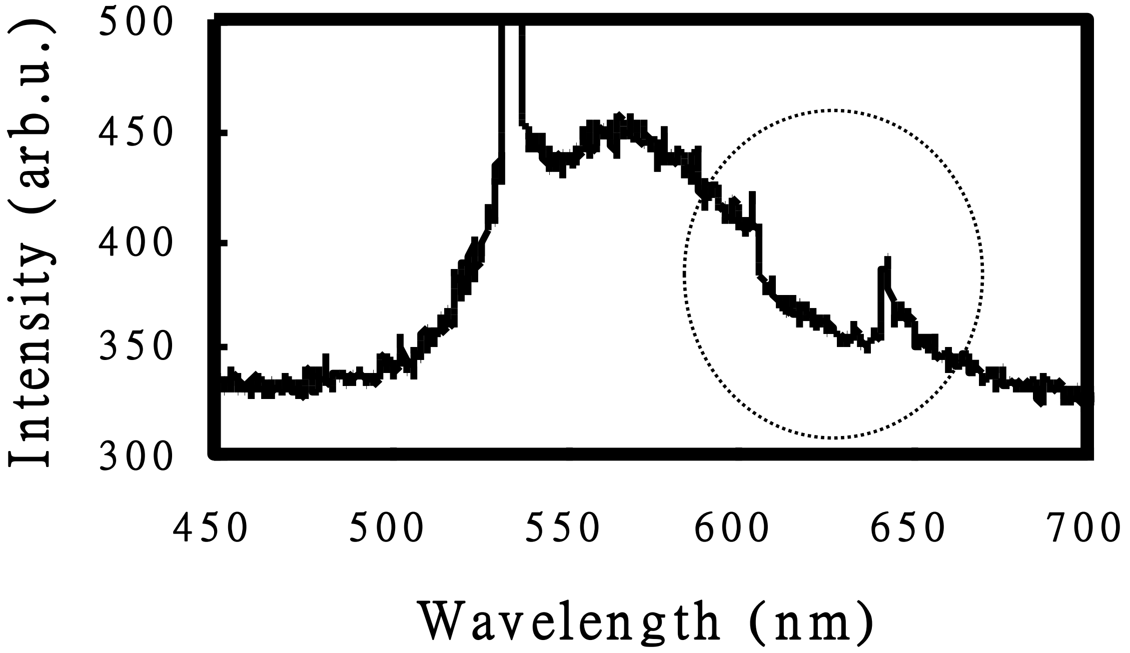
* Negative dielectric anisotropy

$$\Delta\varepsilon \equiv \varepsilon_{\parallel} - \varepsilon_{\perp} < 0$$

Electrically tunable

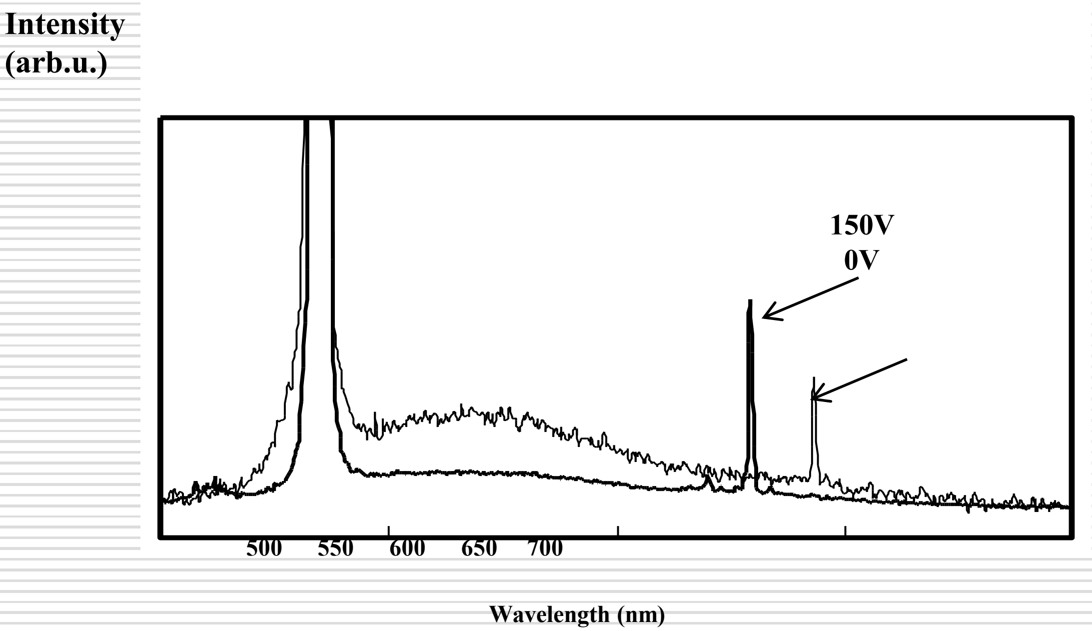


Emission spectrum below lasing threshold



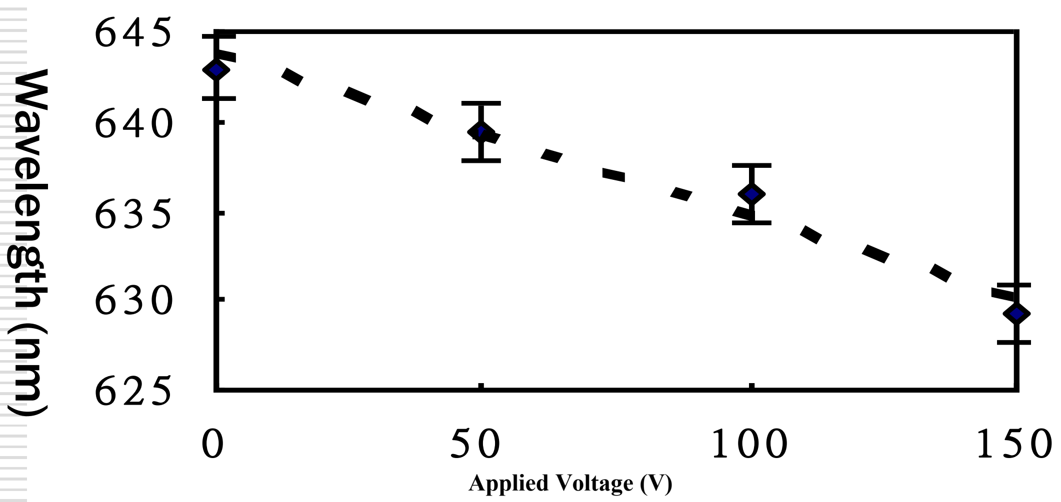
Emission spectrum of dye-doped CLC sample pumped by a single pulse with an intensity below the lasing threshold (~1 μJ).

