Supermolecular Stereochemistry in Liquid Crystals

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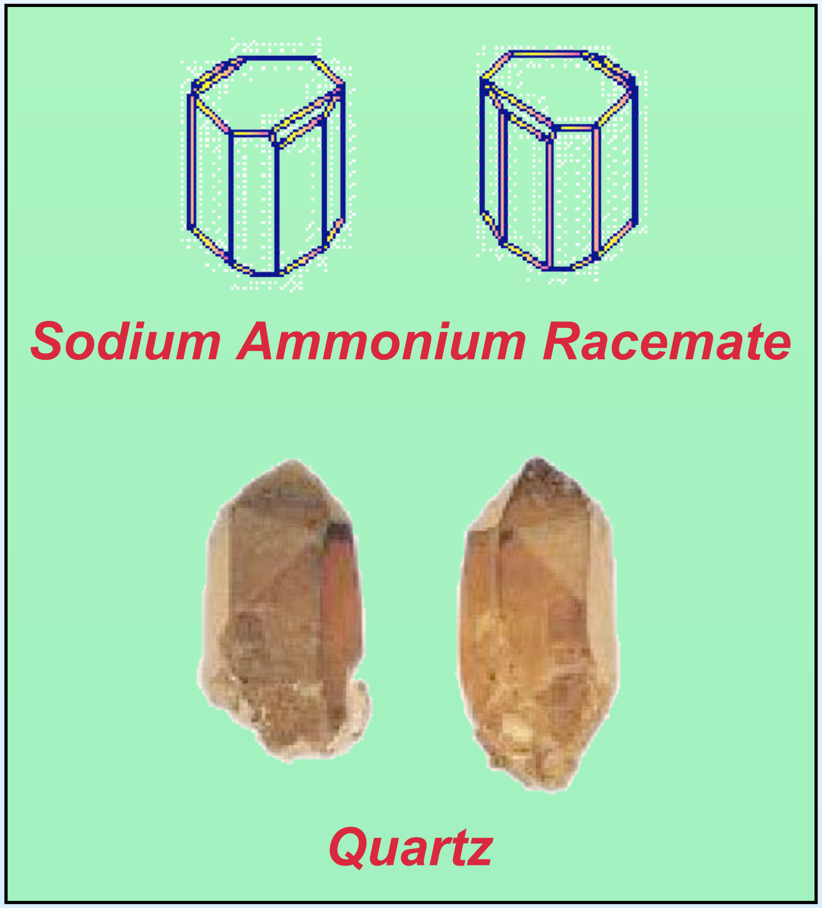
- ***High throughput measurement of ee using FLC EO***
- ***Banana phases and the first fluid conglomerates***

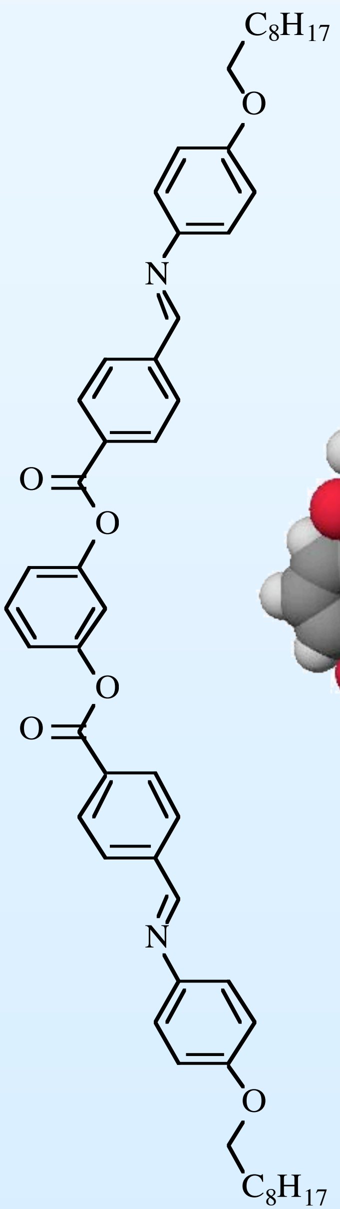
Stereochemical Aspects of Novel Materials
UCSB, August 2005

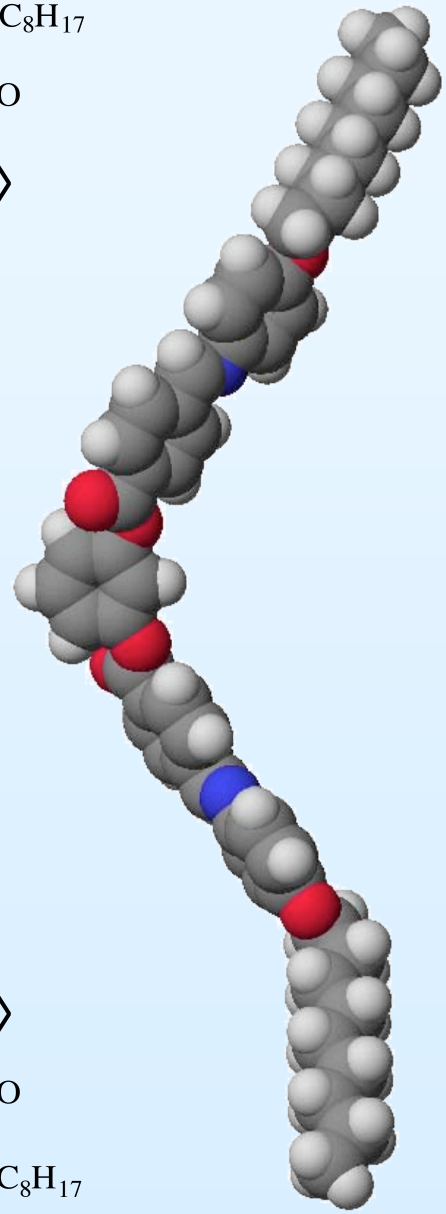
A Liquid Crystal Conglomerate?

- No chiral LC phase from achiral or racemic molecules was known.
- Observation of a chiral LC phase is often used as proof of molecular enantiomeric excess.



Banana Phases



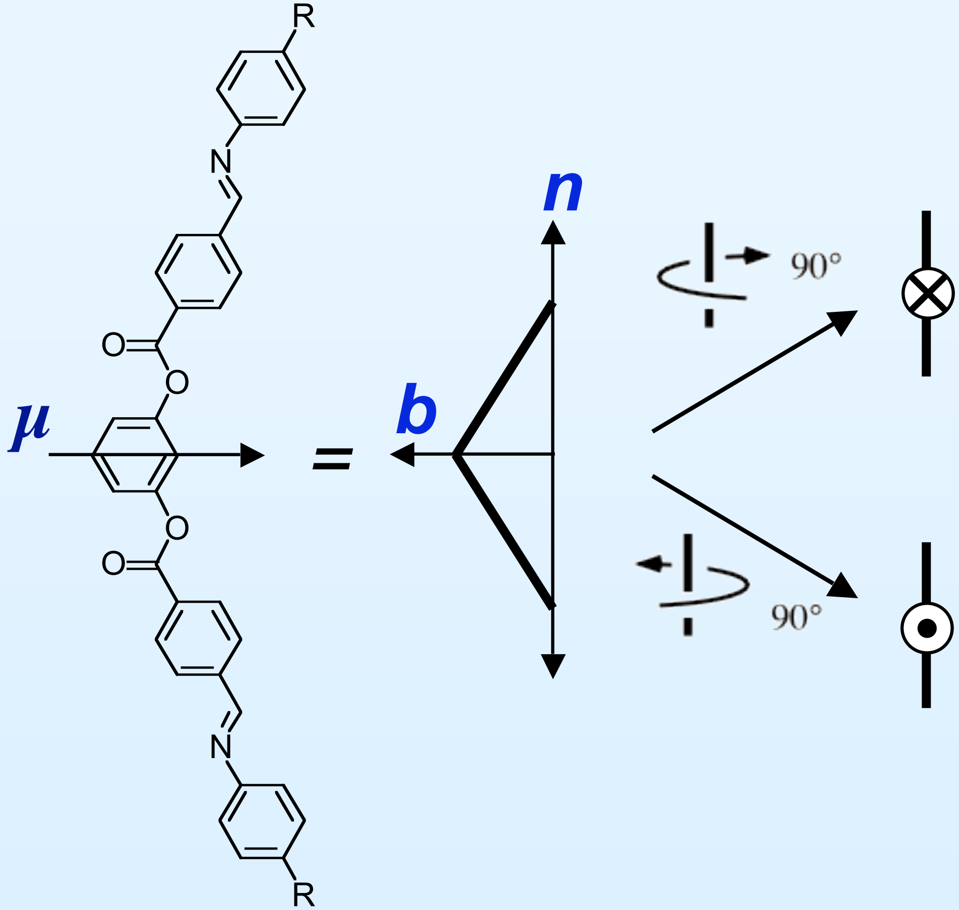


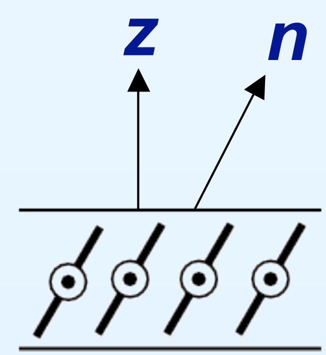
- 1929 Vorländer describes the first banana LCs
- 1992 Cladis, Brand and Pleiner suggest possibility of polar Sm "chevron" bilayer with C_{2v} symmetry and helical chirality
- 1994 Matsunaga reports certain achiral bent mesogens give smectic C phases.
- 1996 Takezoe and Watanabe et al report these "banana-shaped" molecules produce ferroelectric phases with C_{2v} layer structure and helical chirality, starting a wave of banana mania in the FLC community
- 1997 The Boulder Group proposes a chiral layer structure for the B2 phases

NonylOxyBOW (NOBOW): B4 — 155 → B2 — 173 → I

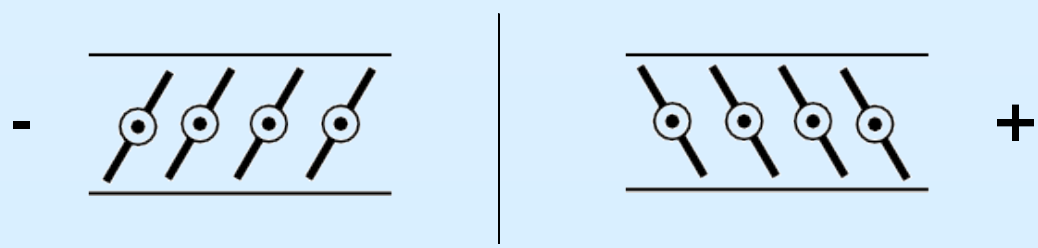
B2 Layer Structure

Spontaneous Nonpolar AND Reflection Symmetry Breaking





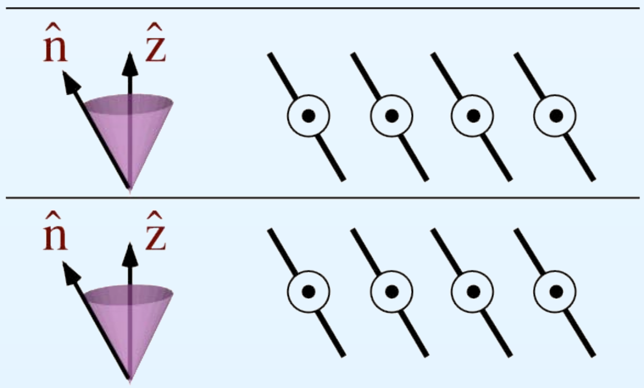
The arrows are all pointing in the same direction, and the director is tilted, giving a C_2 layer structure. This symmetry is both polar and chiral.

