



**The Abdus Salam  
International Centre for Theoretical Physics**



**2037-10**

## **Introduction to Optofluidics**

*1 - 5 June 2009*

**Two case studies on liquid crystal reorientation based applications: holographic data storage and nanotube reorientation**

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Türkiye





MAGNETIC MATERIALS  
OPTICS AND LASERS  
LIQUID CRYSTALS  
SENSORS  
QUANTUM ELECTRONICS  
NANOTECHNOLOGY  
SPINTRONICS  
LOW TEMPERATURE PHYSICS

# SCOPE OF THE TALK

LIQUID CRYSTAL SYSTEMS  
FOR DYNAMIC HOLOGRAPHY

LASER INDUCED DIELECTRIC  
SPECTROSCOPY OF LC. SYSTEMS

LIQUID CRYSTAL - NANOTUBE  
DISPERSIONS

ORGANIC ELECTRONICS BASED  
INSPIRATIONS

# Liquid crystals

Liquid crystal displays (LCD) are found everywhere:

- wristwatches, pocket calculators
- mobile phones
- digital cameras
- desktop and laptop systems
- flat panel television
- .....



These range from simple black&white 7-segment displays to highly sophisticated, full colour, high resolution screens and micro-displays.

Future applications are likely to include:

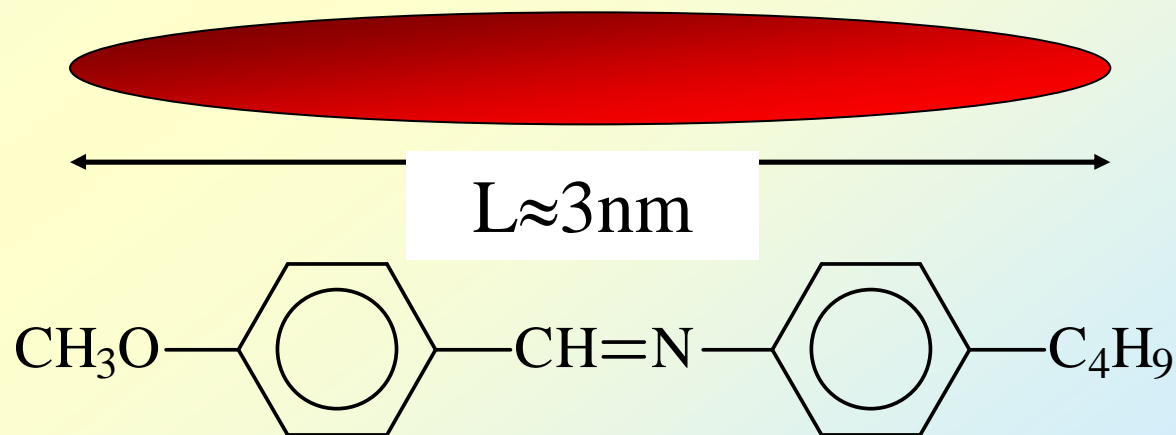
- adaptive optical elements
- 3D holographic displays
- devices in telecommunication
- "electronic paper"
- varieties of sensors
- biological recognition systems

**But, what really are liquid crystals ?**

## Liquid crystals are:

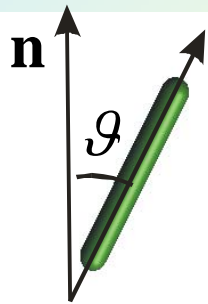
- partially ordered fluids
- thermodynamically located between the liquid and the solid state
- anisotropic liquids, with anisotropic properties
- self-organised systems

Their occurrence is observed for shape-anisotropic molecules:



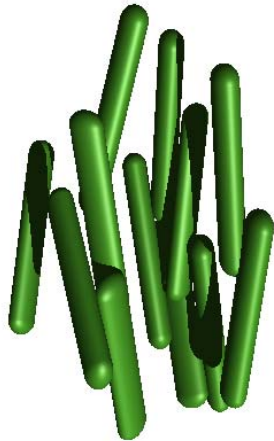
Many different types of liquid crystal phases are known. Here we will only introduce the most basic ones.

### Nematic:



- only orientational order of the long molecular axis

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$$

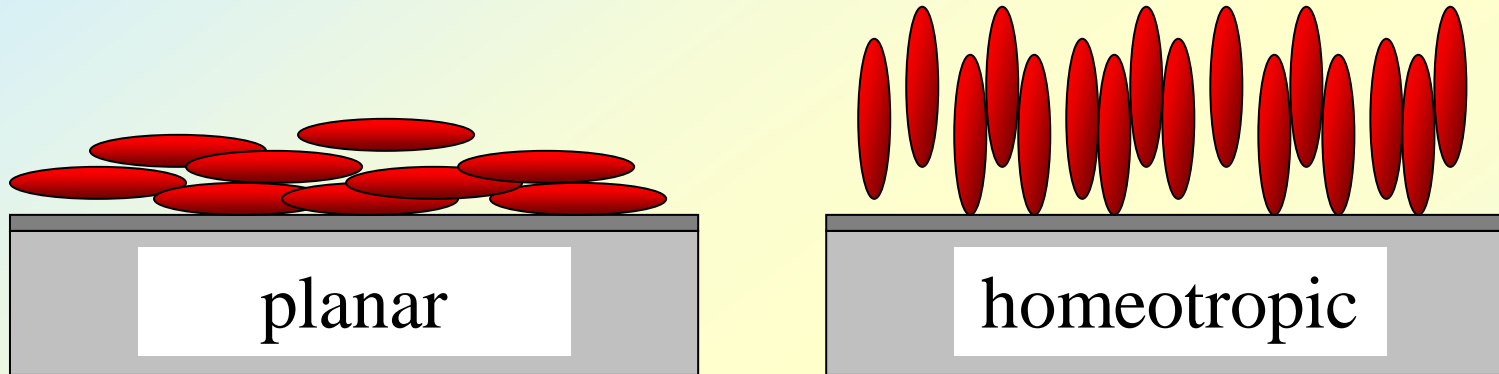


- $S = 0$  no orientational order (isotropic)
- $S = 1$  perfect order

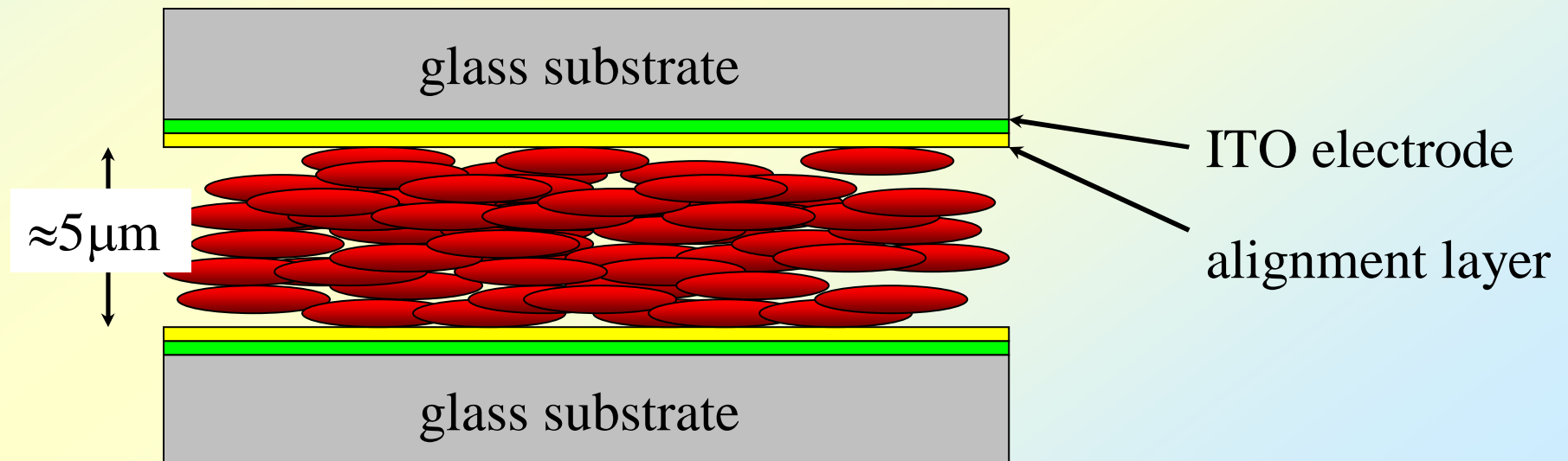
Generally it is  $S=0.5-0.7$ , depending on temperature

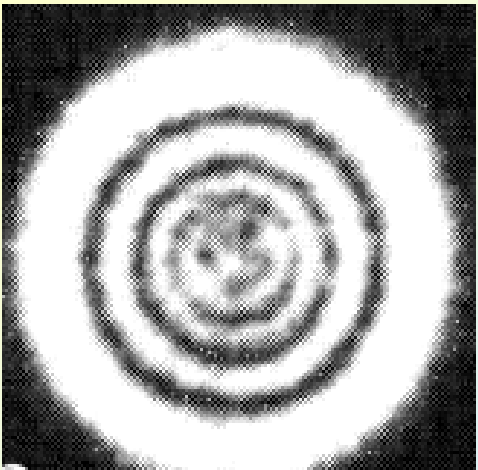
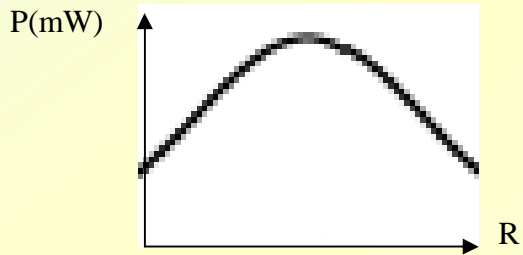
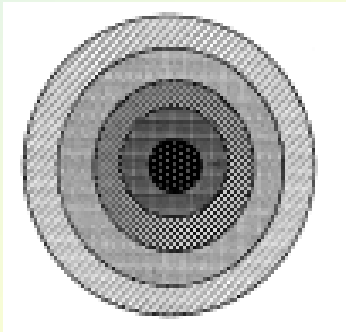
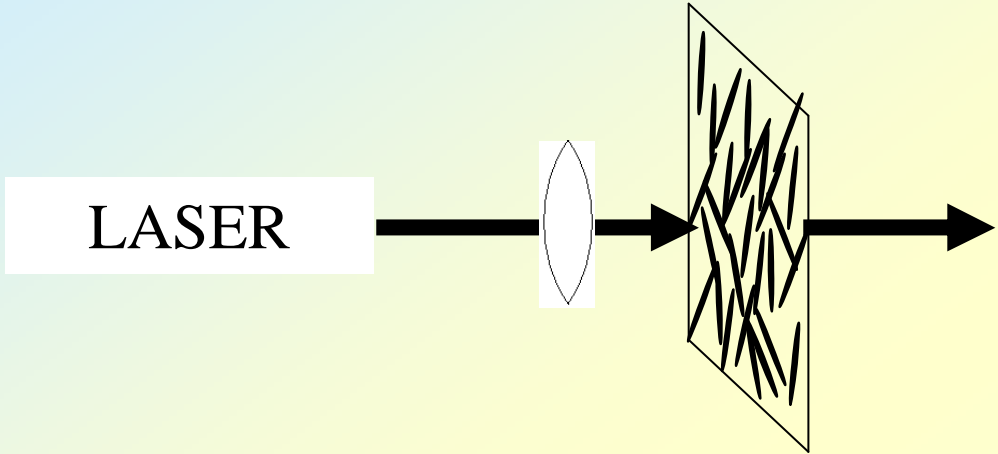


Nematic liquid crystals can easily be aligned uniformly through interactions with treated surfaces



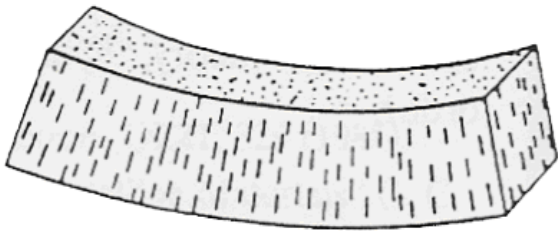
Standard liquid crystal sandwich cell:





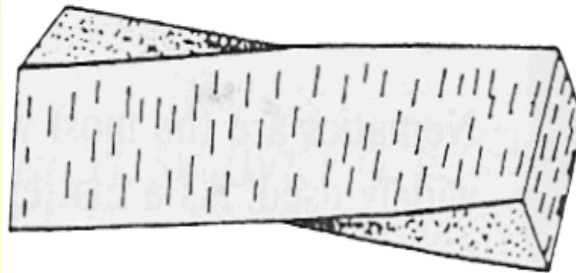
**'Self focusing'**

# Light Scattering



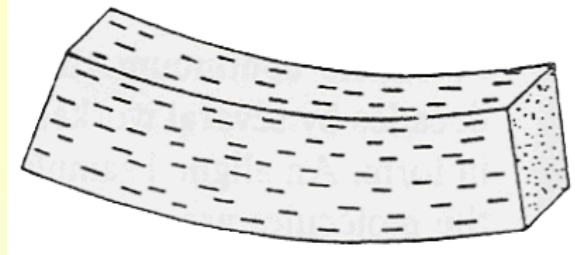
Egilme

$$F_1 = \frac{1}{2} K_1 (\nabla \cdot \hat{n})^2$$



Burulma

$$F_2 = \frac{1}{2} K_2 (\hat{n} \cdot \nabla \times \hat{n})^2$$



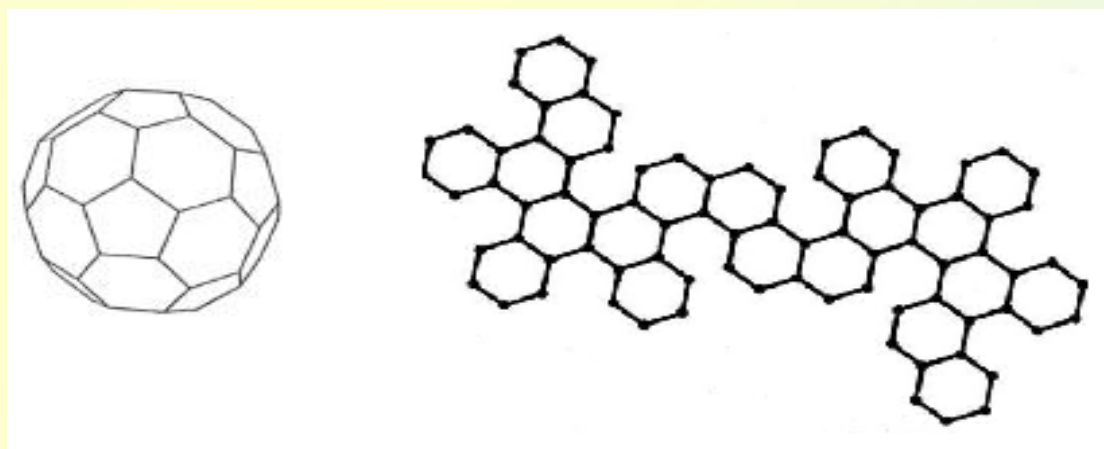
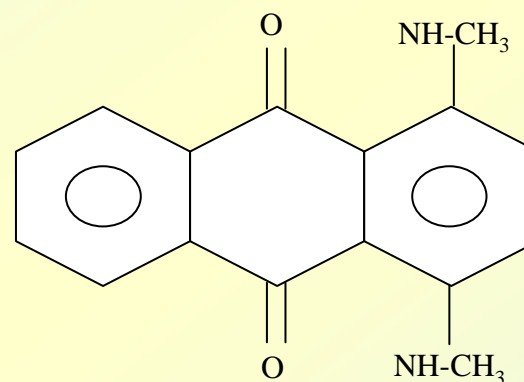
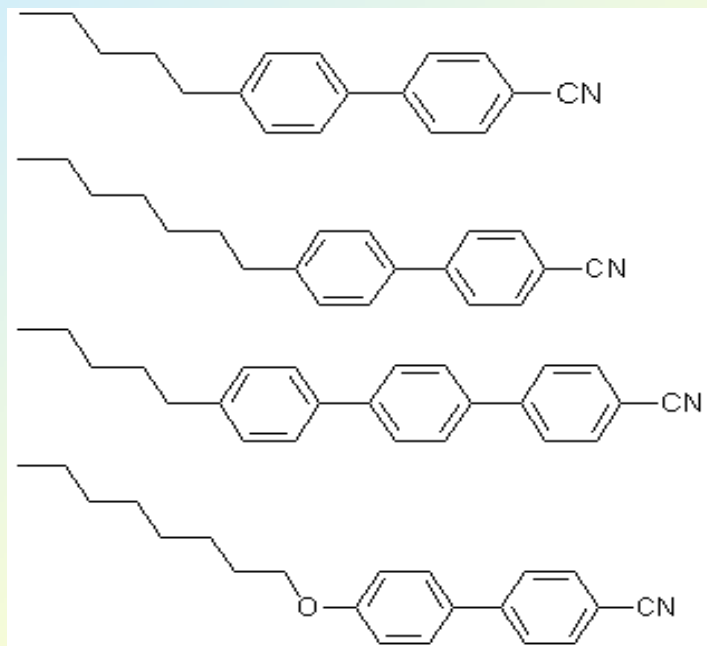
Bükülme