Lasing



Lasing spectra of a CLC cell when 0 and 150V DC are applied.

Electrically (DC) tunnable



Mechanism

- The blue shift is caused by the electrohydrodynamic effect- Helfrich effect.

  $\Delta\varepsilon<0$, $\Delta\sigma>0$

W. Helfrich, J. Chem. Phys. **55**, 839 (1971).

Helfrich Deformation

When the voltage is above a threshold,

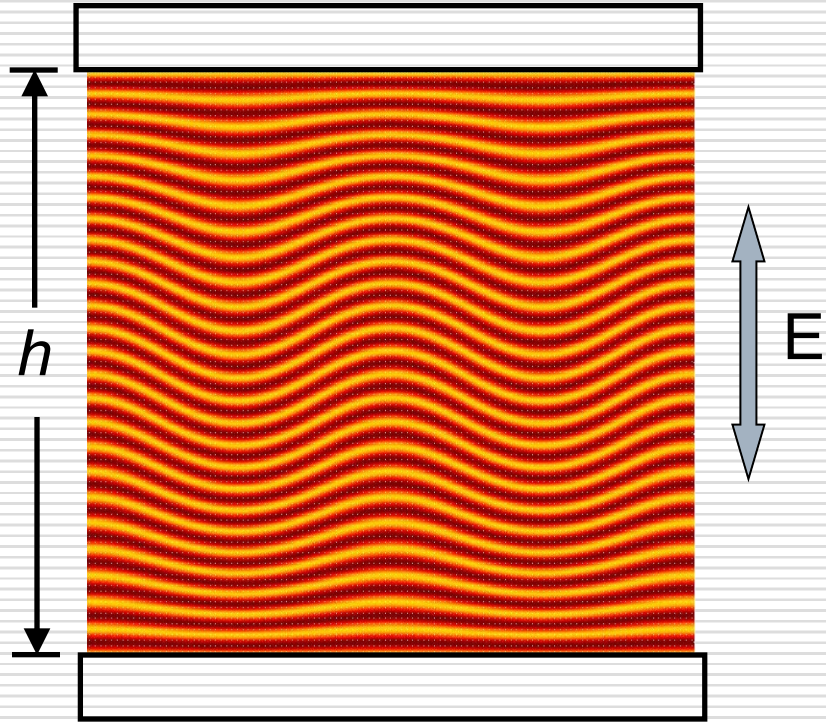
$$V_C = \frac{4\pi^2 (2K_{22}K_{33})^{1/2}}{\Delta\varepsilon\varepsilon_0}\frac{h}{P_0}$$

a 2-D periodical distortion appears.

Spatial period:

$$\lambda = \sqrt{(2K_{33}K_{22})^{1/2} P_0 h}$$

periodical distortion causes
pitch contraction



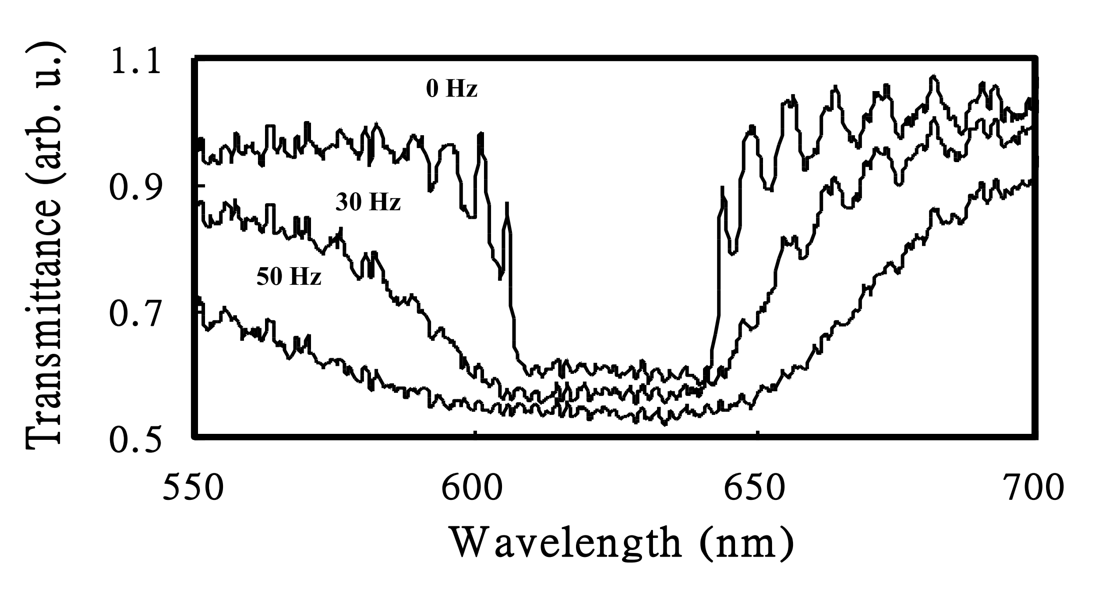
W. Helfrich, *J. Chem. Phys.* **55**, 839 (1971).

Helfrich effect

When a field is applied along the helical axis of a planar CLC cell with a negative dielectric anisotropy and a positive anisotropic electric conductivity, the induced distortion of the liquid crystals causes the segregation of space charges. The space charges interact with the electric field, causing the LCs to flow. The flow is accompanied by a shear stress and then the shear applies a torque on the LC molecules. The shear-induced torque tends to alter the direction of the preferred axis and so reacts to the orientation pattern to form the sinusoidal periodic distortion of a planar CLC cell.

