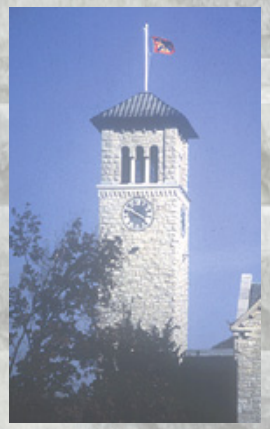
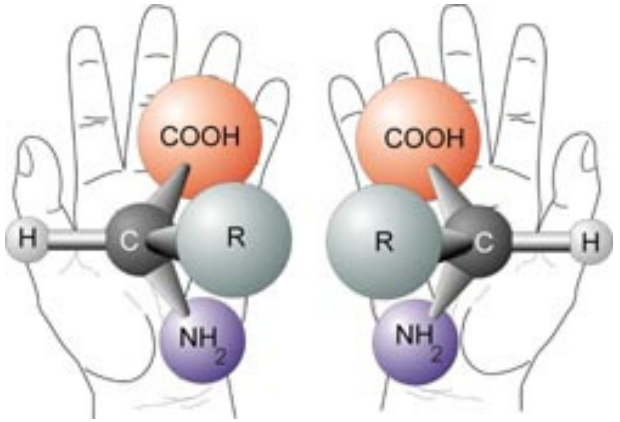
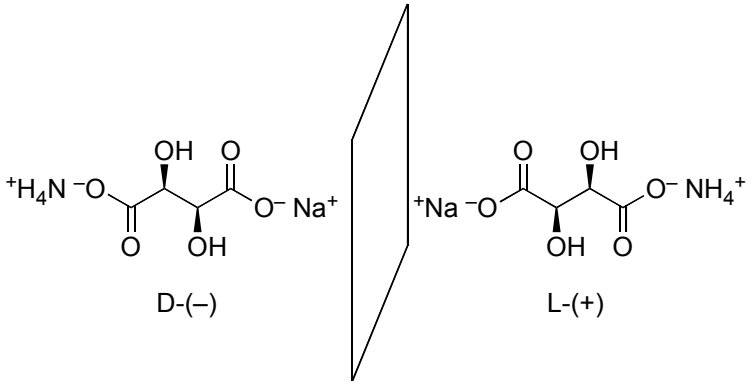


Induction and Modulation of Polarization in Ferroelectric Liquid Crystals.

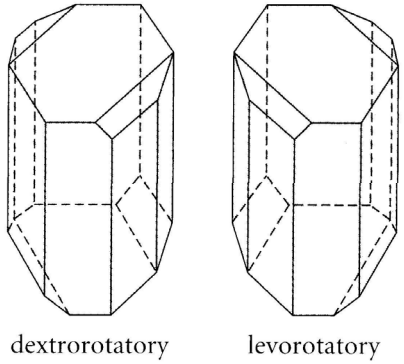
Robert P. Lemieux
Chemistry Department, Queen's University
Kingston, Ontario, K7L 3N6
CANADA

Chirality



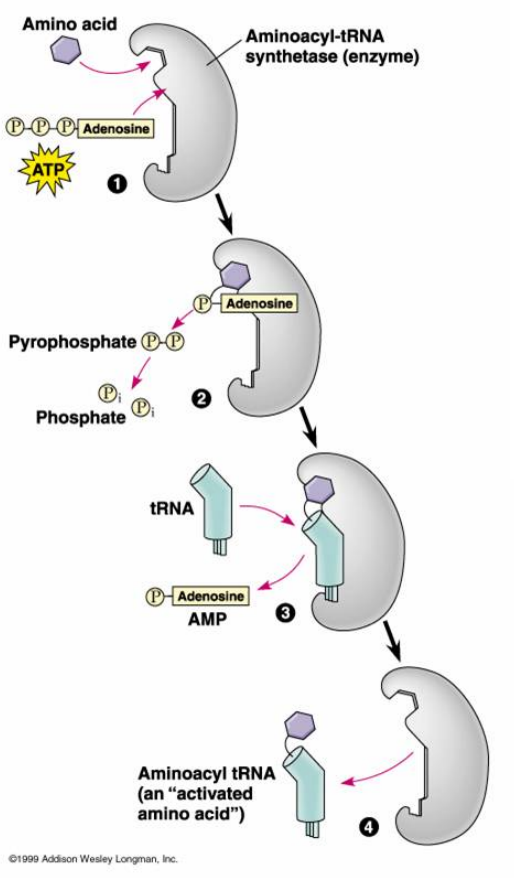


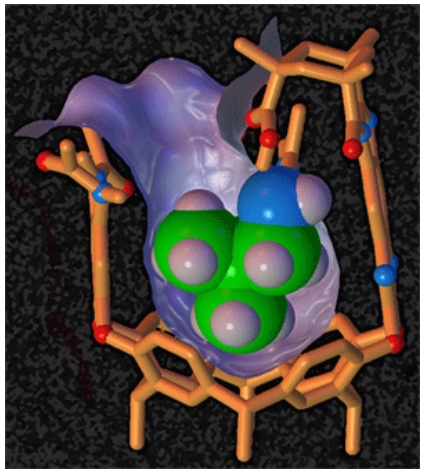
crystallization

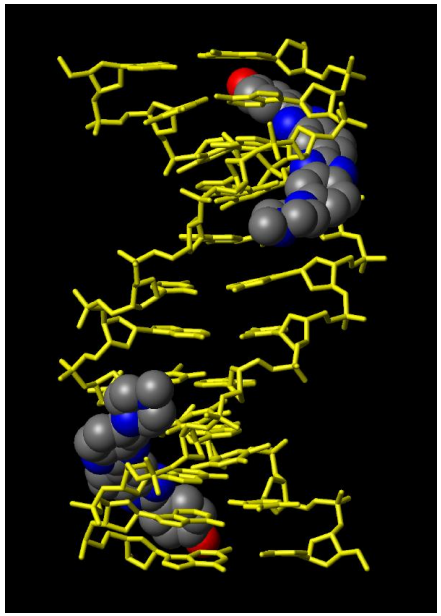


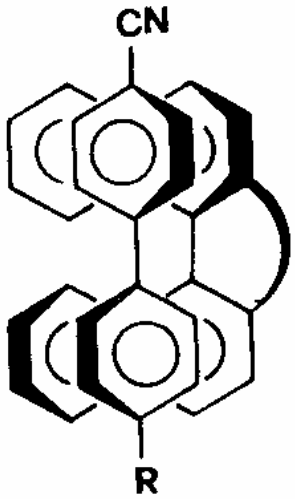
Ranked as the “most beautiful experiment in history”, C&EN, **2003**, *81*, 27-30

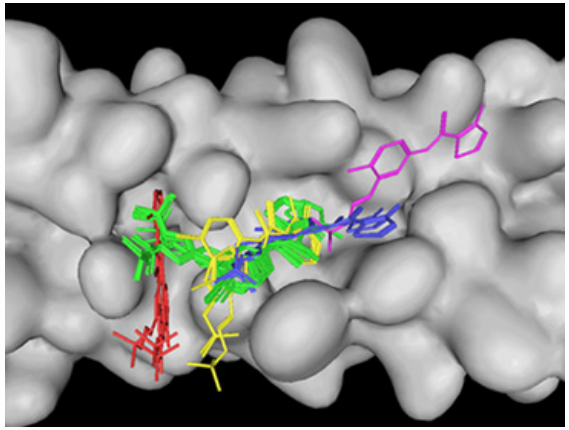
Molecular Recognition



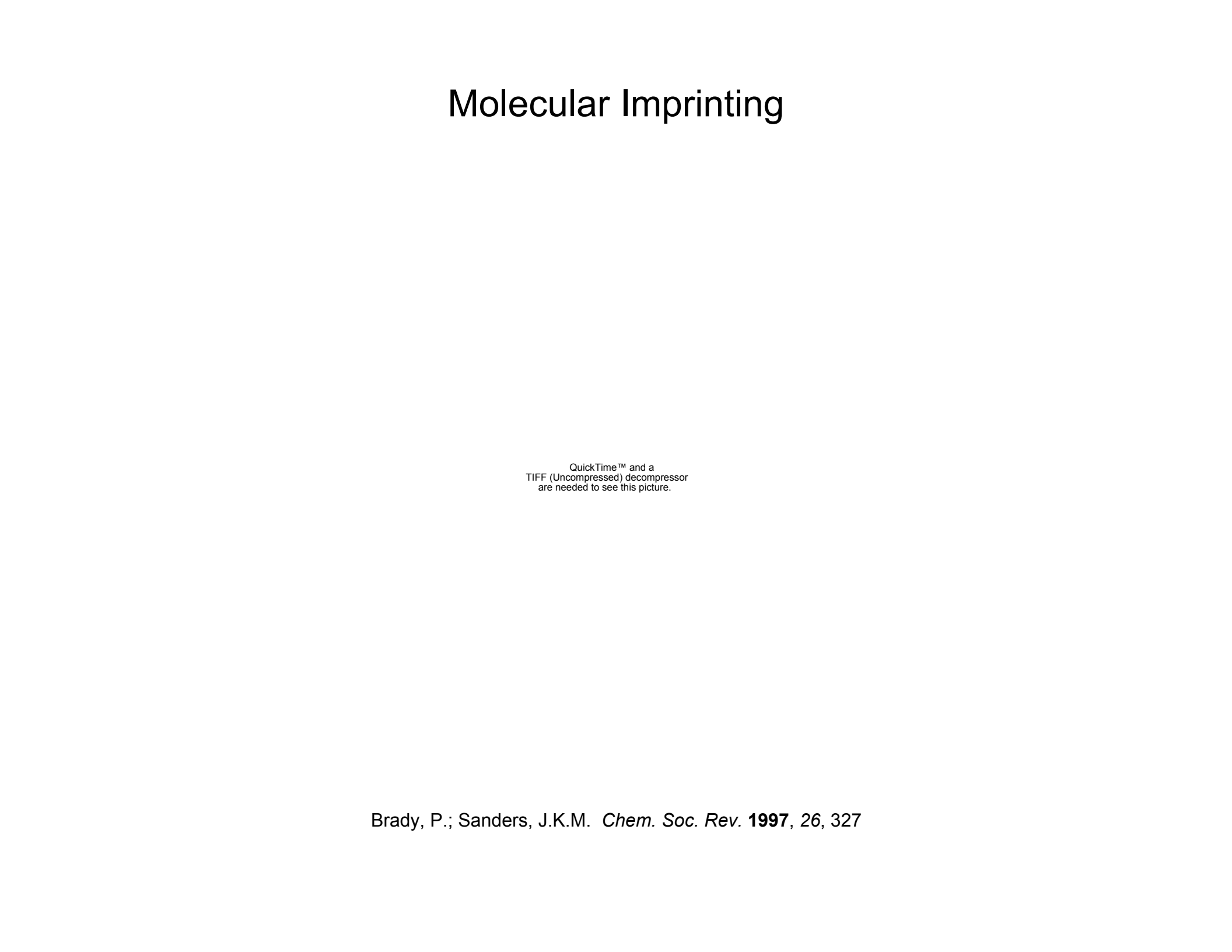






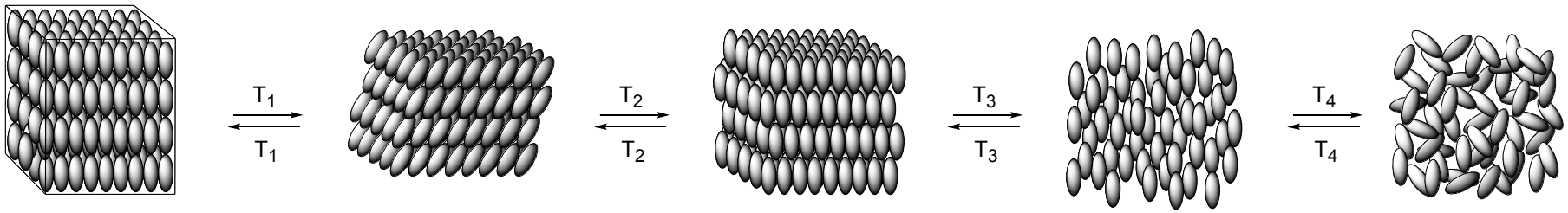


Molecular Imprinting



Brady, P.; Sanders, J.K.M. *Chem. Soc. Rev.* **1997**, *26*, 327

Thermotropic Liquid Crystals



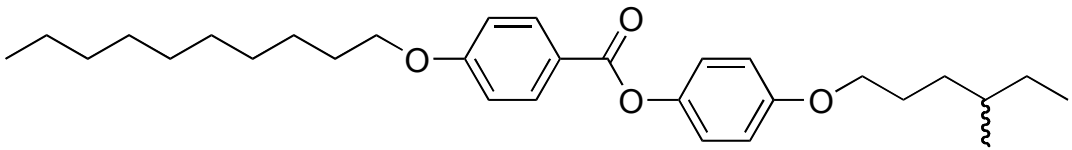
crystal
Cr

smectic C phase
SmC

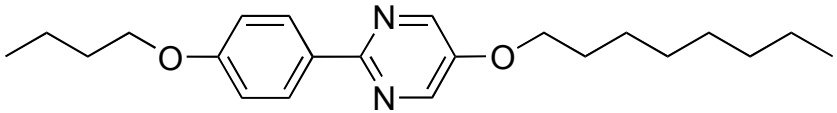
smectic A phase
SmA

nematic phase
N

isotropic liquid
I

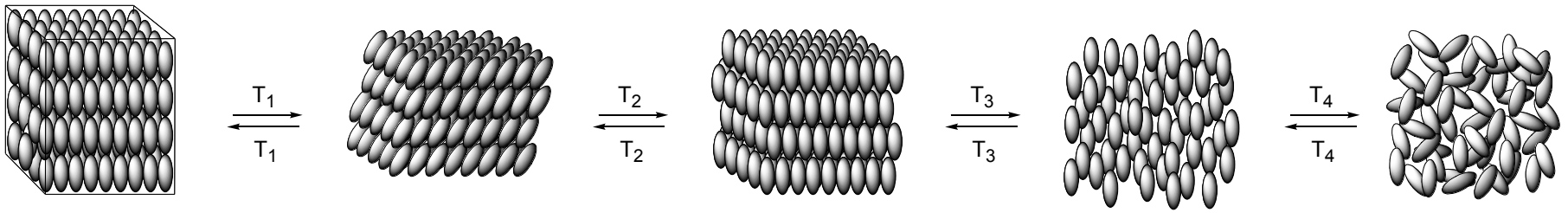


PhB: Cr 35 SmC 70.5 SmA 72 N 75 I



PhP1: Cr 58 SmC 85 SmA 95 N 98 I

Thermotropic Liquid Crystals



crystal
Cr

smectic C phase
SmC

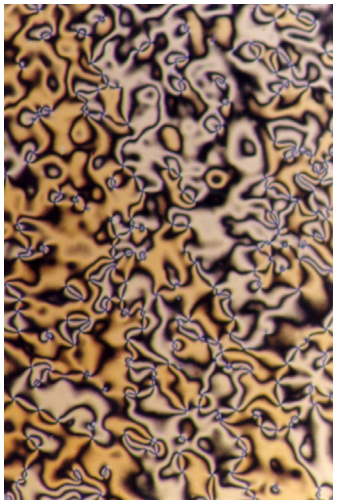
smectic A phase
SmA

nematic phase
N

isotropic liquid
I

QuickTime™ and a
Photo - JPEG decompressor
are needed to see this picture.

QuickTime™ and a
Photo - JPEG decompressor
are needed to see this picture.

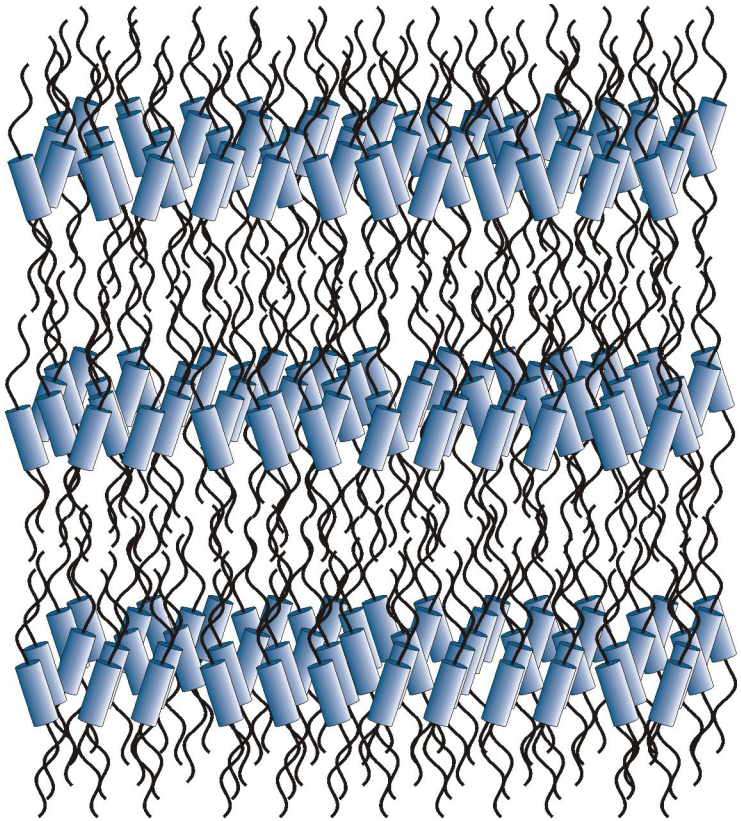


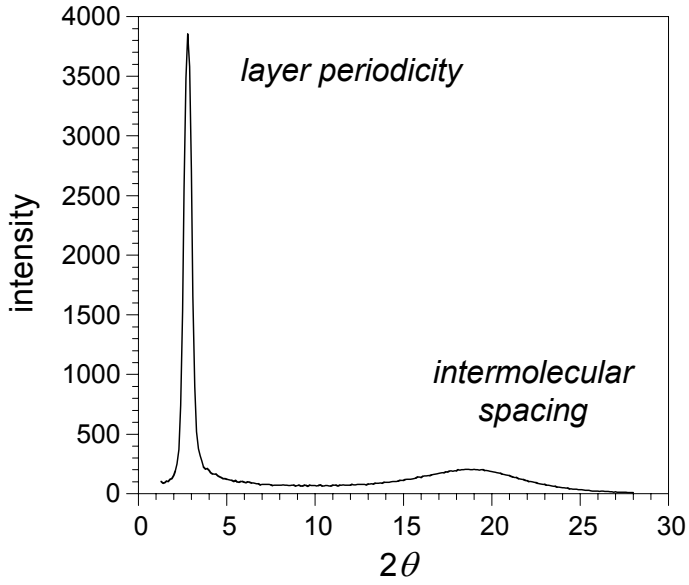
broken fan and schlieren textures

fan texture and homeotropic domains

schlieren texture

Nanosegregation in Smectic A and C Phases



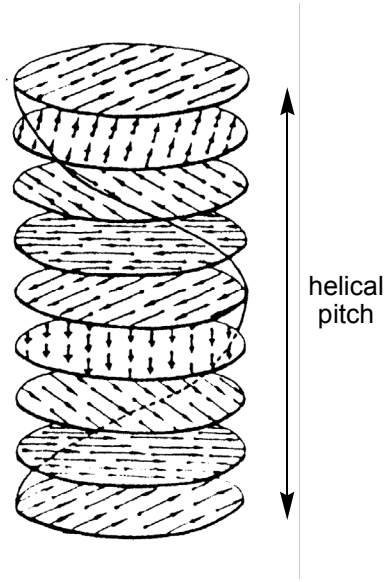


diffuse layer structure

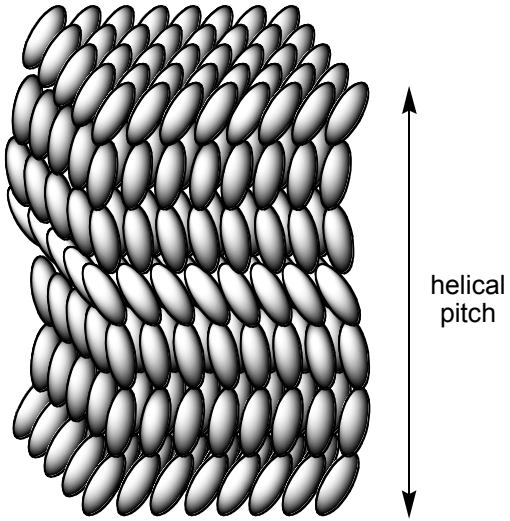
- interlayer fluctuations
- no packing order