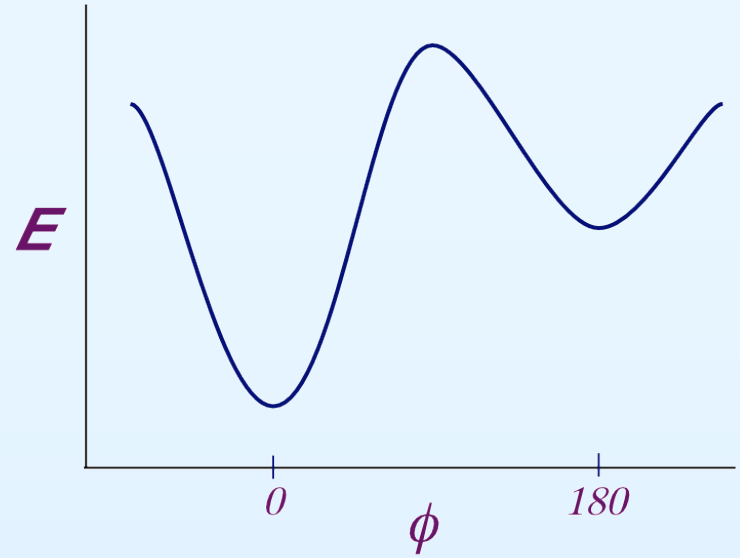


Nonsuperposable Mirror Images

Ferro and Antiferroelectric Chiral Smectics

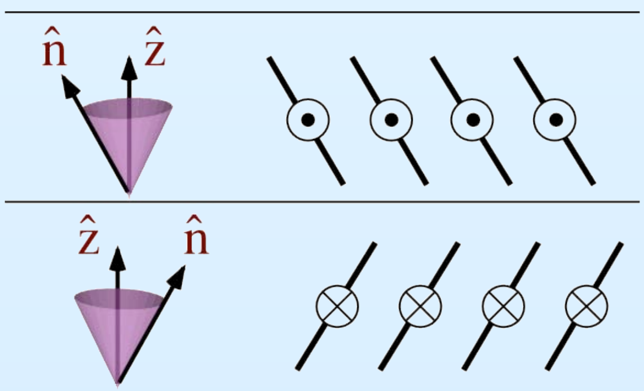
C_2

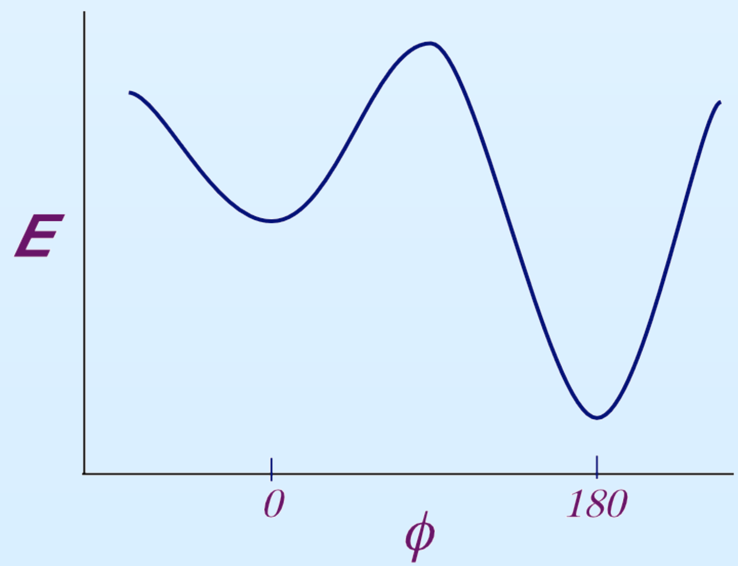




Synclinic Ferroelectric

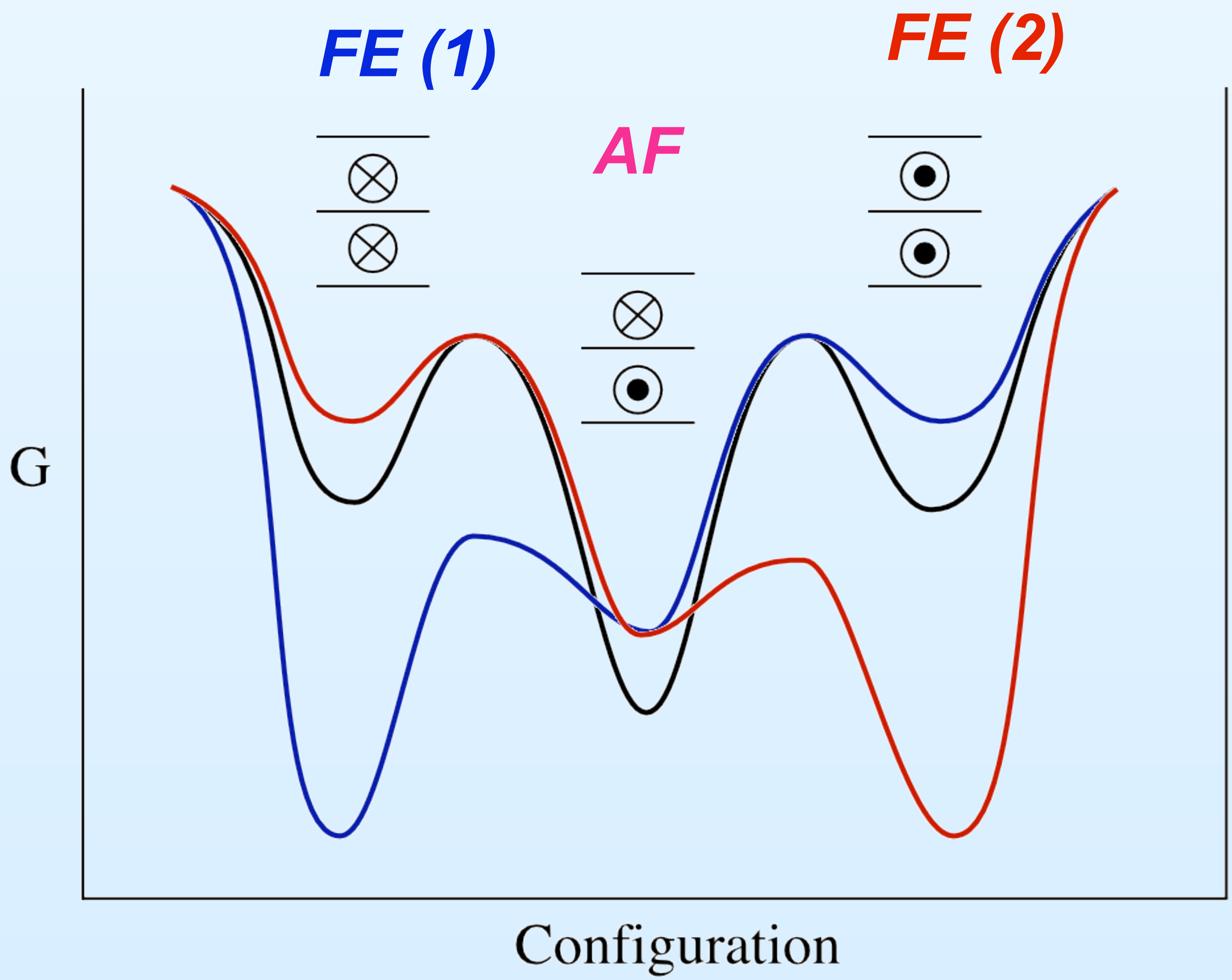
D_2



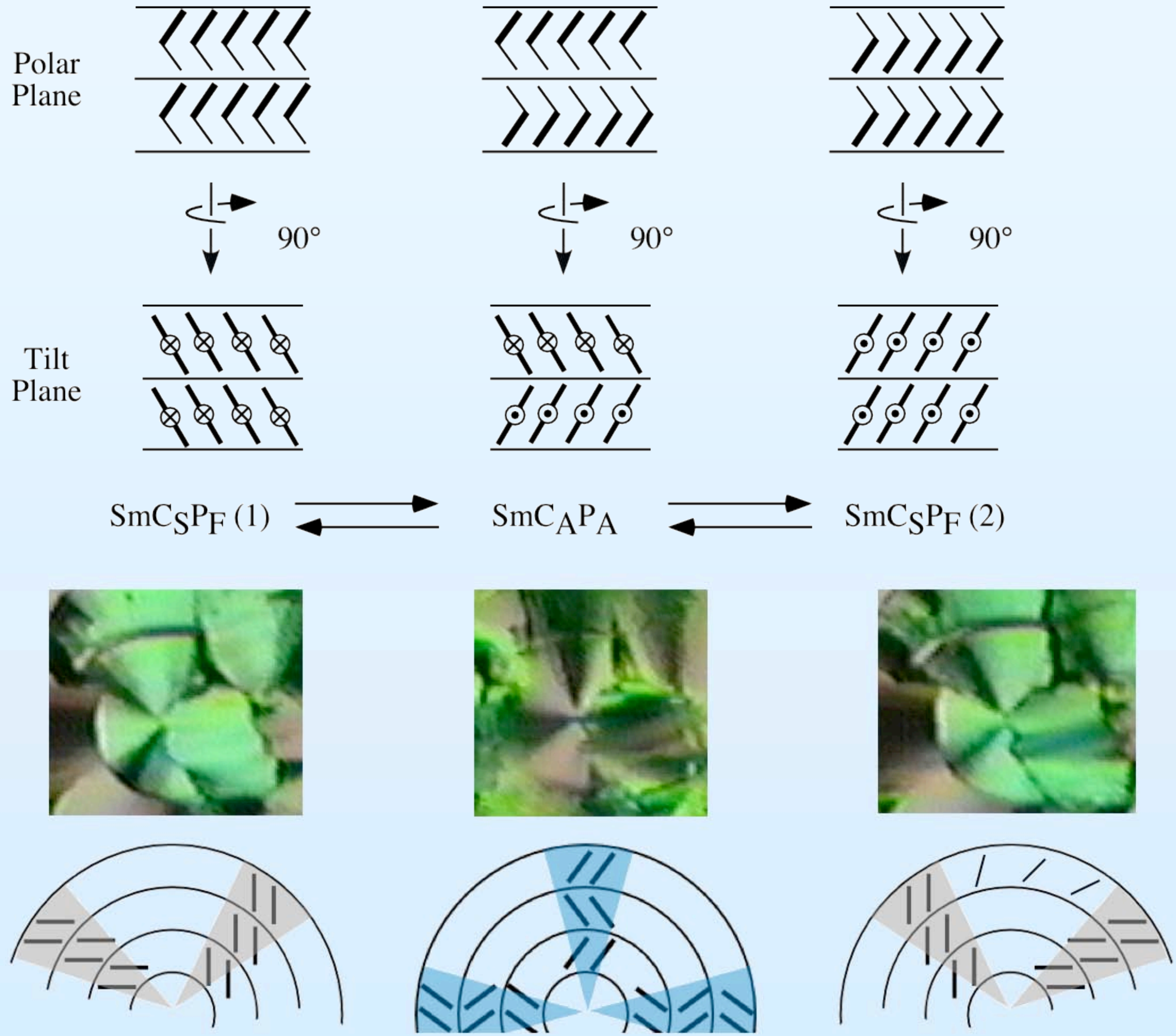


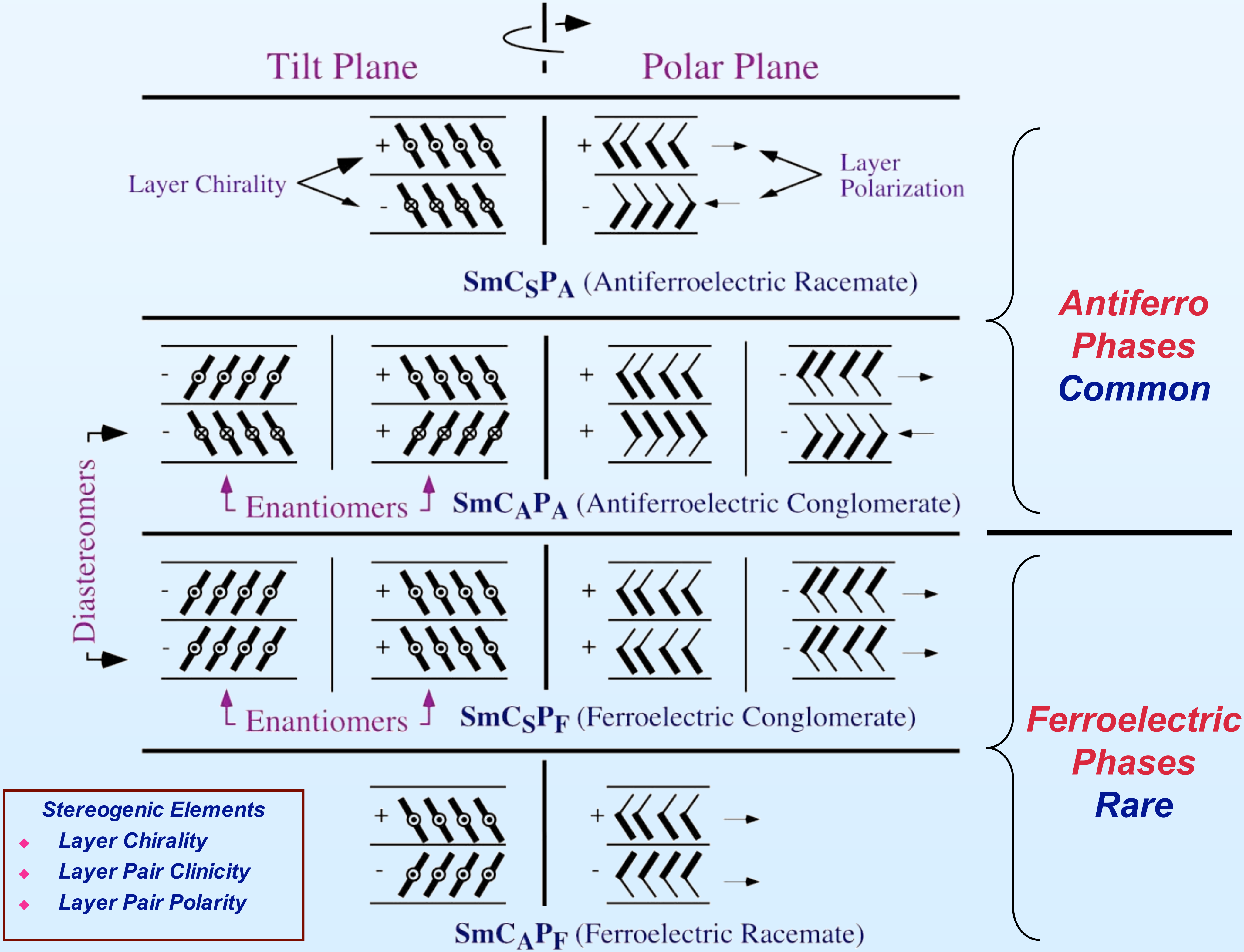
Anticlinic Antiferroelectric

The B2 Conglomerate is Antiferroelectric



(-) NOBOW Antiferro EO Switching



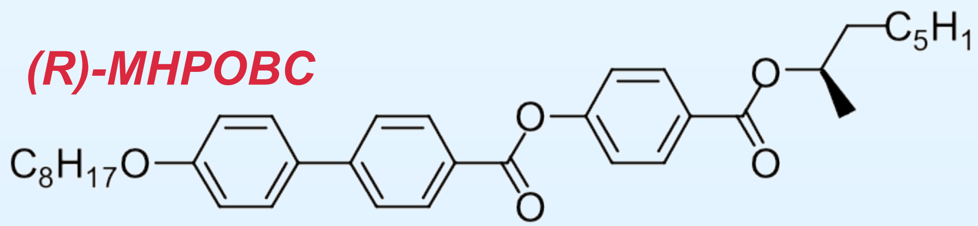


Tilt Plane
Polar Plane
Layer Chirality
Layer Polarization
SmC_SP_A (Antiferroelectric Racemate)
Enantiomers
SmC_AP_A (Antiferroelectric Conglomerate)
Diastereomers
Enantiomers
SmC_SP_F (Ferroelectric Conglomerate)
SmC_AP_F (Ferroelectric Racemate)
Antiferro Phases Common
Ferroelectric Phases Rare
Stereogenic Elements
Layer Chirality
Layer Pair Clinicity
Layer Pair Polarity

A Ferroelectric Banana?