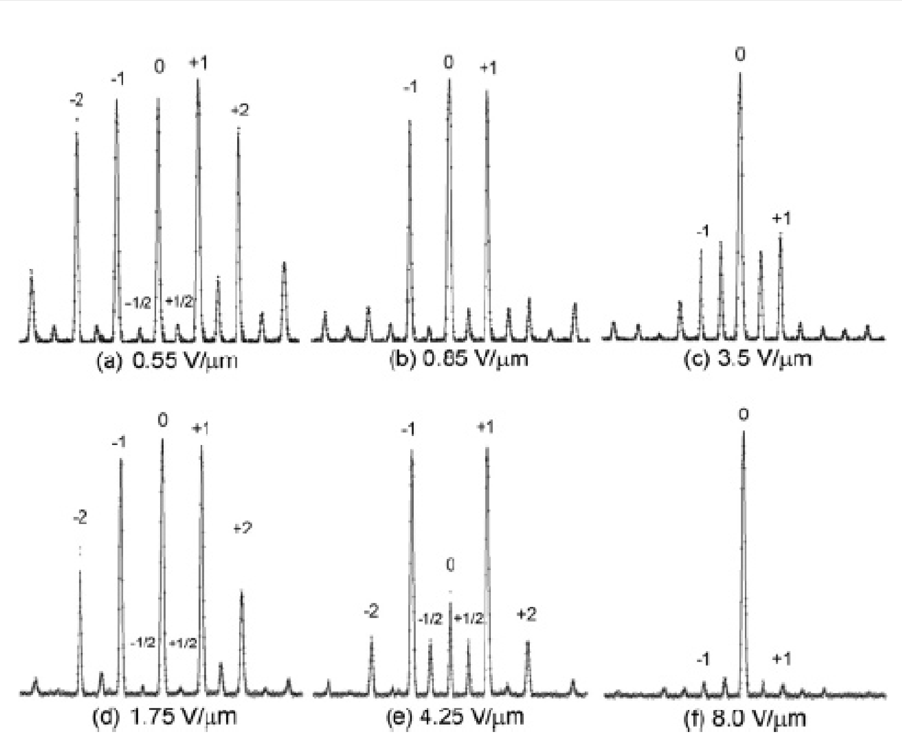
Electrical-frequency switchable

The decline in the transmission and the broadening of the reflection band are caused by dynamic scattering of the sample.

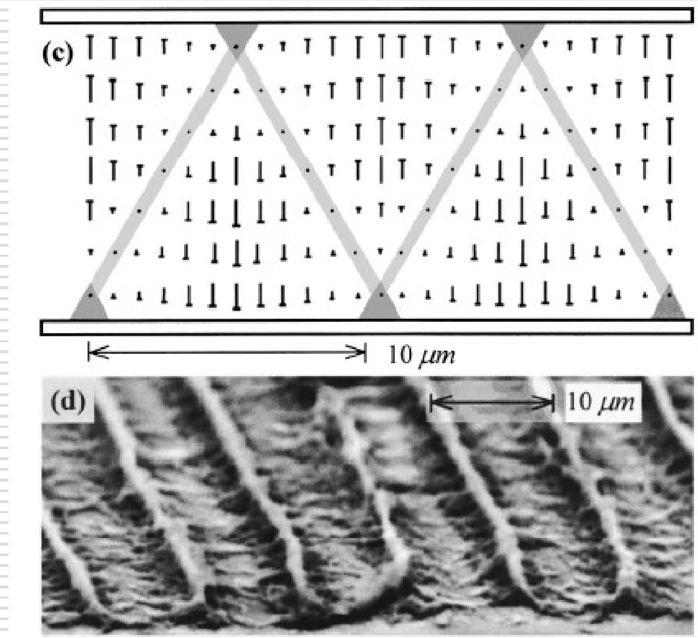


CLC lasing can be switched on (off) by varying the frequency of the applied 100 V between 0 and 50 Hz.

A model for the director structure suggested by the network morphology



Chem. Mater., Vol. 18, No. 18, 2006



Appl. Phys. Lett., Vol. 76, No. 24, 12 2000

Outline

1. Introduction
   - Photonic crystals
2. Experiments: results and discussion
   - Lasing in dye-doped Cholesteric LC

   2.1 Optically tunnable

   2.2 Electrically-controllable

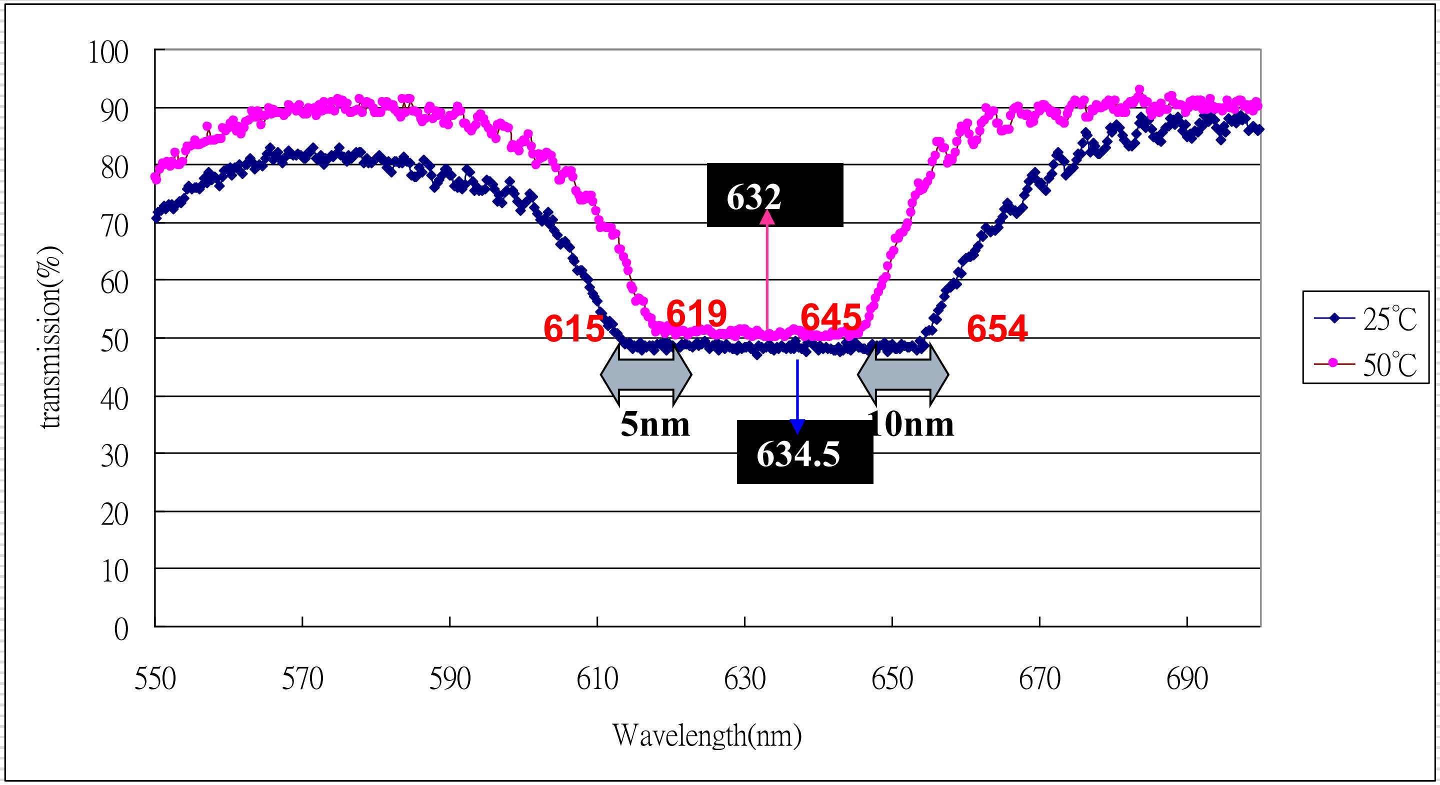
   2.3 Thermally tunable
3. Conclusions

Experiment : Sample

- Dye-doped L-CLC =
 ZLI 2293(76.3wt%)+S811(22.7wt%)+DCM(1wt%)
 λ=630nm

- Q-switch Nd-YAG pulse laser (Second Harmonic Generation λ=532nm τ~8ns)