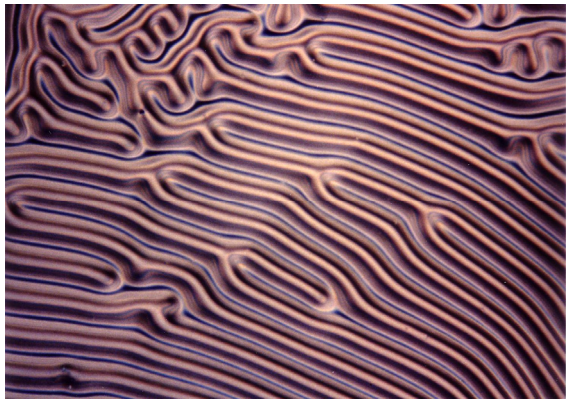
Chiral Liquid Crystals

N*

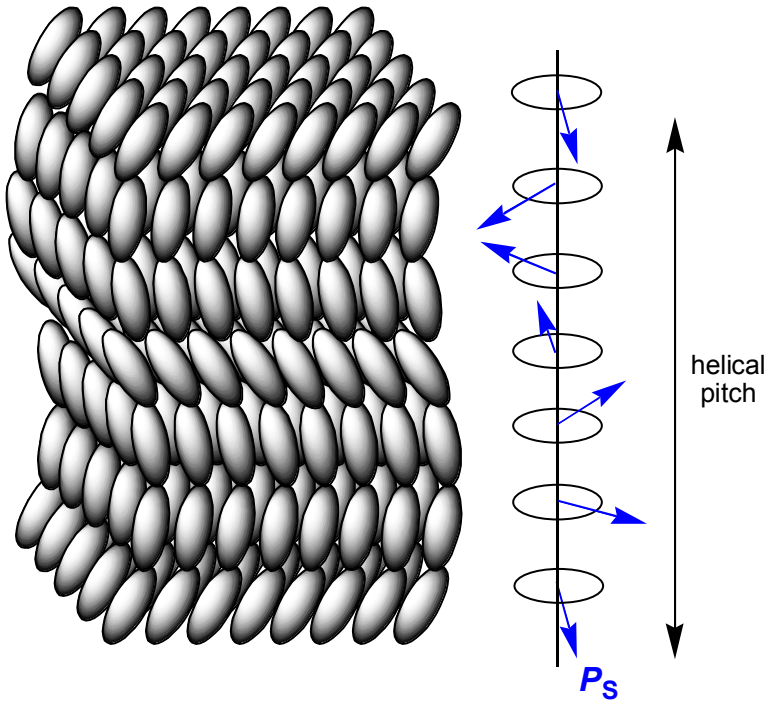


SmC*

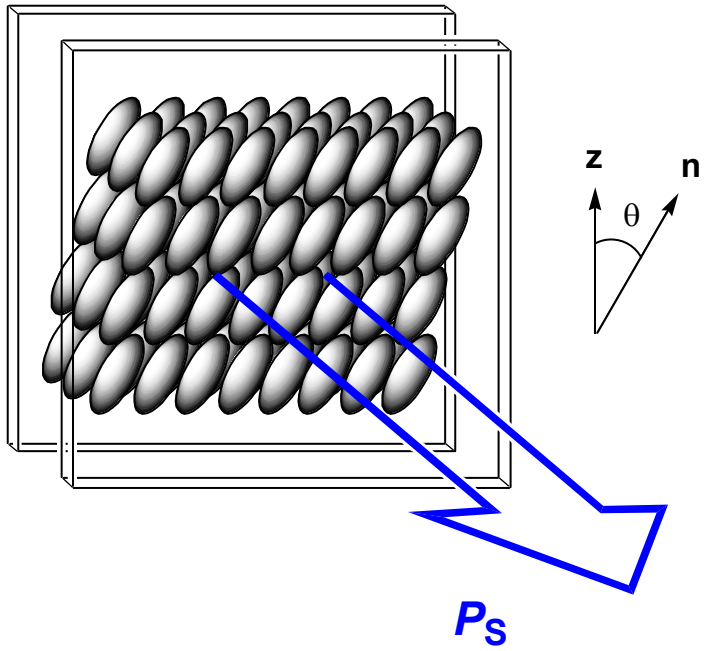




Polar Order in the SmC* Phase

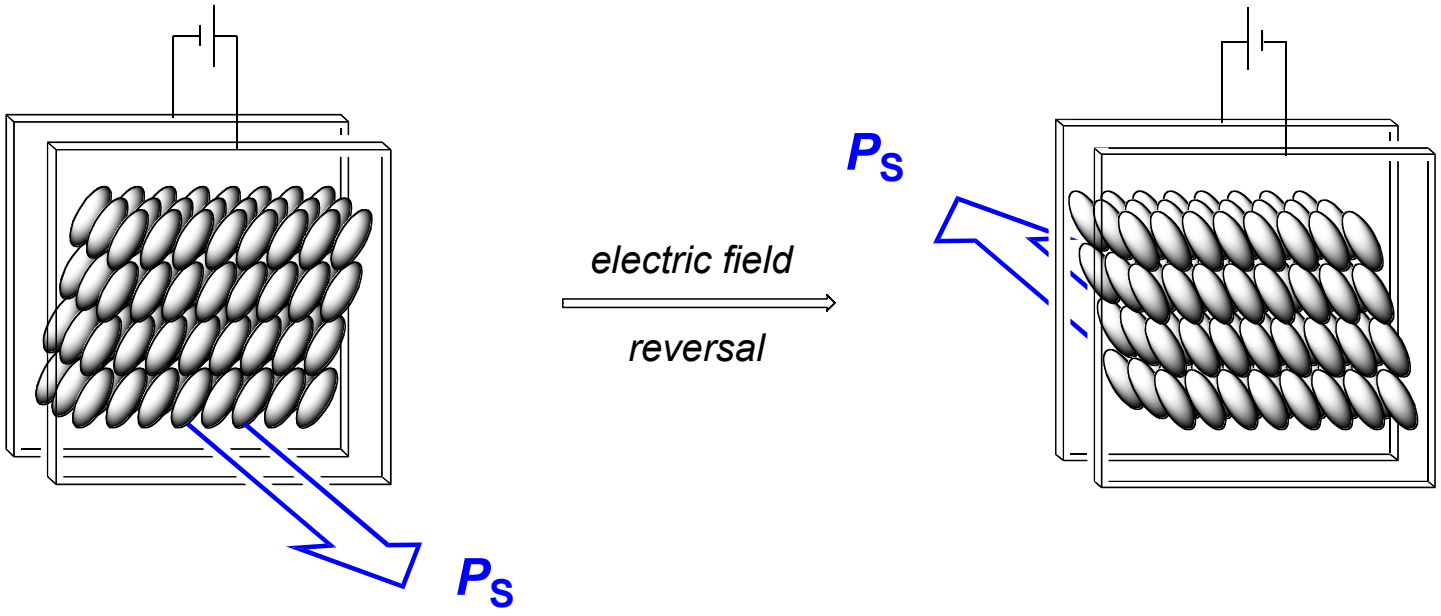


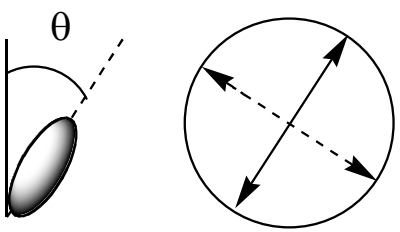
Helical State (Non-Ferroelectric)

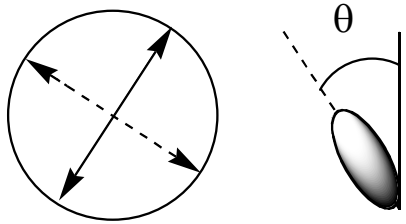


Surface-Stabilized Ferroelectric State
Clark & Lagerwall *Appl. Phys. Lett.* **1980**, *36*, 899

SSFLC Light Shutter







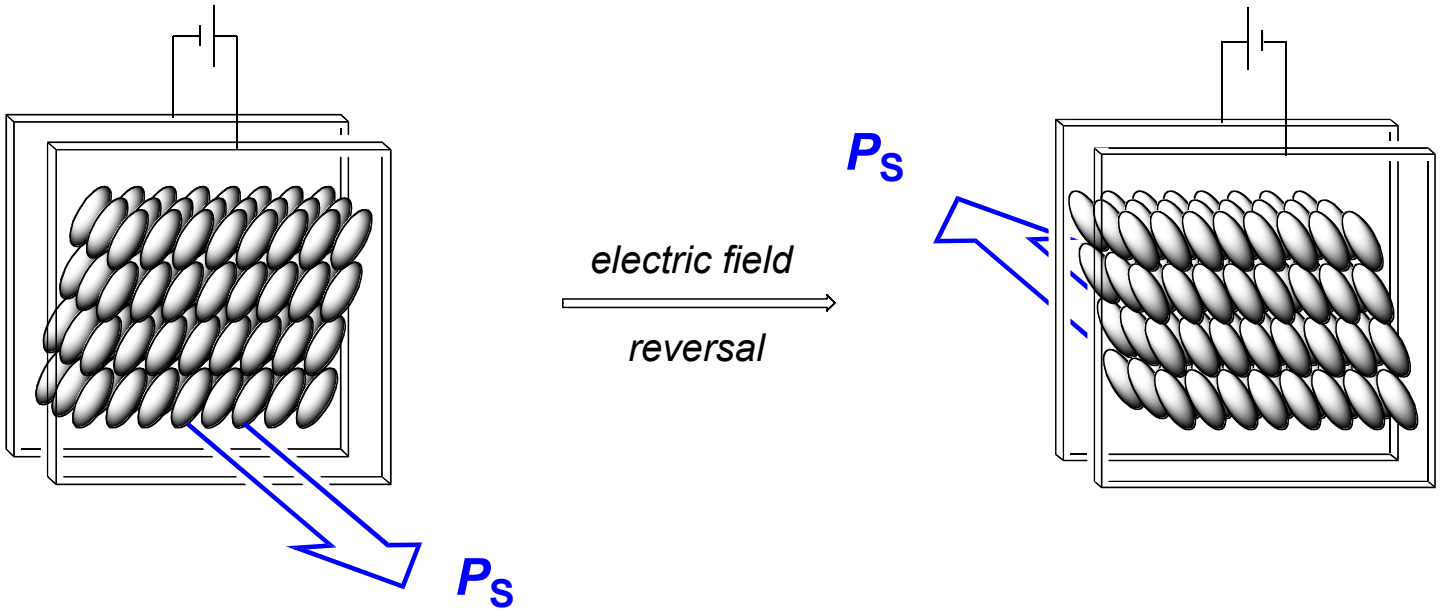
"OFF" state

no light transmission through cross polarizers

"ON" state

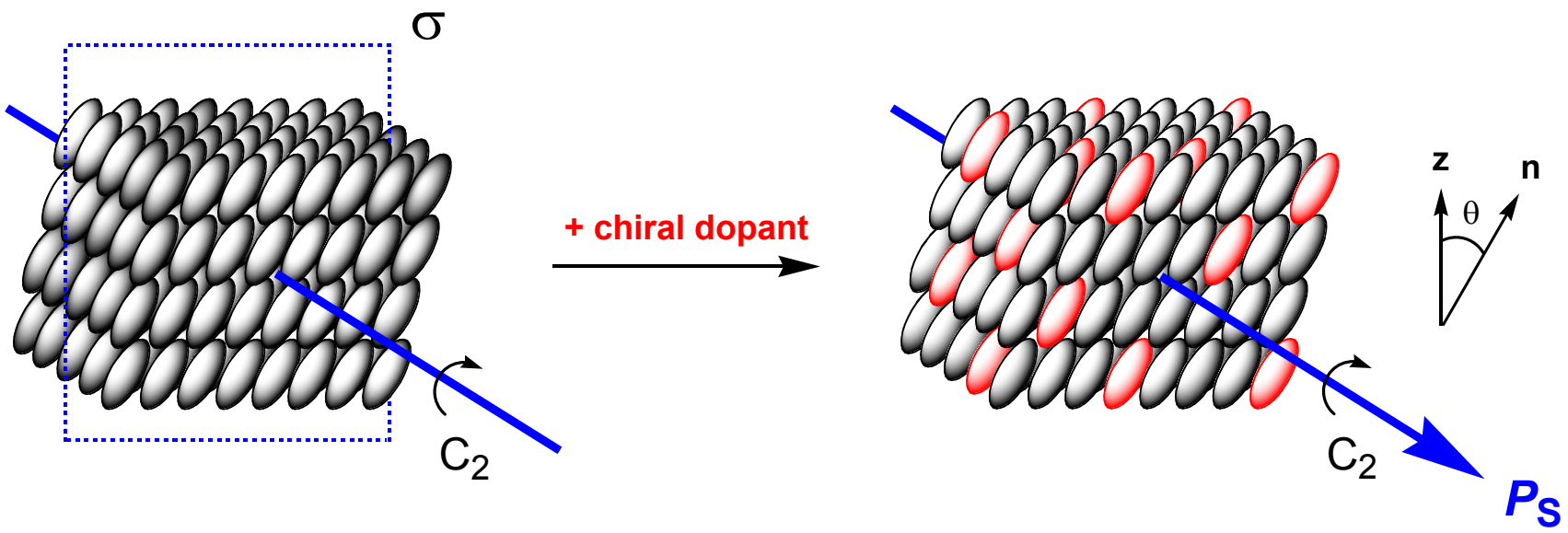
light transmission through cross polarizers

SSFLC Light Shutter



$$\textbf{switching time} \propto \frac{\eta}{P_S \bullet E}$$

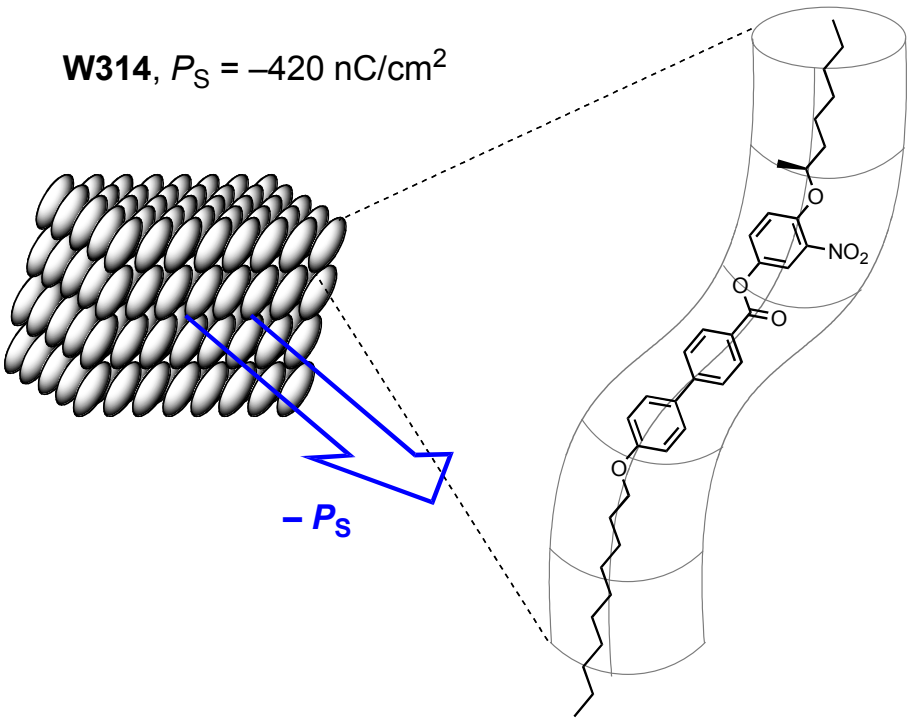
Induction of a Chiral SmC* Phase

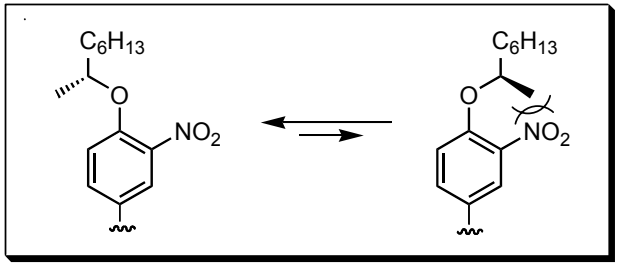


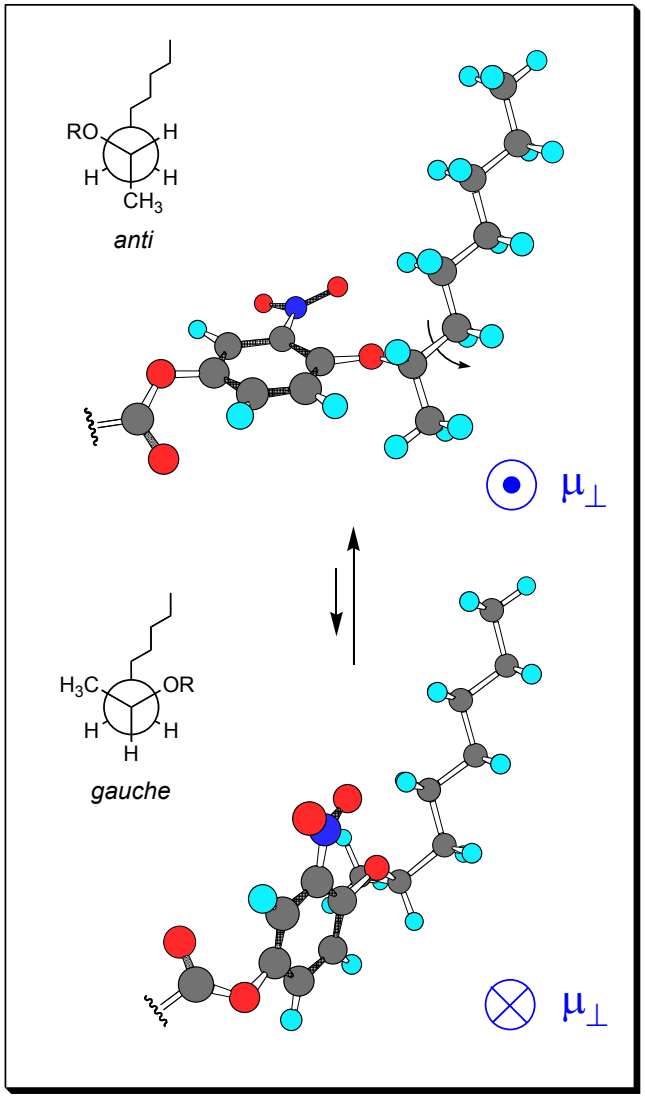
reduced polarization	*polarization power*
$P_o = \frac{P_S}{\sin\theta}$	$\delta_p = \frac{dP_o}{dx_d}$