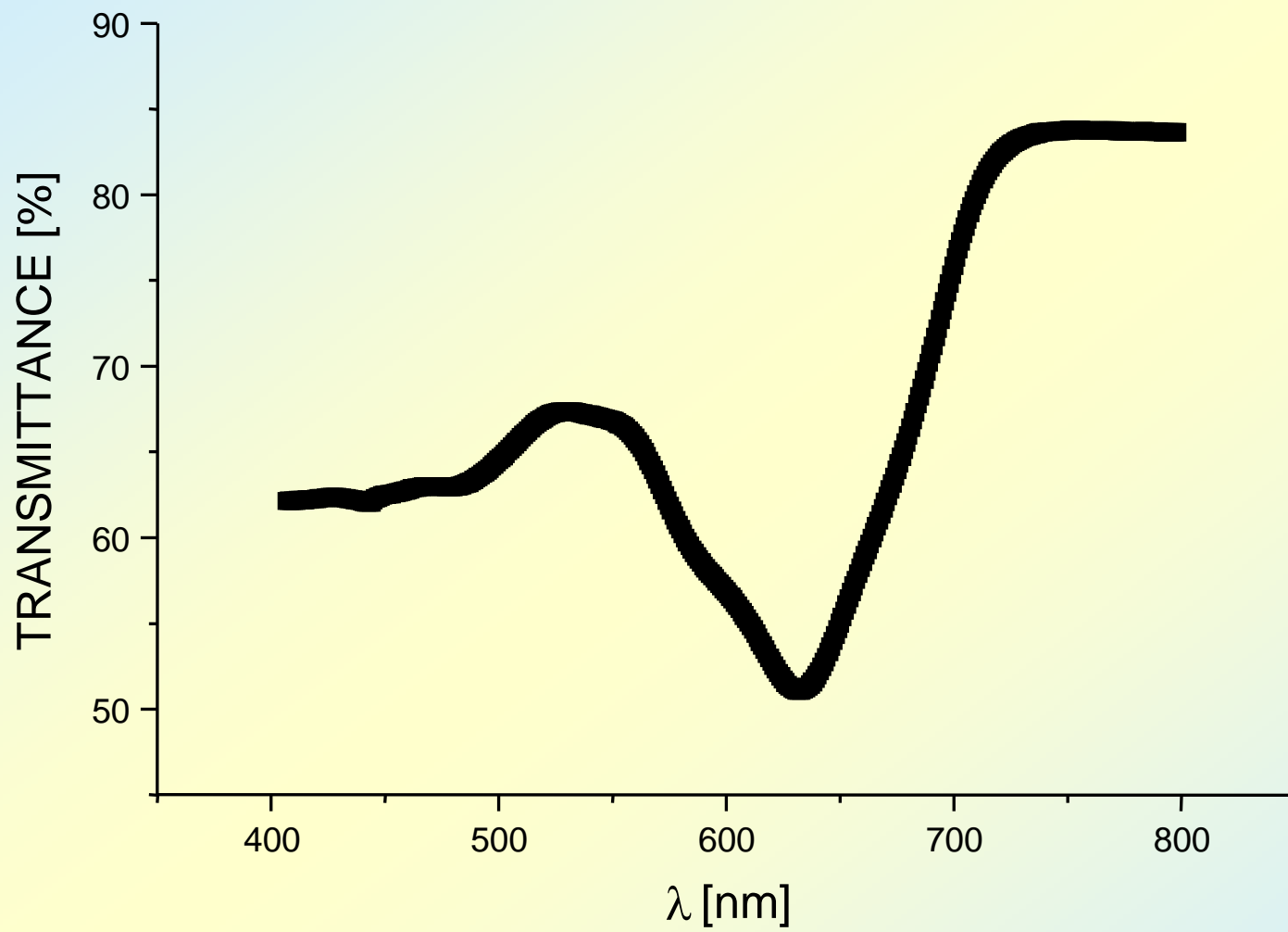
$$F_3 = \frac{1}{2} K_3 (\hat{n} \times (\nabla \times \hat{n}))^2$$

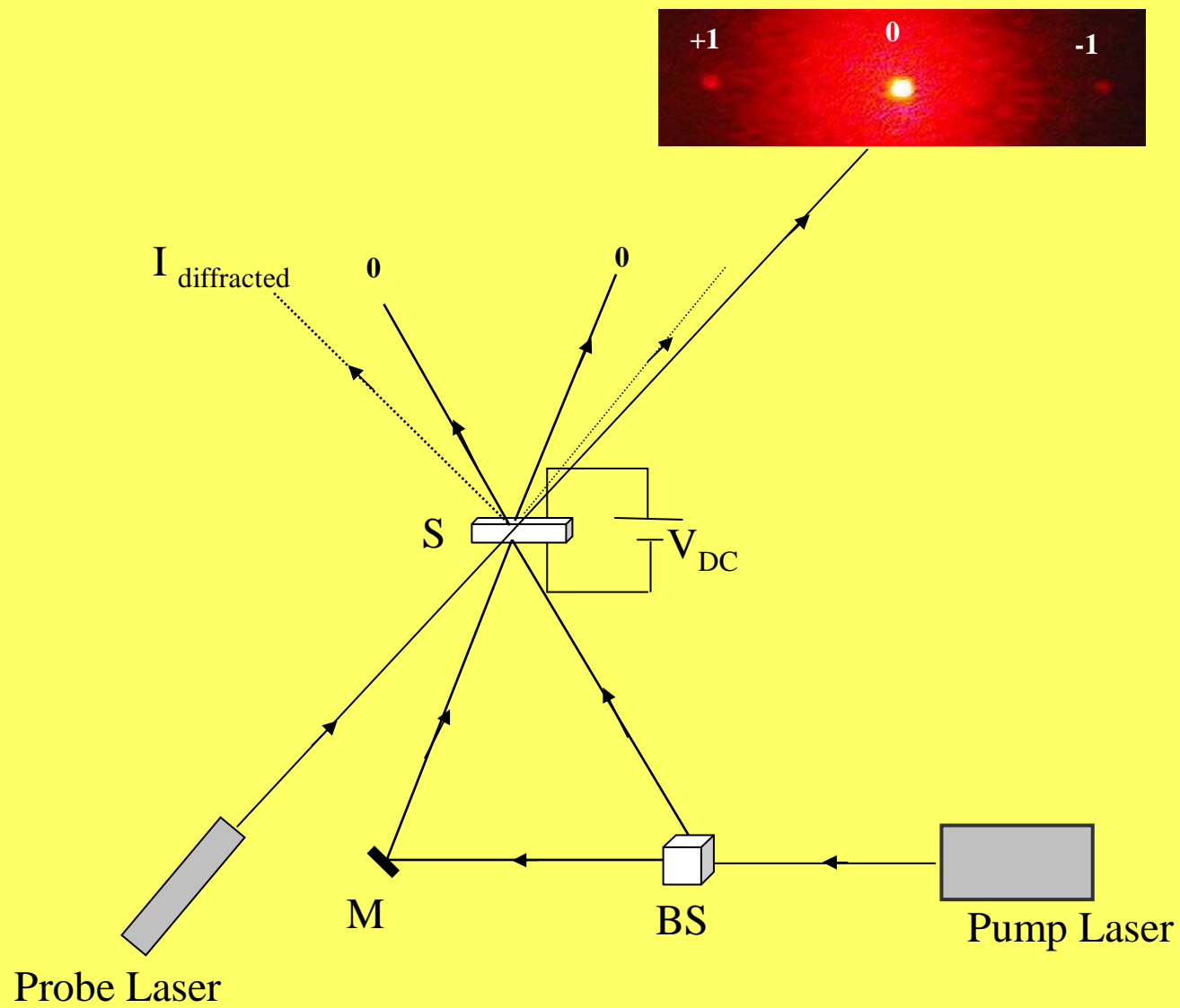
Free Energy

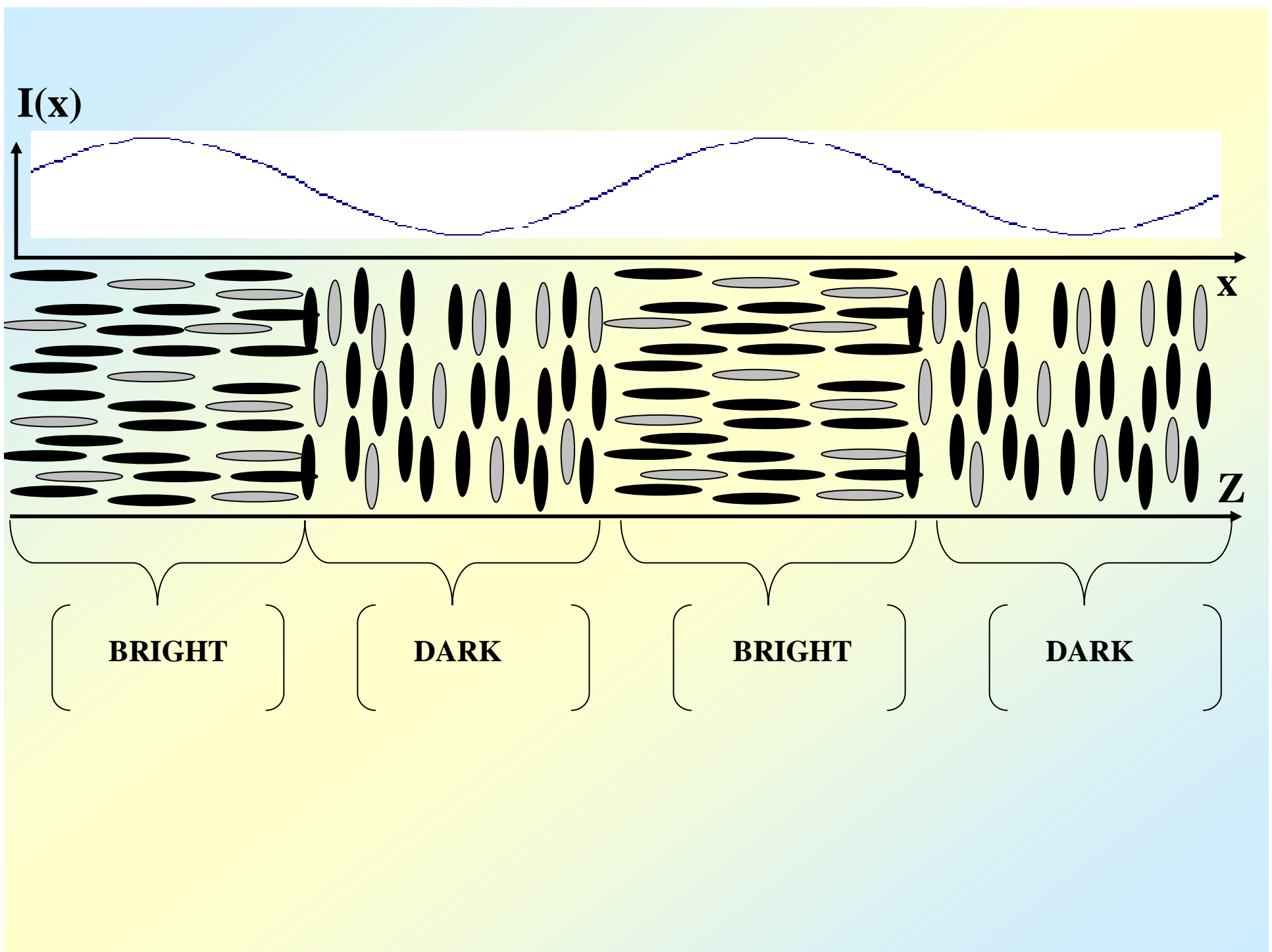
$$F_T = \frac{1}{2} K_1 (\nabla \cdot \hat{n})^2 + \frac{1}{2} K_2 (\hat{n} \cdot \nabla \times \hat{n})^2 + \frac{1}{2} K_3 (\hat{n} \times \nabla \times \hat{n})^2$$