Result: ***Reflection band changed***



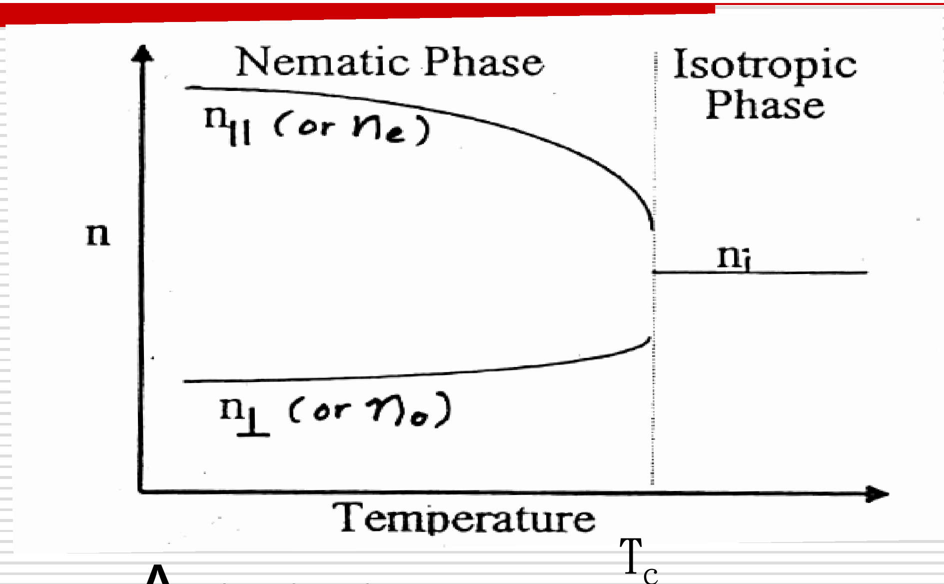
Reflection bands at 25, 50^{o}C

- Note:

  1). Central wavelengths of the reflection bands: remain almost unchanged, i.e. dP/dT~0 (due to boundary anchoring effect)

  2). Reflection bandwidth: 👎 ● (~Δn)↓ as Temp.↑

Refractive Index of a typical nematic LC



$\Delta n = n_e - n_o$

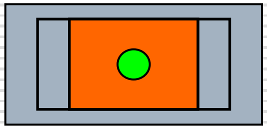
$\Delta n = \text{constant} \cdot \rho^{1/2} \cdot S$

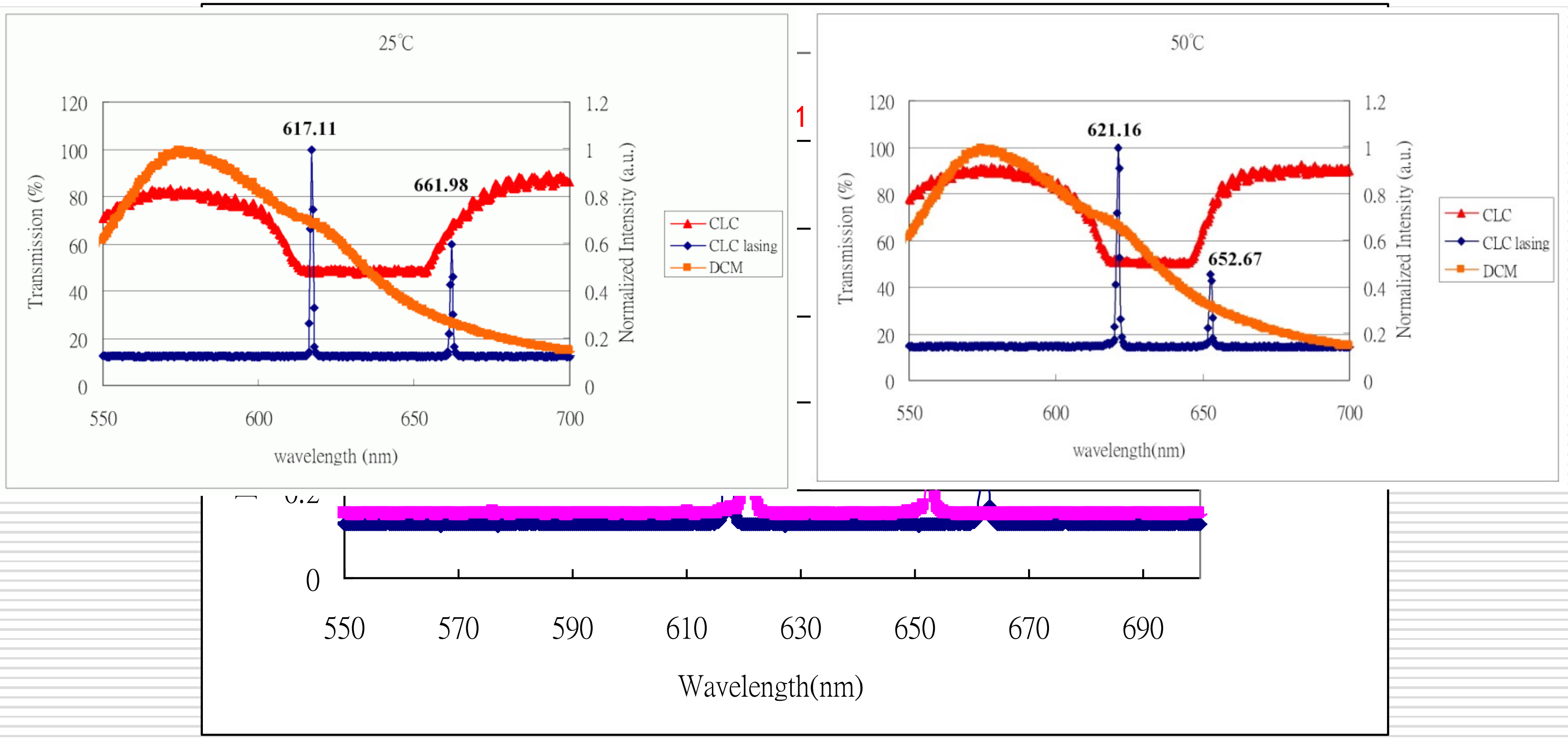
ρ=density

S= degree of order

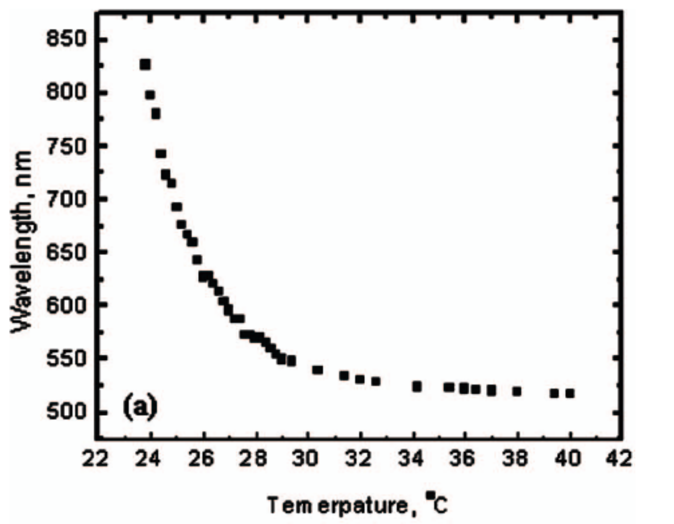
$$S = \left(1 - \frac{T}{T_c}\right)^{\beta} \quad ; \beta \sim 0.25$$