Siemensmeyer, K.; Stegemeyer, H. *Chem. Phys. Lett.* **1988**, *148*, 409

Molecular Origins of Polarization: The Boulder Model



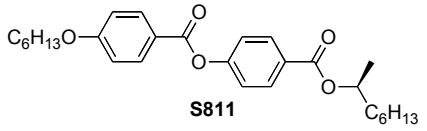




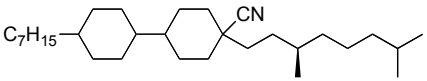
Walba, D. M. et al. *J. Am. Chem. Soc.* **1991**, *113*, 5471

Molecular Recognition in the SmC* Phase

Dopant

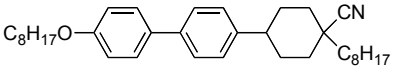


S811

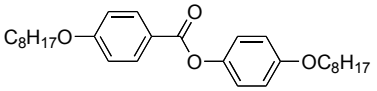


C7D

SmC Host



NCB8O8



8OO8

δ_p is independent of host structure

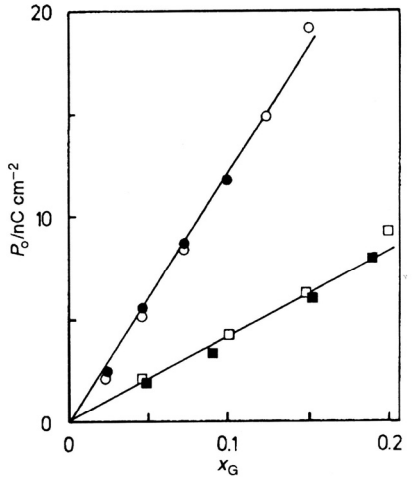
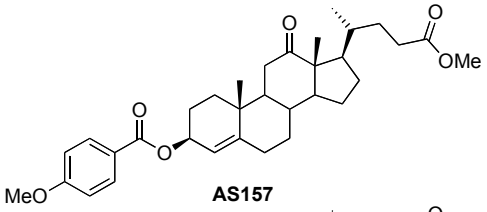
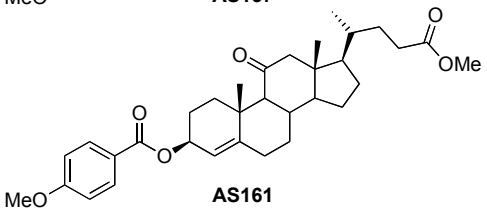


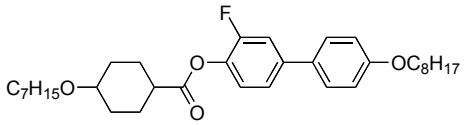
Fig. 6 Tilt-angle-reduced polarization, P_O *vs.* x_G for the chiral dopants C7D (□, ■) and S811 (○, ●) in different host phases[6] (*cf.* Fig. 5)



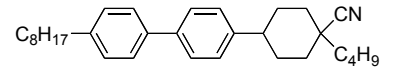
AS157



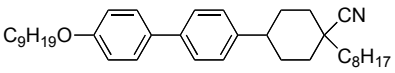
AS161



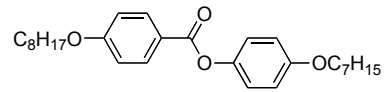
BDH-o-F



NCB84



NCB9O8



8OO7

δ_p varies with host structure

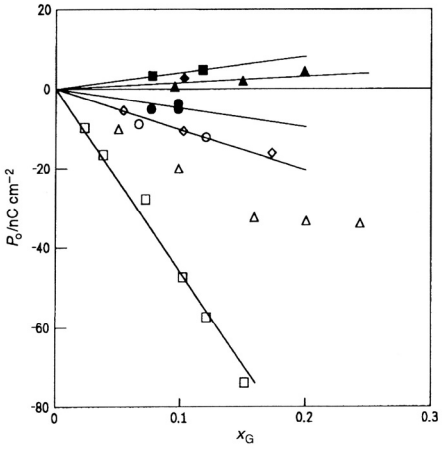
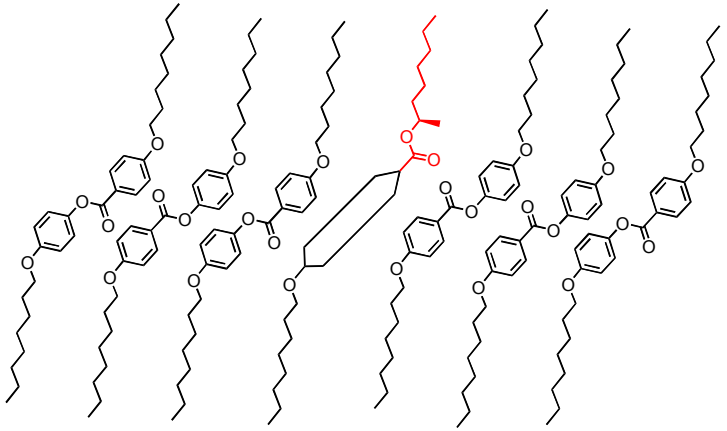


Fig. 11 Polarization, P_O *vs.* x_G for the type II-2 dopants AS157 (open symbols) and AS161 (filled symbols) in different host phases; ΔT = 5 K. Host phases: ○/●, 8007; ◇/◆, BDH-o-F; □/■, NCB84; △/▲, NCB908.

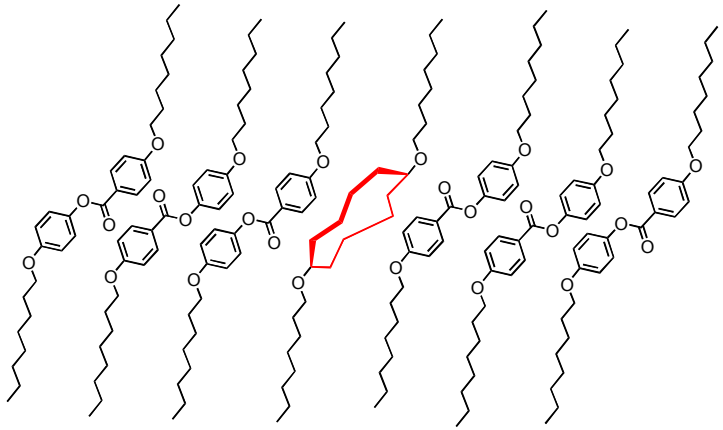
Stegemeyer, H.; Meister, R.; Hoffmann, U.; Sprick, A.; Becker, A. *J. Mater. Chem.* **1995**, *5*, 2183

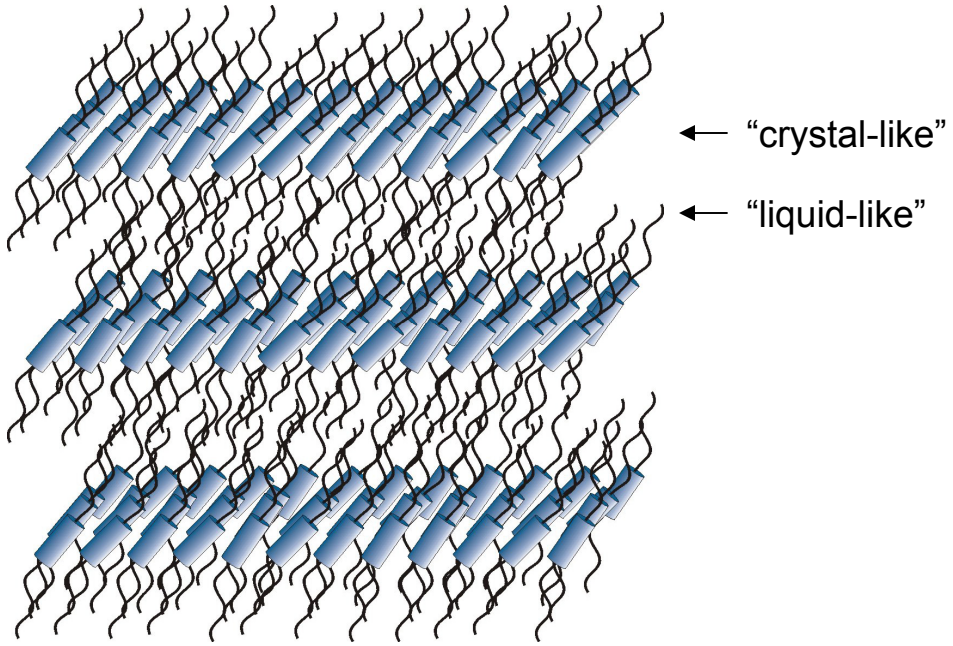
Molecular Recognition in the SmC* Phase

Type I



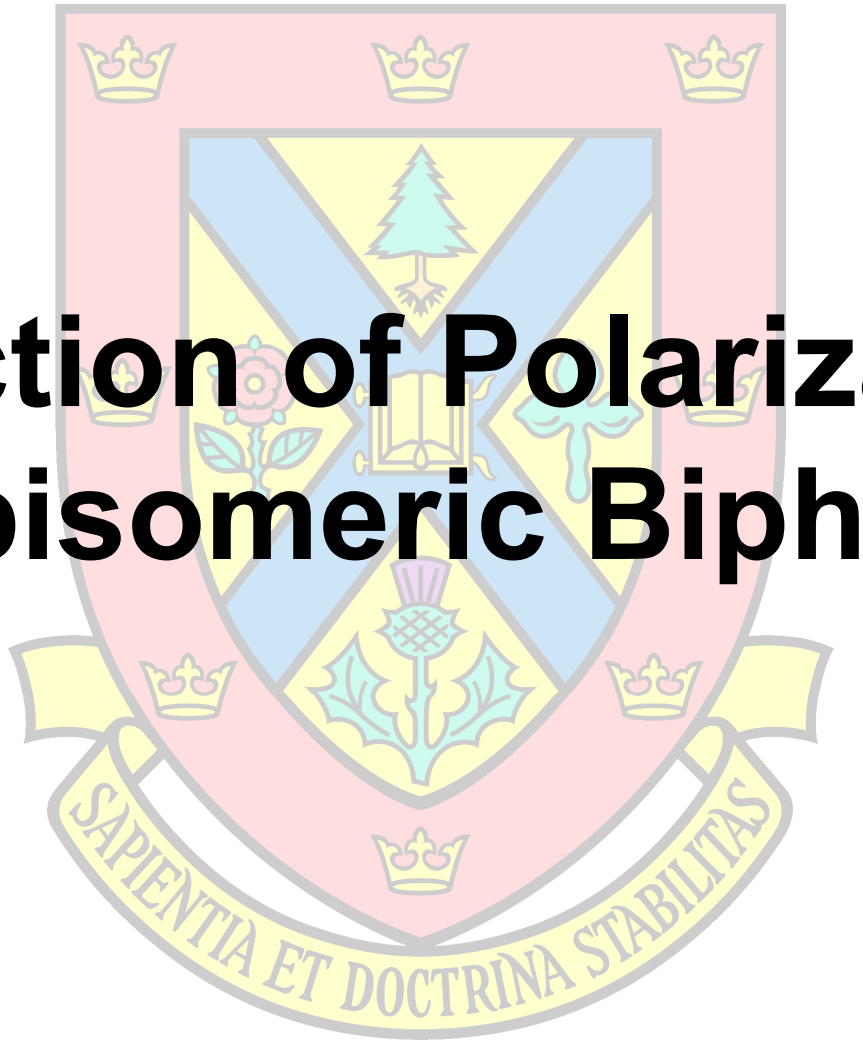
Type II



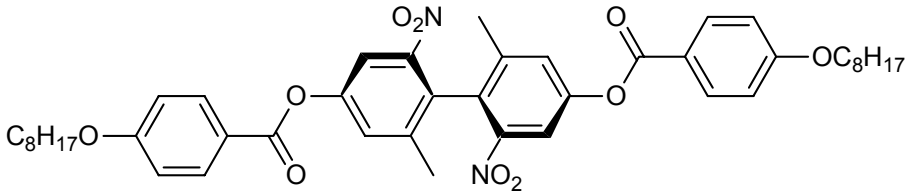


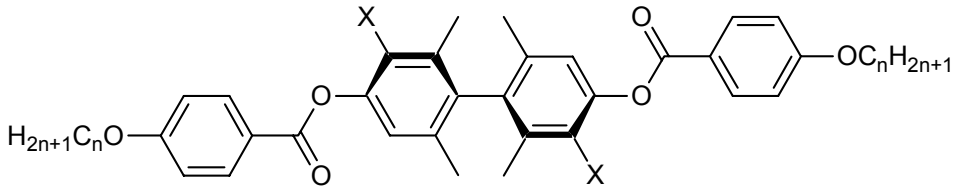
Stegemeyer, H.; Meister, R.; Hoffmann, U.; Sprick, A.; Becker, A. *J. Mater. Chem.* **1995**, *5*, 2183

Induction of Polarization: Atropisomeric Biphenyls



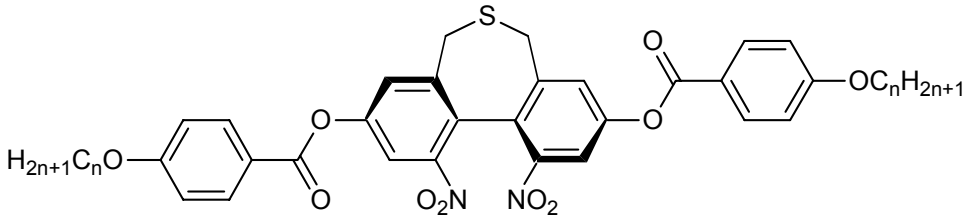
Atropisomeric Biphenyl Dopants





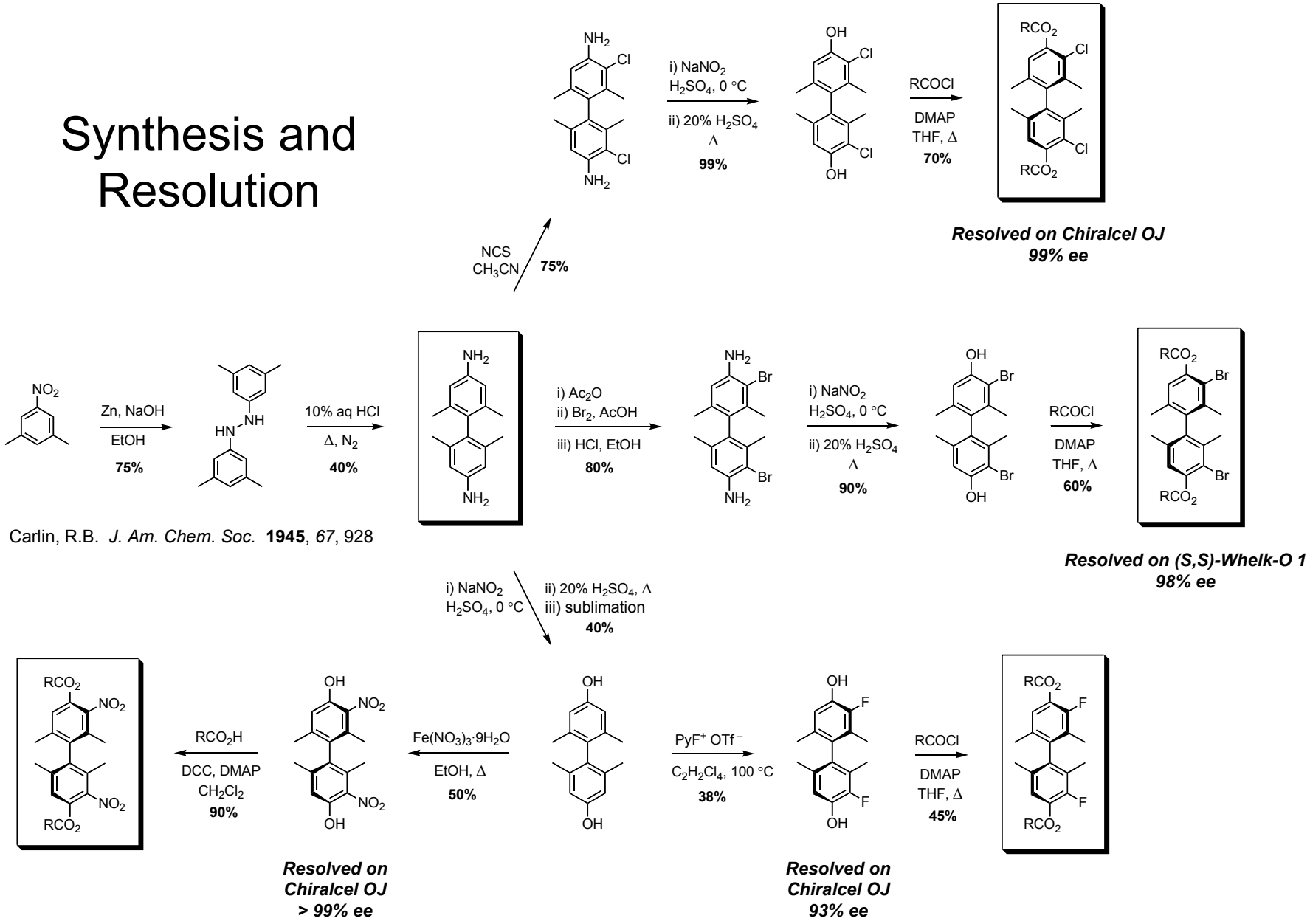
X = NO_2, F, Cl, Br, CH_3

QuickTime™ and a
GIF decompressor
are needed to see this picture.