I	II	III	IV
Pure E7	1 % DB14 in E7	1 % C60 in E7	0.5 % DB14 + 0.5 % C60 in E7









$I(x)$

$x$

$z$

BRIGHT

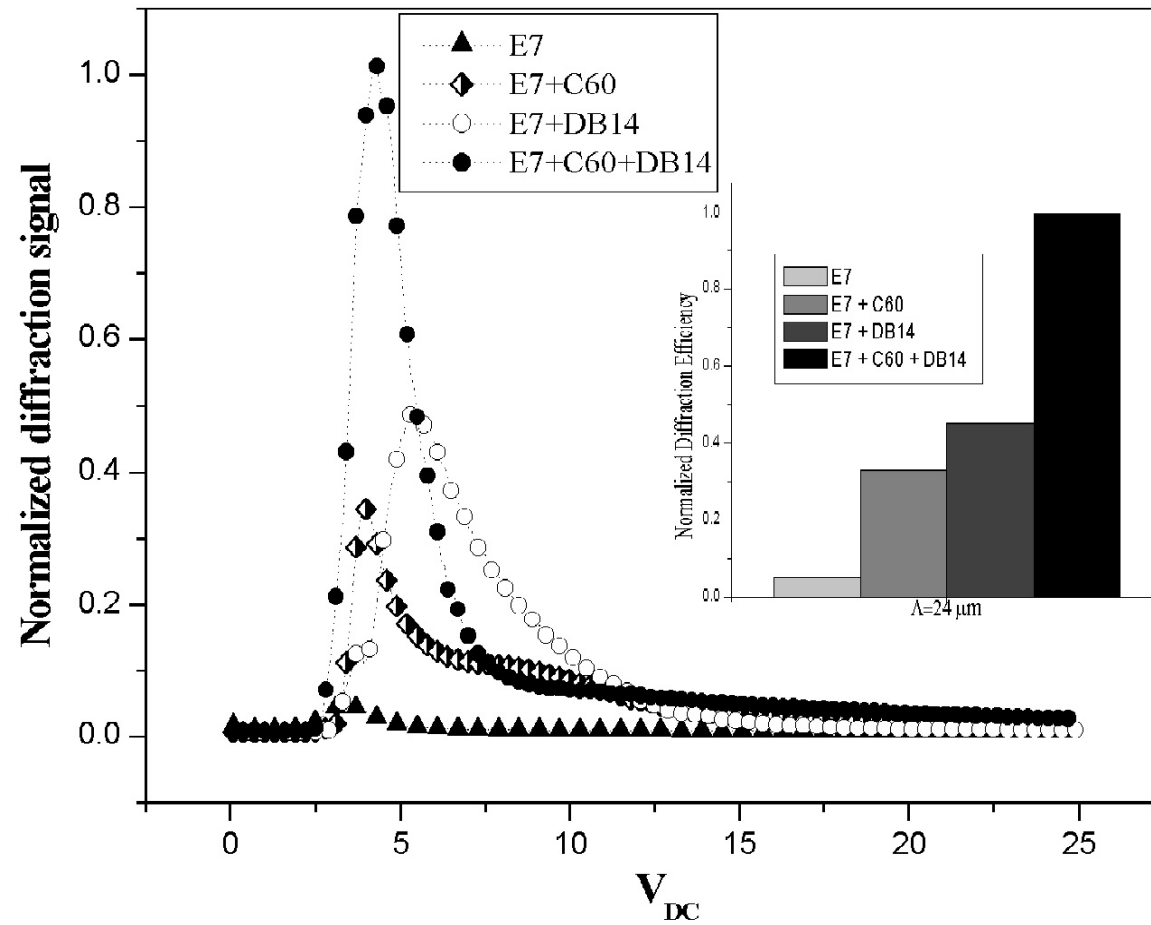
DARK

BRIGHT

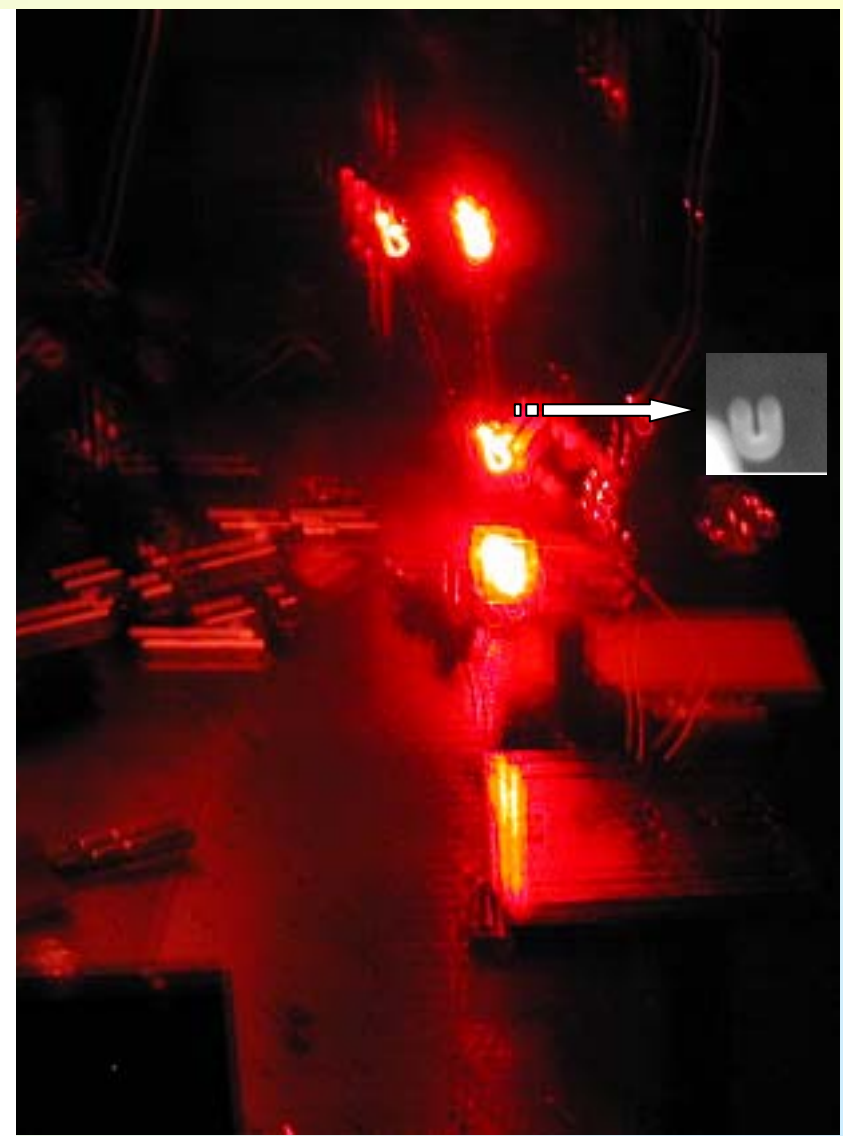
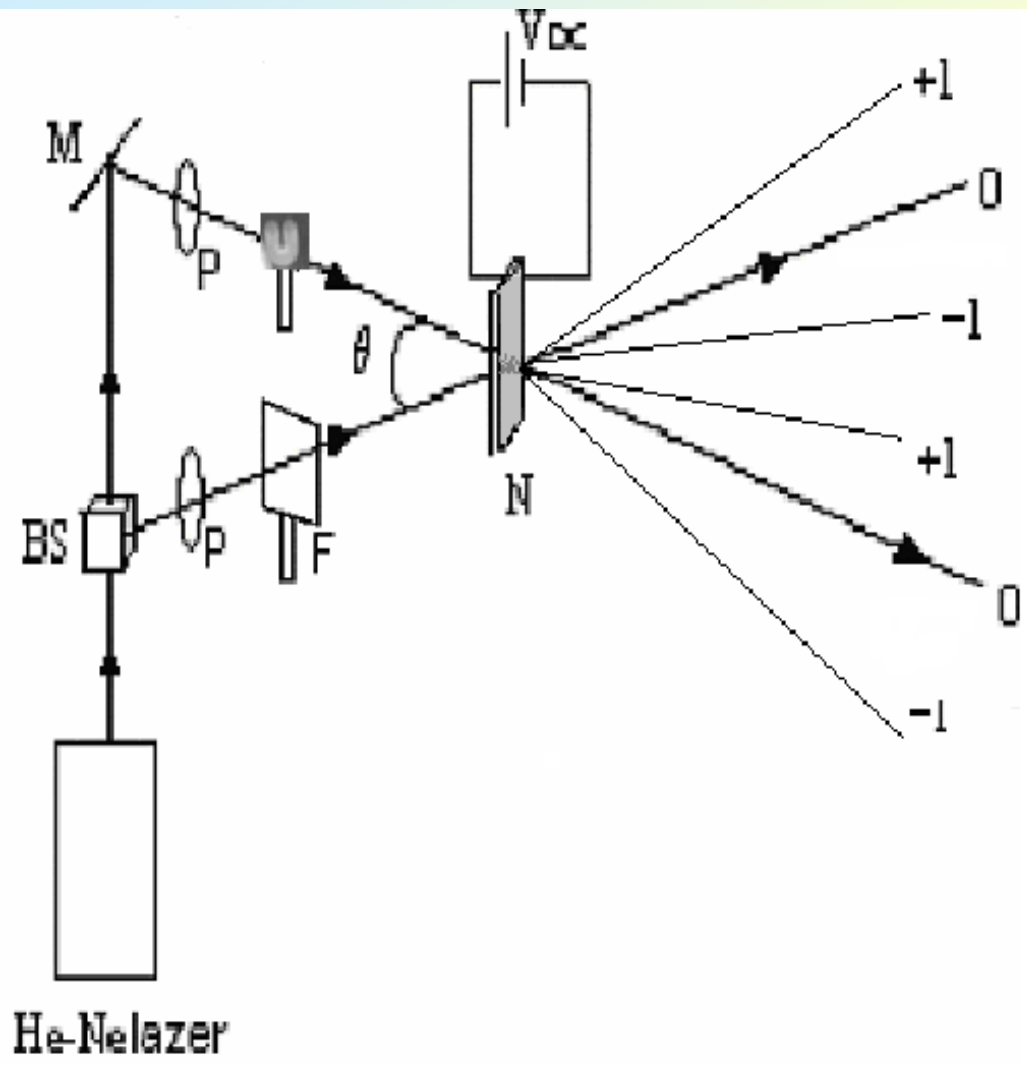
DARK

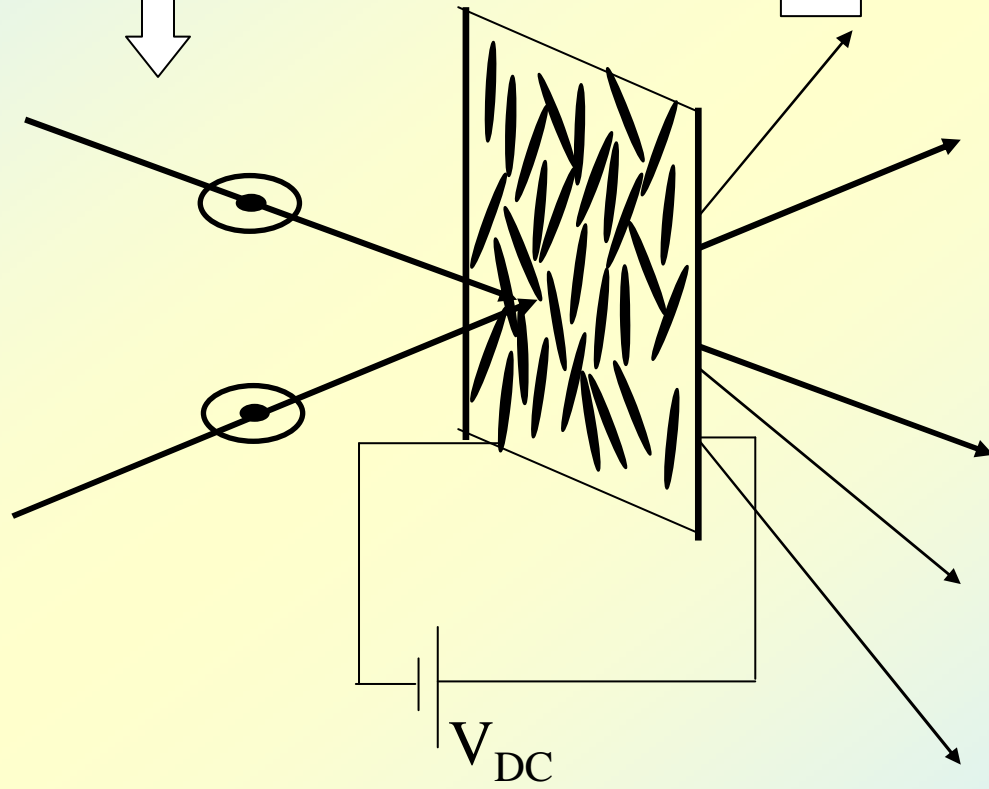
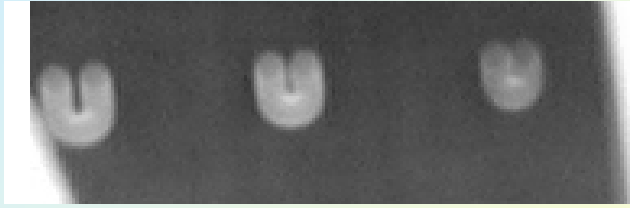






S. Eren San et.al. Synthetic Metals 142 (2004) 283-286





**Laser induced dielectric  
spectroscopy of a hybrid liquid  
crystal composite made up of  
methyl red and fullerene C<sub>60</sub>**

# Motivation

- Light-molecule & voltage-molecule interaction mechanisms (A tool for understanding the molecule scale events in such systems)
- Optimization basis for new designs  
(Opto-electronic applications: displays, optical switches, holographic mediums, phase retarders, filters etc.)

# Outline

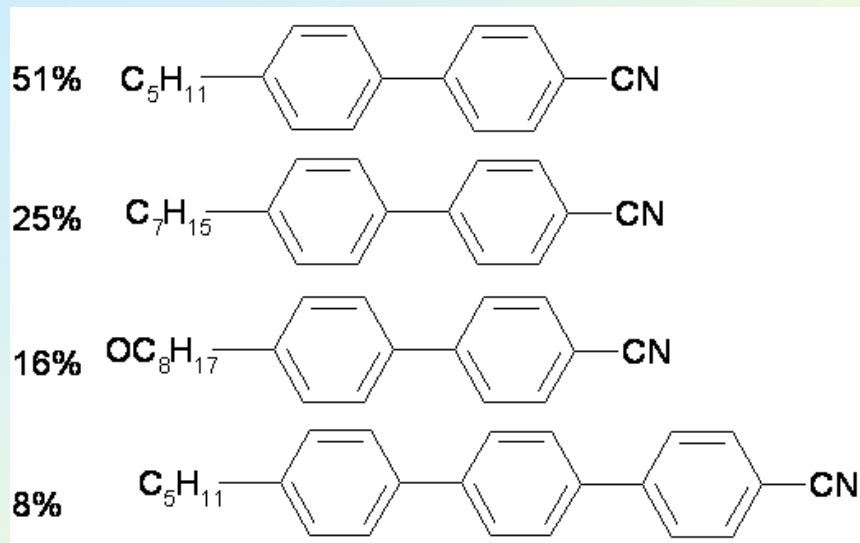
- Liquid Crystals ←
  - Doping
  - Dyes (Methyl Red)
  - Fullerene
  - Application
- Material
  - Experimental
  - Results