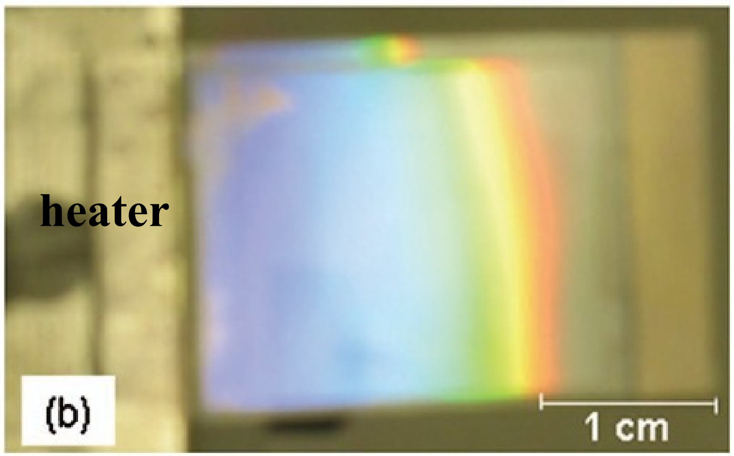
CLC lasing V.S. Temperature





Prof. S.-T. Wu's group (Central U. Florida)



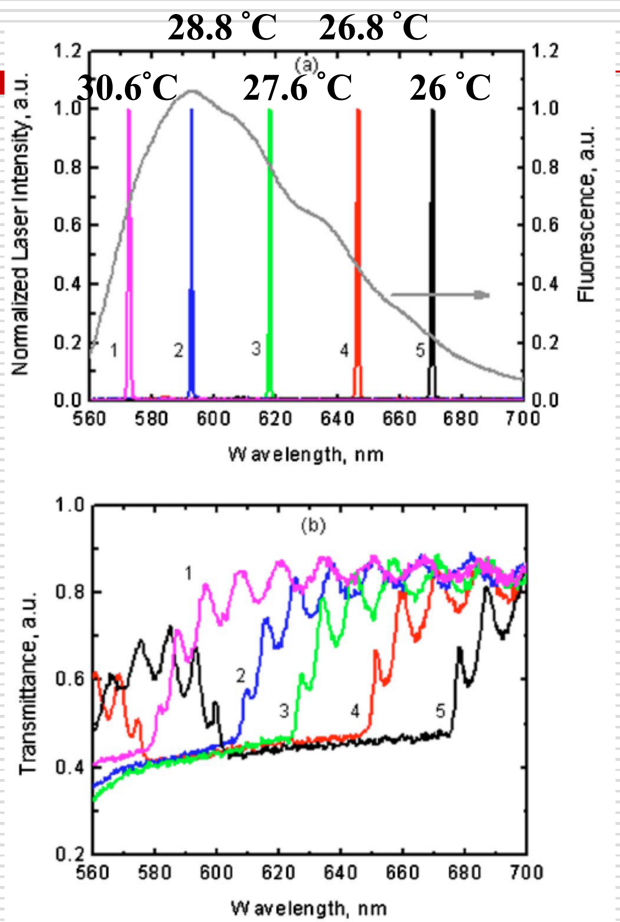


BL006(65wt%)+**S811(34wt%)**+DCM(1wt%)

over the maximum solubility(25%) at room temperature

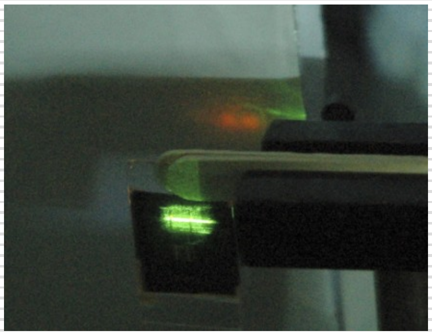
Yuhua Huang, Ying Zhou, and Shin-Tson Wu , " Spatially tunable laser emission in dye-doped photonic liquid crystals ", Appl. Phys. Lett. **88**, 011107 (2006)

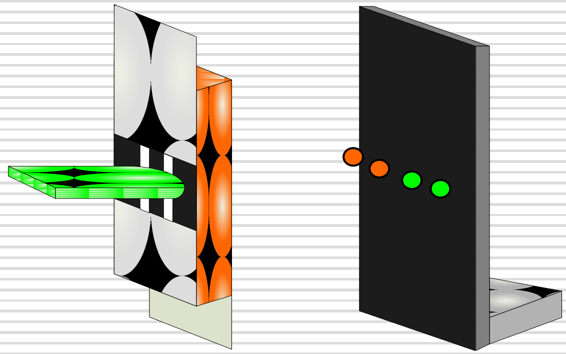
Prof. S.-T. Wu group

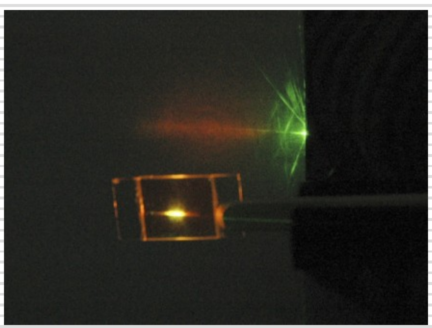


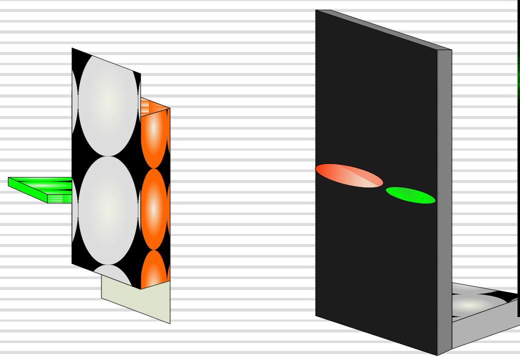
Yuhua Huang, Ying Zhou, and Shin-Tson Wu , “ Spatially tunable laser emission in dye-doped photonic liquid crystals “,APPLIED PHYSICS LETTERS **88**, 011107 (2006)