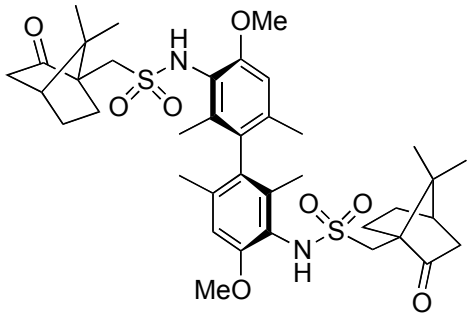
Lemieux, R.P. *Acc. Chem. Res.* **2001**, *34*, 845

Synthesis and Resolution

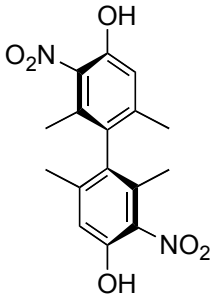


Vizitiu, D.; Lazar, C.; Radke, J.P.; Hartley, C.S.; Glaser, M.A.; Lemieux, R.P. *Chem. Mater.* **2001**, *13*, 1692

Assignment of Absolute Configuration



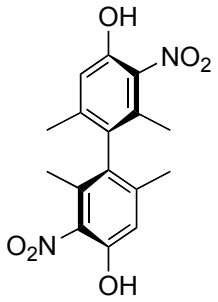
(*S,S,R*)



(*R*)

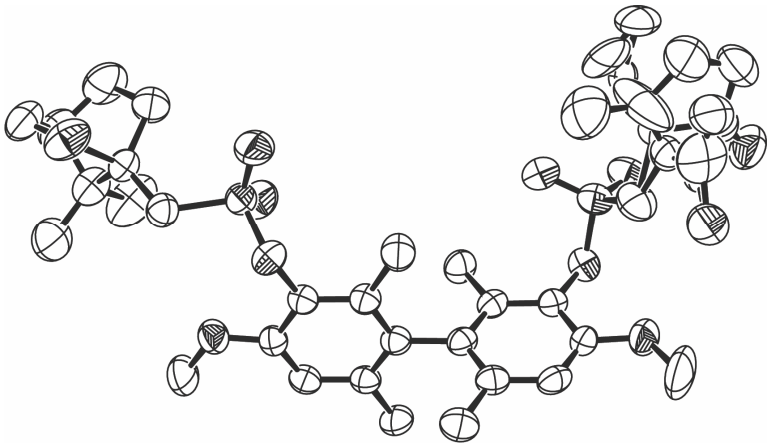
first eluant

+



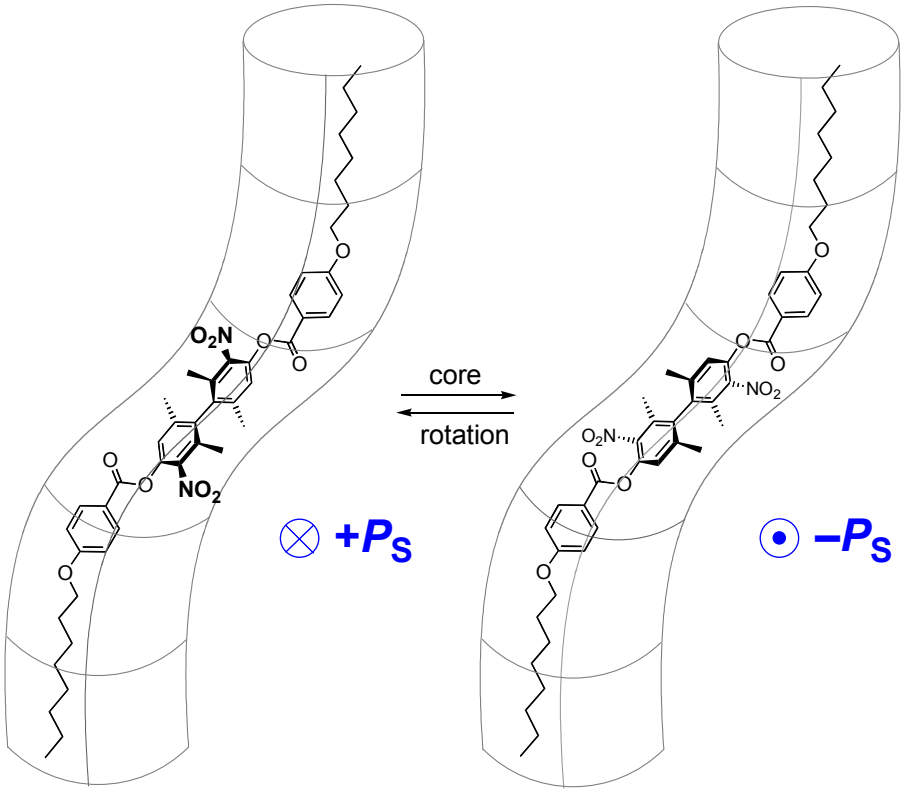
(*S*)

second eluant

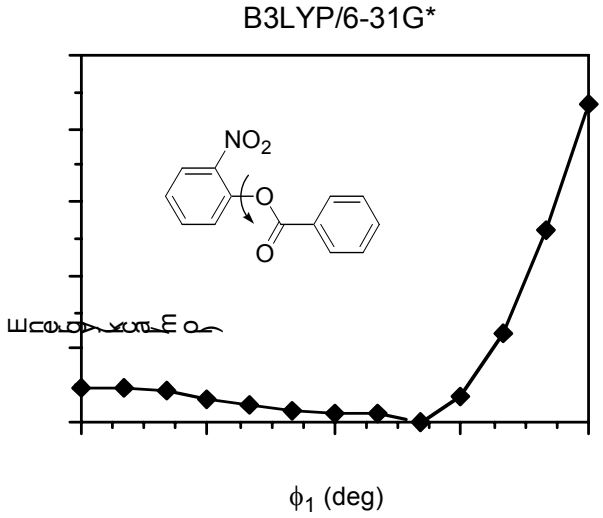


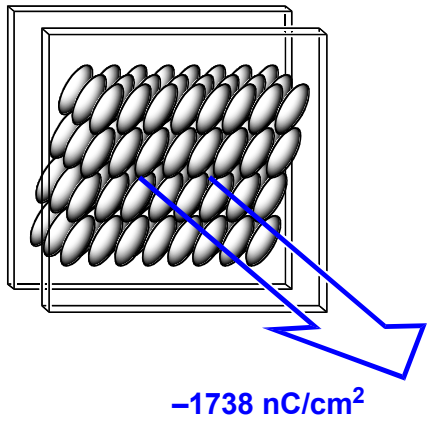
Hartley, C.S.; Wang, R.; Lemieux, R.P. *Chem. Mater.* **2004**, *16,* 5297

Conformational Asymmetry



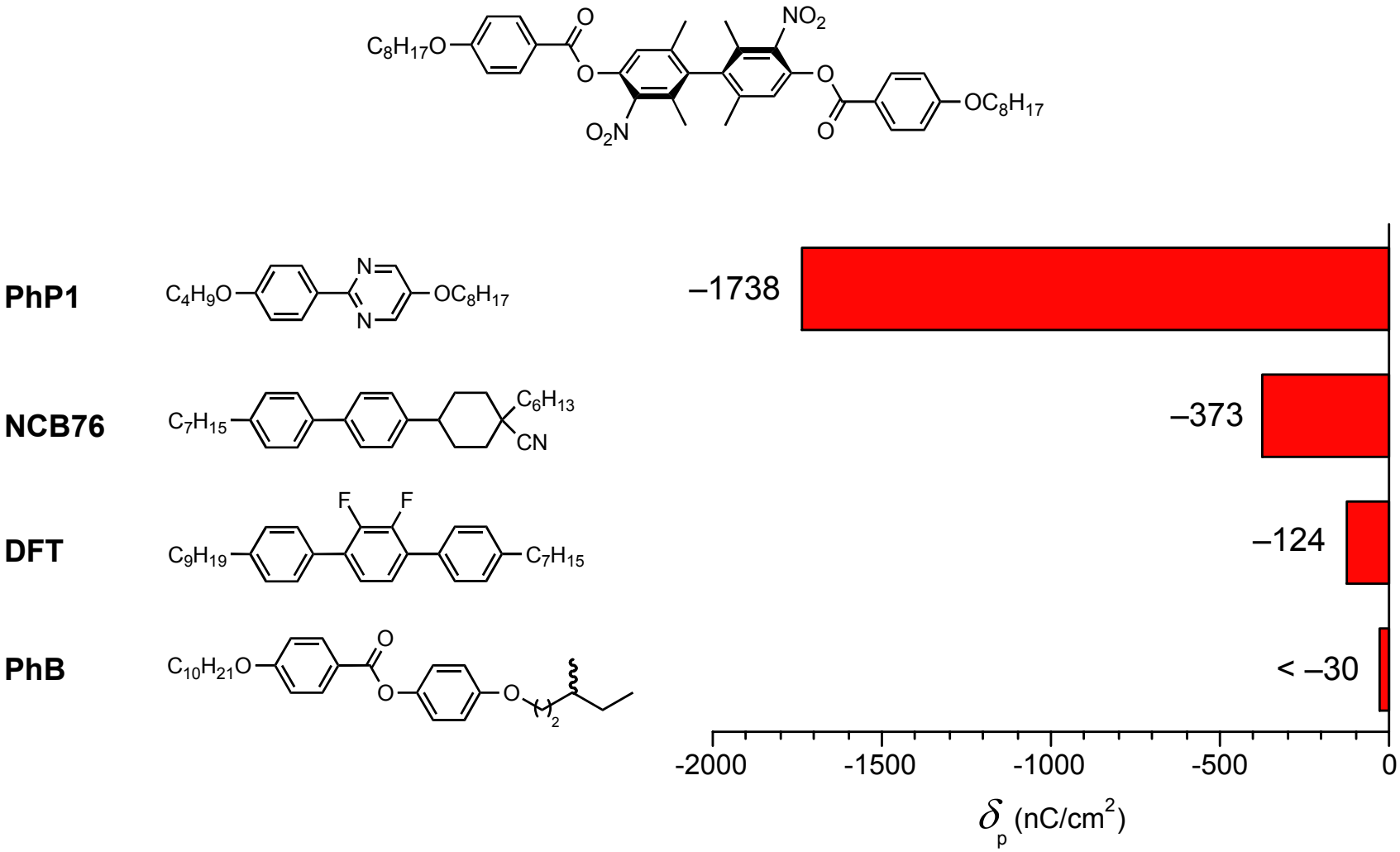
(*R*) enantiomer





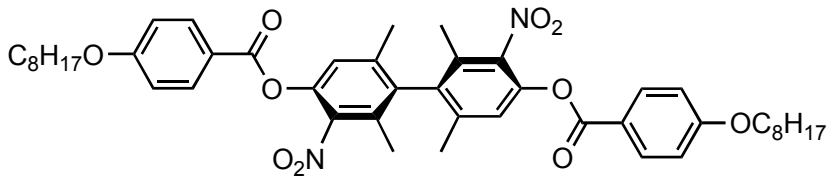
D. Vizitiu, C. Lazar, J.P. Radke, C.S. Hartley, M.A. Glaser, R.P. Lemieux *Chem. Mater.*, **2001**, *13*, 1692

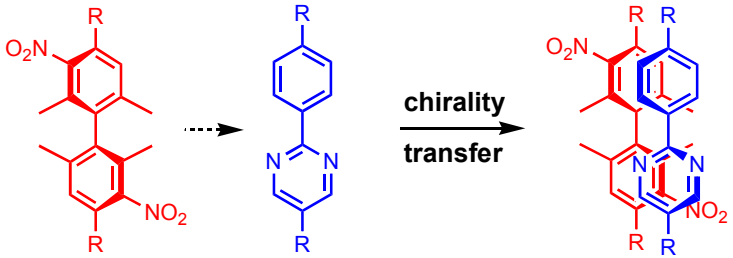
Polarization Power: Host Dependence



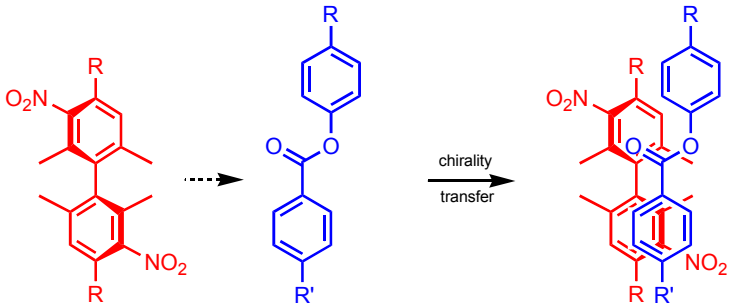
D. Vizitiu, C. Lazar, B.J. Halden, R.P. Lemieux *J. Am. Chem. Soc.* **1999**, *121*, 8229

Polarization Power: Host Dependence

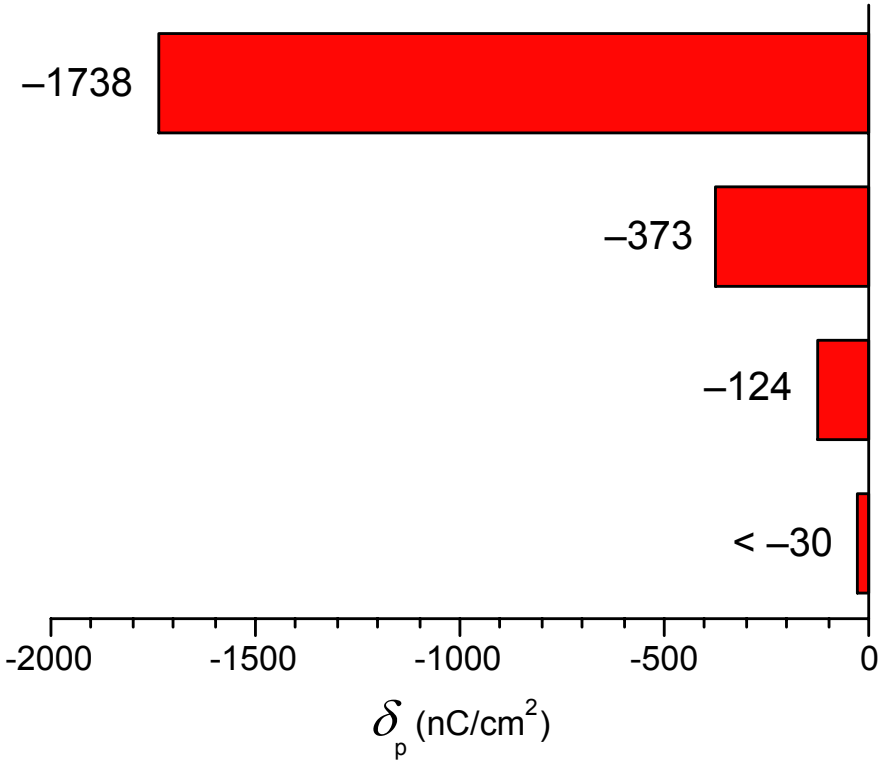




chirality transfer

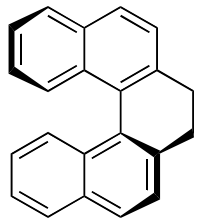


chirality transfer



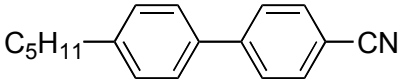
D. Vizitiu, C. Lazar, B.J. Halden, R.P. Lemieux *J. Am. Chem. Soc.* **1999**, *121*, 8229