Dielectric  
Spectroscopy

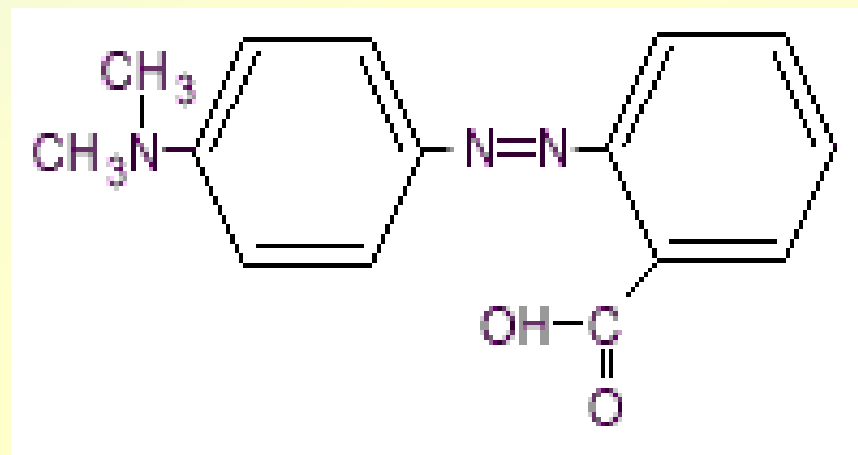


**HP4194A IMPEDANCE  
GAIN PHASE ANALYZER**

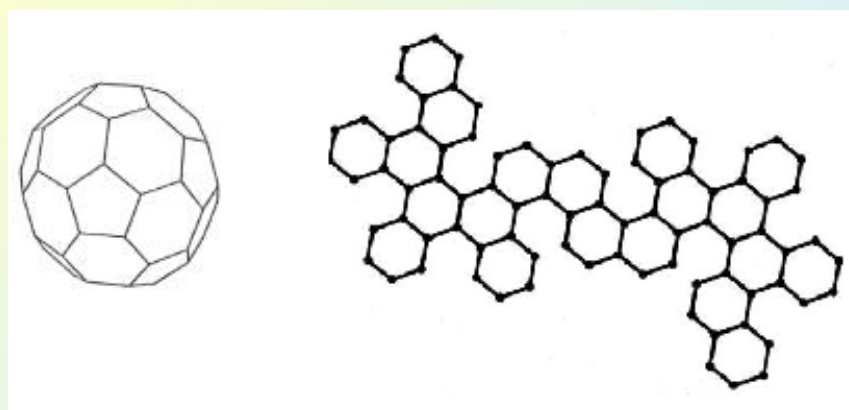
# E7



# MR



# C60



I (MR)	II (MR+C60)
1 % MR in E7	0.5 % MR + 0.5 % C60 in E7

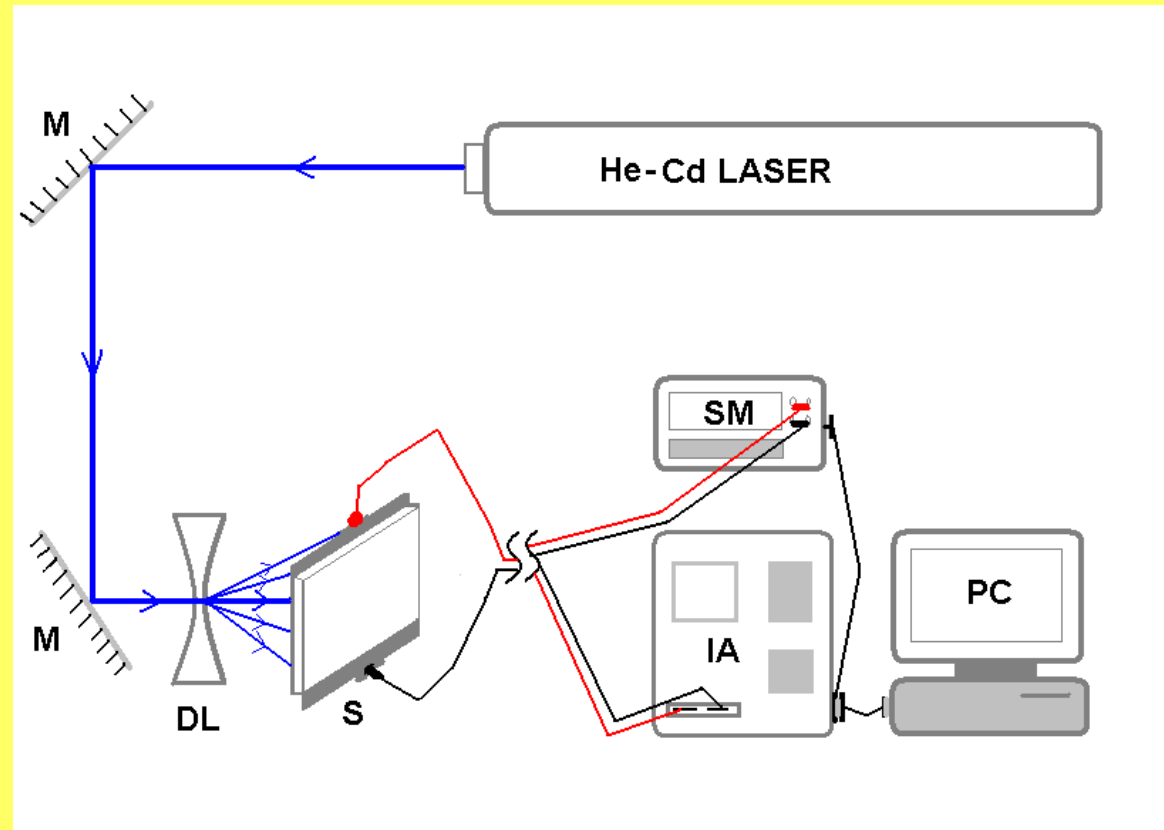
# Diffraction efficiency





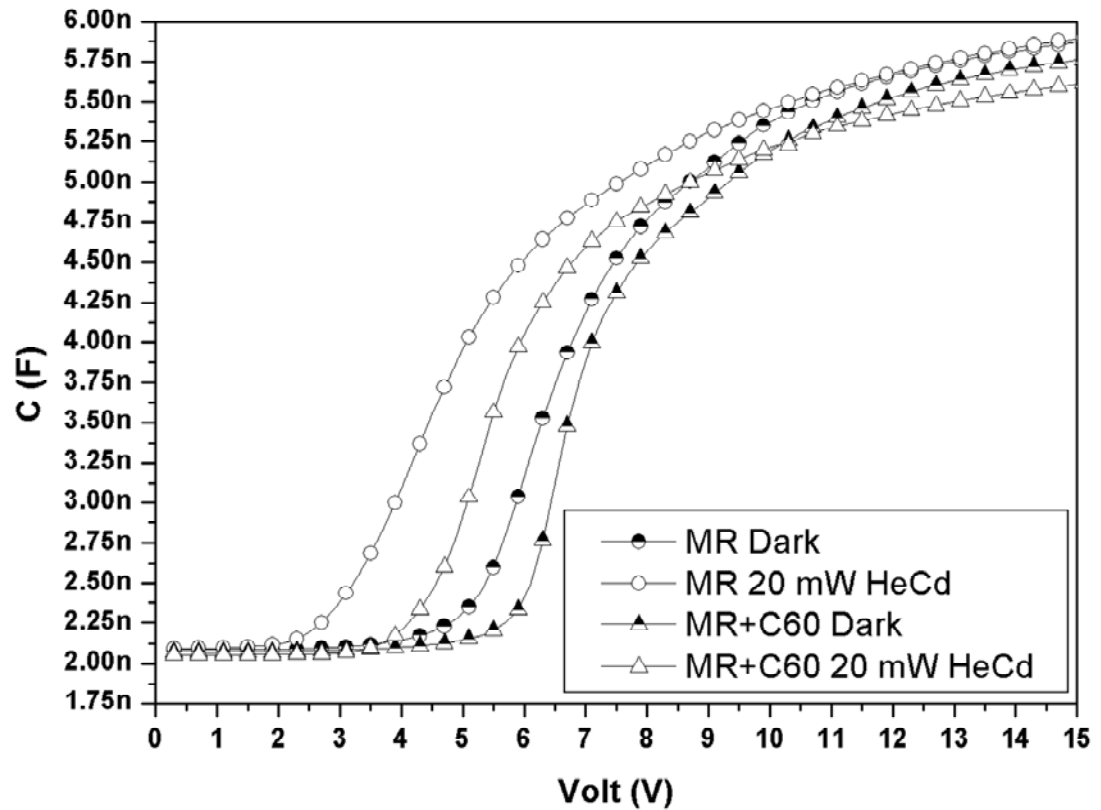
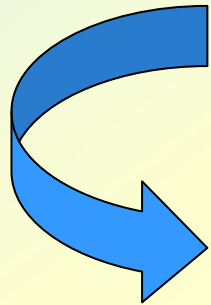
# Experimental set-up

- 10k Hz spot frequency whose rms amplitude is  $\sim 495$  mV
- 20 mW He-Cd  $\lambda=441.6$  nm
- The time lag between successive measurements was arranged to be at the order of 10 seconds



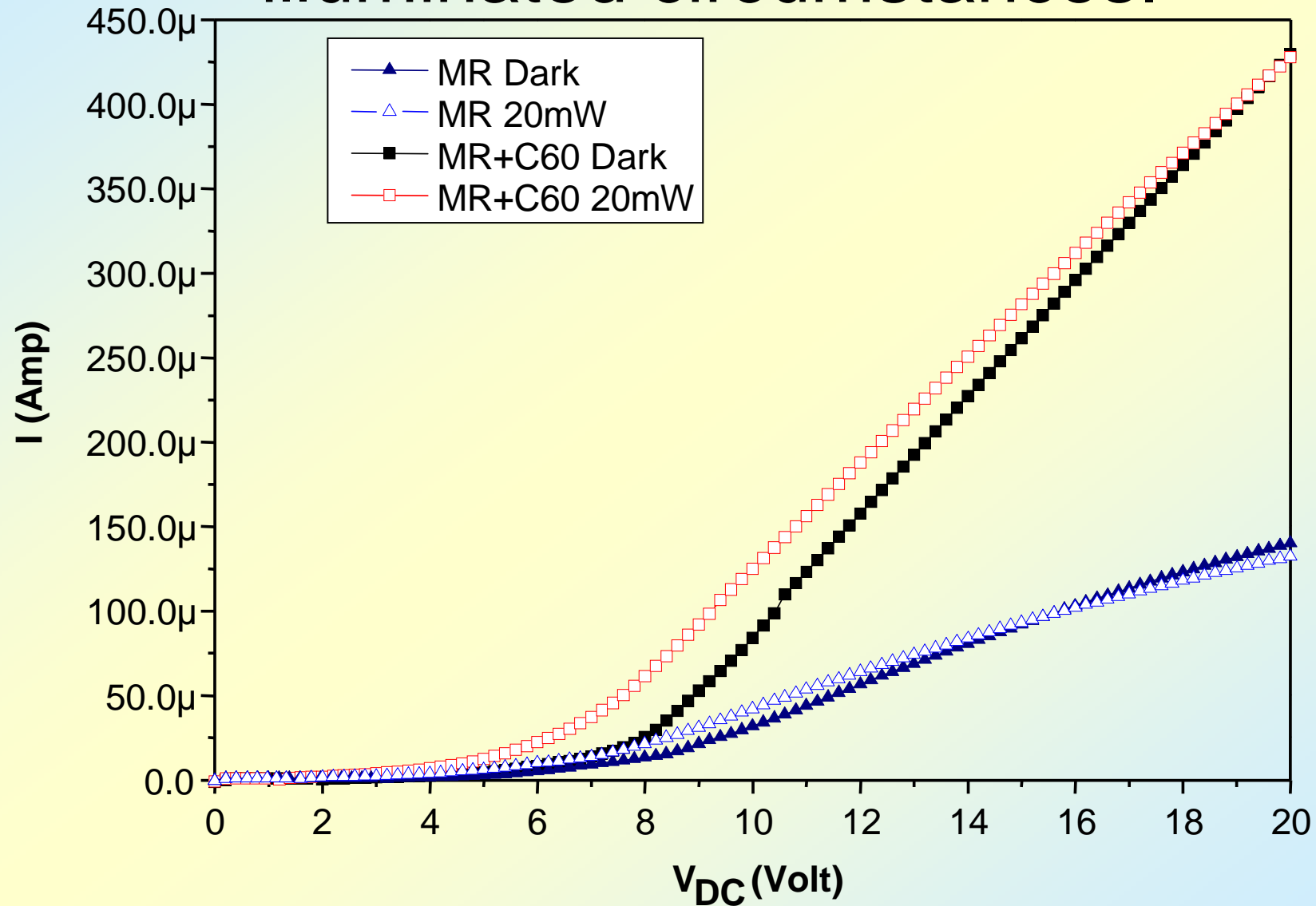
# Capacitance measurements

$$C = \epsilon_0 \cdot \epsilon \cdot \frac{A}{d}$$



$\Delta\epsilon$	MR	MR+C60
<i>Dark</i>	12.68	12.44
<i>20 mW HeCd</i>	10.56	9.87

# I / V plot of samples under dark and illuminated circumstances.



# Results

- C60 doping enlarges the bandwidth of impedance peak while it gets narrower by **laser pumping**
- Switching voltage was shifted to lower values as the **laser pumping** occurs
- The lowest amount of capacitance was acquired by **MR+C60 doped sample** after the saturation threshold
- The **MR+C60 doped sample** has **superiority over the others** according to the satisfied  $\Delta\varepsilon$  value both in dark and in illuminated conditions. Decreasing trend of  $\Delta\varepsilon$  value is also explicit **under the laser illuminated case**
- $\Delta\varepsilon$  is inferred from the extreme values (Capacitance graph) (Dielectric constant along the director axis is larger than that of it along the axes perpendicular to the director)  $\Delta\varepsilon > 0$   
So our system to be determined as **p-type**
- **Laser illumination** increases the **photoconductivity** in both of the samples as it also shifts the switching voltages of reorientation to lower voltage values.

**Dielectric spectroscopy of a hybrid composite; constituted by doping a side-chain liquid crystalline polymer; in laser induced circumstances**