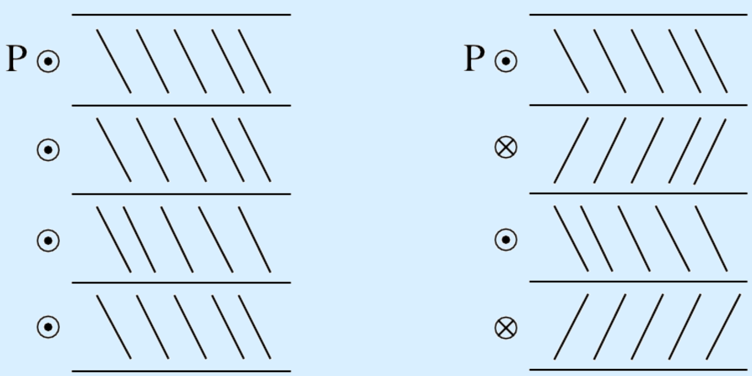
- *Most calamitic chiral smectics are ferroelectric (antiferroelectrics are very rare)*
- *Most bananas are antiferroelectric*
- *Glaser theory: Syn-clinicity is favored entropically due to out-of-layer fluctuations*
- *Suppression of OLFs by the molecular structure allows anticlinic layer interfaces to appear in the phase sequence.*
- *By far the best way to achieve this: The famous MHOC tail*
- *The SmC_A anticlinic phase occurs in both unichiral and racemic MHPOBC*

(R)-MHPOBC



X 84 C_A* 118 Cγ* 119 C* 121 Cα* 122 A 148 I

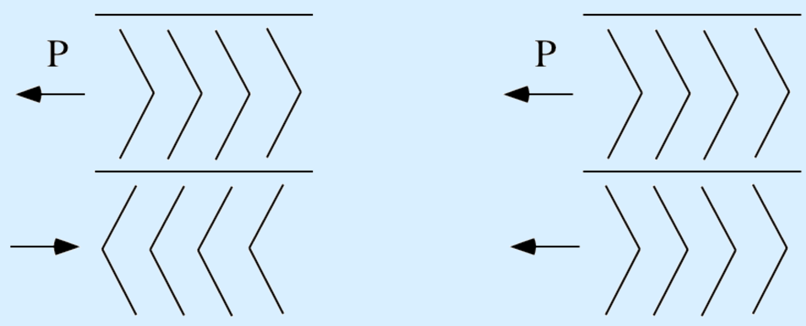
Calamitic Smectics



*Ferroelectric SmC**
Common

*Antiferro SmC_A**
Rare

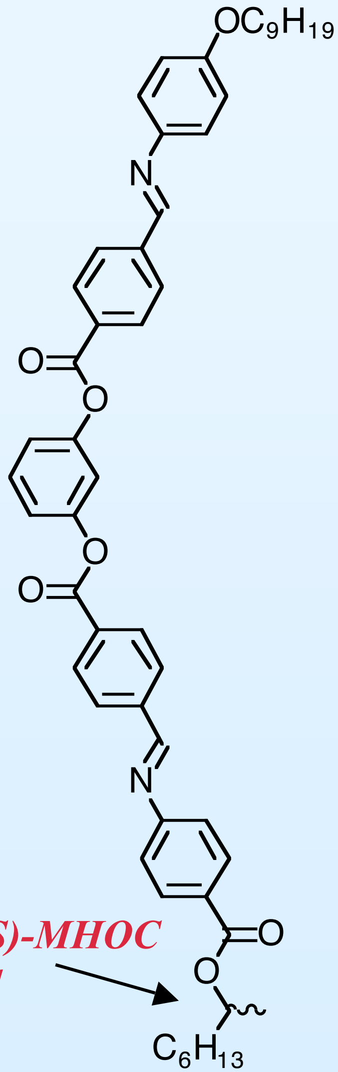
Bananas



Antiferro SmC_SP_A
Common

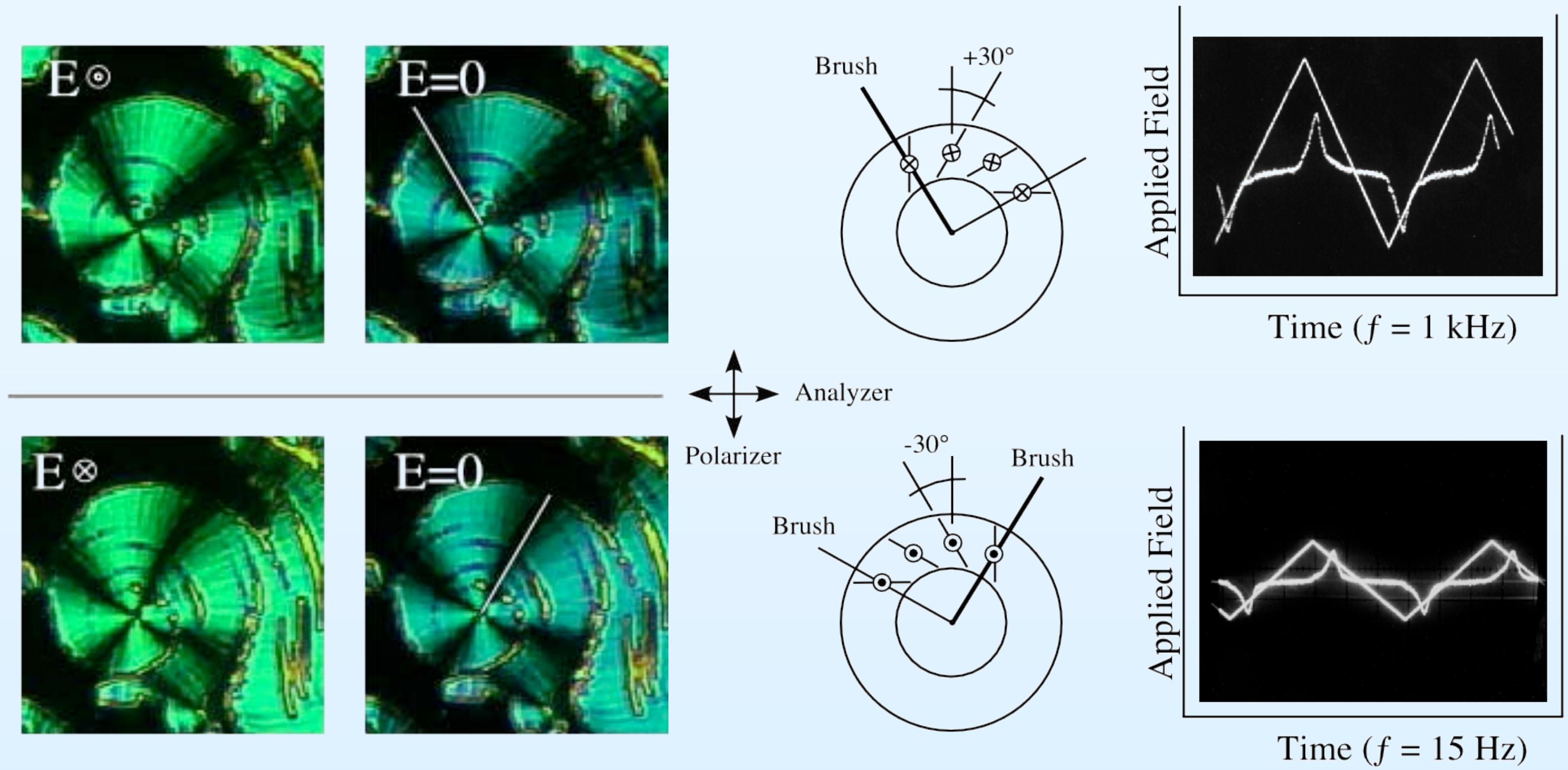
Ferroelectric SmC_SP_F
Rare

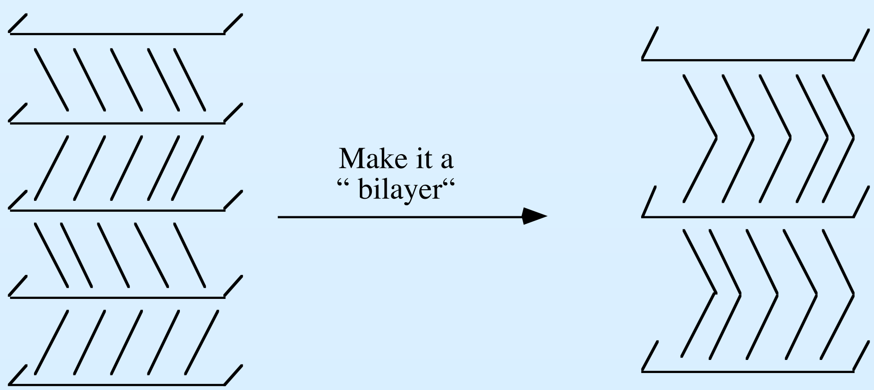
MHOBOW: A SmC_SP_F by Control of Clinicity



(R,S)-MHOC Tail

B4 $\underset{90}{\overset{120}{\rightleftharpoons}}$ B7 $\overset{139}{\rightleftharpoons}$ Iso

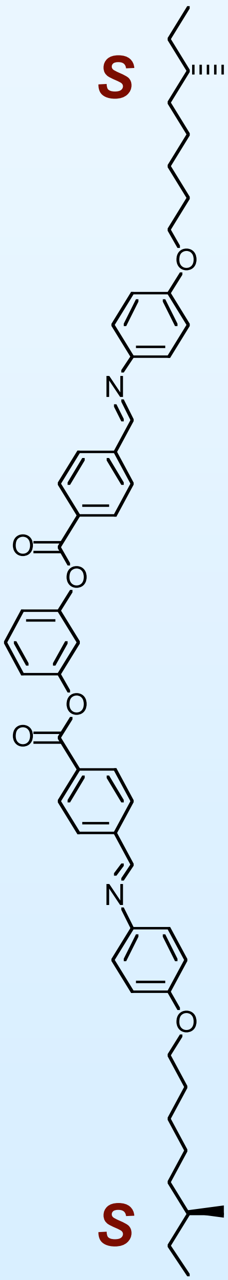




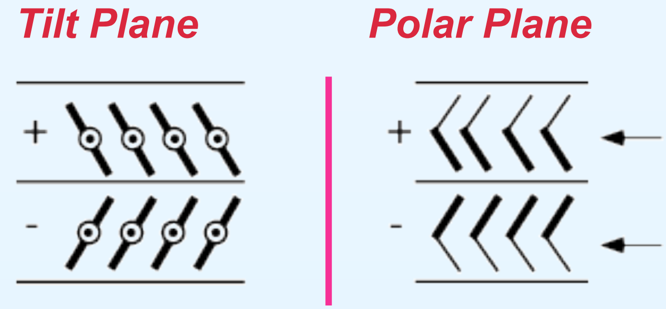
Tilt plane of SmC_A

Bow plane of SmC_SP_F

The Amazing KYOBOW from Tokyo Tech!

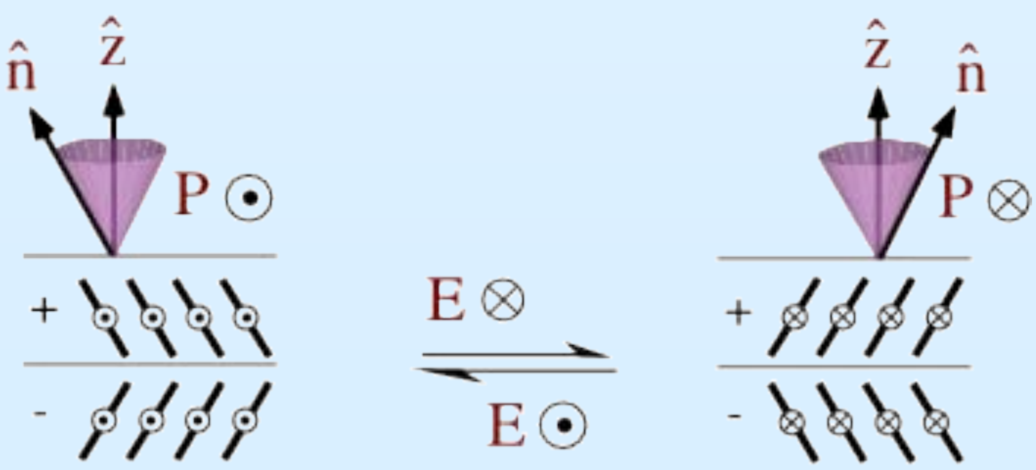


$$X \overset{146.8}{\rightleftharpoons} Sm_Y \underset{147.4}{\overset{154.8}{\rightleftharpoons}} SmC_AP_F \overset{154.9}{\rightleftharpoons} Iso$$



KYOBOW is Unichiral, but forms a SmC_AP_F Ferroelectric Racemate!

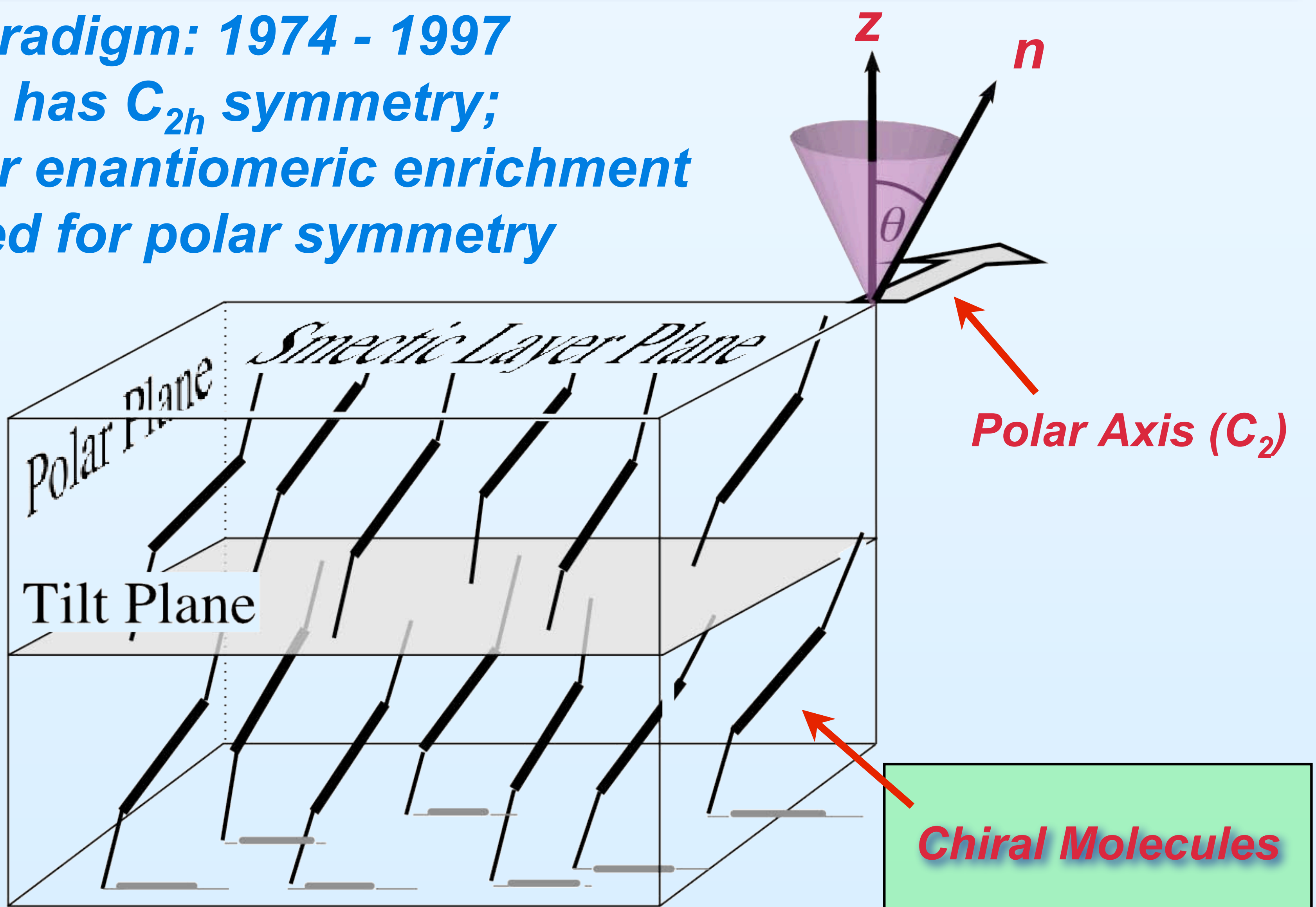
- *Minority domains are a conglomerate showing the chiral EO of a SmC_SP_F phase.*
- *Majority domains show no EO switching, but a strong ferroelectric polarization reversal current.*
- *Focal conic domains are immiscible with the NOBOW SmC_SP_A phase in the absence of a field, but become miscible upon application of a field, where both materials are in the SmC_AP_F structure.*