Chiral Nematics Analogy



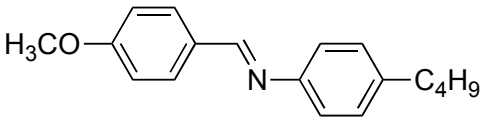
P-helicity

in

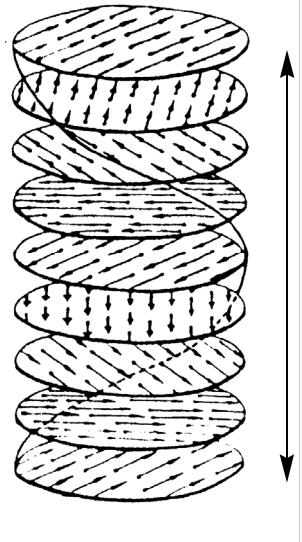


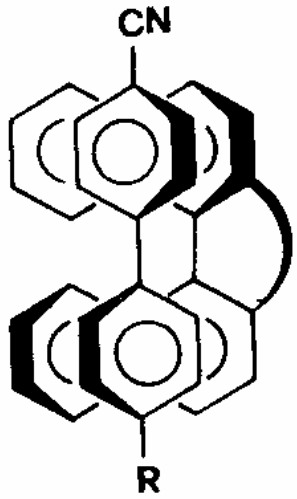
Helical Twisting Power

+76 μm^{-1}



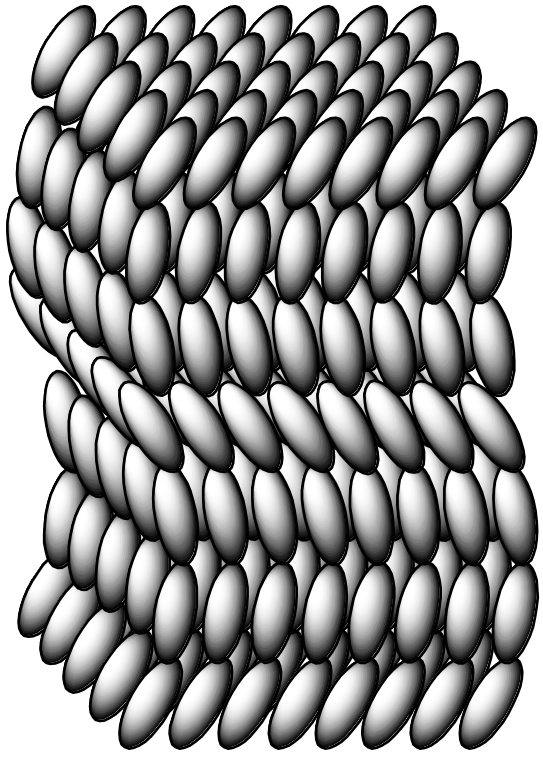
+37 μm^{-1}





Gottarelli, G.; Hibert, M.; Samori, B.; Solladié, G.; Spada, G.P.; Zimmermann, R. *J. Am. Chem. Soc.*. **1983**, *105*, 7318

Polarization Power: Correlation with SmC* Pitch

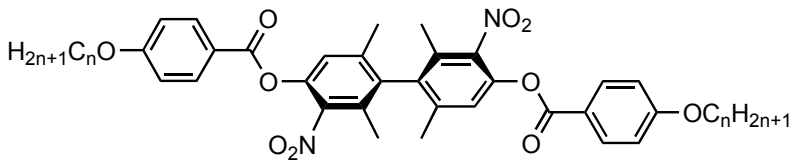


helical
pitch

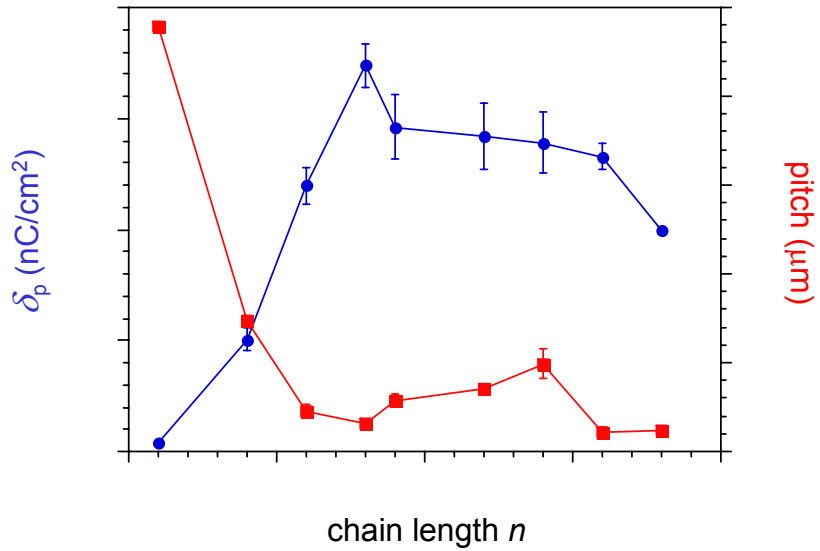
QuickTime™ and a
Photo - JPEG decompressor
are needed to see this picture.

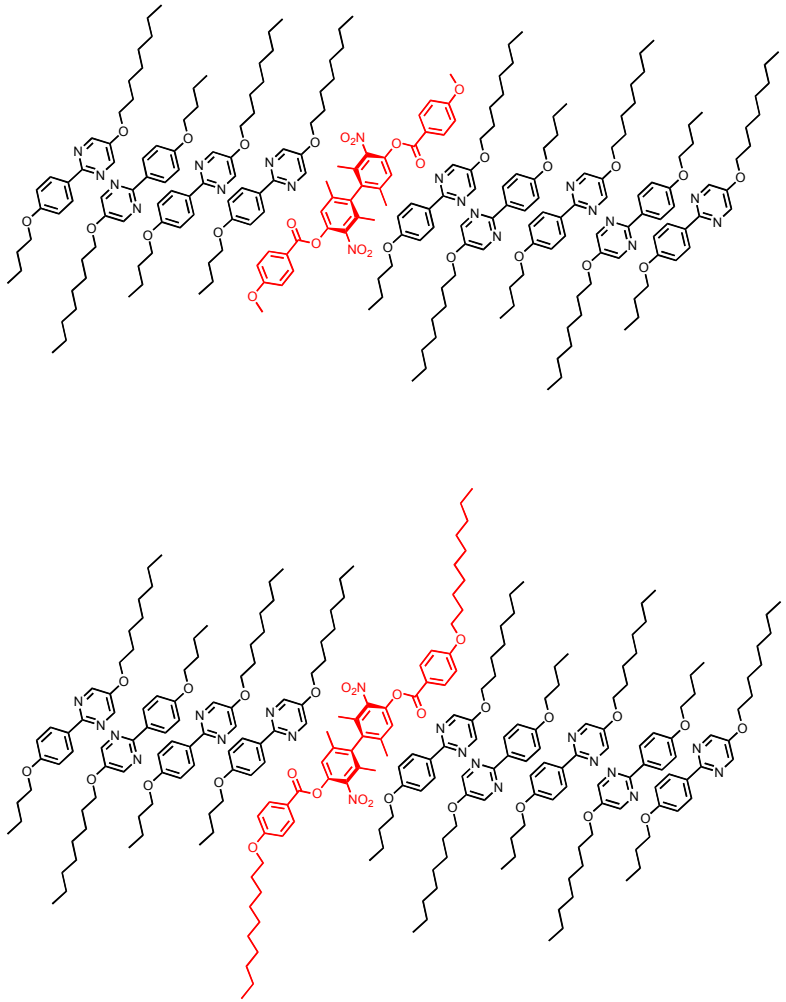
150 μm film viewed by polarized microscopy (100 ×)

Polarization Power: Correlation with SmC* Pitch



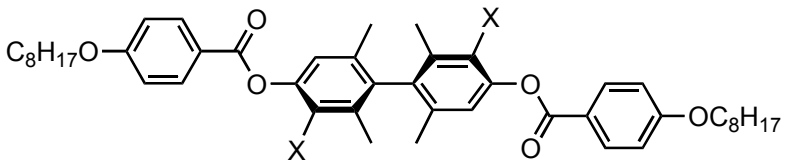
in **PhP1**



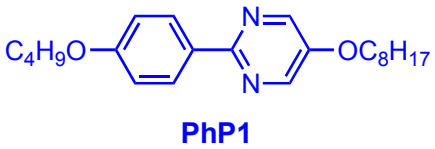


D. Vizitiu, C. Lazar, B.J. Halden, R.P. Lemieux *J. Am. Chem. Soc.* **1999**, *121*, 8229

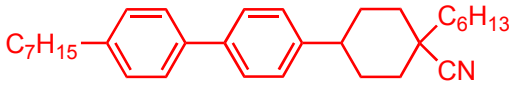
Polarization Power: Correlation with SmC* Pitch



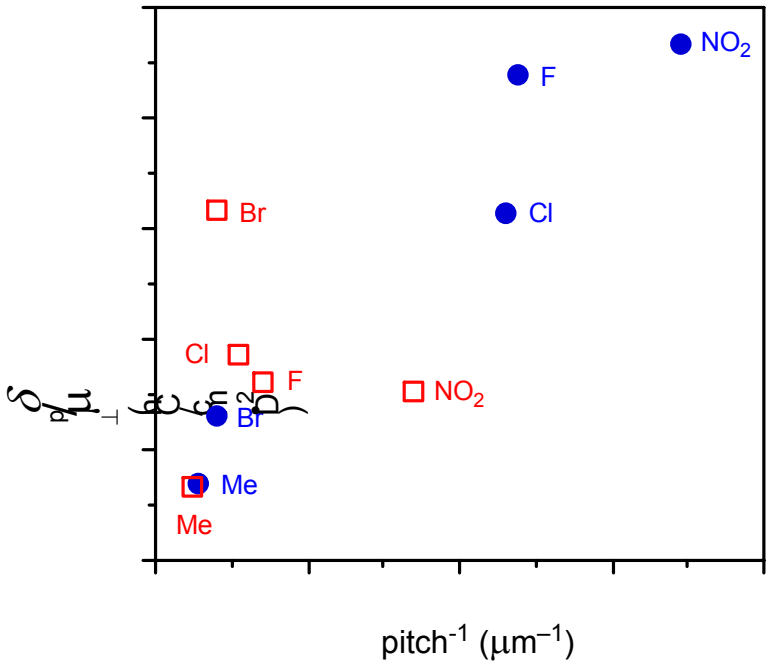
X = NO_2, F, Cl, Br, CH_3



PhP1



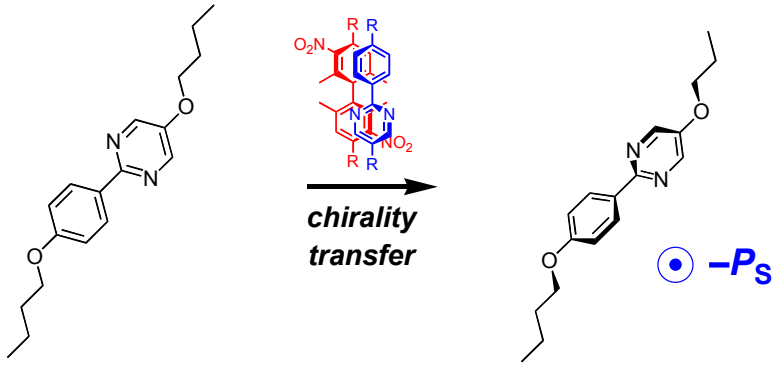
NCB76



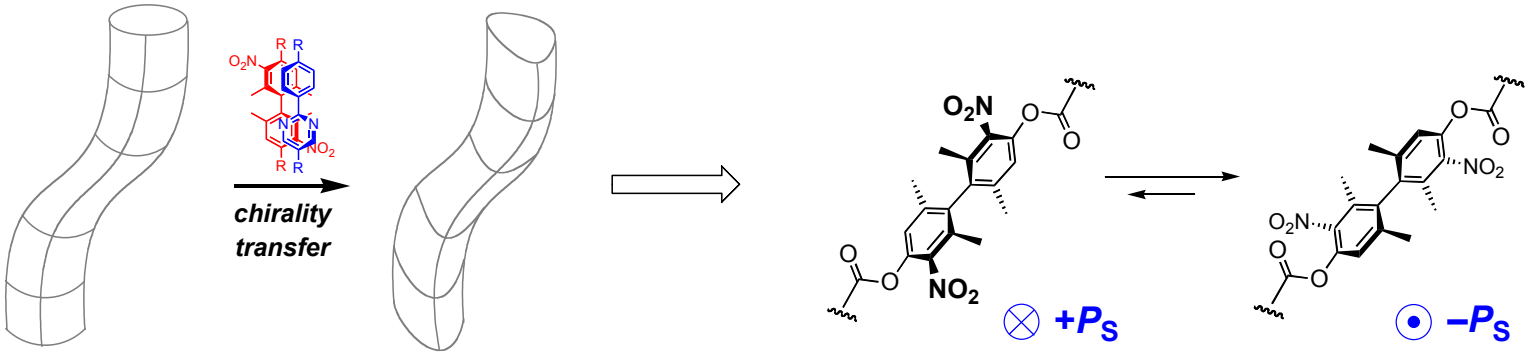
Vizitiu, D.; Lazar, C.; Radke, J.P.; Hartley, C.S.; Glaser, M.A.; Lemieux, R.P. *Chem. Mater.* **2001**, *13*, 1692

Effect of Chirality Transfer

(i) Polar Ordering of the Host

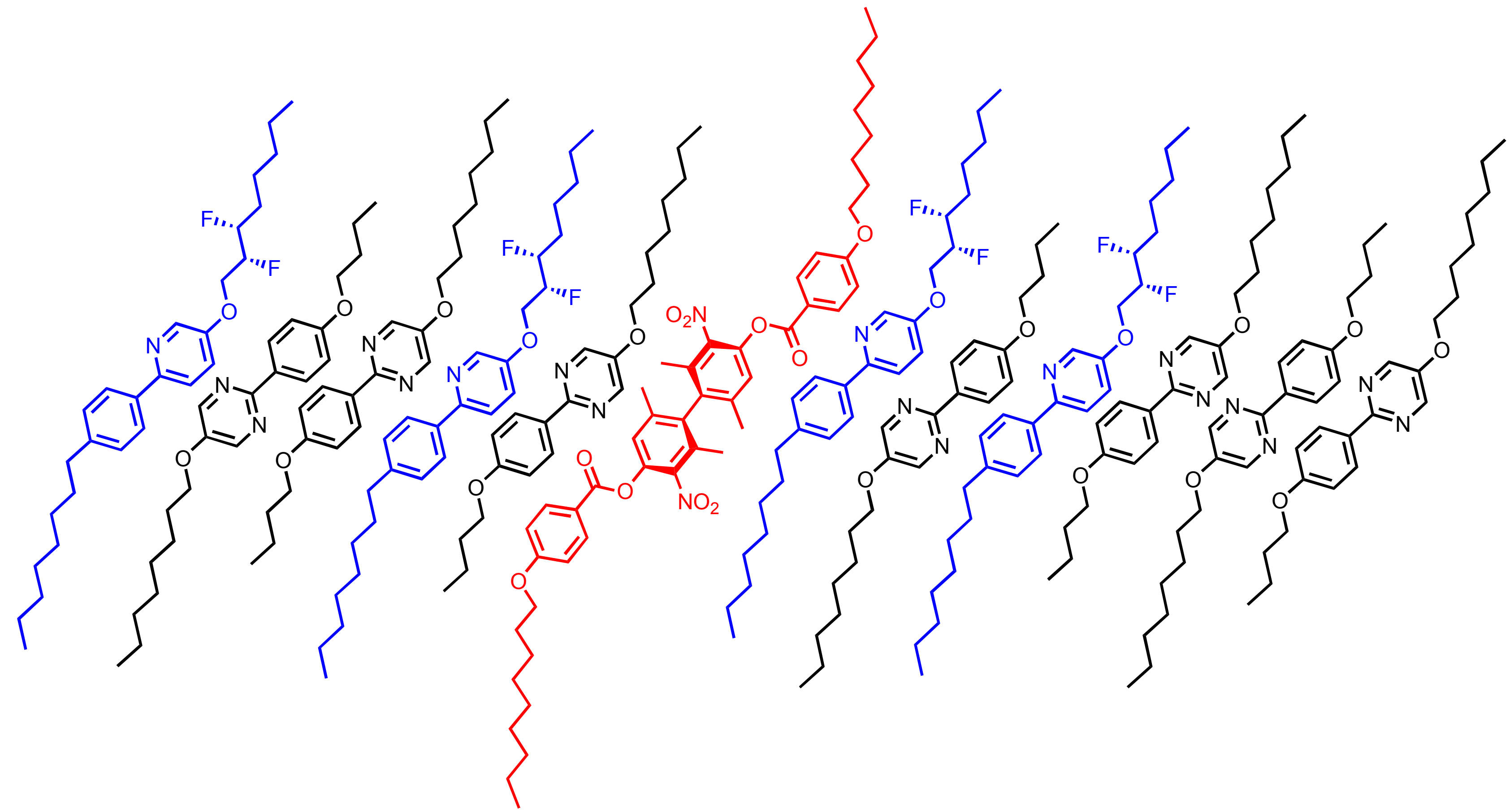


(ii) Chirality Transfer Feedback



shift in conformational equilibrium

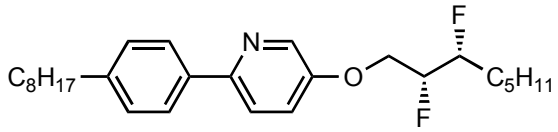
Probe Experiment: **PhP1** Mimic



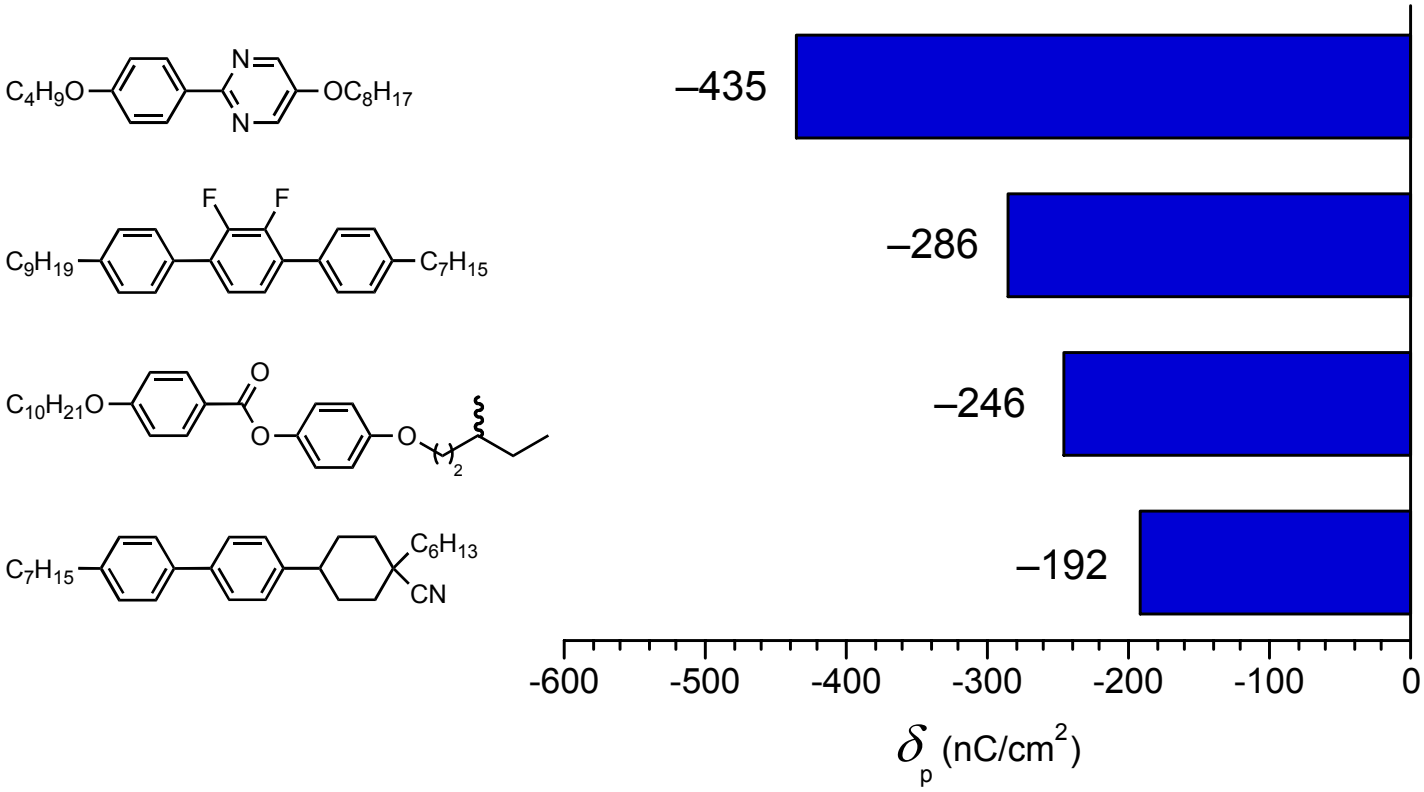
Total Polarization = P_S (**C9**) + P_S (**MDW950**)