# Material

**E7**

51%



25%



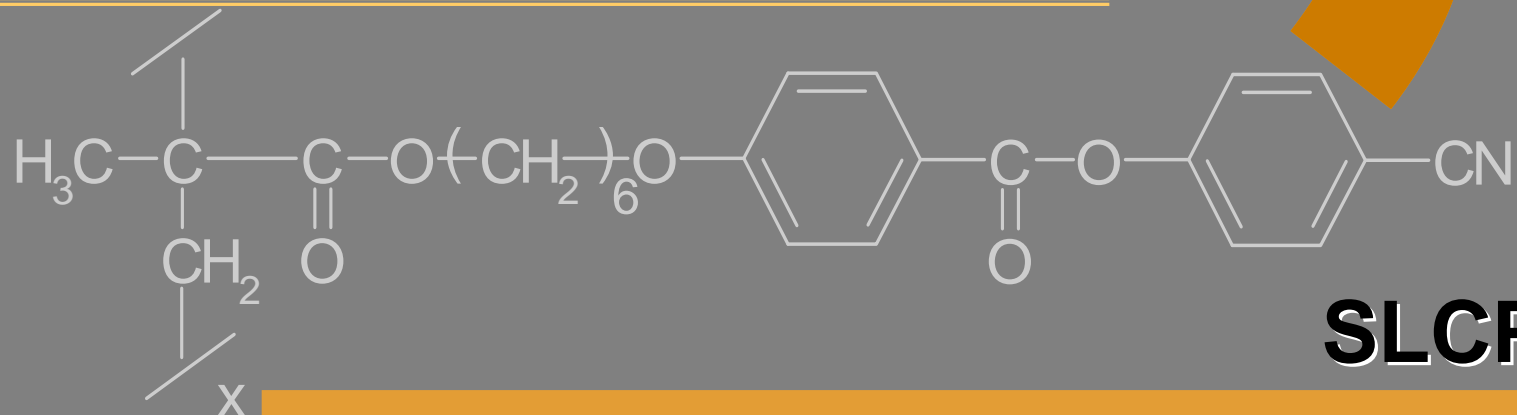
16%



8%

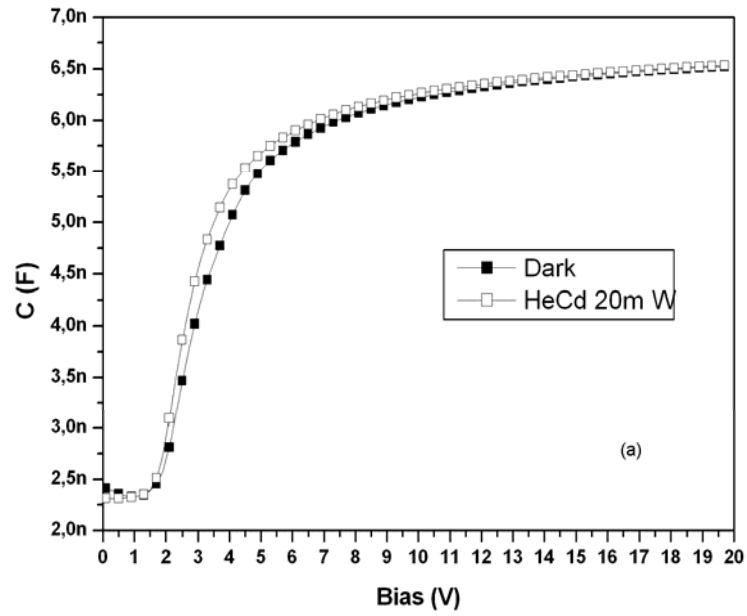


**10 % SLCP in E7  
wt/wt**



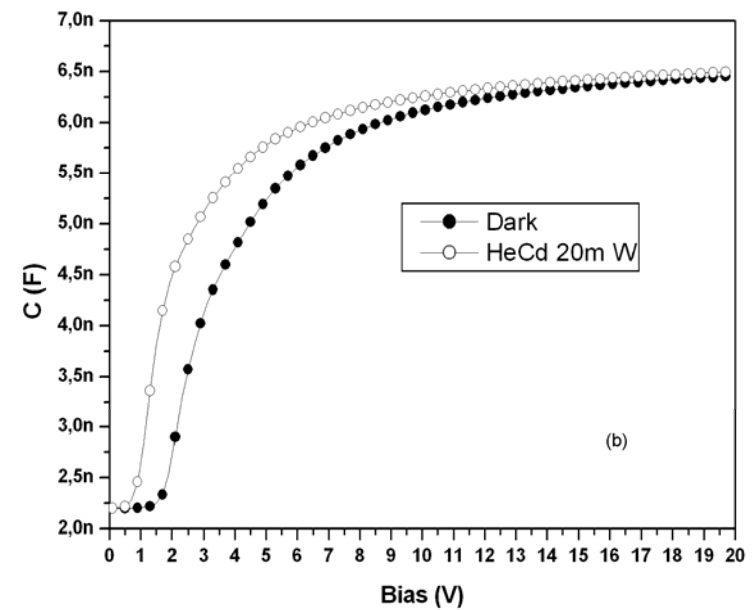
**SLCP**

# Dependency of capacitance on DC voltage

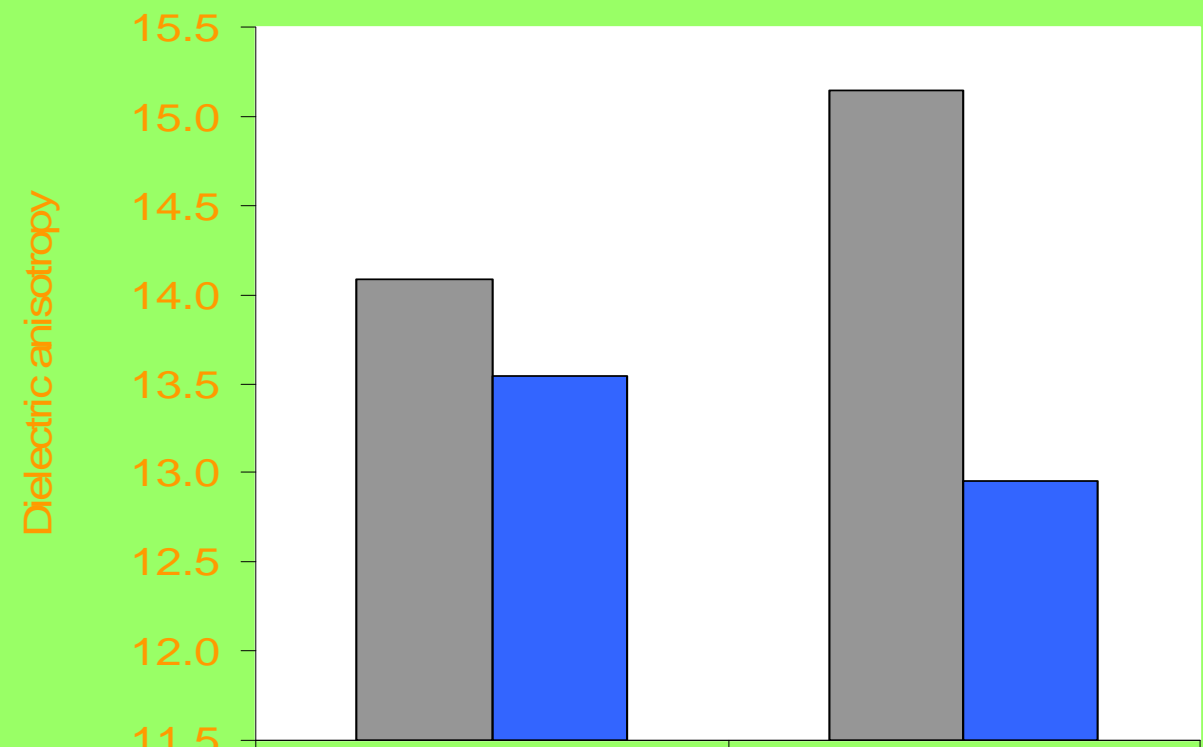
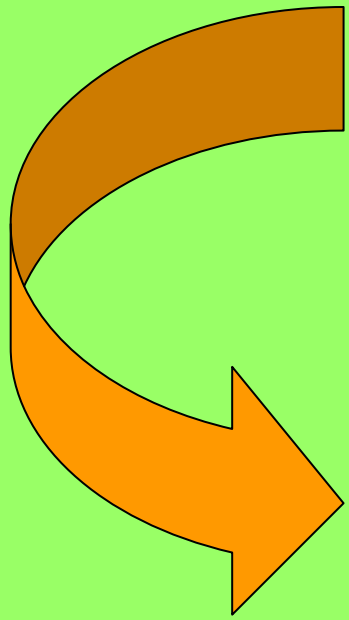


← E7

SLCP →



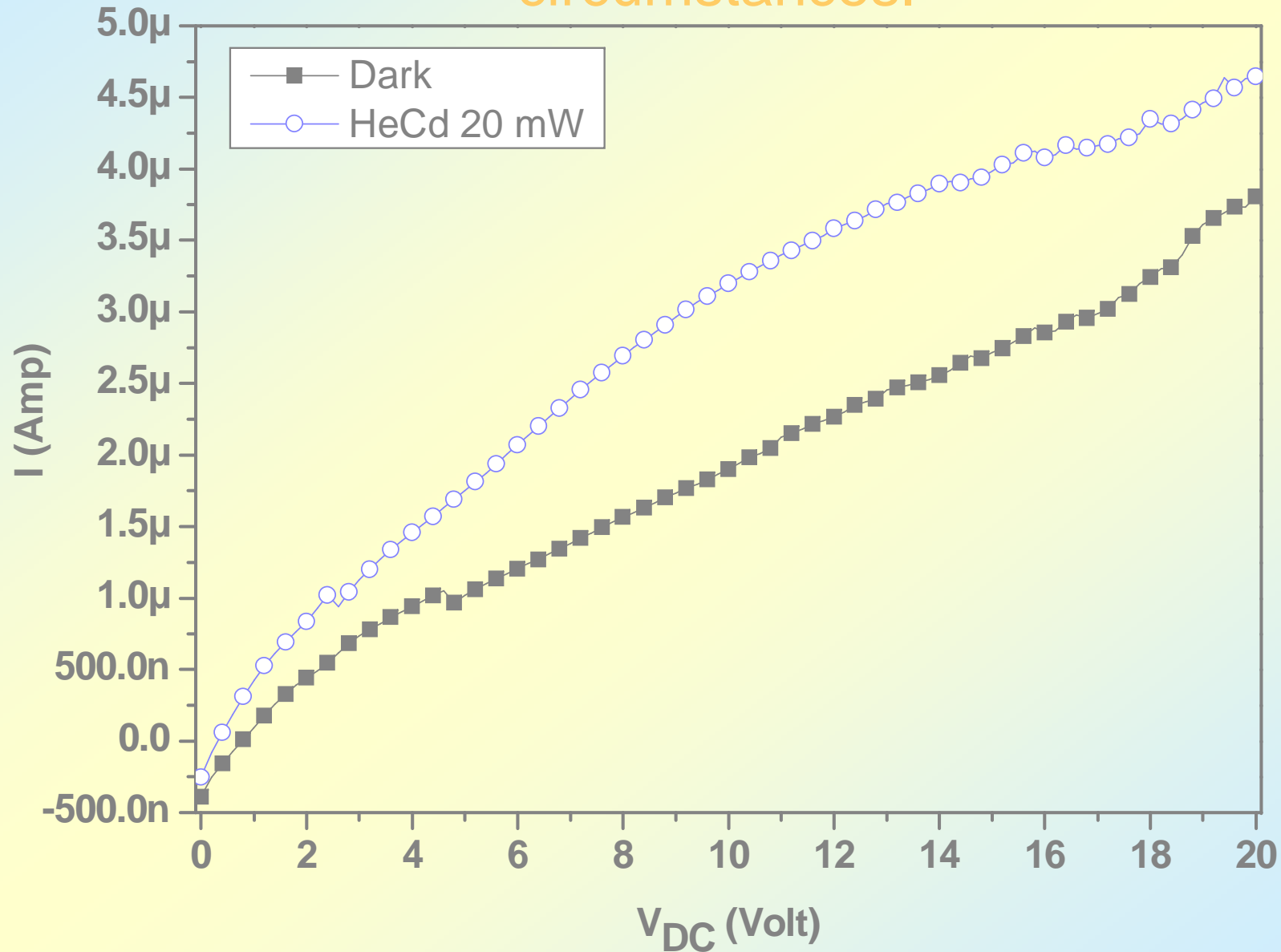
$$C = \epsilon_0 \cdot \epsilon \cdot \frac{A}{d}$$



■ Dark	14.08	15.15
■ 20m W HeCd	13.54	12.95



# I / V plot of SLCP under dark and illuminated circumstances.



# Results

- **Laser pumping** causes a considerable decrease on the required amount of voltage for saturation in **SLCP**
- $\Delta\varepsilon$  value of **SLCP** is more and its response to **laser illumination** is larger than **pure E7**; the minimum dielectric anisotropy case holds for the **illuminated SLCP** sample
- **Laser pumping** has a noteworthy effect on the conductivity in **SLCP**

S. Eren San et.al. Journal of Non-Crystalline Solids 351  
(2764-2767)

# Liquid crystal - nanotube dispersions

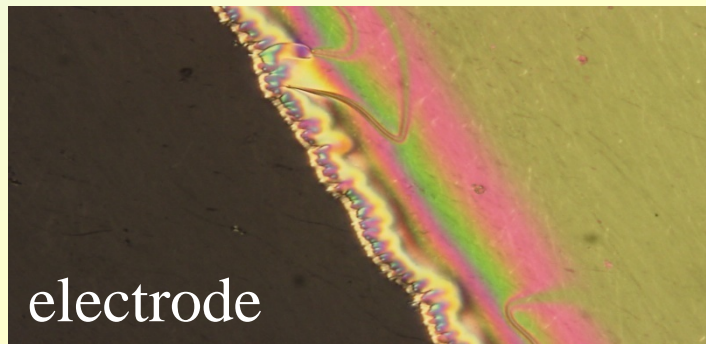
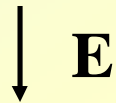
# Contents

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- Combining two modern materials
- Reorienting nanotubes
- Possible applications

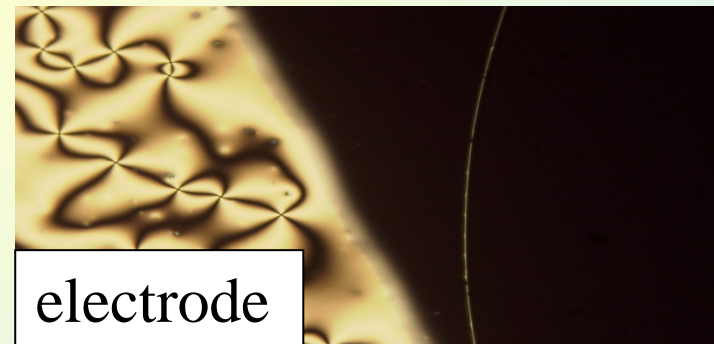
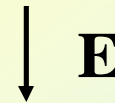
The liquid crystal director  $n$  (optical axis) can be reoriented by application of external fields: electric, magnetic, mechanical, optic ...

**E7 ( $\Delta\varepsilon > 0$ )**



**planar  $\rightarrow$  homeotropic**

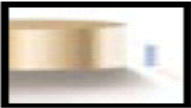



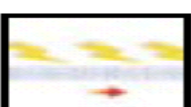
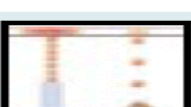
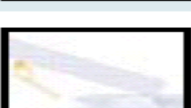

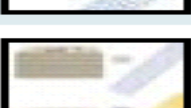
**ZLI-2806 ( $\Delta\varepsilon < 0$ )**



**homeotropic  $\rightarrow$  planar**

## Properties of Carbon Nanotubes

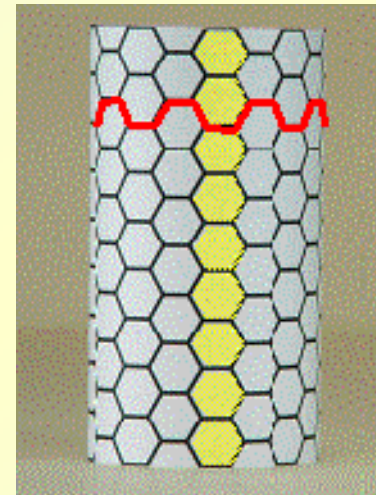
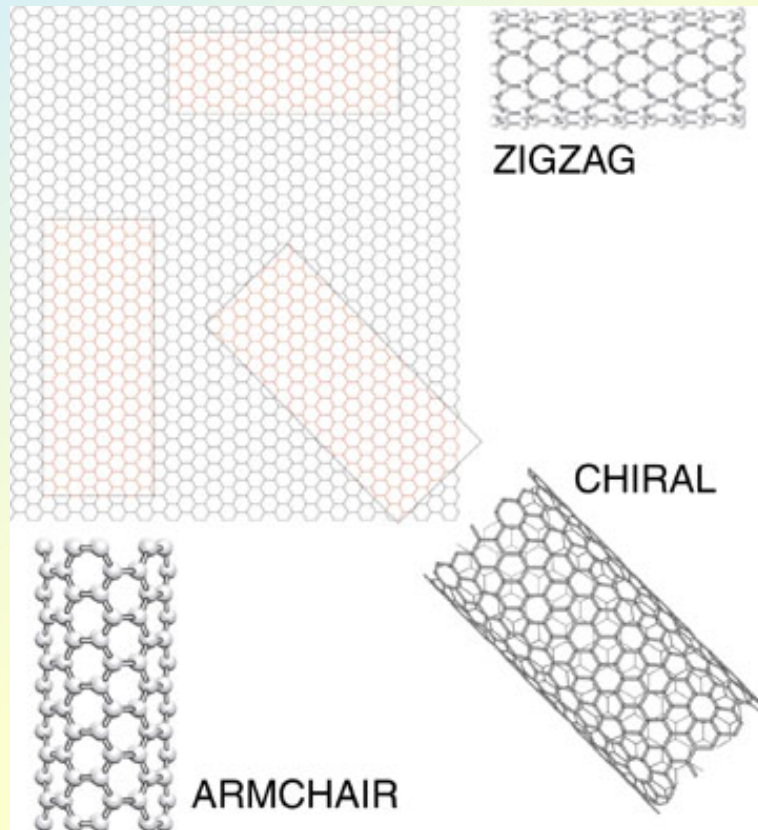
# Going to Extremes