H. Takezoe
J. Watanabe
M. Nakata
D.R. Link
Et al

The SmCP Story was an FLC Paradigm Shift

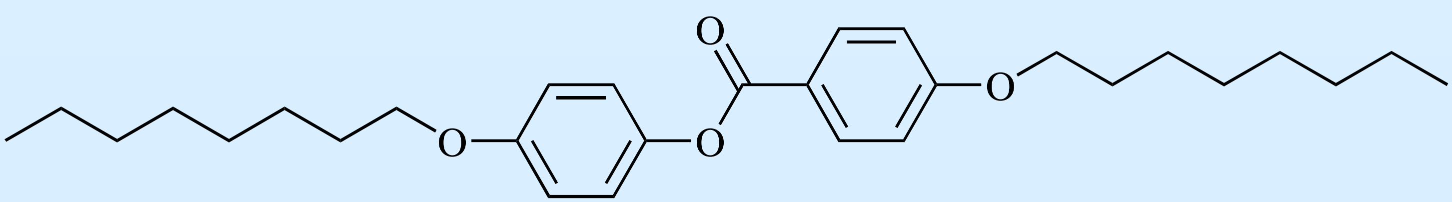
Meyer paradigm: 1974 - 1997
The SmC has C_{2h} symmetry;
molecular enantiomeric enrichment
is required for polar symmetry



Tilt Plane ≡ Normal to C_2
Polar Plane ≡ Contains C_2 and z

FLC Paradigm Shifting Runs Amuck

- **Claims of parity violation**
  - Goodby 2005 Chem. Commun. (unichiral FLC from a racemate)
  - Goodby 2001 J. Mater. Chem. (unichiral FLC from achiral mesogen)
- **Claims of spontaneous reflection symmetry breaking**
  - Kishikawa 2005 JACS (achiral calamitic phenylbenzoate makes a chiral SmC phase!)
  - Niori 2004 MCLC (chiral nematic from an achiral bent-core mesogen)
  - Takezoe and Watanabe 2002 JACS (doping an achiral bent-core mesogen into a chiral nematic tightens the pitch)
  - Takezoe 1999 Angew. Chem. IE (spontaneous de-racemization of enantiomers in a SmC)
  - Komitov 1998 Liq. Cryst. (chiral nematic from achiral mesogen)



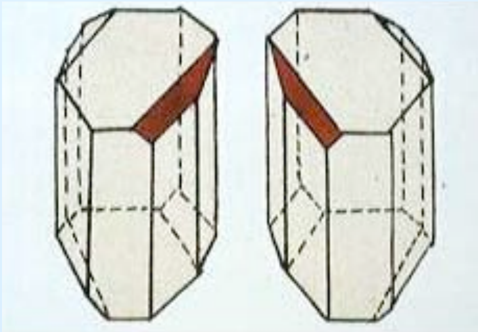
The conformational chirality hypothesis in LCs

Mauguin's Twisted Nematic

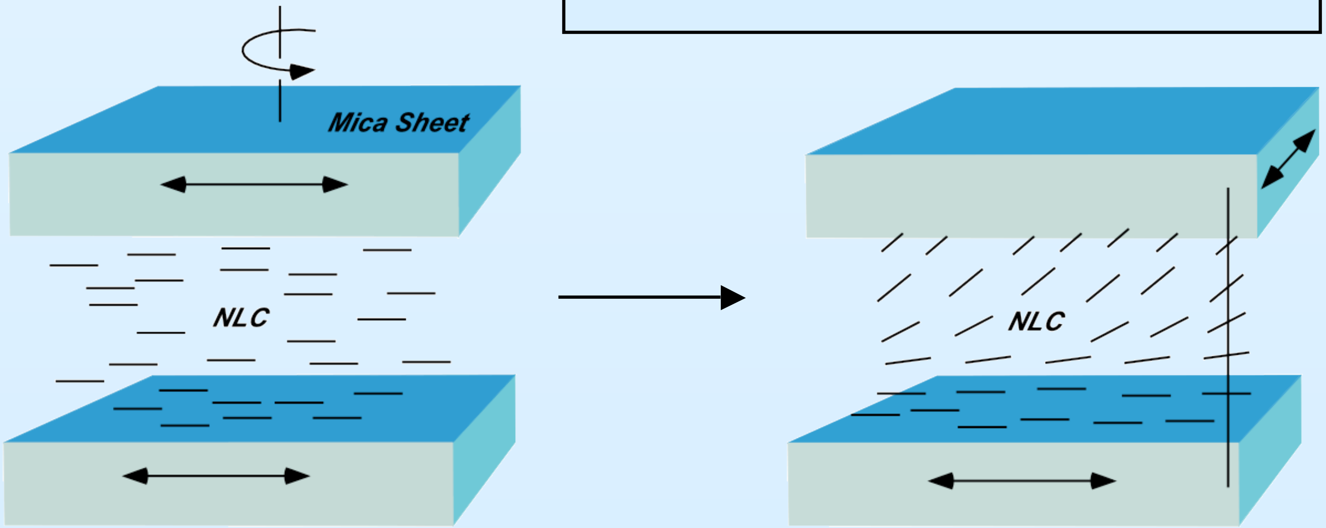
Louis Pasteur

Charles Mauguin

- Spontaneous reflection symmetry breaking in LC systems driven by surface constraints is very common.
- But, no chiral LC phase from achiral or racemic molecules had been seen.
- Observation of a chiral LC phase is often used as proof of molecular enantiomeric excess.

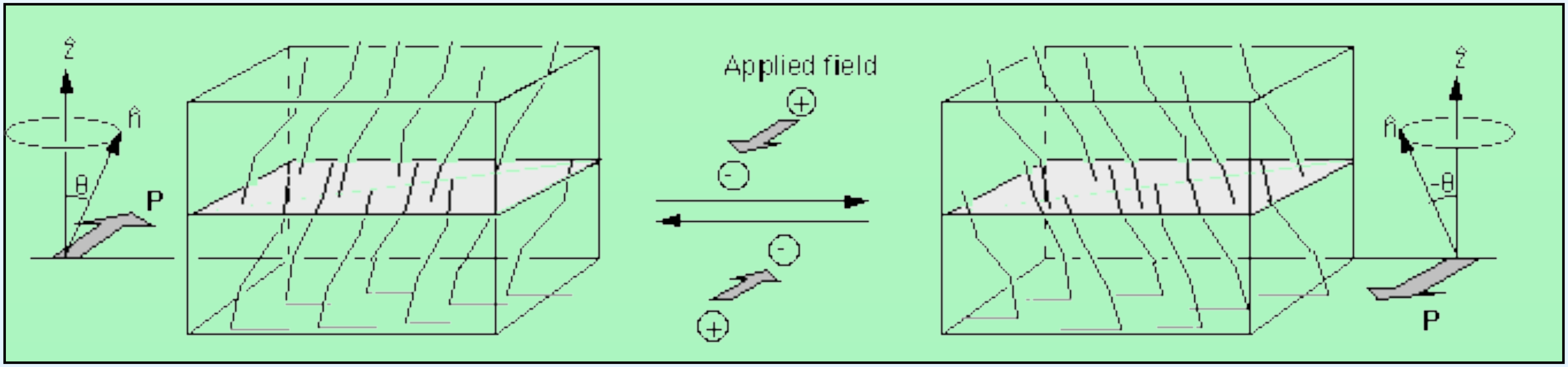


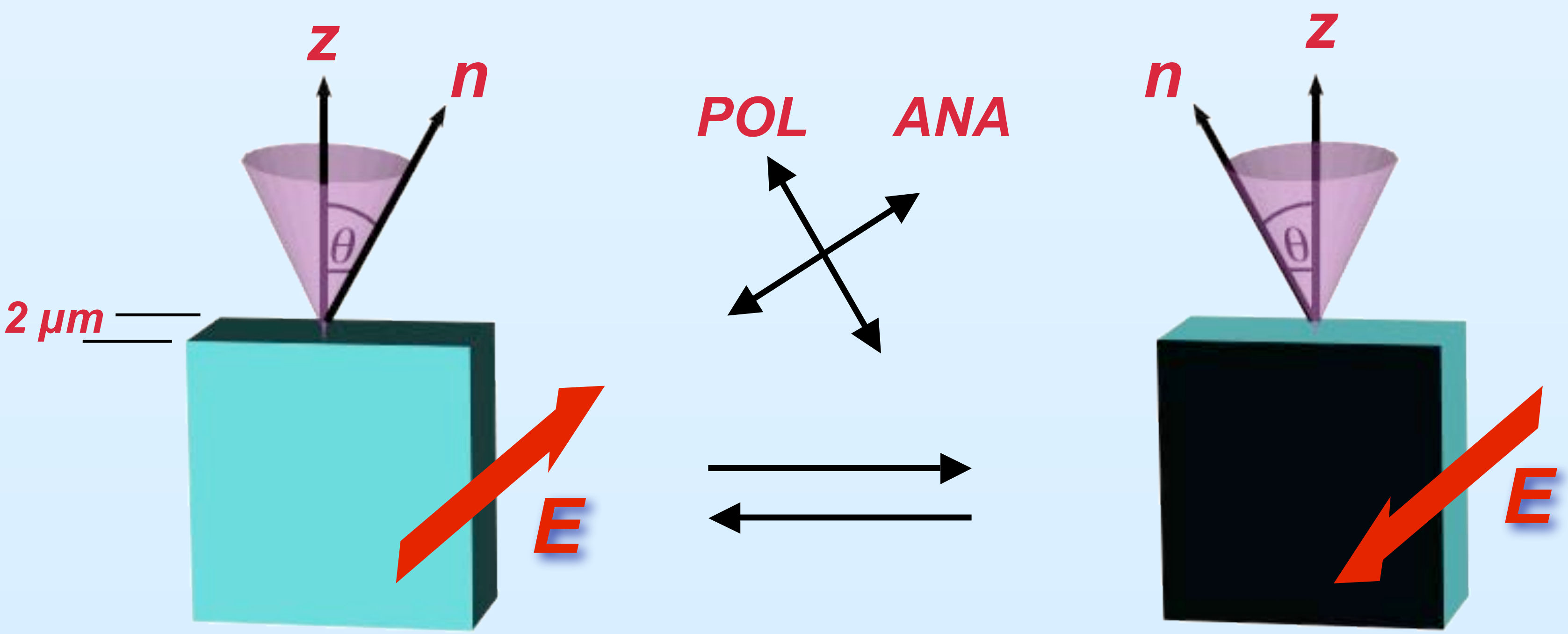
Chiral Sodium Ammonium Racemate Crystals, 1848



Mauguin's Twisted Nematic Liquid Crystal, 1911

Unichiral SSFLC Electro-optics





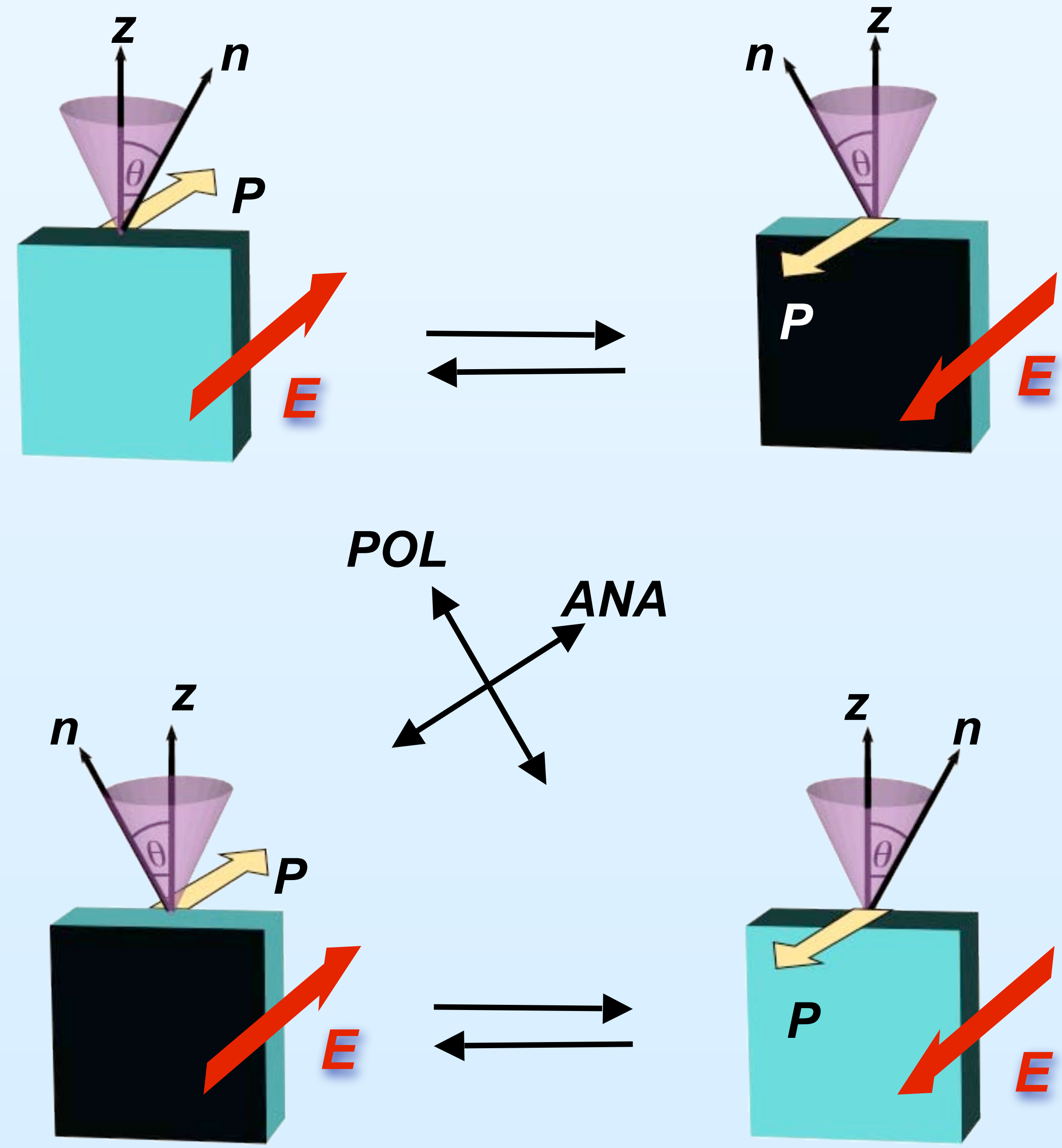
P > 0 (right-handed)