Hartley, C.S.; Lazar, C.; Wand, M.D.; Lemieux, R.P. *J. Am. Chem. Soc.* **2002**, *124*, 13513

Probe Experiment: **PhP1** Mimic

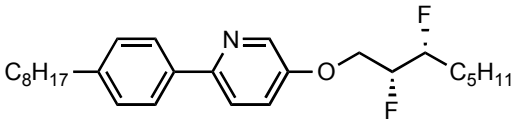


MDW950 (Displaytech)

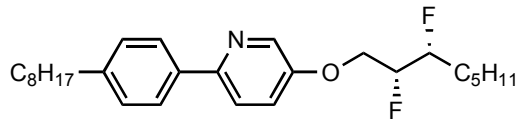


Thompson, M.; Hegmann, T.; Lemieux, R.P., unpublished results

No Perturbation: Hypothetical

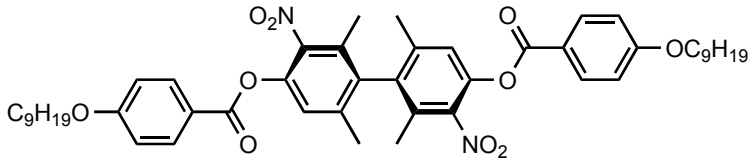


MDW950

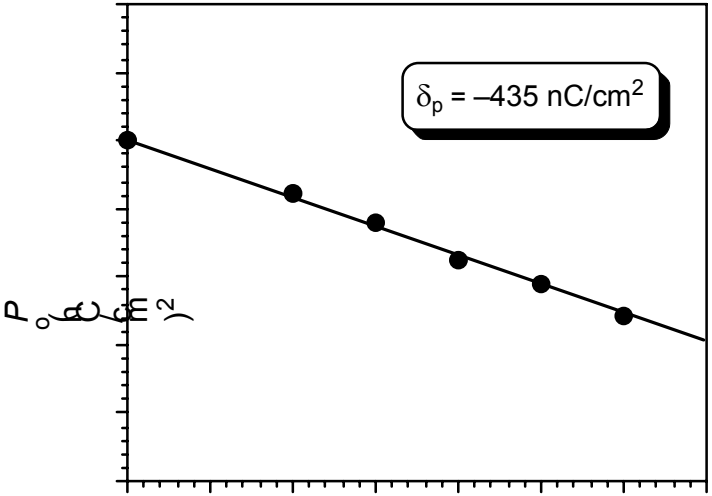


MDW950

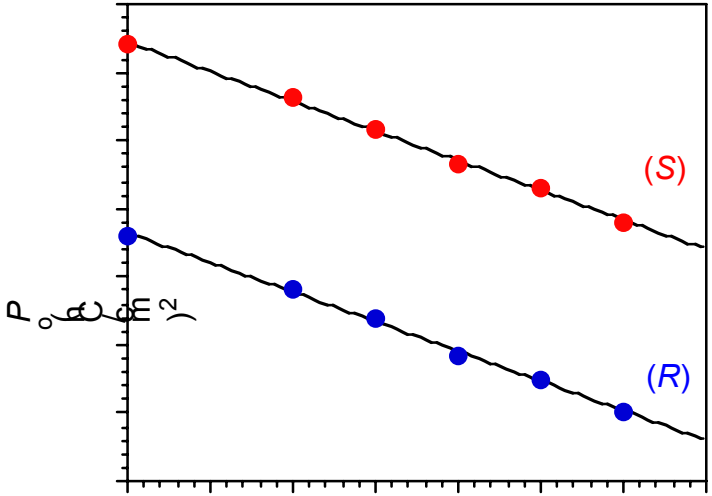
+



C9, 4 mol%

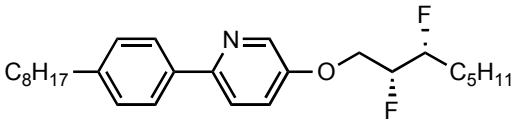


x_d (MDW950)

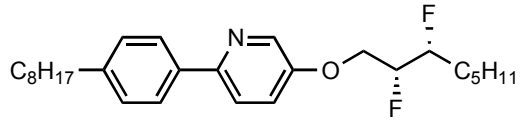


x_d (MDW950)

No Perturbation: Hypothetical

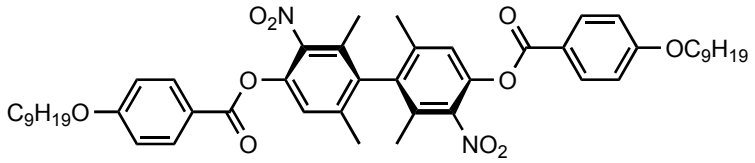


MDW950

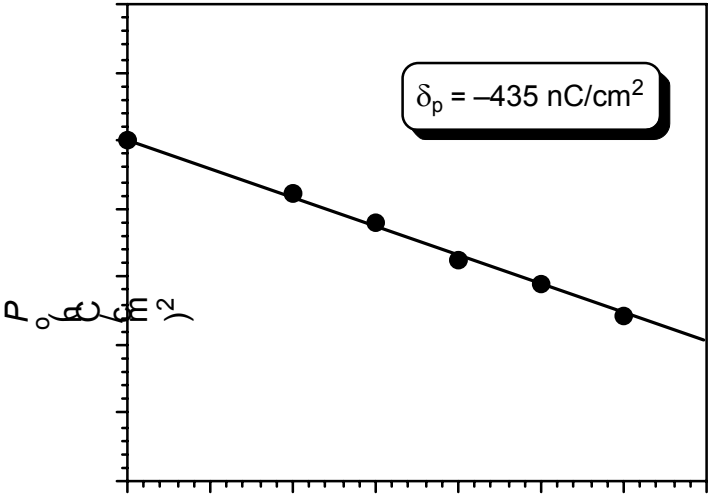


MDW950

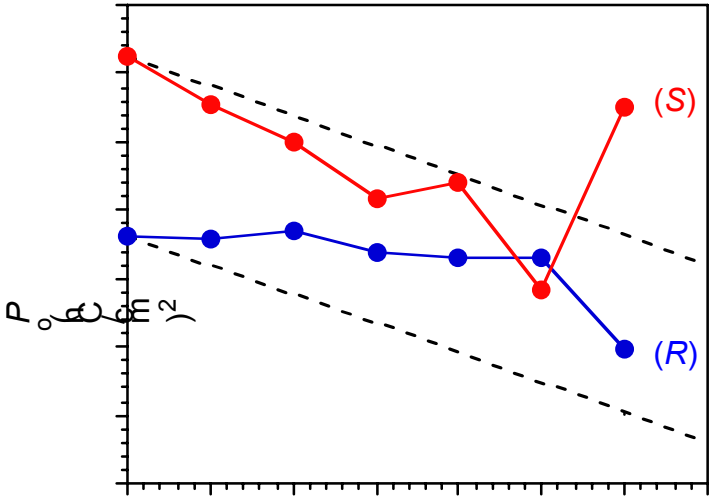
+



C9, 4 mol%



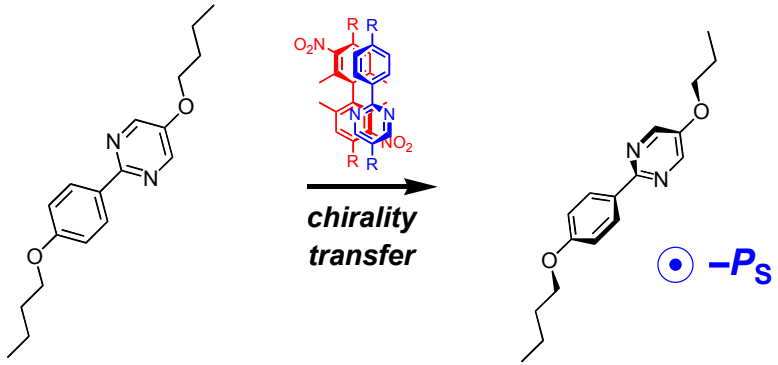
x_d (MDW950)



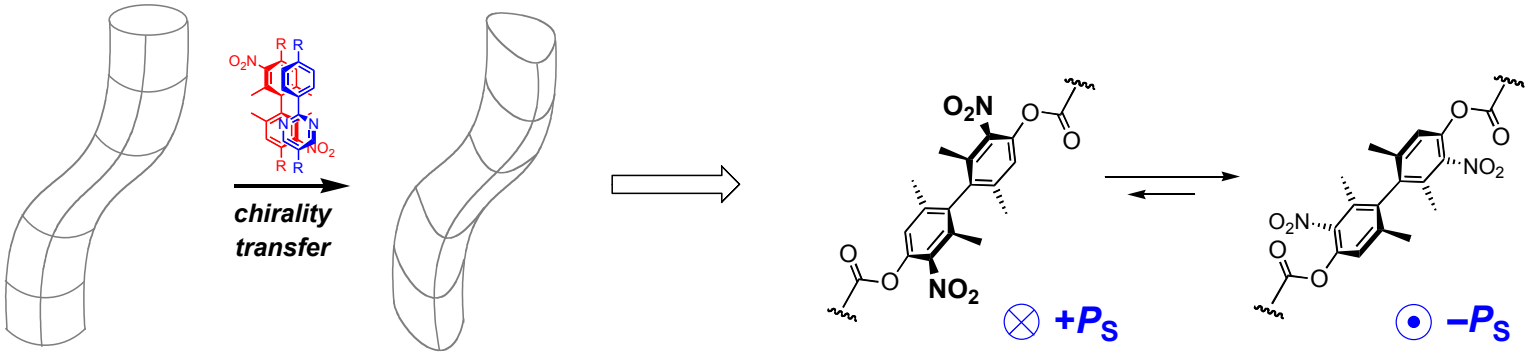
x_d (MDW950)

Effect of Chirality Transfer

(i) Polar Ordering of the Host

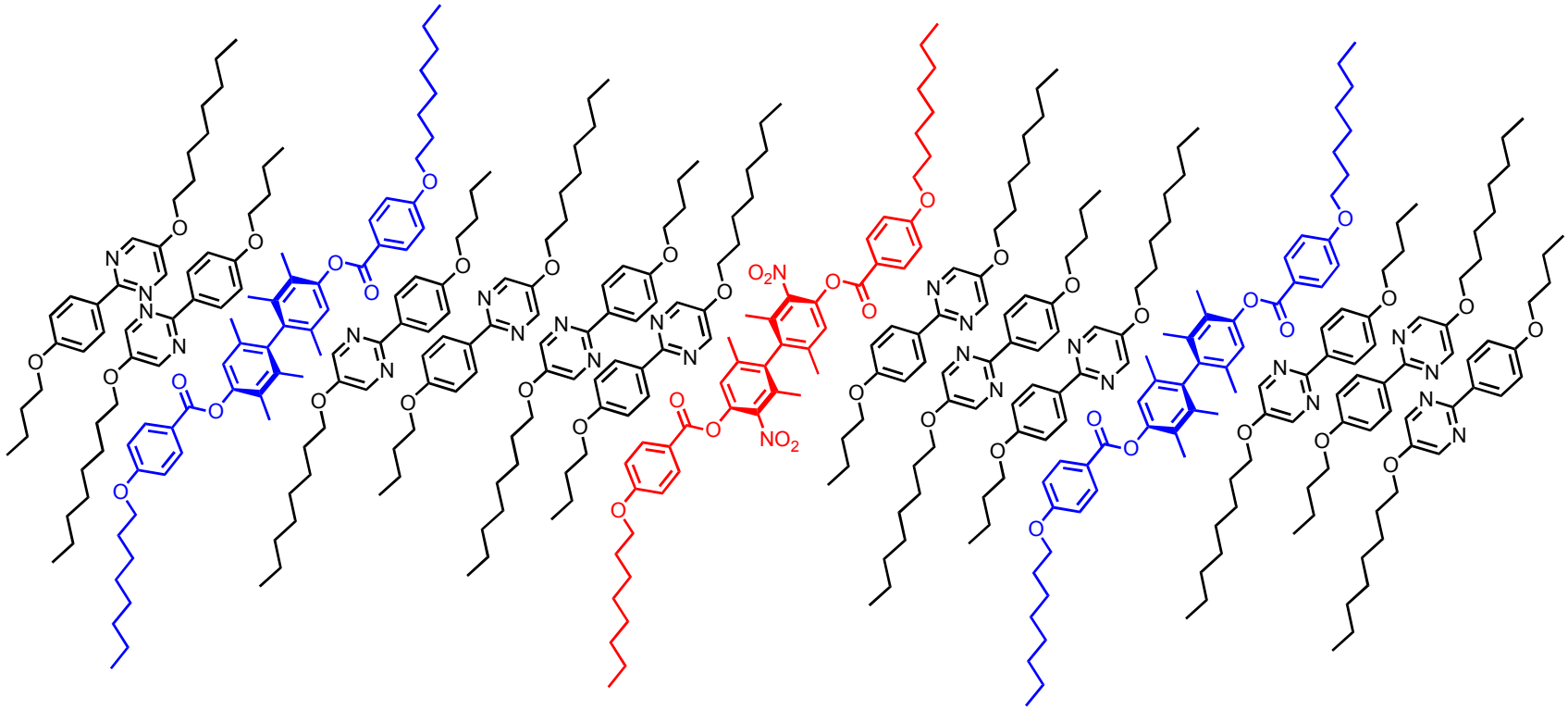


(ii) Chirality Transfer Feedback



shift in conformational equilibrium

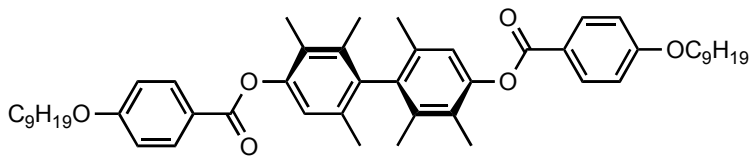
Probe Experiment: Hexamethyl Dopant



$\delta_p/\mu_\perp$ = 440 nC/cm^2•D $\delta_p/\mu_\perp$ = 70 nC/cm^2•D

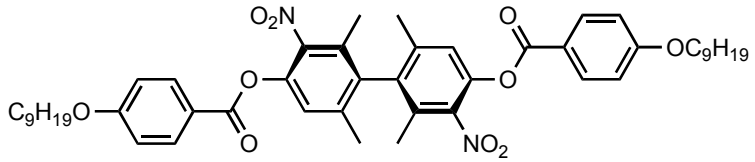
Hartley, C.S.; Lazar, C.; Wand, M.D.; Lemieux, R.P. *J. Am. Chem. Soc.* **2002**, *124*, 13513

Probe Experiment: Hexamethyl Dopant

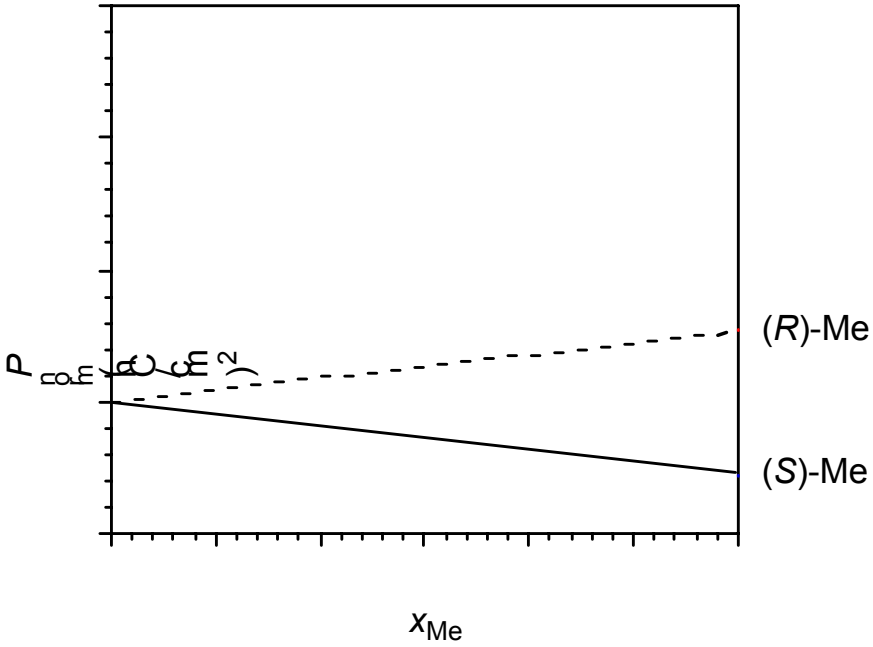


(*R*)- and (*S*)-Me probe

+

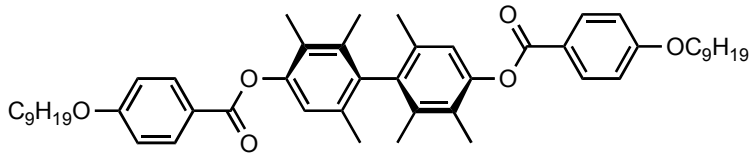


(*S*)-C9, 4 mol%



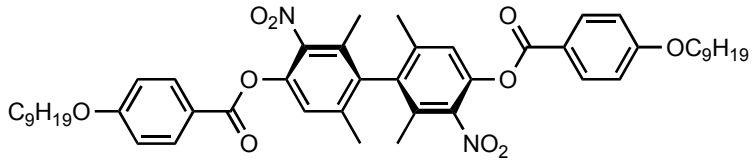
Hartley, C.S.; Lazar, C.; Wand, M.D.; Lemieux, R.P. *J. Am. Chem. Soc.* **2002**, *124*, 13513