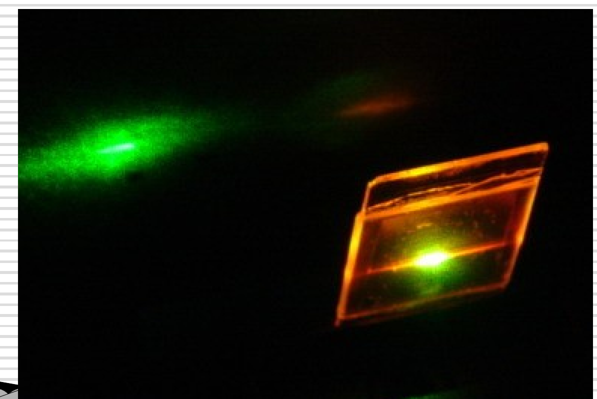
Changing beam-shape of CLC lasing (My group)



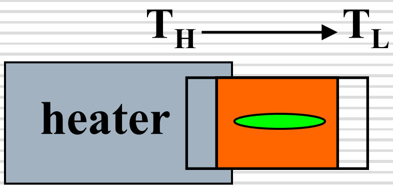


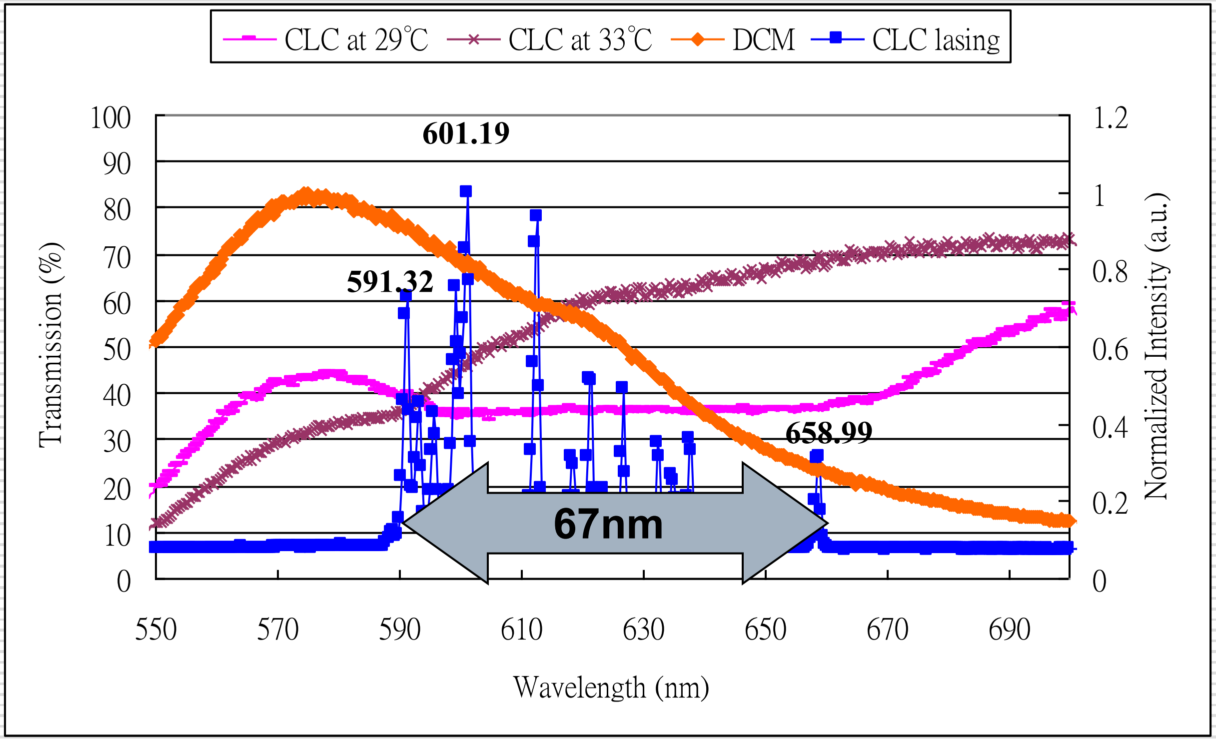






Multi-spot CLC lasing





Lasing peaks span over 65nm

Conclusions

- Both of the optically, electrically and thermally tunable CLC lasings are demonstrated.

The tunable range is dependent on the LC employed.

In the present case:

- Optically tunable: ~110nm
- Electrically tunable: ~20 nm
- Thermally tunable: ~10 nm
- Multi-spot lasing

Thank you

for your attention!

Introduction: Photonic crystals

- Photonic crystals (PCs) : periodic structure having lattice constants comprable with the wavelength of visible and infrared photons.
- A PC exhibits a “photonic bandgap” analogous to the electronic bandgap in semiconductors.