Enantiomeric EO Response

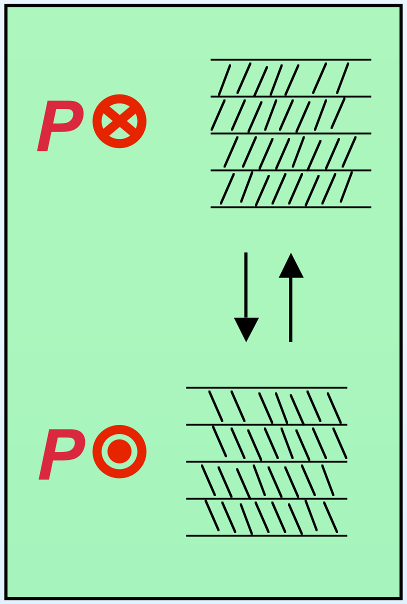
P > 0 (right-handed)

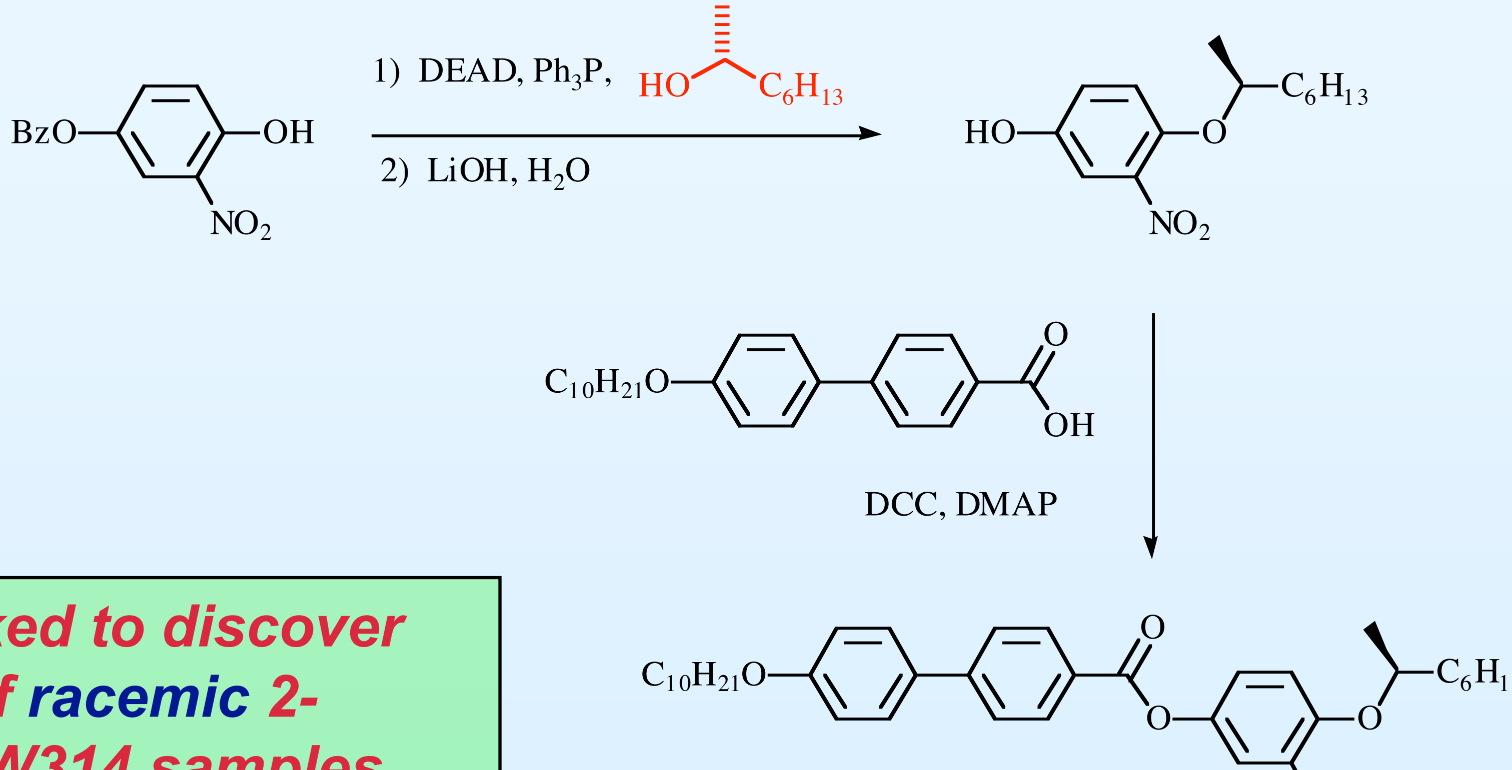
$$P = f(ee)$$

P < 0 (left-handed)



Weird Observation from the '90s





(S)-W314

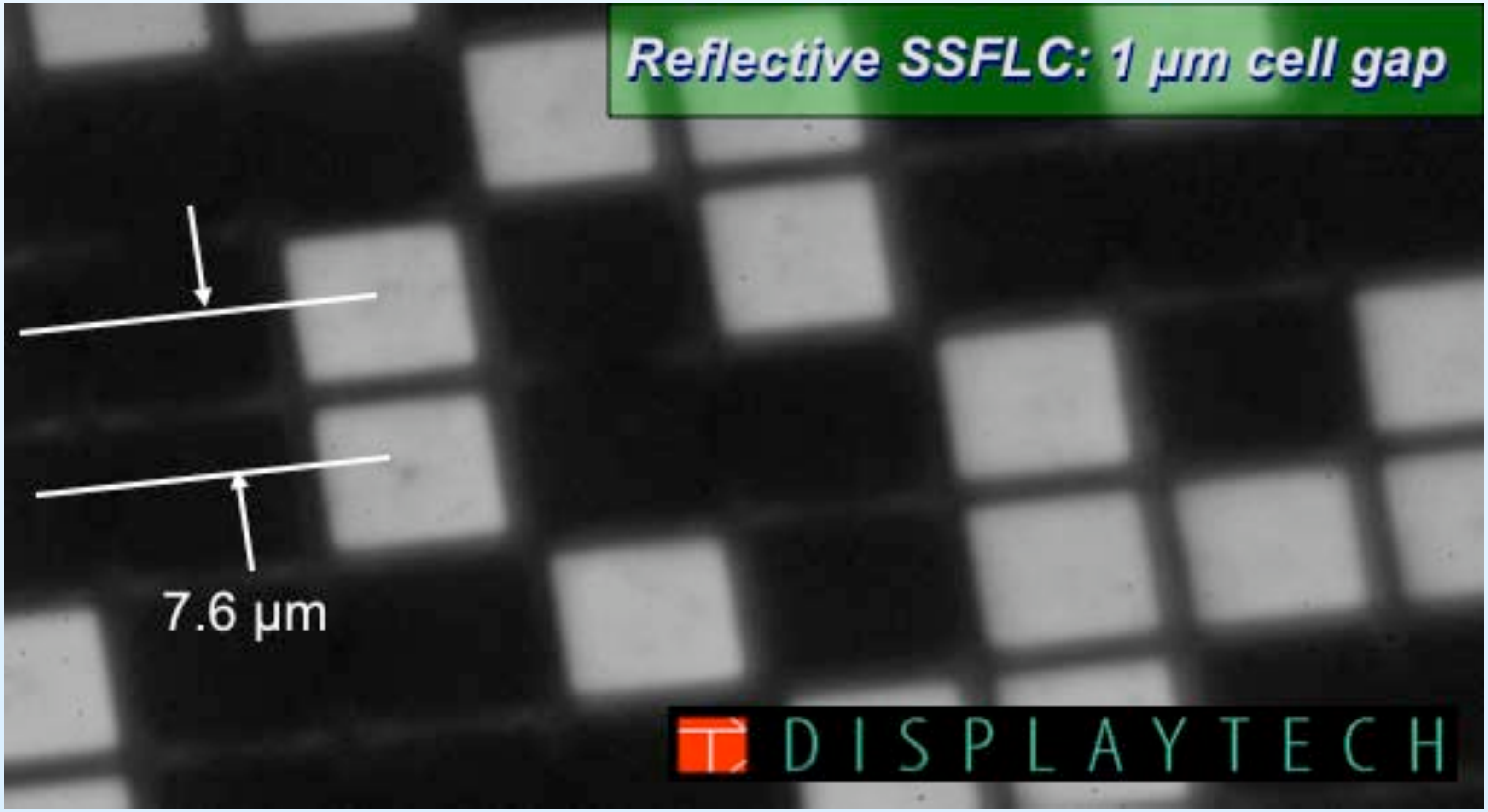
P ~ -500 nC/cm²

*We were shocked to discover that samples of **racemic 2-octanol** led to W314 samples showing **unichiral** electro-optics in SSFLC cells!*

Response suggests ~0.3% ee?

- ***Parity violation? We think NOT.***
- ***SSFLC switching is one of the most sensitive detectors of chirality...***

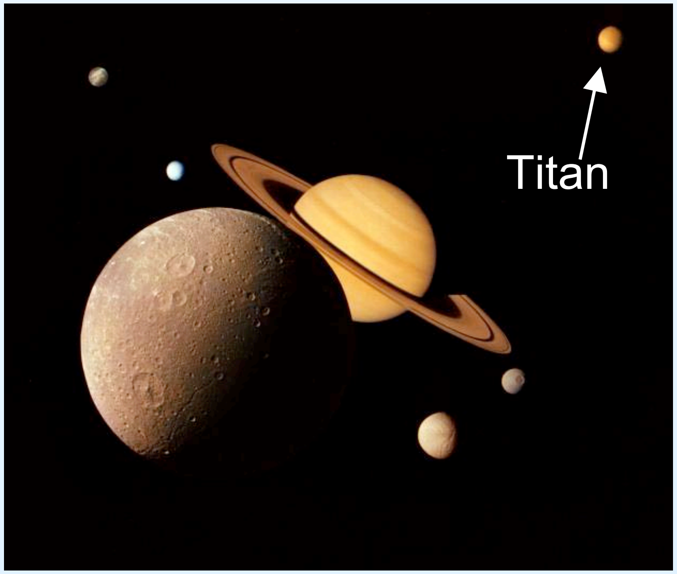
…and the Volume of Material in the Pixels is Small

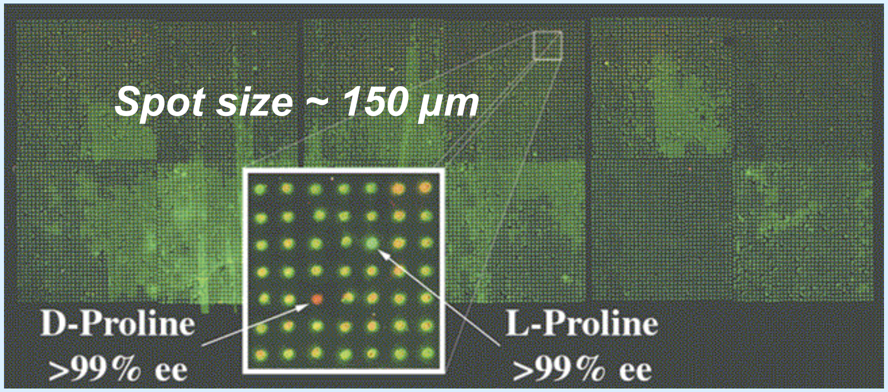


Pixel volume as small as 25 µm^3 = 25 Fl ~ 25 pg

…Suggests Possible New Applications

- Search for enantio-enrichment on Titan
  - Requires fast, high sensitivity method for sensing ee remotely
- Chirality detectors for combinatorial asymmetric catalyst development
  - Key to development of asymmetric catalysts using combinatorial methods
  - Requires high throughput and good discrimination in the 50% - 100% ee range
  - Conventional method: 15,000 analyses in several months by HPLC
  - Current published state of the art: 15,000 analyses in 48 hrs using reaction microarrays





The Harvard chirality detector

M. Shair et al. J. Am. Chem. Soc., 123, 361 (2001)

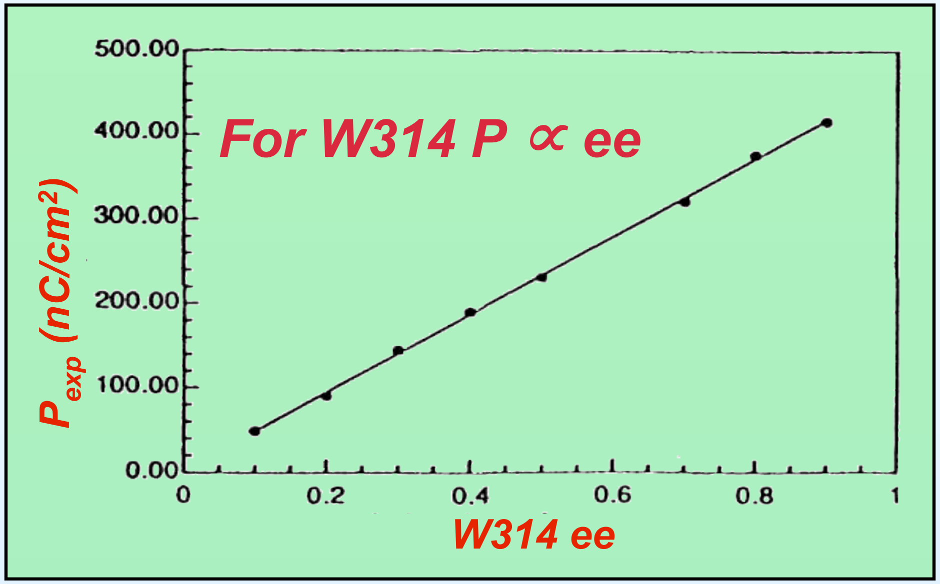
First Approach to FLC Chirality Detector