Probe Experiment: Hexamethyl Dopant



(*R*)- and (*S*)-Me probe

+



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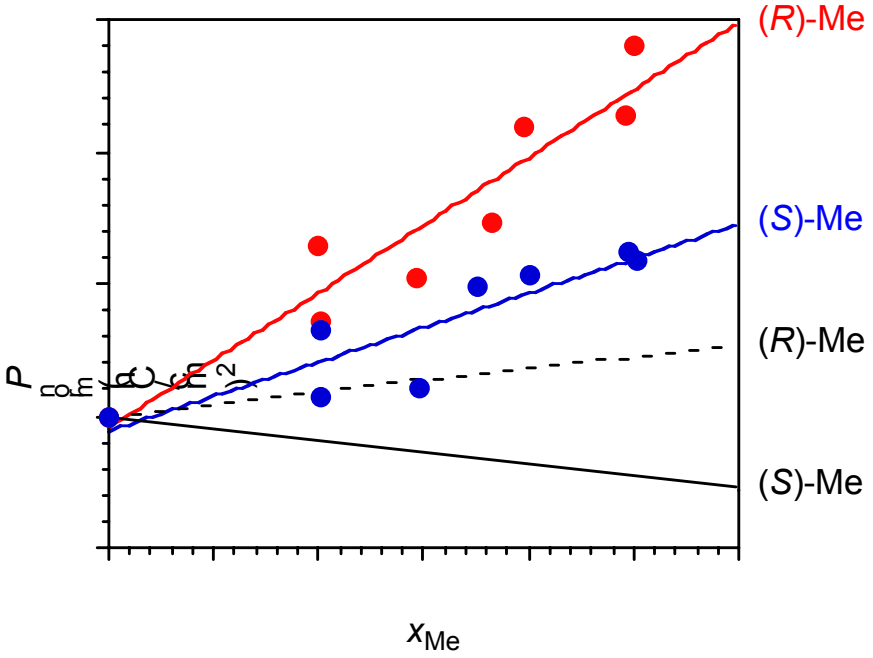

Hartley, C.S.; Lazar, C.; Wand, M.D.; Lemieux, R.P. *J. Am. Chem. Soc.* **2002**, *124*, 13513

Effect of Chirality Transfer

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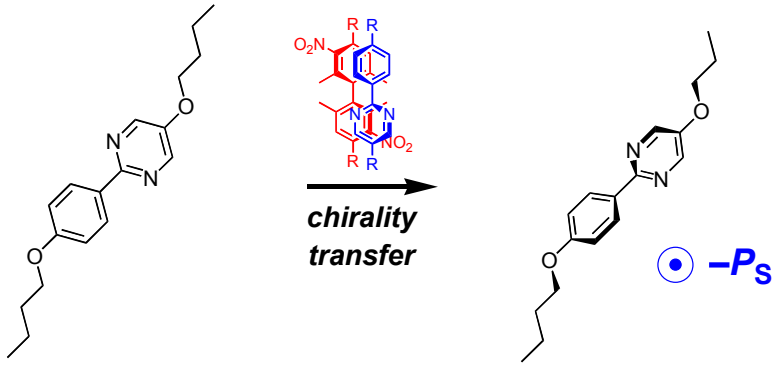
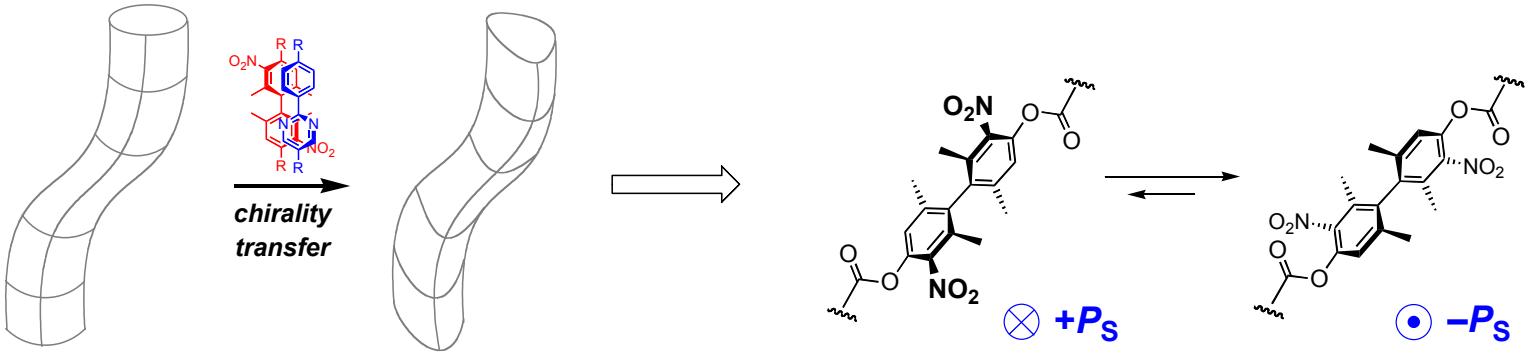


(ii) Chirality Transfer Feedback



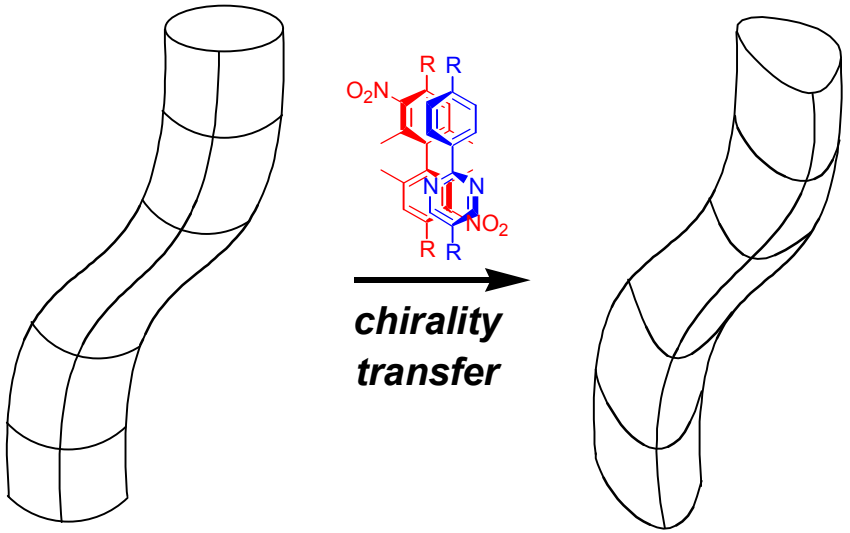
shift in conformational equilibrium

Analogy to Molecular Imprinting ?

Chiral Molecular Imprinting

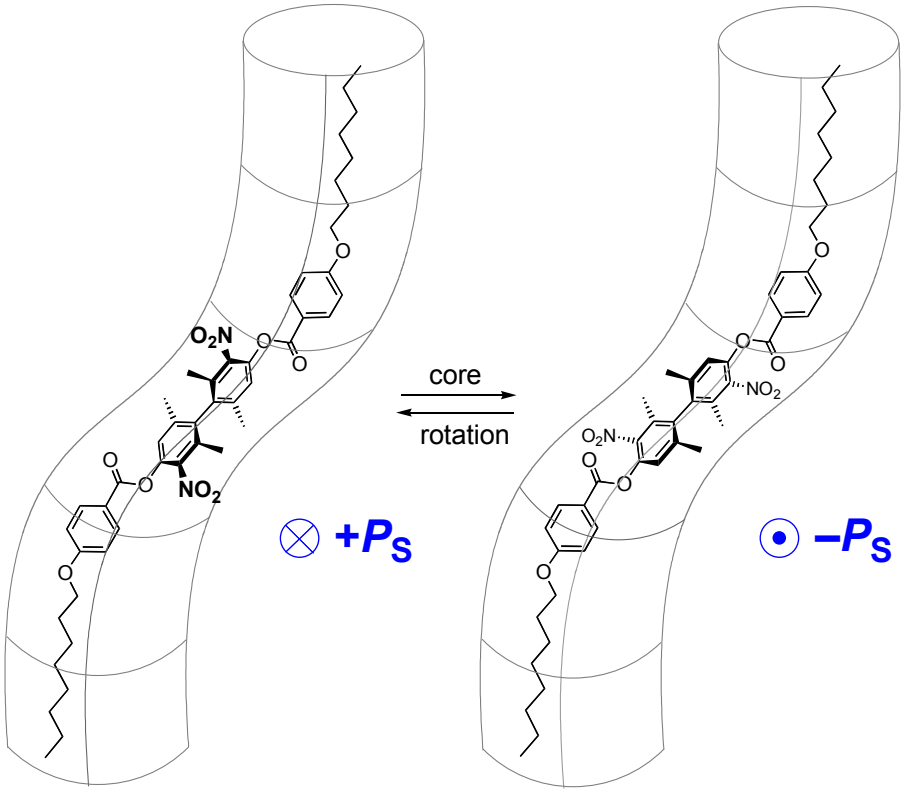
QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

Chirality Transfer Feedback

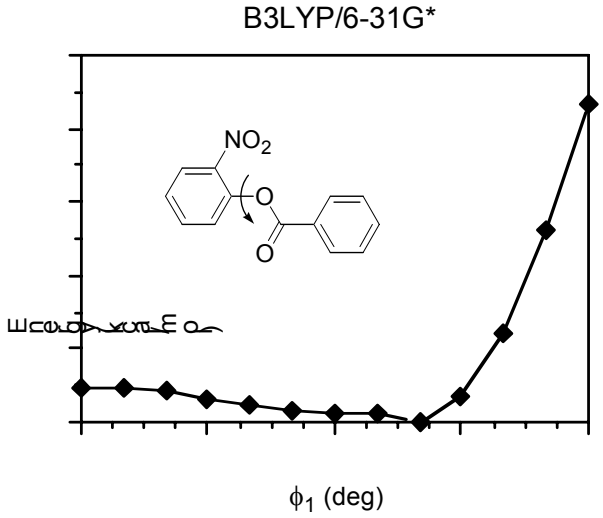


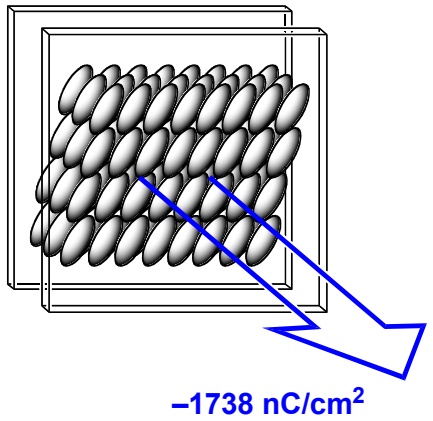
Induction of Polarization: 2,2’-Spirobiindan-1,1’-diones

Conformational Asymmetry



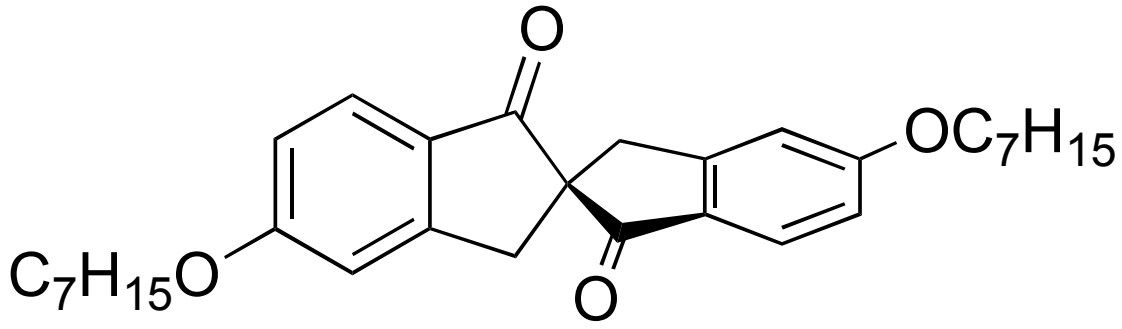
(*R*) enantiomer



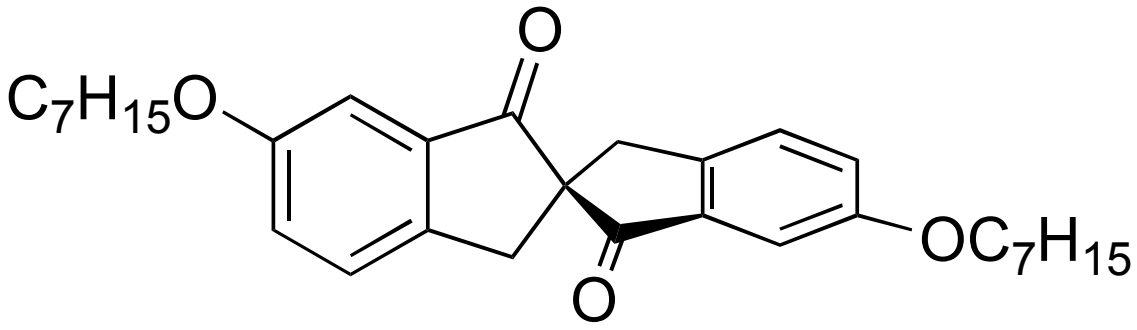


D. Vizitiu, C. Lazar, J.P. Radke, C.S. Hartley, M.A. Glaser, R.P. Lemieux *Chem. Mater.*, **2001**, *13*, 1692

2,2’-Spirobiindan-1,1’-dione Dopants

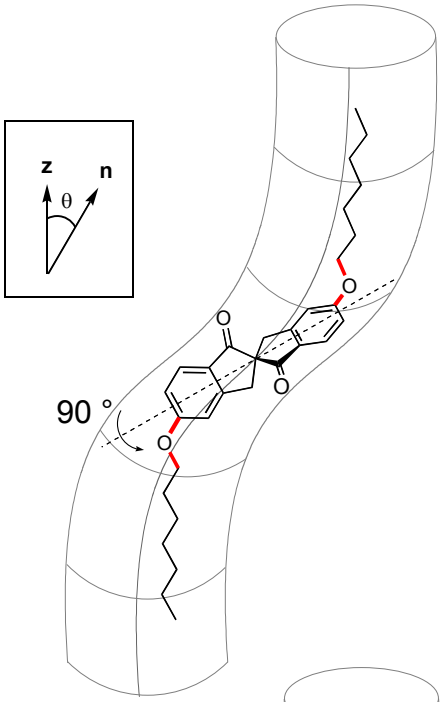


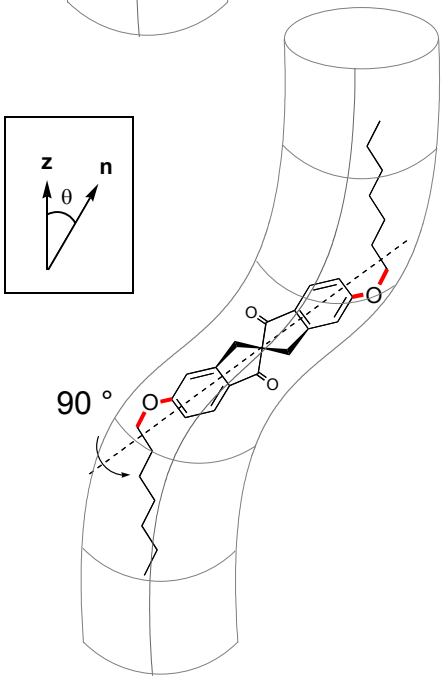
5,5’

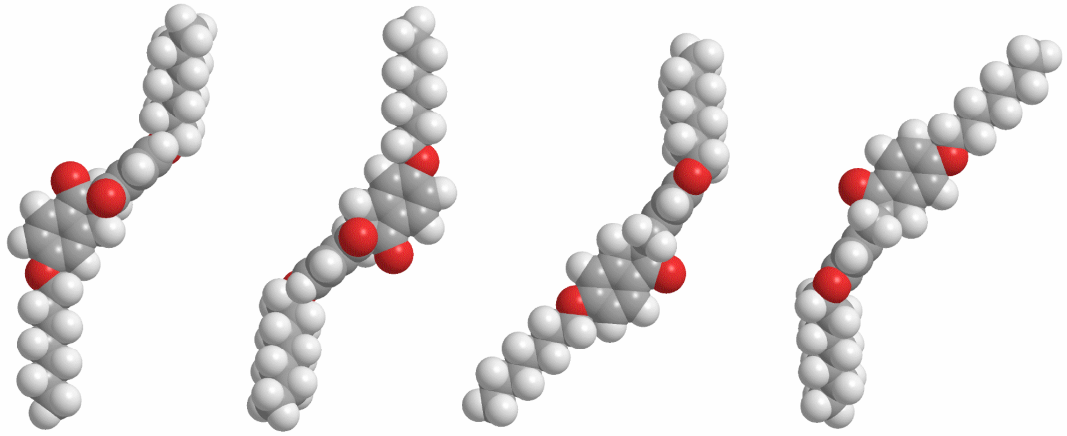


6,6’