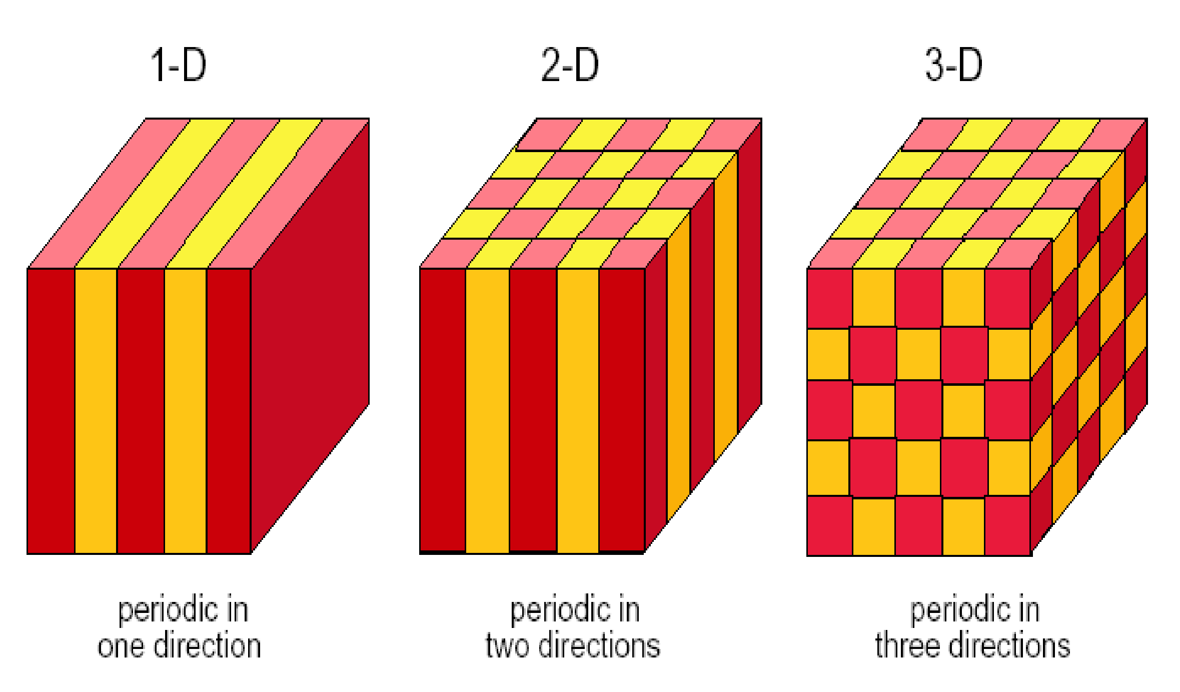
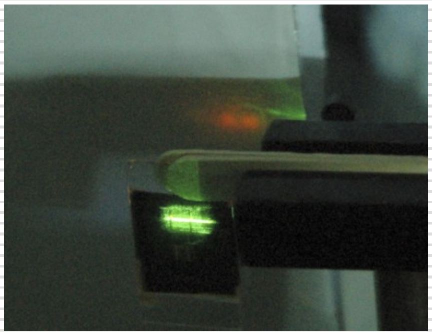
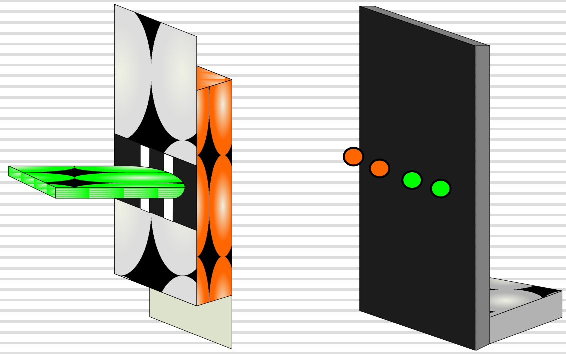
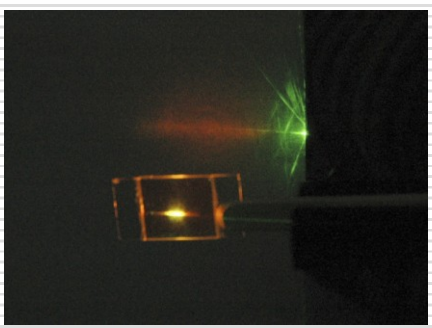


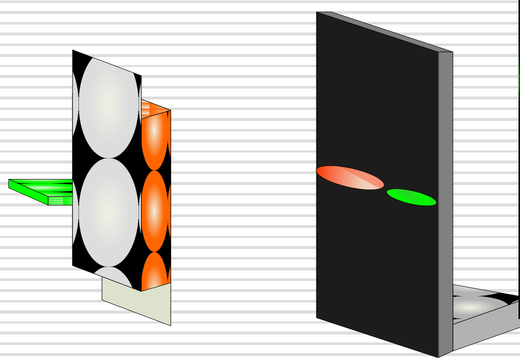
Illustration of 1-D, 2-D and 3-D Photonic crystals