PROPERTY	SINGLE-WALLED NANOTUBES	BY COMPARISON
 <b>Size</b>	0.6 to 1.8 nanometer in diameter	Electron beam lithography can create lines 50 nm wide, a few nm thick
 <b>Density</b>	1.33 to 1.40 grams per cubic centimeter	Aluminum has a density of 2.7 g/cm <sup>3</sup>
 <b>Tensile Strength</b>	45 billion pascals	High-strength steel alloys break at about 2 billion Pa
 <b>Resilience</b>	Can be bent at large angles and restraightened without damage	Metals and carbon fibers fracture at grain boundaries
 <b>Current Carrying Capacity</b>	Estimated at 1 billion amps per square centimeter	Copper wires burn out at about 1 million A/cm <sup>2</sup>
 <b>Field Emission</b>	Can activate phosphors at 1 to 3 volts if electrodes are spaced 1 micron apart	Molybdenum tips require fields of 50 to 100 V/μm and have very limited lifetimes
 <b>Heat Transmission</b>	Predicted to be as high as 6,000 watts per meter per kelvin at room temperature	Nearly pure diamond transmits 3,320 W/m-K
 <b>Temperature Stability</b>	Stable up to 2,800 degrees Celsius in vacuum, 750 degrees C in air	Metal wires in microchips melt at 600 to 1,000 degrees C
 <b>Cost</b>	\$1,500 per gram from BuckyUSA in Houston	Gold was selling for about \$10/g in October

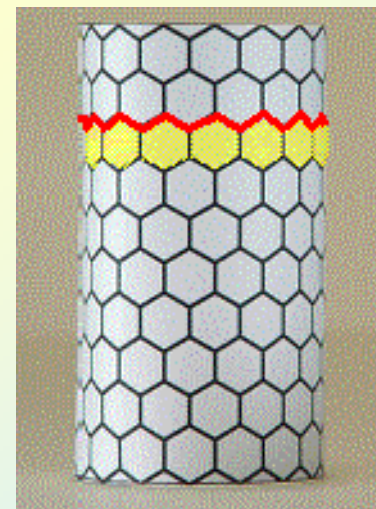


There are two basic forms: **single-wall nanotubes** (SWNT):

**Basically: rolled up sheets of atomic carbon**



**armchair**

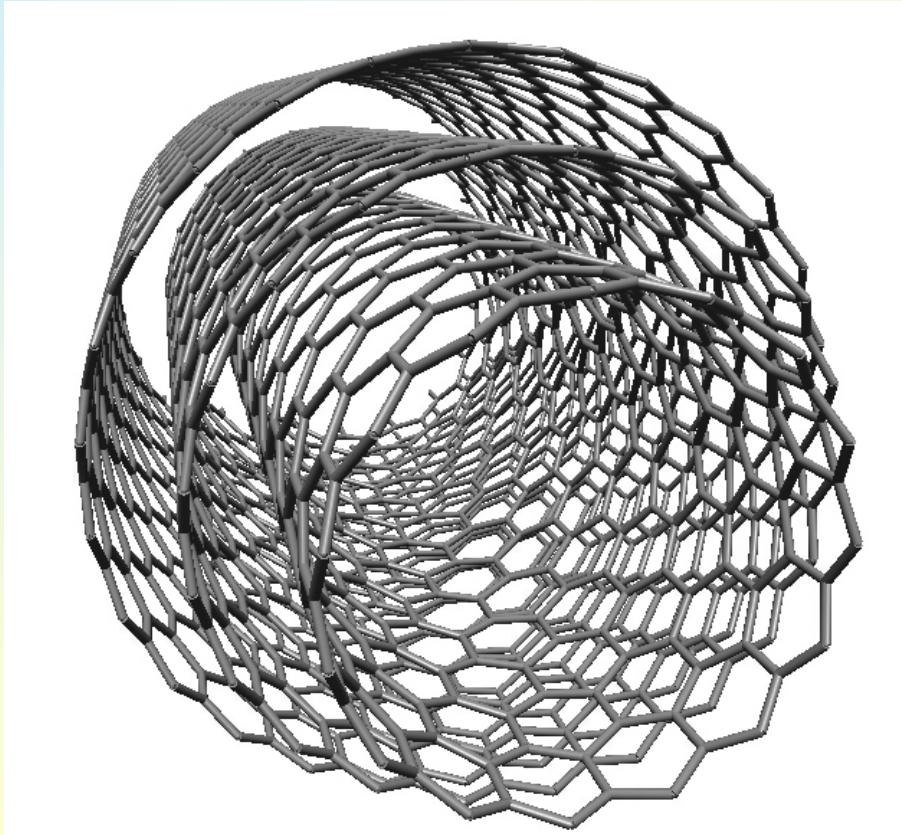


**zigzag**

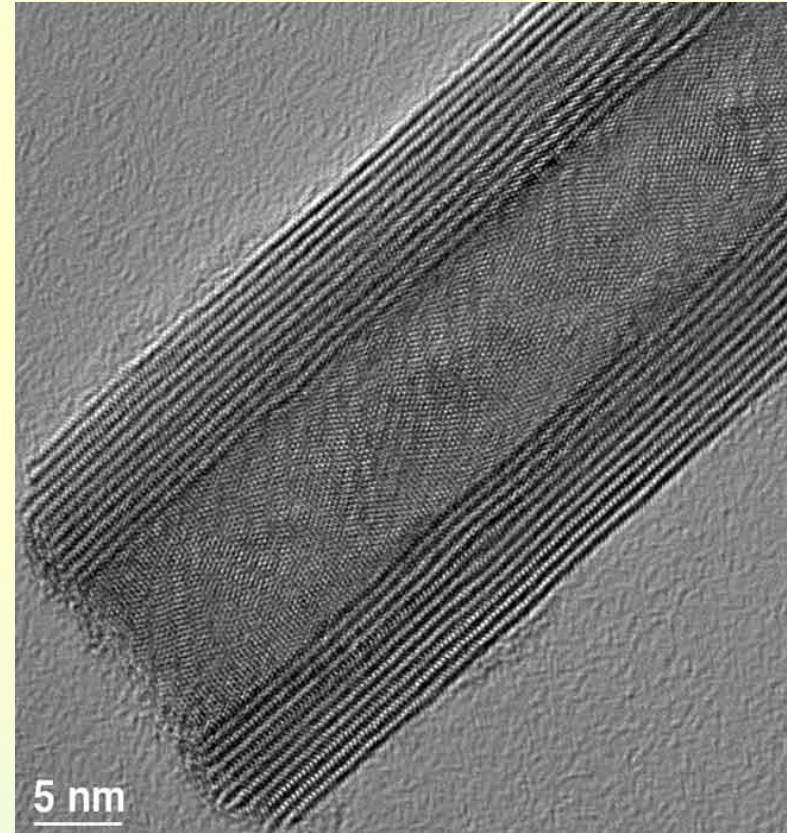
<http://www.seas.upenn.edu/mse/images/>

<http://www.arc.eee.tut.ac.jp/research/nanotube/paperfold/pic/>

and **multi-wall nanotubes** (MWNT):



<http://www.ahwahneetech.com/technology/images/>



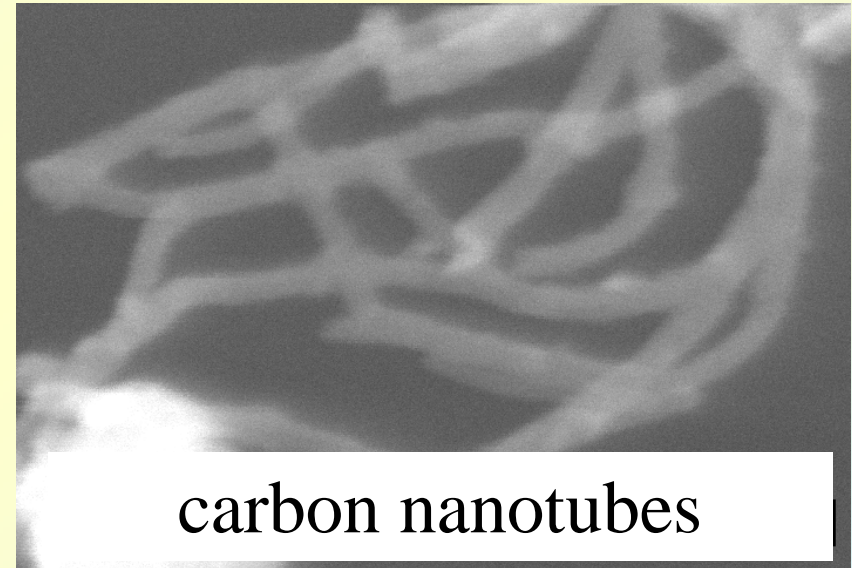
<http://www.weizmann.ac.il/materials/msg/>



# Combining two modern materials



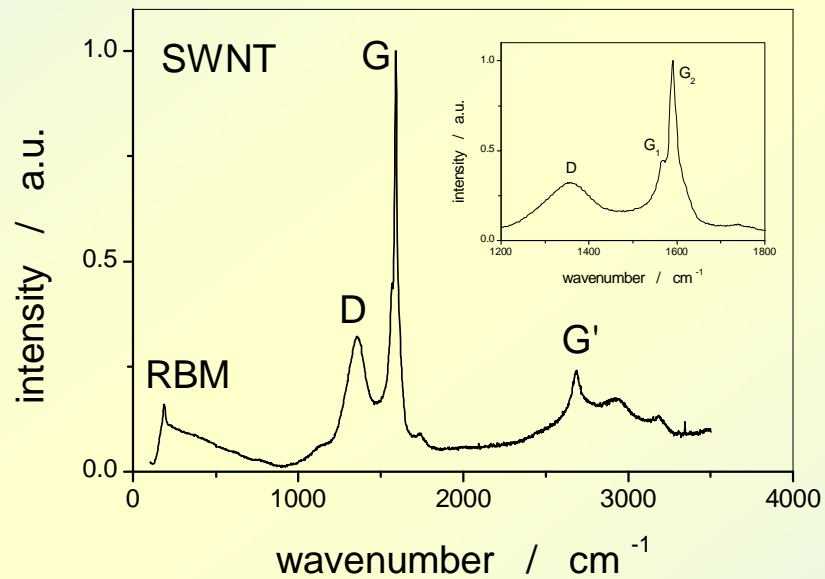
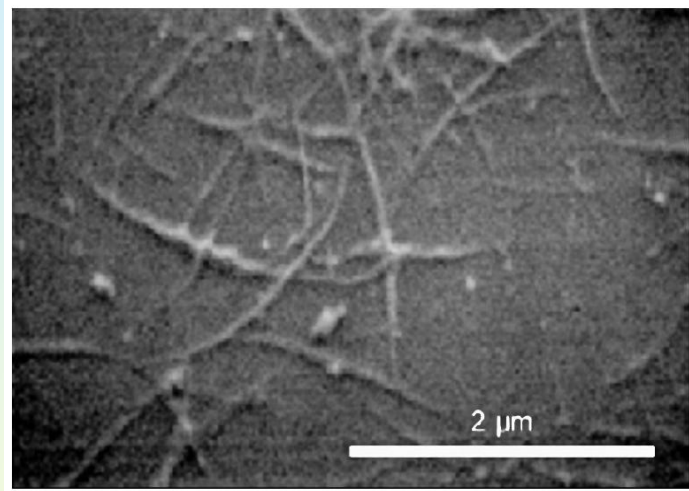
+



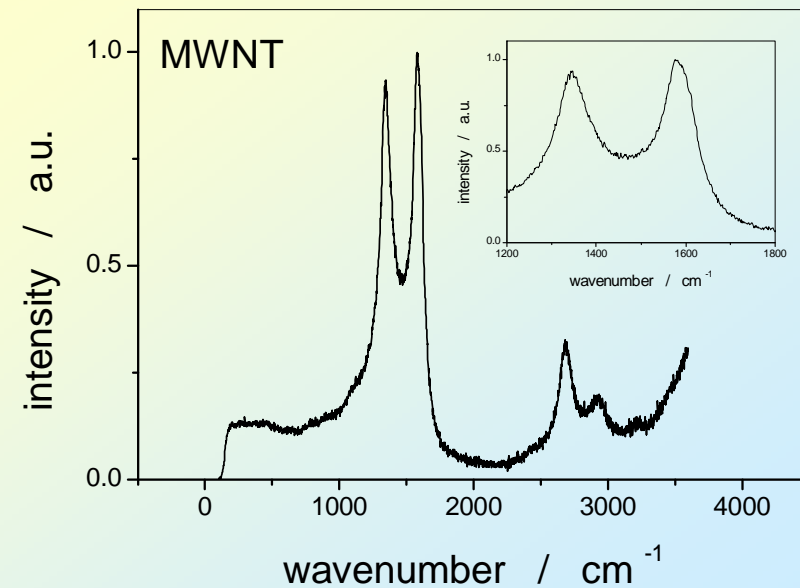
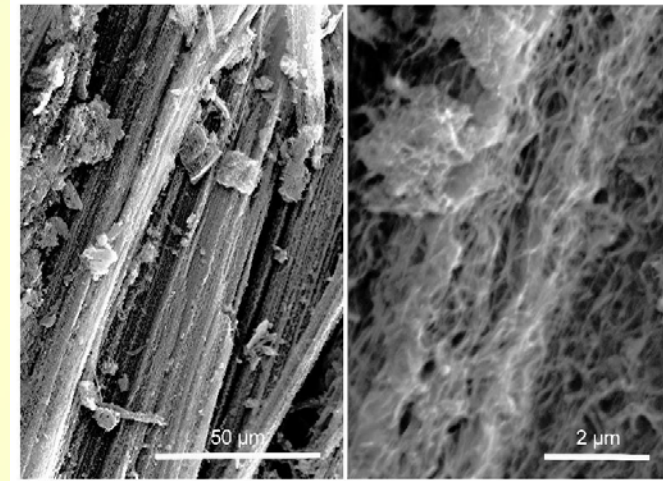
- mixing at low nanotube concentrations ( $<0.1\%$ )
- use of spectroscopically pure solvents
- ultra-sonification for at least half an hour