- Pick an achiral or racemic SmC host (e.g. racemic W314)
- Dope with sample of unknown ee
- Determine ee using SSFLC electro-optics
- Adapt the method for use in a large array of physically separated pixels

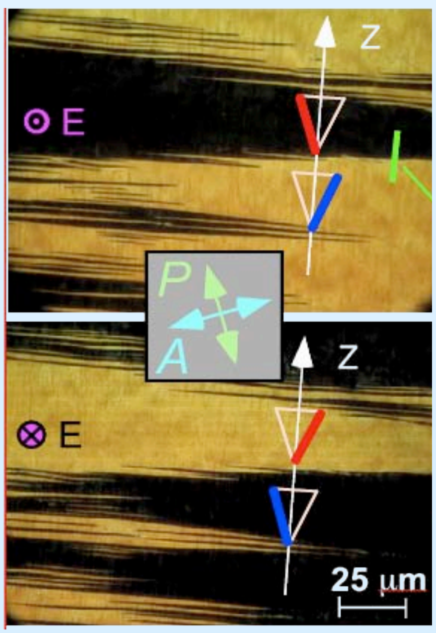
$$\tau = \frac{\eta}{P * E}$$

$$P = f(ee)$$

Behavior of the Authentically Racemic Host is Surprising

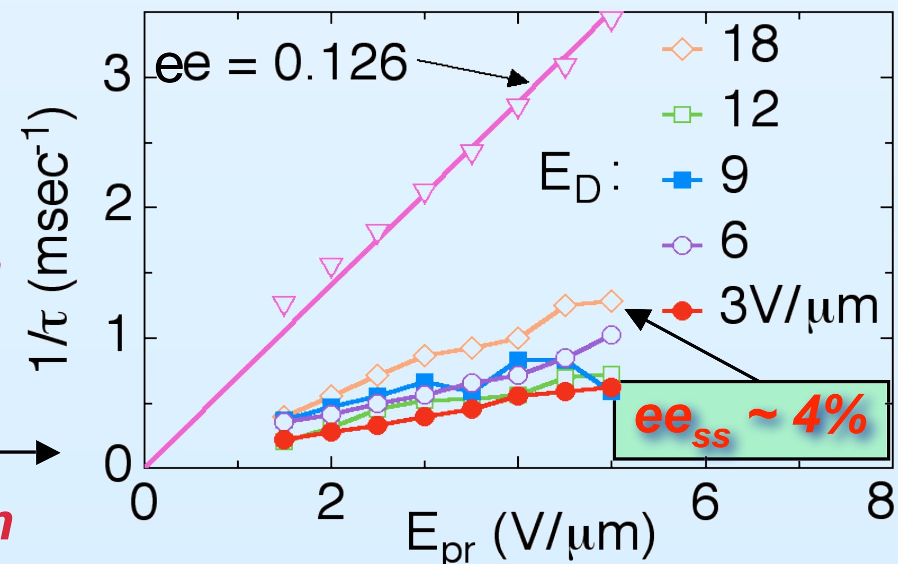


- **The EO response of authentic rac-W314 is complex**
  - ***After a few hours under drive, chiral domains can be observed***
  - ***After a month under drive, the entire sample segregates into two heterochiral domains***



Hetereochiral domains formed in rac-W314 ←

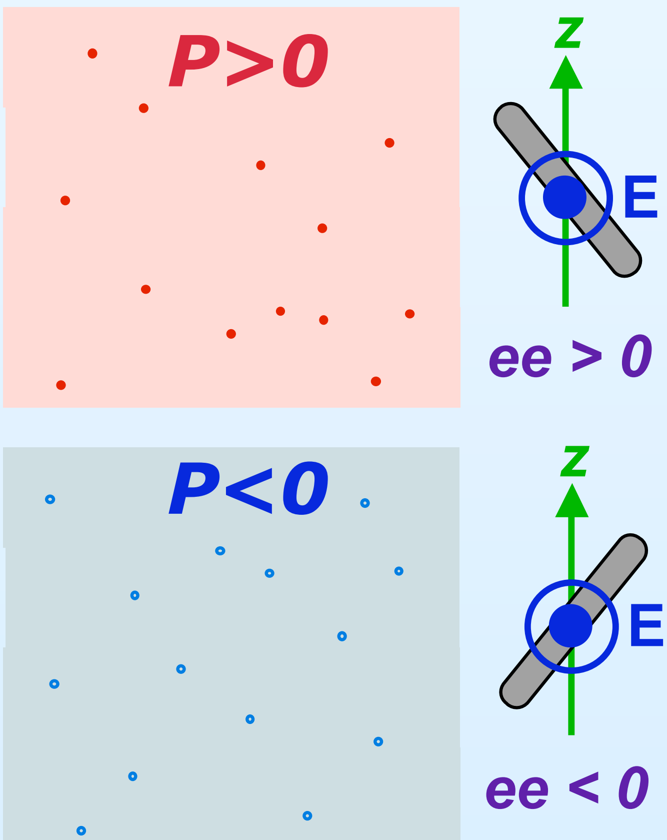
Determination of ee in domains from careful risetime measurements →

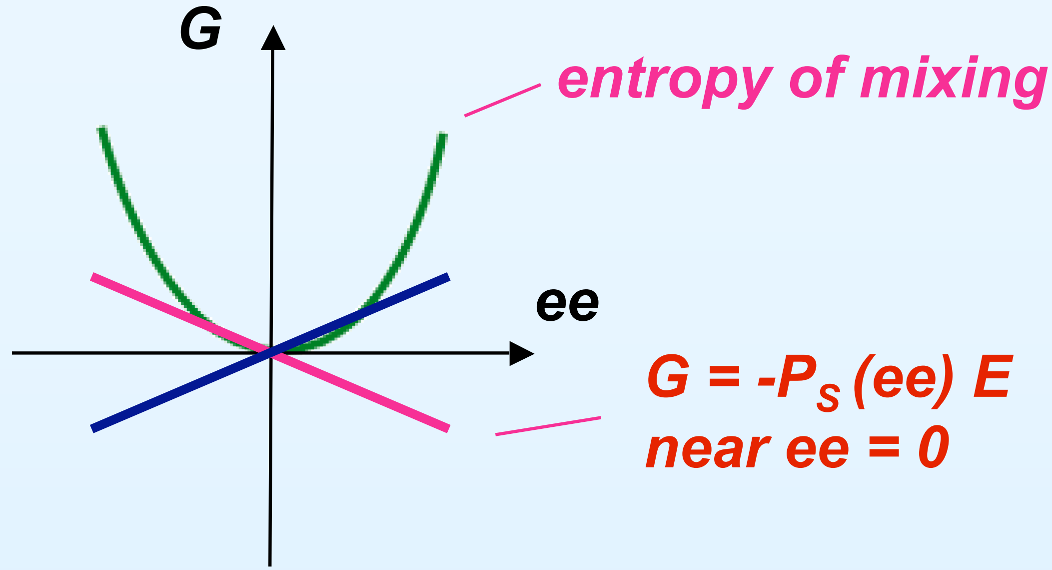


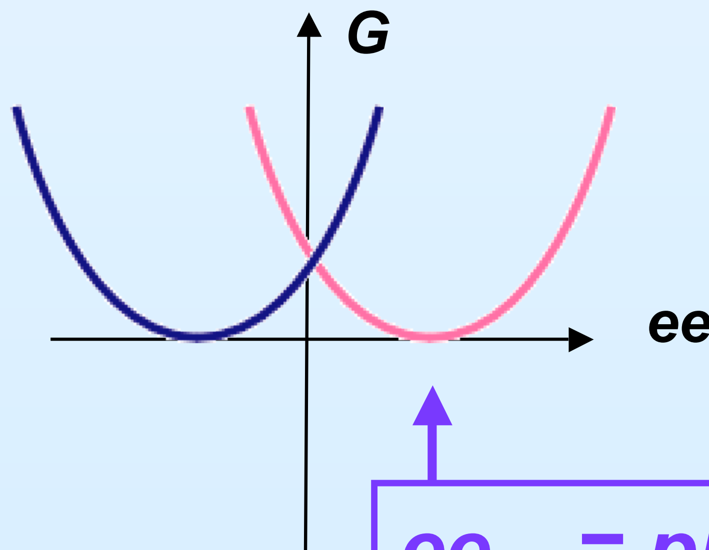
$$\frac{1}{\tau} = \left(\frac{P}{\eta}\right) E$$

PE Can Drive Partial Deracemization (~4% ee)

"extras" in a smectic C







$ee_{ss} = pE/\, k_B T$

$p = P_S$ /molecule

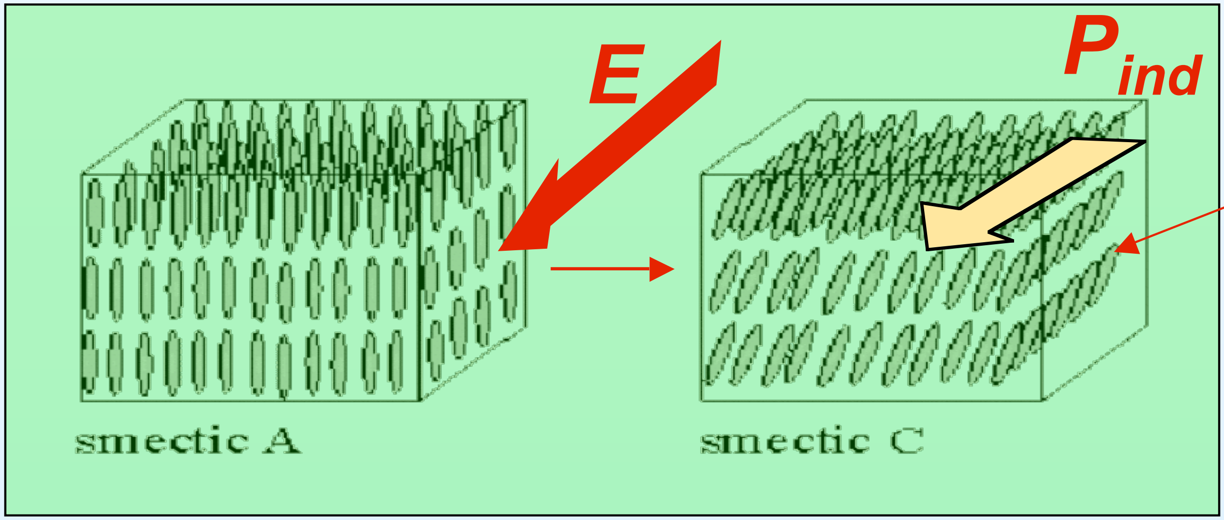
In the presence of a field

$G = -P_s\,(ee)\,E + 1/2\, kT\, ee^2$

For Chirality Detector SmC is Problematical
G2 Approach: Electroclinic Chirality Detection

- *E-field induced deracemization is cool, but chirally doped racemic W314 is not useful for measurement of ee in our hands*
- *Preliminary work using achiral SmC hosts uncovered several other interesting complexities (i.e. it doesn't work)*
- *Can the electroclinic effect in doped achiral SmA hosts produce a useful chiral signal?*

The Electroclinic Effect in the SmA*



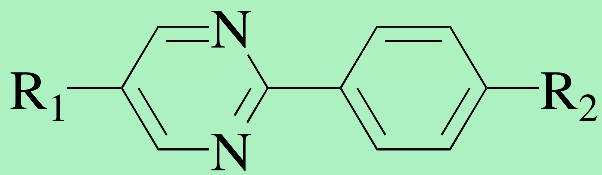
Effectively an E-field induced SmC with collective polarization*

Only happens with chiral liquid crystal

- *Bob Meyer also predicted the electroclinic effect in SmA* materials*
- *At E = 0 there is no net tilt in a SmA**
- *Due to free energy gain from combining an applied E field with the collective polarization in tilted chiral smectics, a tilt is induced in the SmA* with applied E*
- $\theta \propto E$ *for small E*

Doping a SmA Host (EK992)

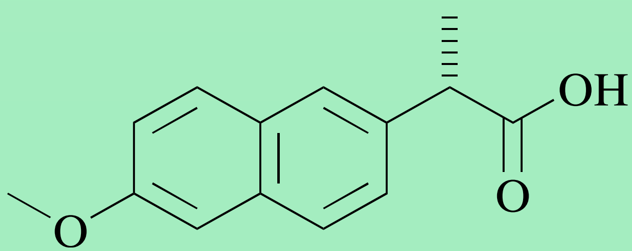
Host: EK992



80% $R_1 = C_8H_{17}$; $R_2 = OC_6H_{13}$
5% $R_1 = C_8H_{17}$; $R_2 = OC_{12}H_{25}$
15% $R_1 = C_{10}H_{21}$; $R_2 = OC_6H_{13}$