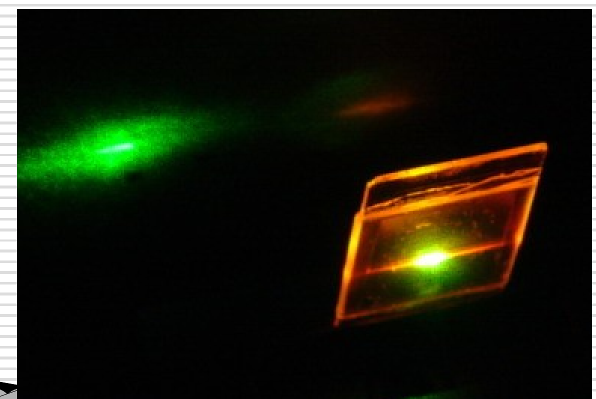
Changing beam-shape of CLC lasing



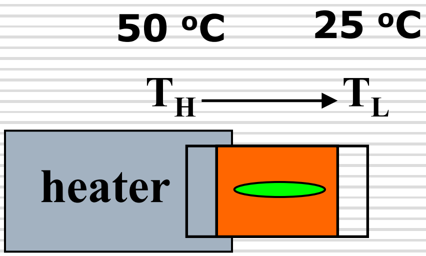


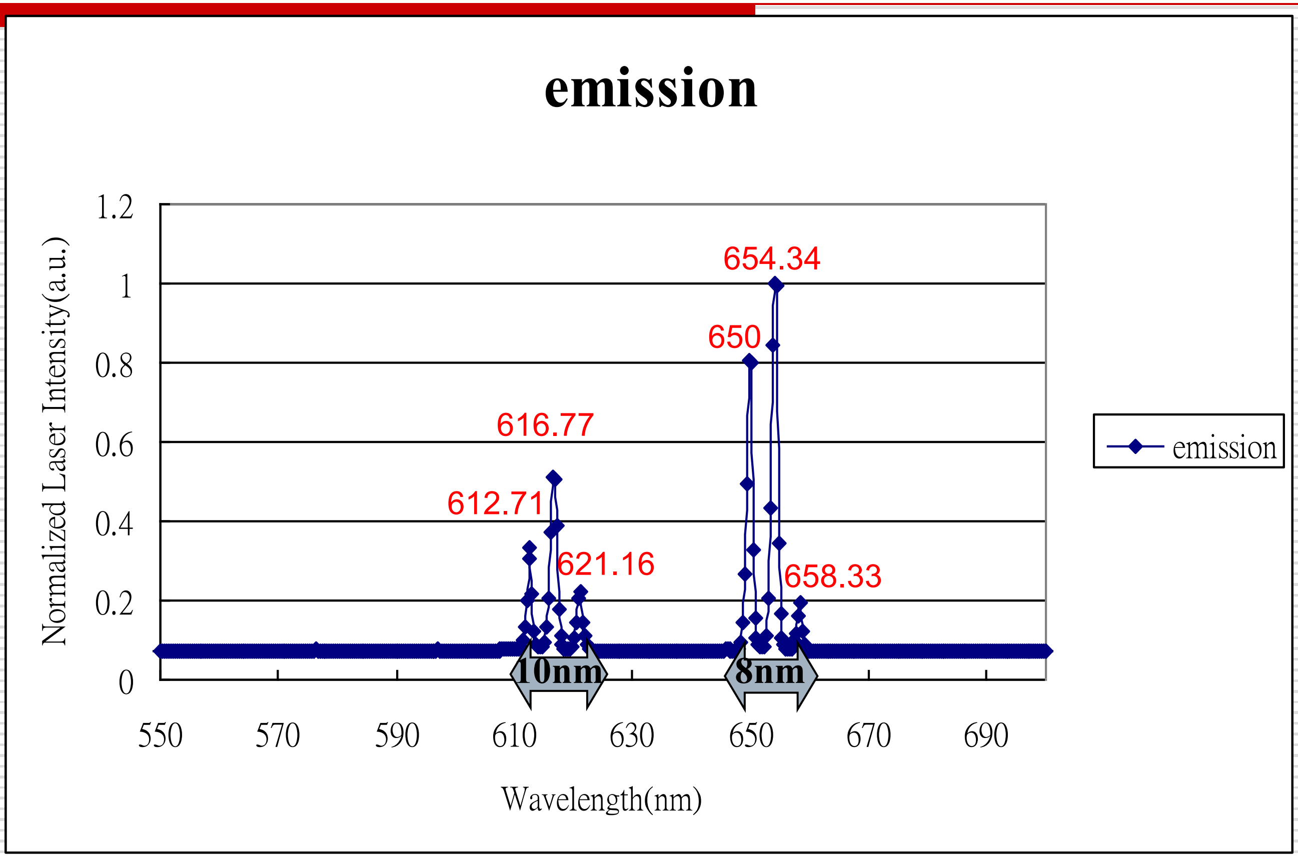




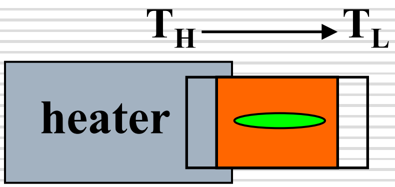


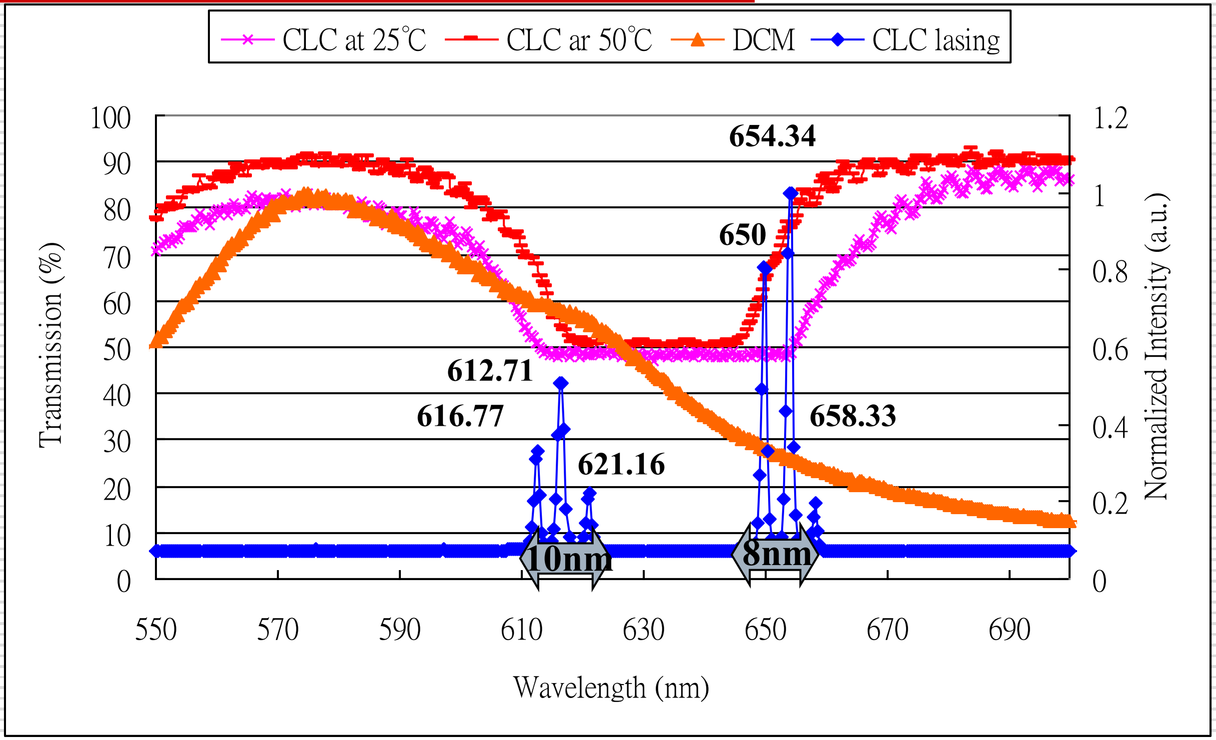
Pumped with an elliptical-shaped beam: Multi-spot CLC lasing





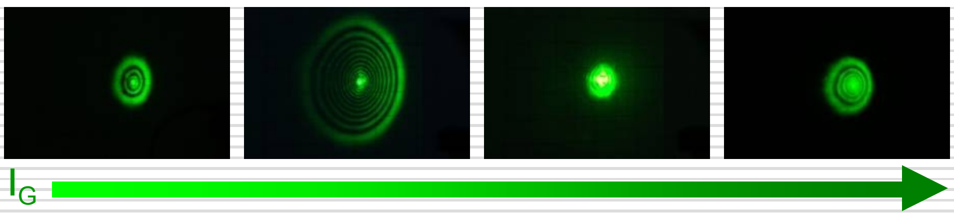
Multi-spot CLC lasing





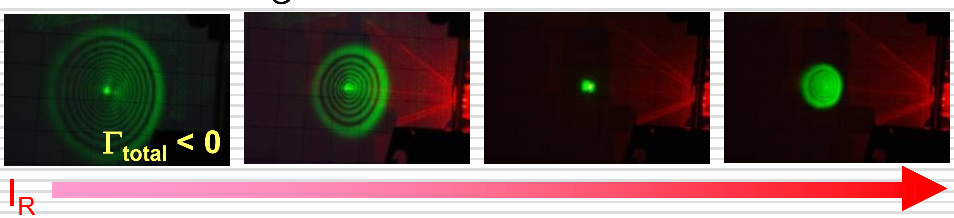
Conclusion

- The photo-induced reorientation in ADDLC films was studied by observing the diffraction patterns resulting from self-phase modulation.



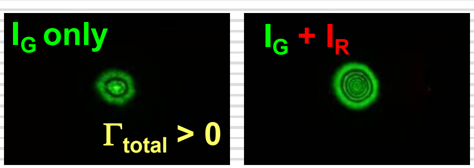
$$\eta = \eta_t(1 - X) + \eta_c X$$

- With a fixed I_G = 0.7 W/cm^2



Cis-isomer absorb red light

$\tau_{c \to t}\downarrow$, $\eta_c\uparrow$, $\vec{\Gamma}'$



- The thermal effect can be ignorable.