# Characterisation of nanotubes

## Single wall nanotubes



## Multi-wall nanotubes

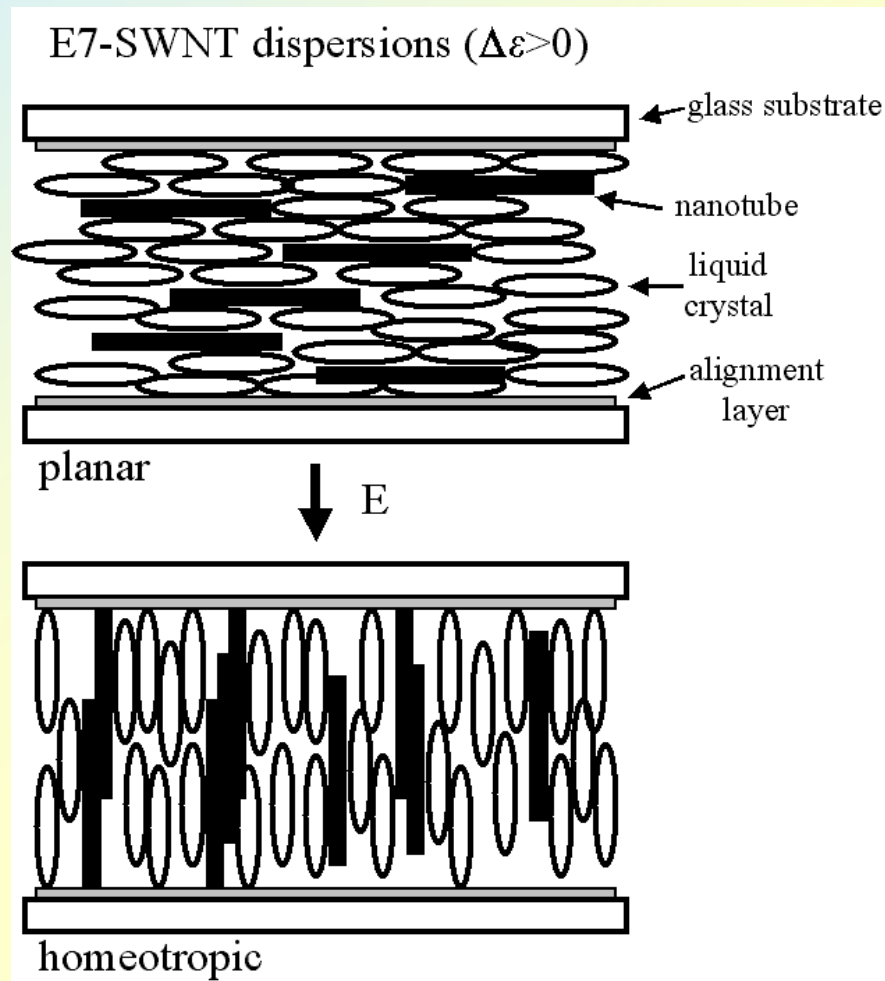


# Re-orienting nanotubes

## Liquid crystal - single-wall nanotube dispersions:

LC: nematic E7

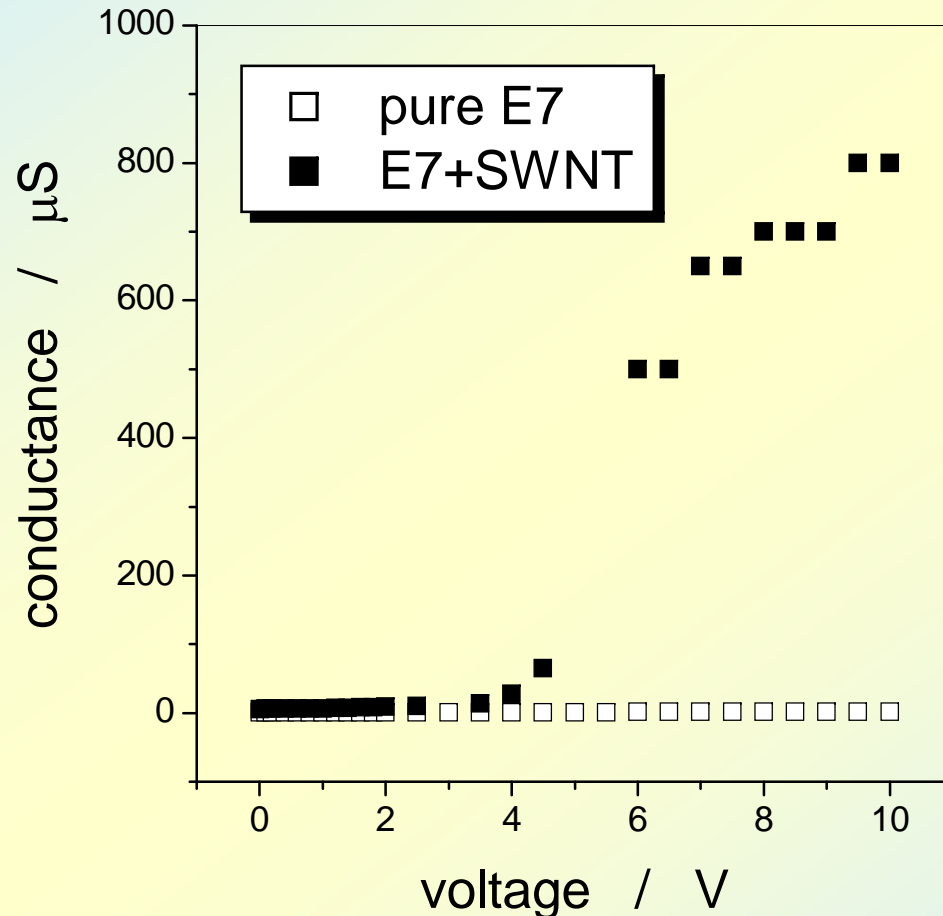
positive dielectric anisotropy  $\Delta\epsilon > 0$



## *electrically steered*

- The liquid crystal re-orientation is easily verified by polarising microscopy. Also capacitance measurements are employed for double check.
- But how can we verify that also the nanotubes are re-oriented?

## → **conductance measurements**



- The conductance of the LC-nanotube dispersion increases drastically, as the threshold voltage for the liquid crystal Fredericksz transition (planar to homeotropic) is exceeded.

→ **Nanotubes re-orient from the non-conductive in-plane orientation to the conductive out-of-plane orientation.**

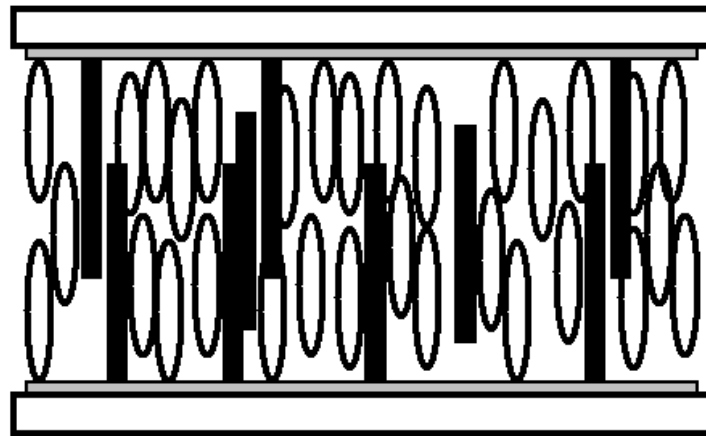
# The counter-experiment:

*electrically steered*

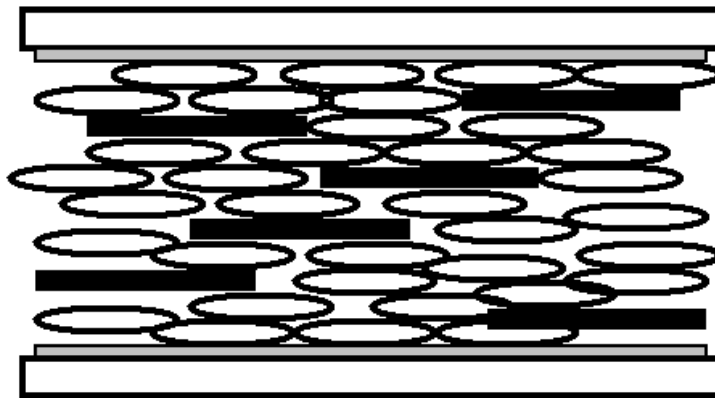
LC: nematic ZLI-2806

negative dielectric anisotropy,  $\Delta\epsilon < 0$

ZLI2806-nanotube dispersion ( $\Delta\epsilon < 0$ )



homeotropic

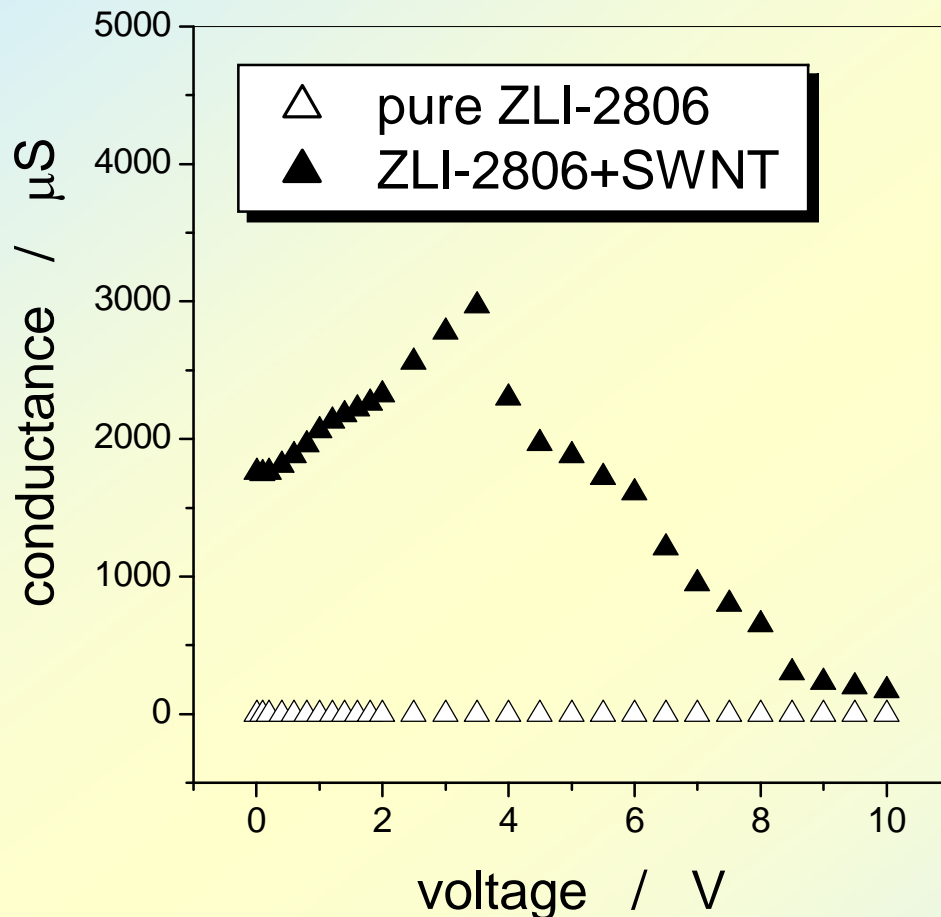


planar



*electrically steered*

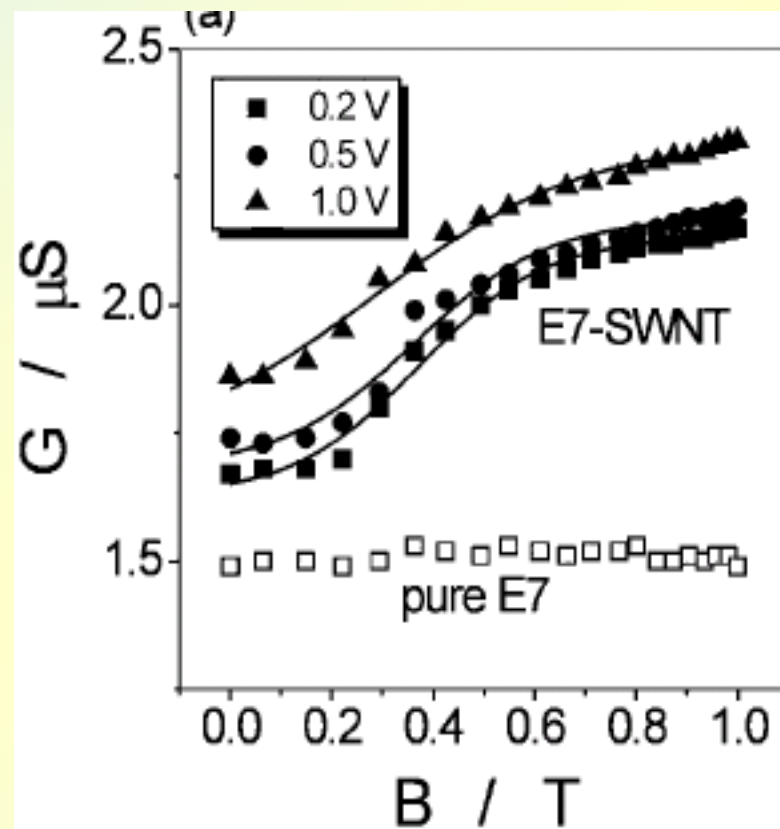
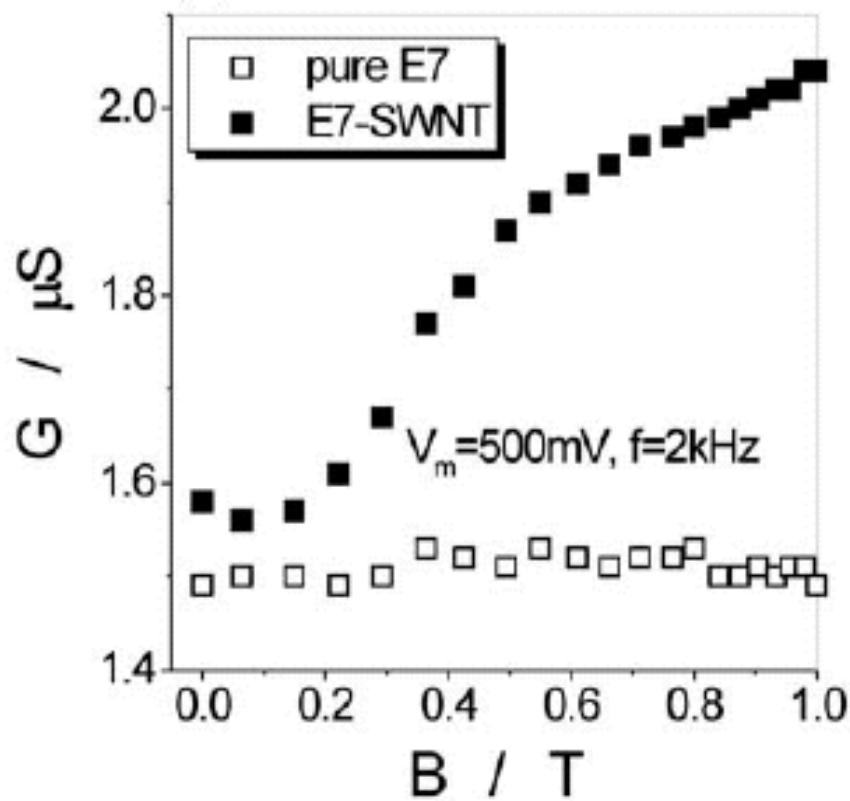
## Conductance measurements:



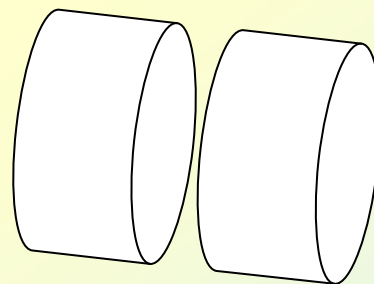
- The conductance of the LC – nanotube dispersion strongly decreases, as the threshold voltage for the liquid crystal homeotropic to planar transition is exceeded.