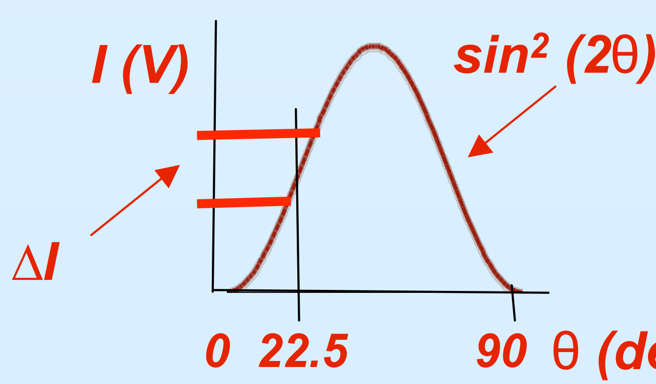
SmC - 43 - SmA - 59 - N - 65 - I

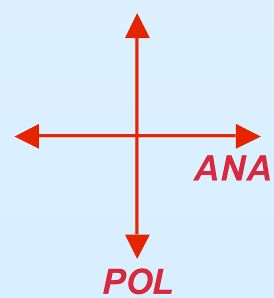
Dopant: Naproxen



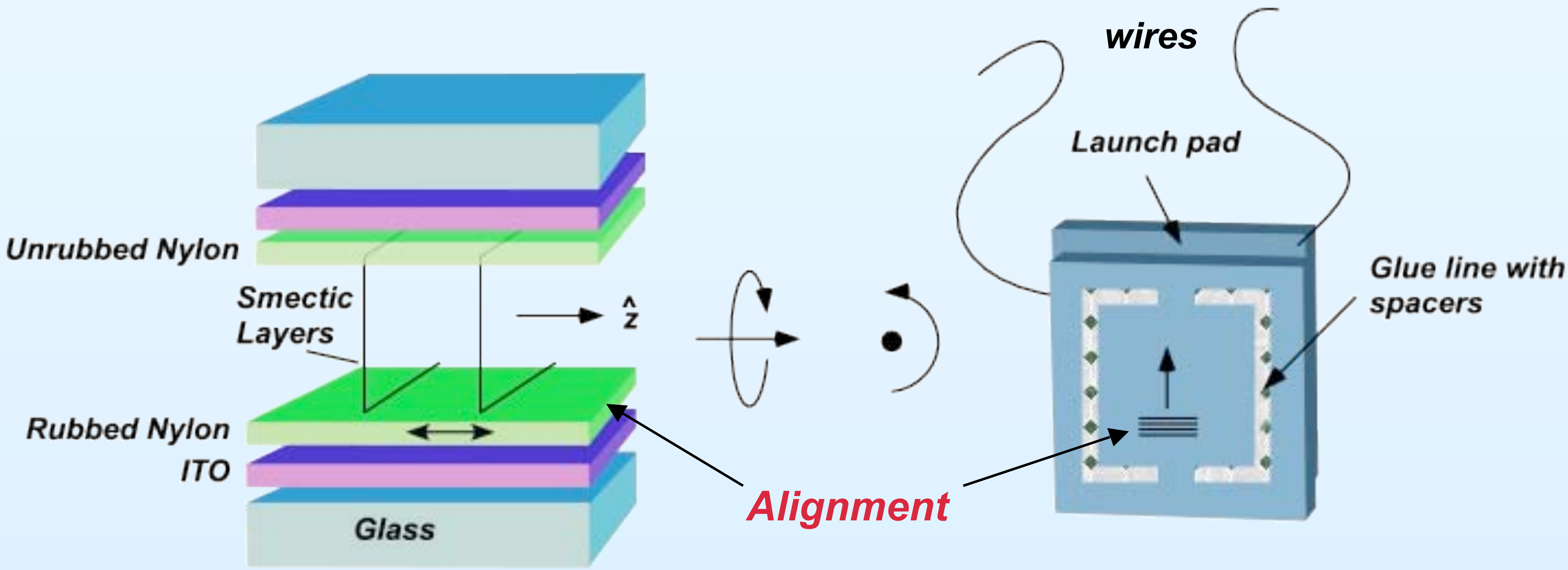
Various ee, enriched in (S)

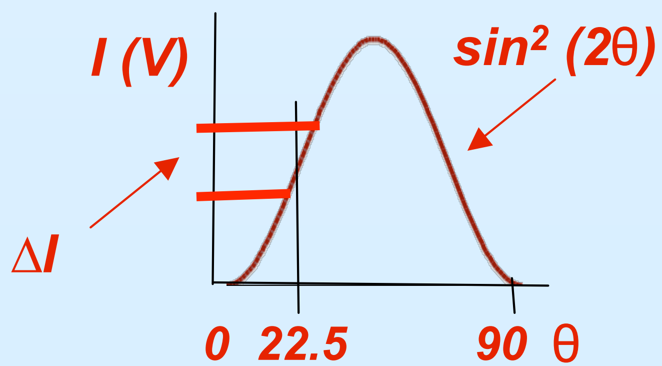
- ***The chiral signal***
  - *Electroclinic electro-optic modulation depth ΔI between crossed polarizers ($I_{E\ on}$ - $I_{E\ off}$ with the cell oriented for maximum ΔI)*
- ***Conditions of the measurements***
  - *Sample: Host doped with 1% by weight naproxen samples of various ee*
  - *EO cell: 3.7 μm gap ITO/glass with parallel-rubbed low pretilt PI alignment layers*
  - *EO measurement: V_{App} = ± 10V square-wave drive @ 1KHz, HeNe laser probe (spot size 20 x 20 μm), I measured with a photodetector (V)*

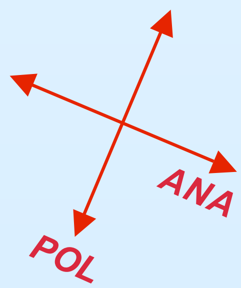




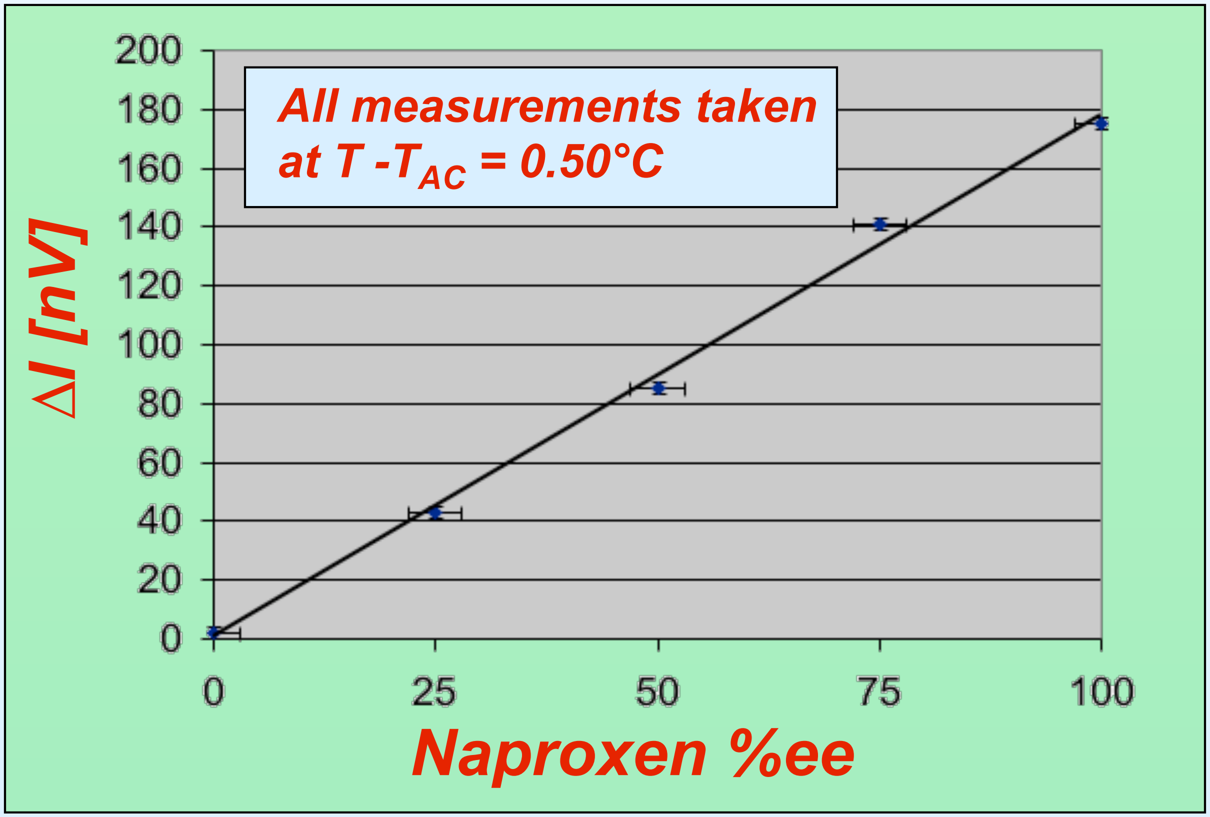
A deVries Cell

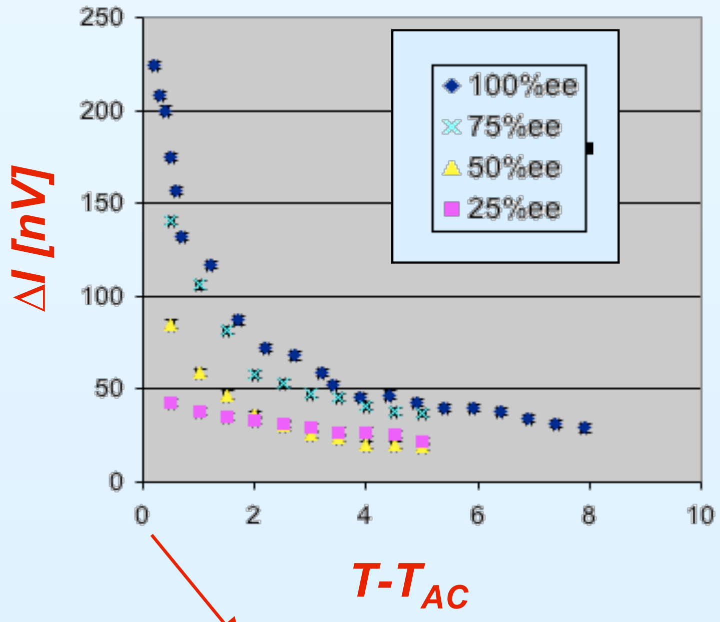






Data Obtained with EK992 Host





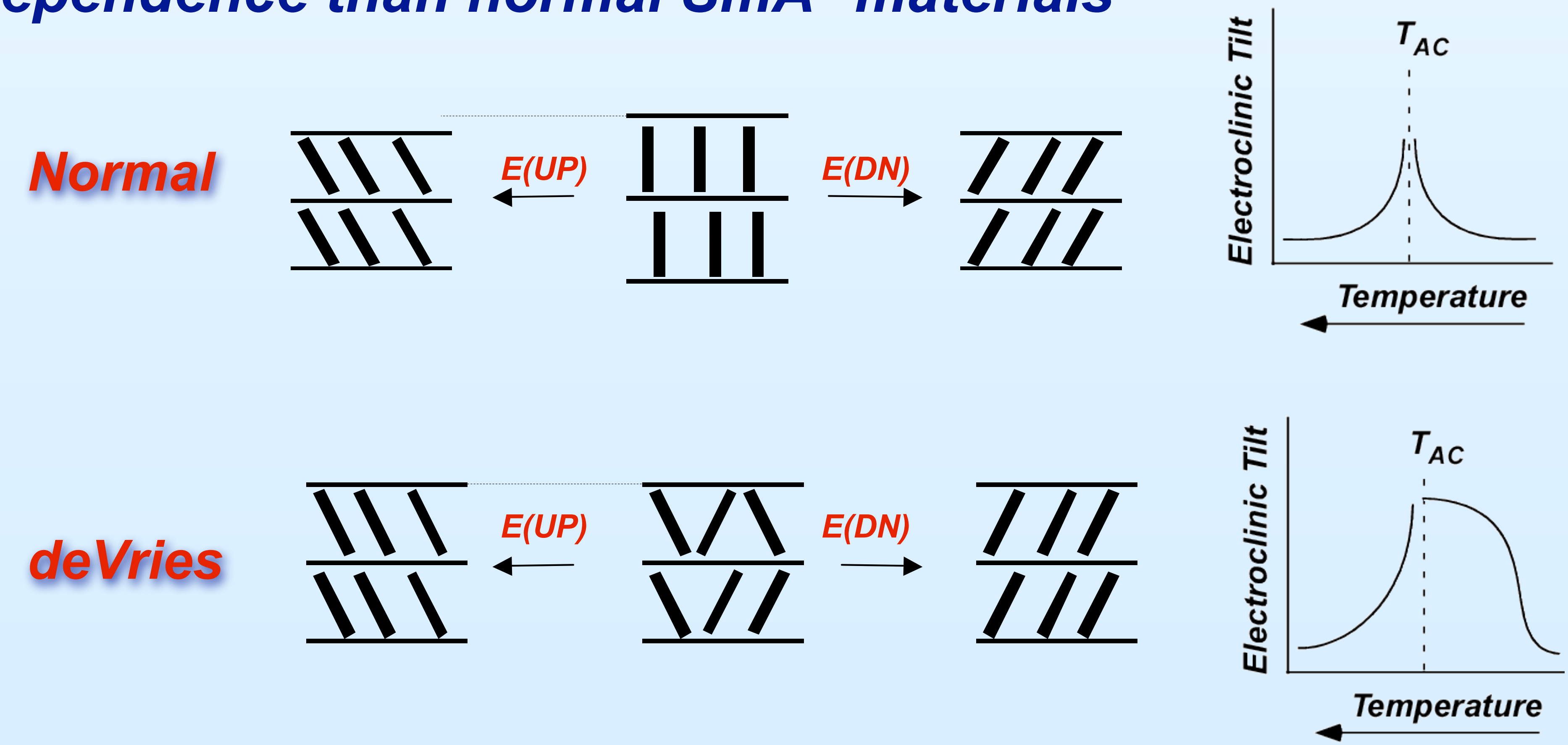
The good news: The chiral signal provides a good measure of naproxen ee.

The bad news: T_{AC} is different for each sample. Since the electroclinic effect is strongly dependent upon reduced temperature, the data had to be taken at a constant reduced temperature, which was a different absolute temperature for each sample.