**→ Nanotubes re-orient from the conducting to the non-conducting orientation.**





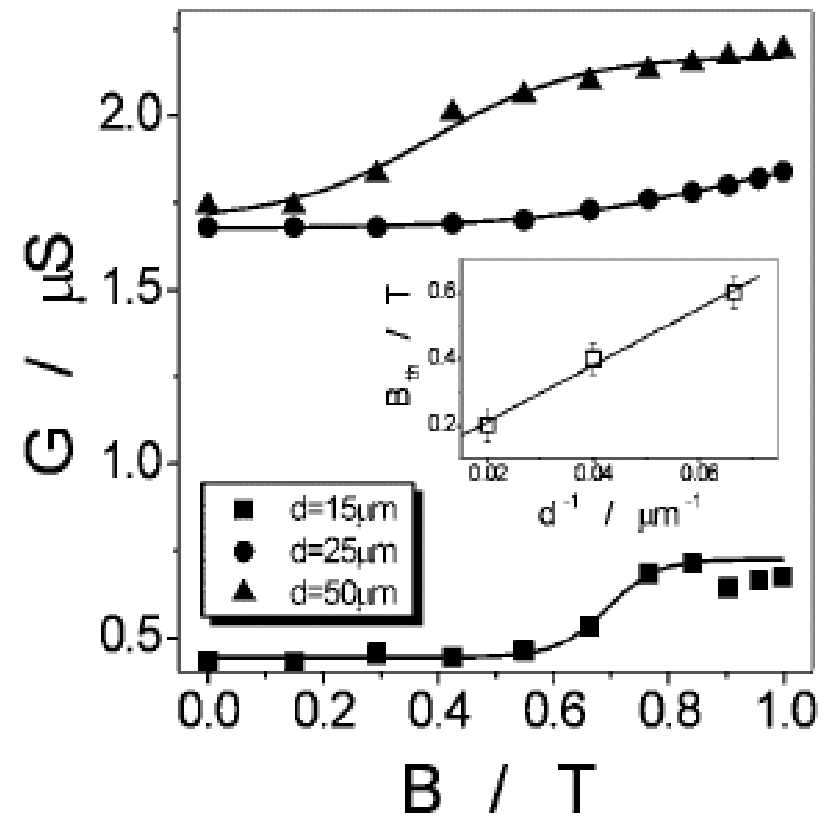
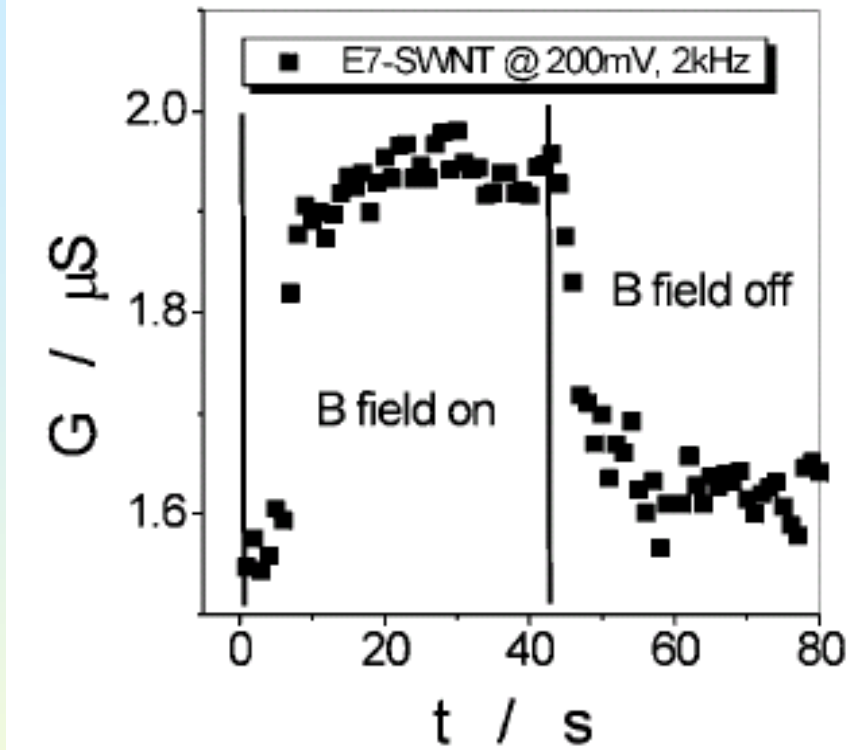
1 Tesla



*magnetically steered*

I. Dierking, S. Eren San et.al. Appl. Phys. Lett. 87, 233507

*magnetically  
steered*





- ⇒ The anisotropic liquid crystal environment imposes orientation onto the dispersed nanotubes.
- ⇒ A change of the liquid crystal director field causes an elastic torque on the dispersed nanotubes.
- ⇒ The dispersed nanotubes are re-oriented through *elastic interactions* with their host

**Note that:**

The reported conductivity behaviour is **NOT** observed in the isotropic phase of E7 or ZLI-2806, nor in glycerine!

# Possible applications

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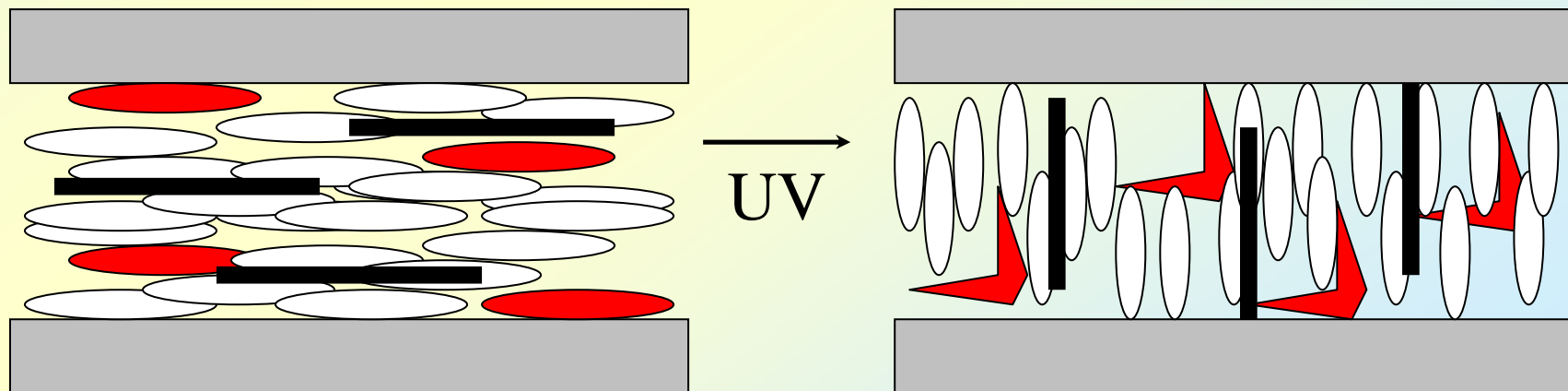
**electrically steered** liquid crystal – nanotube switches, in both OFF-ON (planar-homeotropic) and ON-OFF (homeotropic-planar) configuration. Note that the electric threshold voltage is **independent** on cell gap. → **Nano-electronics ... ?**

**magnetically steered** liquid crystal – nanotube switches, OFF-ON (planar-homeotropic) configuration .  
→ **Magnetic field sensors ... ?**

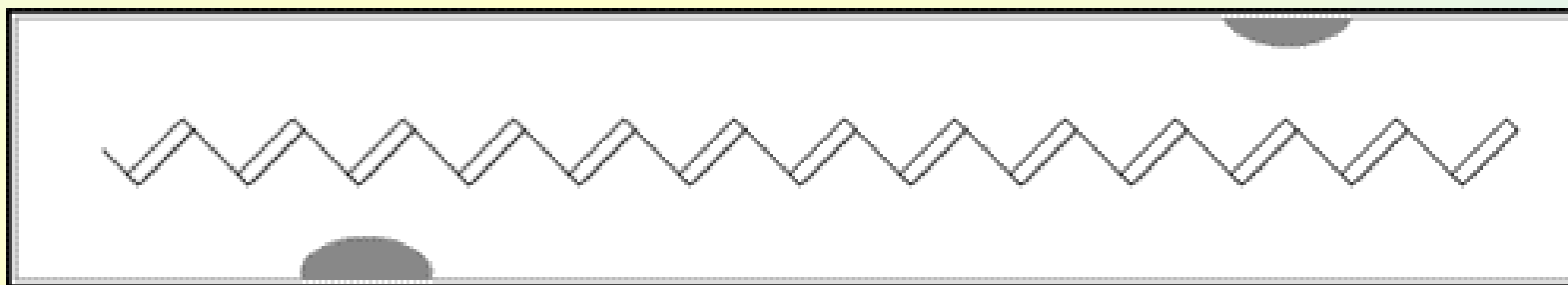
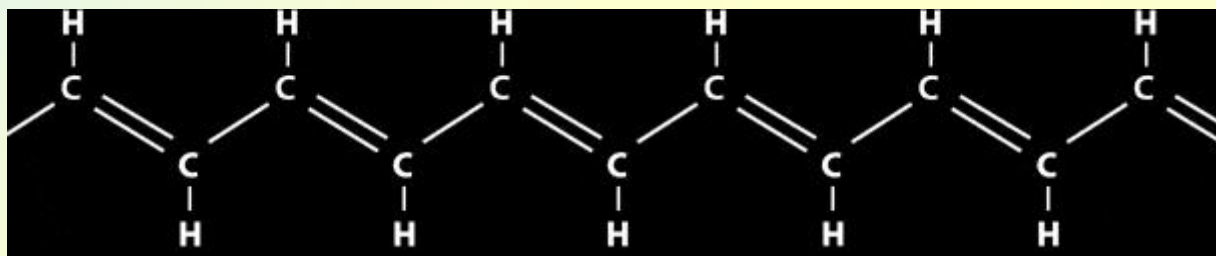
One can also think of **optically steered** electric switches:

- dope the liquid crystal with special azo-compounds
- illumination with UV light causes molecular cis-trans isomerisation
- this in turn causes a macroscopic reorientation of the liquid crystal from planar to homeotropic
- thus switching from a non-conducting to a conducting state

→ **LC-nanotube UV sensors ... ?**

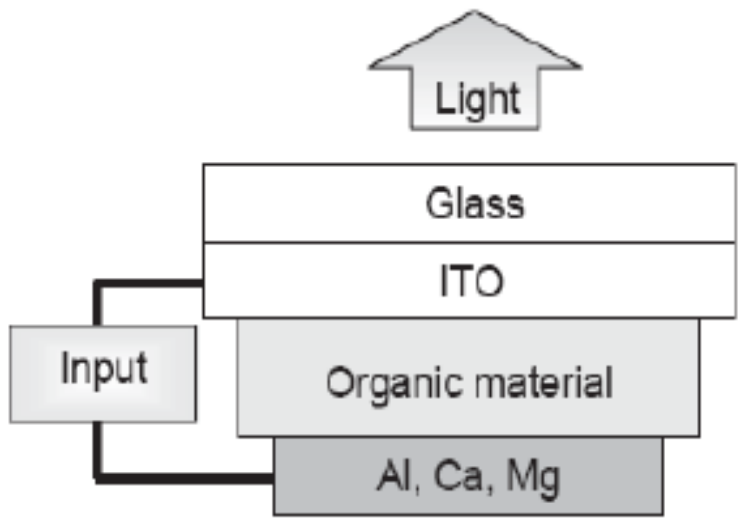
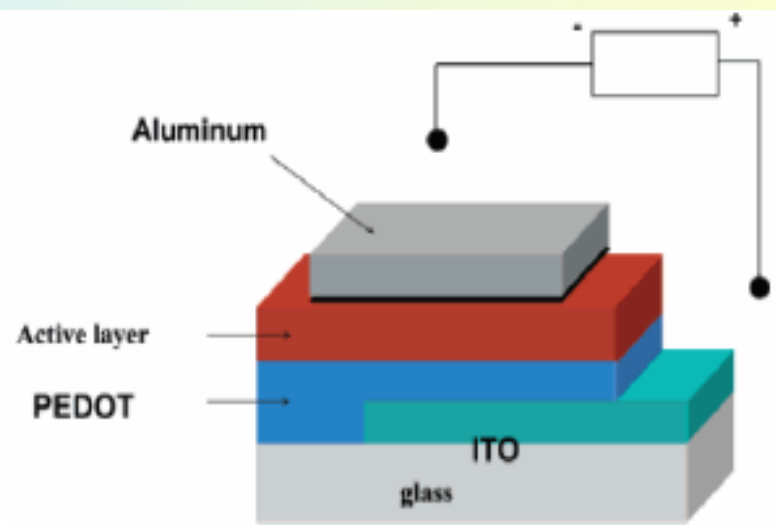


# Conjugated polymers

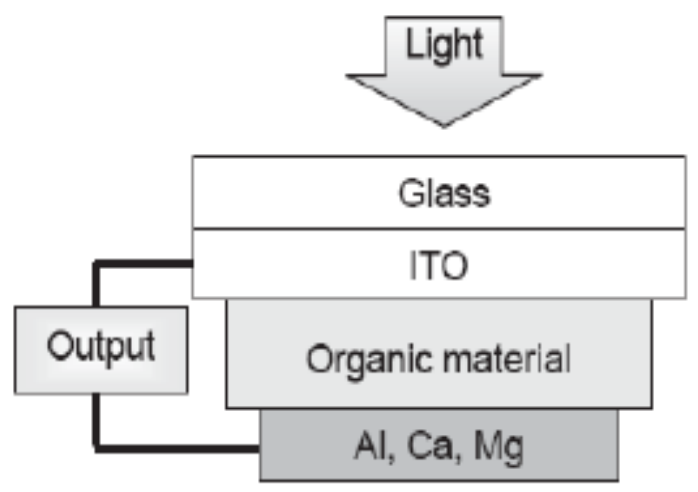


# Organic Electronics

- OLEDs
- Organic Solar Cells OSCs
- OFETs
- LCs for OFETs



**LED mode**



**Photovoltaic mode**

Ongoing with preliminary results:

Analogy from pipes to circuits

OSC+OFET Light to Voltage to  
Light (wavelength switch)

OSC+OFET Light to Voltage to  
Current (sensors or light induced  
control )

LC FETs

# Acknowledgements for CNT work

- My coworker: **Dr. I. Dierking,**

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- Our collaborators: **Dr. Giusy Scalia, Dr. Piero Morales**

Unità Tecnico Scientifica, Materiali e Nuove Tecnologie (ENEA)

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[1] *Adv. Mater.*, **16**, 865, (2004).

[2] *J. Appl. Phys.*, **97**, 044309, (2005).

[3] *Appl. Phys. Lett.* **87**, 233507, (2005).



THANK  
YOU