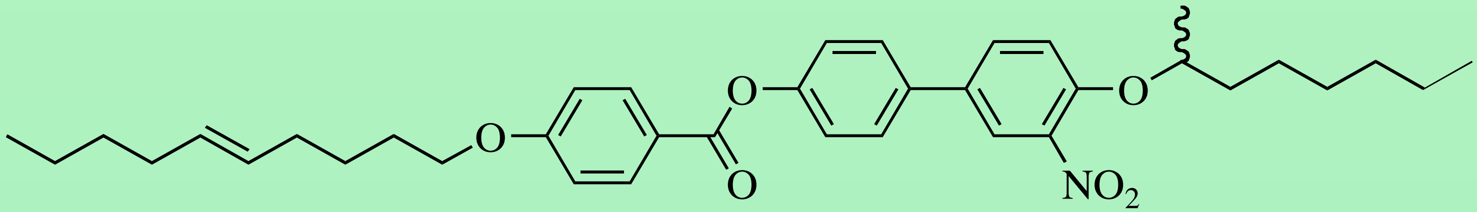
This method cannot be applied to a high throughput measurement device.

deVries Smectics to the Rescue

- For "normal" SmA* materials the electroclinic tilt is small, and highly dependent on $T\text{-}T_{AC}$
- deVries SmA* materials (very rare) in general seem to show a much larger tilt, and much less temperature dependence than normal SmA* materials



Host W435 (a deVries material)



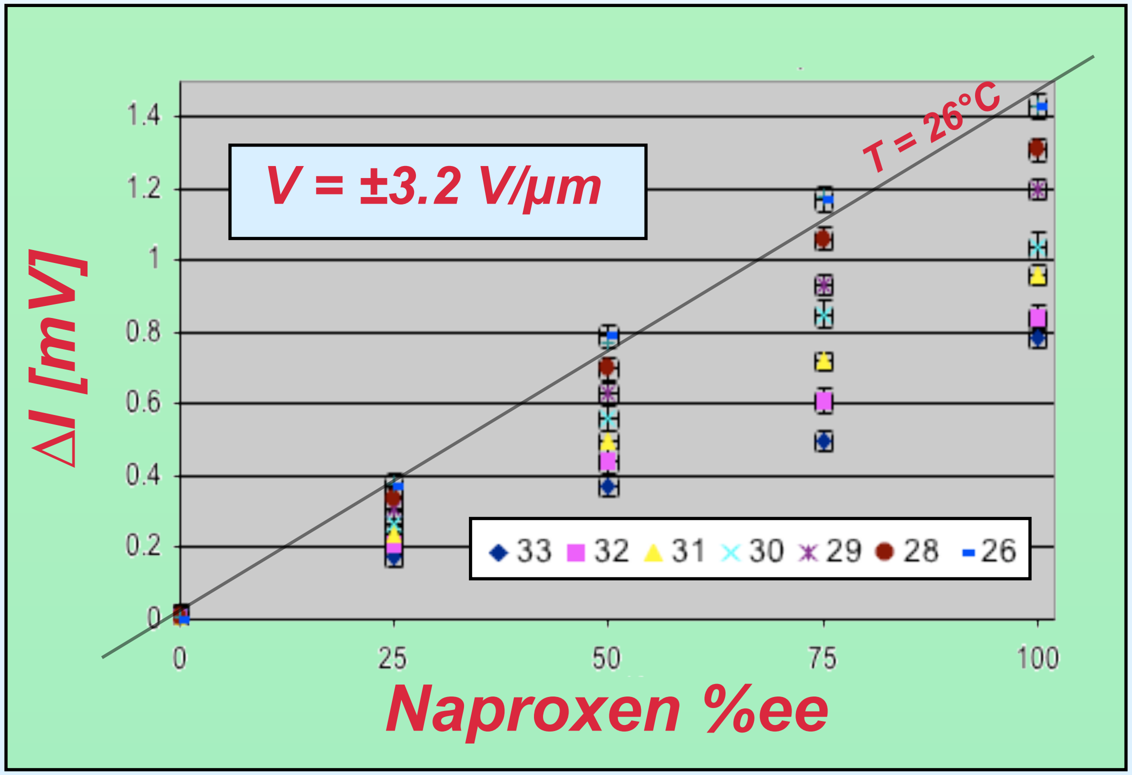
W435 (racemic W415)

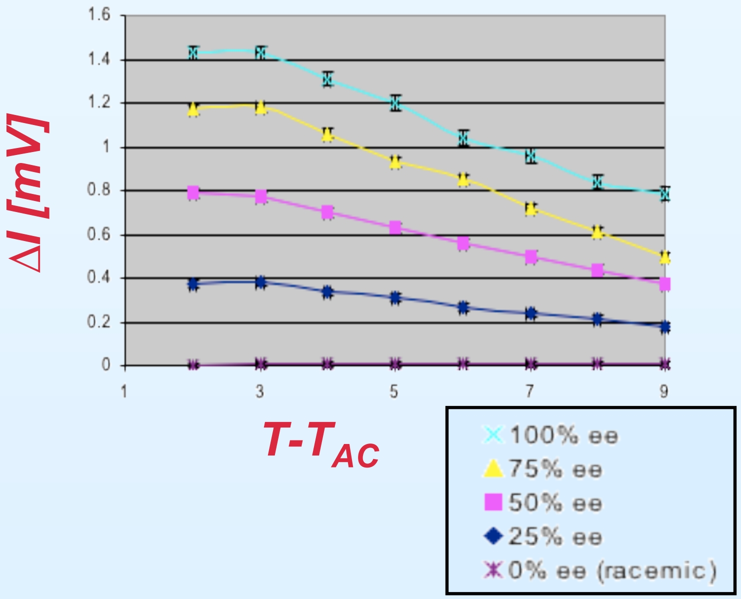
SmC - 24 - SmA - 33 - I

- **Conditions used for the measurements**
  - *Host doped with 1% by weight of several naproxen samples of various ee*
  - *Sample filled into an ITO/glass LC cell with one rubbed and one unrubbed nylon (elvamide) alignment layers*
  - *ΔI measured as before*

This method can be amazingly sensitive (W415 of ~ 0.01 % ee detectable)

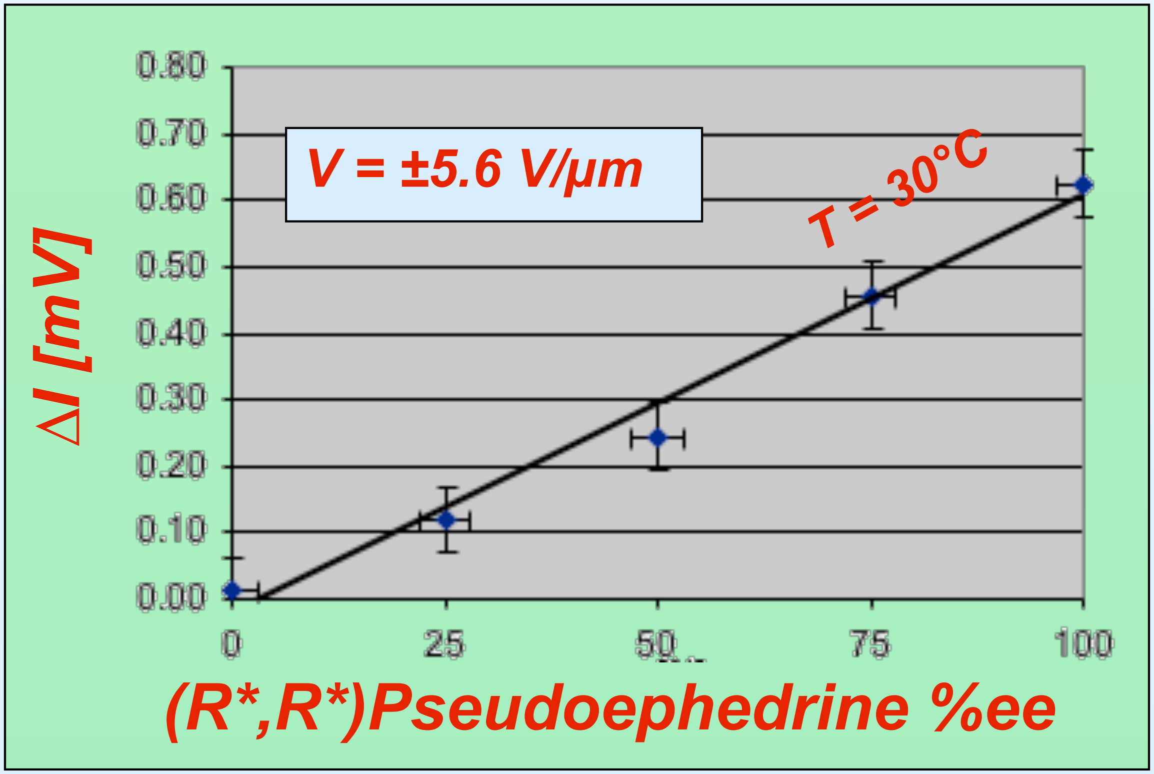
Method works at a single temperature





- *Chiral signal from 1% Naproxen in achiral deVries SmA host*
- *Measurement good to about ± 5% ee*
- *Signal from about 10 pgm of Naproxen*
- *Adaptable to really high throughput measurement of ee*

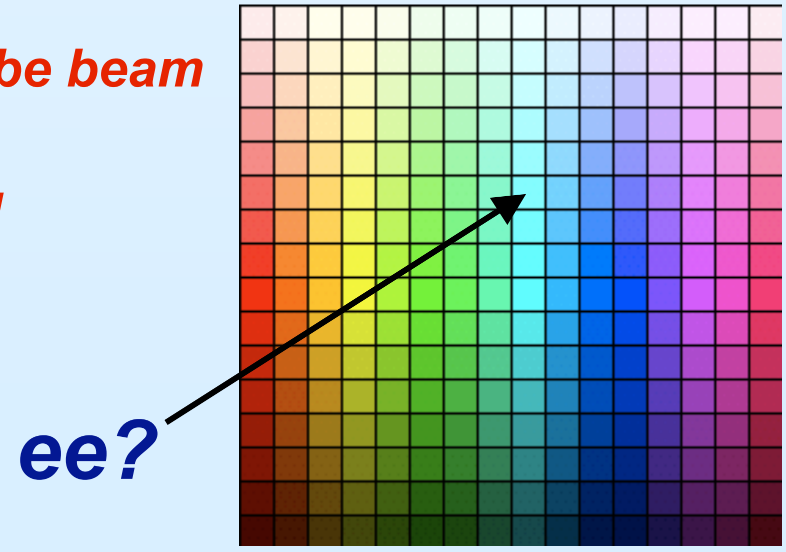
Results with Pseudoephedrine



- *1% by weight pseudoephedrine in W435 gives a smaller signal than naproxen*
- *Consistent data was difficult to obtain, due to the volatility AND insolubility of the pseudoephedrin in W435*

Conclusions

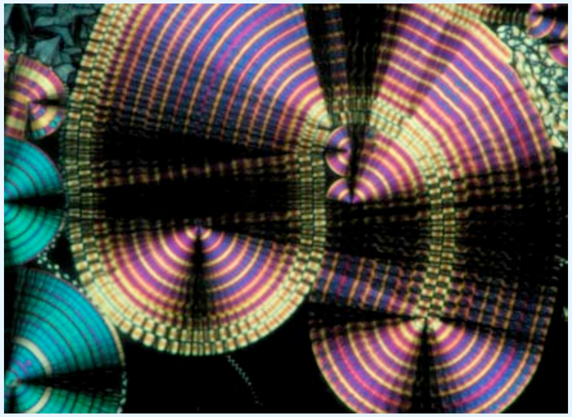
- *The achiral deVries host gives a huge signal compared to the non-deVries host*
- *The signal is linear with ee of the dopant*
- *Though the $T\text{-}T_{AC}$ was different for the mixtures, in the deVries host the signal was relatively temperature independent, allowing for measurement of the ee of multiple samples at one absolute temperature*
- *It is necessary to "scan around" the cell to find a well-aligned region*
- *This method could in principle be applied to a large number of samples in parallel (in physically separated "pixels") if uniform alignment could be obtained*
- *The actual amount of naproxen in the probe beam is ~ 10 pgm (10^{-11} gm)*
- *This method could be applied to ~ 0.25 pg (5 x 5 μm pixels)*
- *Optimization of the host is possible*

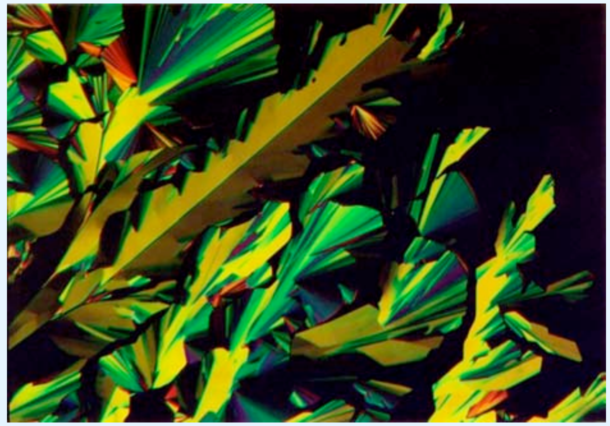


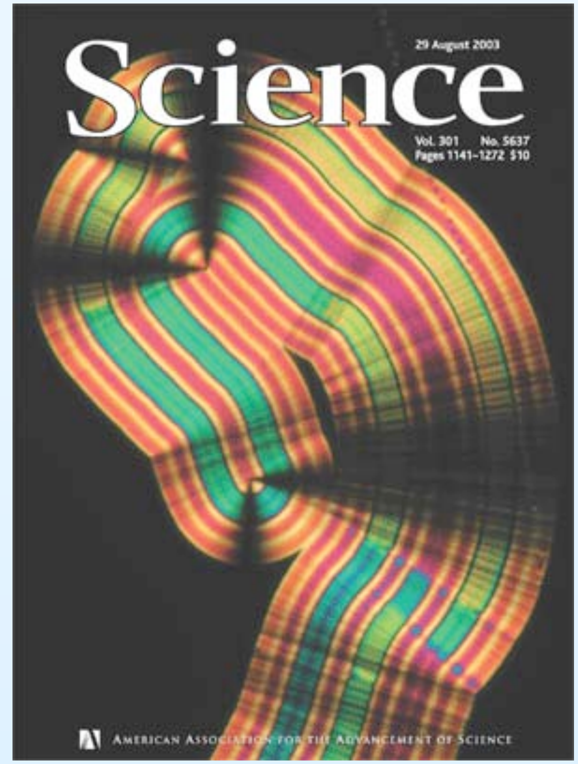
What Now?

- **Measure ee of the product of some asymmetric reactions**
  - Homogeneous mixture?
  - Interference from catalyst?
- **Develop a parallel method - measurement "pixels" in an array**
  - ee microdisplay has physically separated pixels, uniform electronics (should be much less expensive than video microdisplays)
  - Very relaxed lifetime specification suggests high yield manufacturability…
  - Is it possible to get the required "clean molecular alignment"?
- **Key issue - low conversion is indistinguishable from low enantioselectivity**

Banana Mania







<u>**Design, Synthesis, PLM**</u>

Dave Walba, Eva Körblova

<u>**PLM , X-ray, DRLM, FFTEM, Simulations**</u>

Noel Clark	**Joe Maclennan**	**Matt Glaser**
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Michi Nakata	**Renfan Shao**	**John Fernsler**

$$ The Liquid Crystal Materials Research Center (NSF MRSEC)

Chirality Detector

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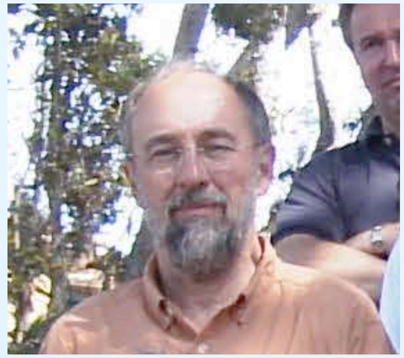
Jan Lagerwall
Alex Kane



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