Conformational Analysis: AM1



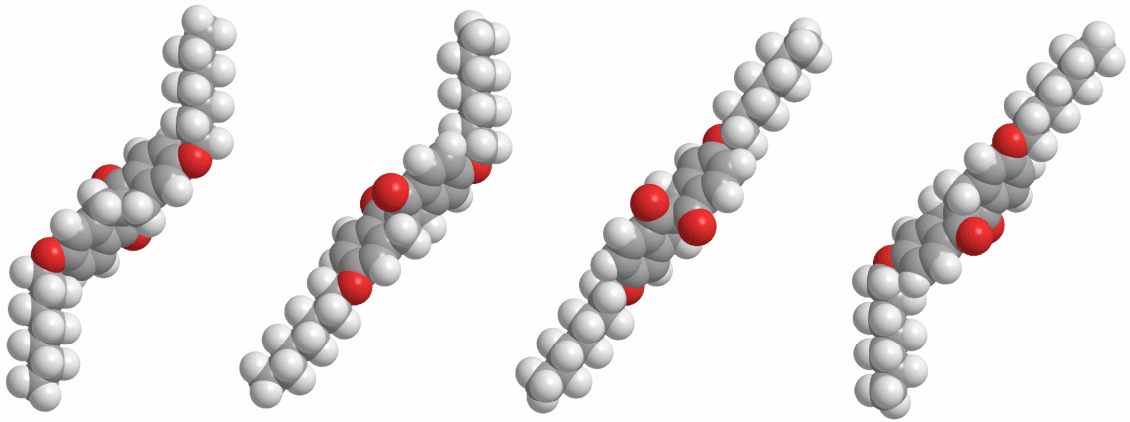




PI **PI'** **PII** **PII'**

ΔH_f −162.30 kcal/mol −162.17 kcal/mol

$\mu_\perp$ +1.61 D ⊗ −1.61 D ⊙

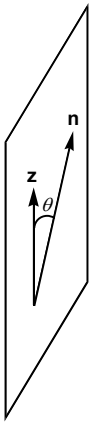


C_2I **C_2II** **C_2III** **C_2IV**

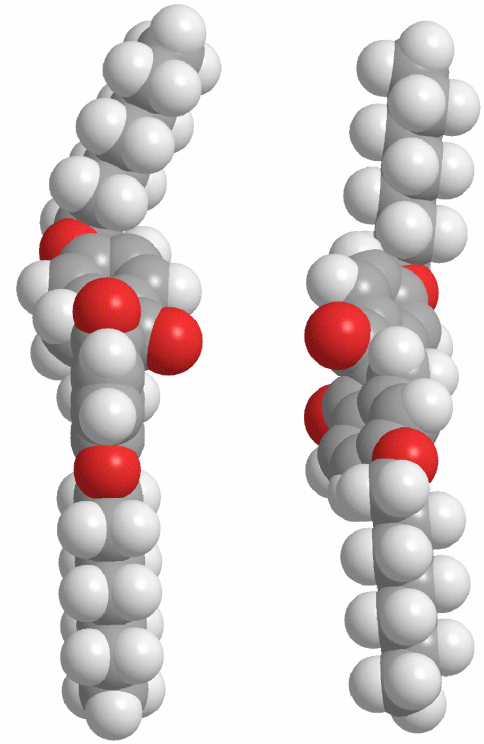
ΔH_f −162.30 kcal/mol −162.34 kcal/mol −162.34 kcal/mol −162.35 kcal/mol

$\mu_\perp$ −2.70 D ⊙ 0.00 D +2.68 D ⊗ 0.00 D

Conformational Analysis: 5,5’ vs 6,6’



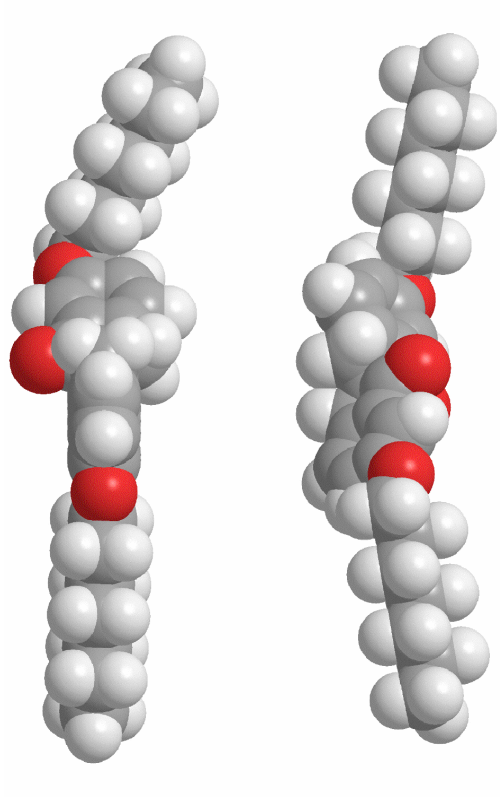
(*R*)-5,5’



P ⊕ ← ⊖ **C$_2$** ⊖ → ⊕

	P	C$_2$
$\mu_\perp$	**+1.61**	**–2.70**
ΔH_f	**–162.17**	**–162.31**

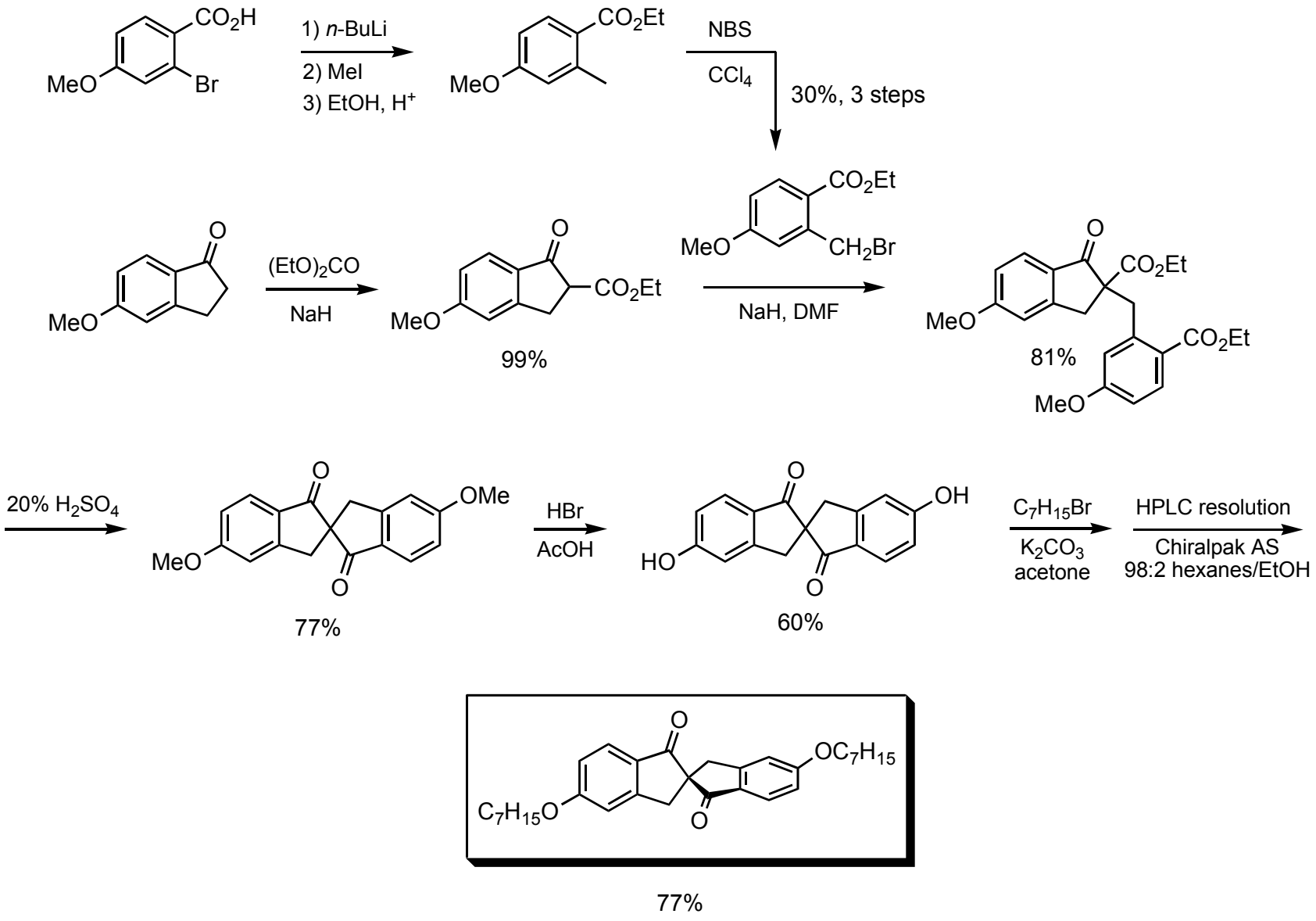
(*R*)-6,6’



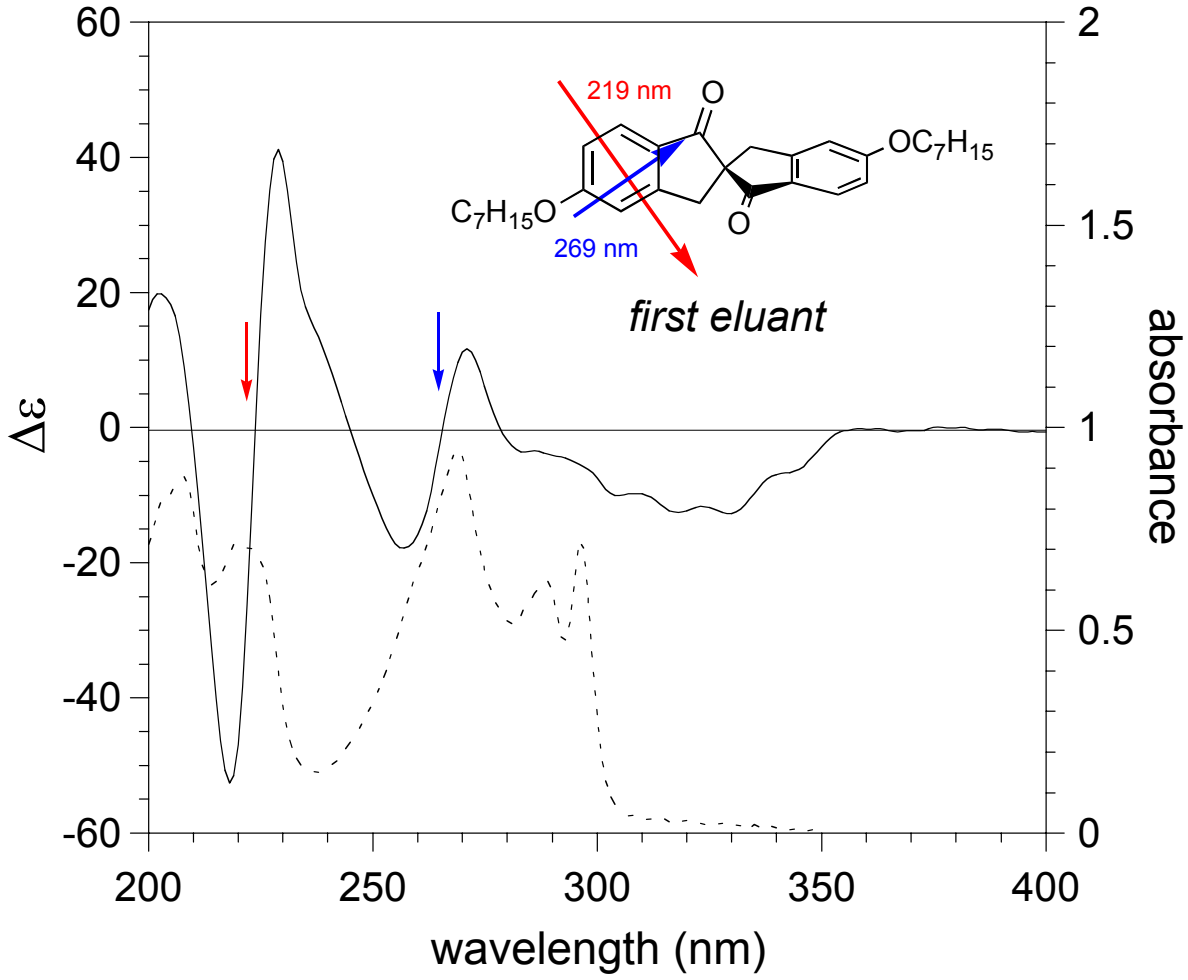
P ⊖ → ⊕ **C$_2$** ⊕ ← ⊖

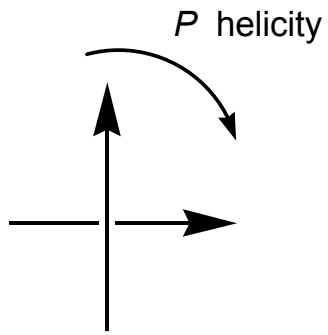
	P	C$_2$	
$\mu_\perp$	**–3.52**	**+4.30**	(D)
ΔH_f	**–159.68**	**–159.44**	(kcal/mol)

Synthesis


CO2H
MeO
Br
1) n-BuLi
2) MeI
3) EtOH, H+
CO2Et
MeO
NBS
CCl4
30%, 3 steps
CO2Et
MeO
CH2Br
O
MeO
(EtO)2CO
NaH
O
CO2Et
MeO
99%
NaH, DMF
O
CO2Et
MeO
CO2Et
81%
MeO
20% H2SO4
O
OMe
MeO
O
HBr
AcOH
O
OH
HO
O
C7H15Br
K2CO3
acetone
HPLC resolution
Chiralpak AS
98:2 hexanes/EtOH
77%
60%
O
OC7H15
C7H15O
O
77%

Stereochemistry: Exciton Chirality



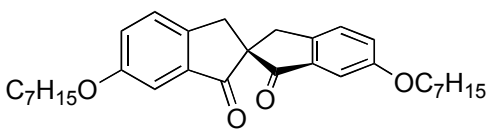


positive split
Cotton effect

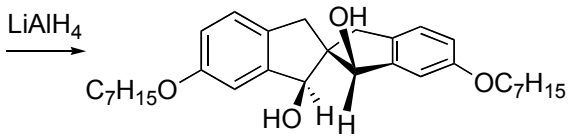
(*R*)

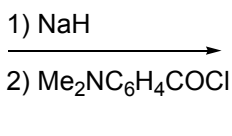
N. Harada and K. Nakanishi, *Circular Dichroic Spectroscopy: Exciton Coupling in Organic Photochemistry*, University Science Books, New York, 1983

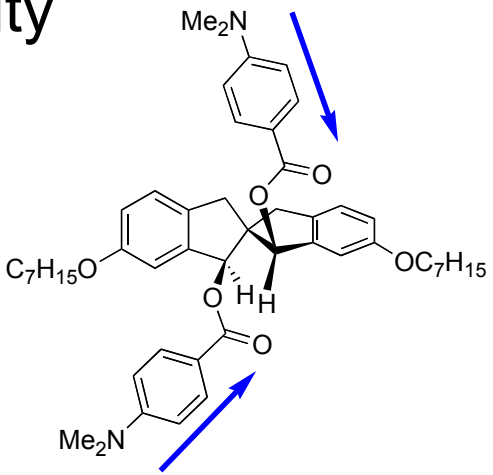
Stereochemistry: Exciton Chirality

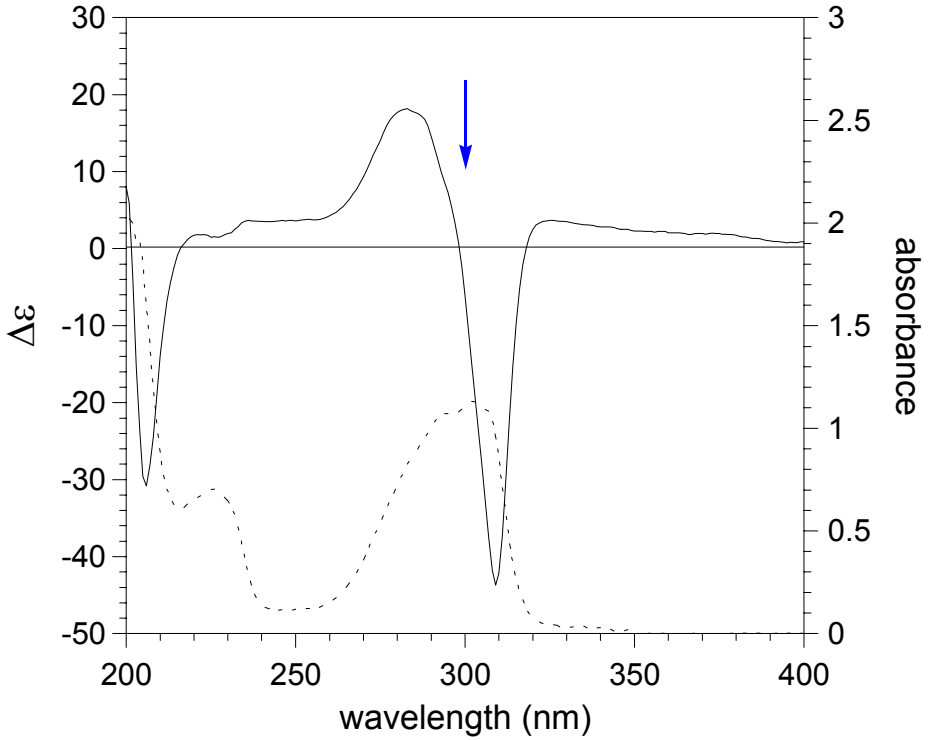


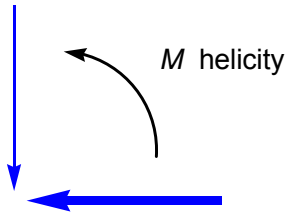
second eluant







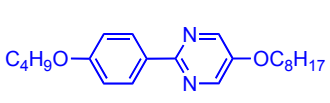




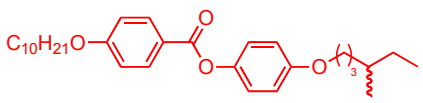
negative split
Cotton effect

(*S*)

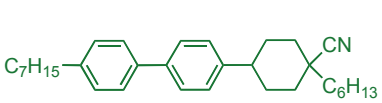
Dopant-Host Compatibility



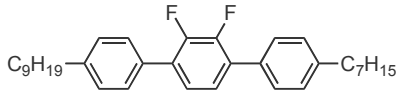
PhP1



PhB

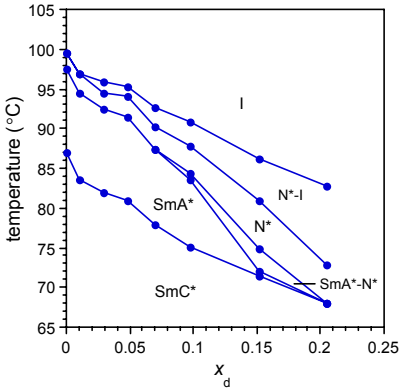


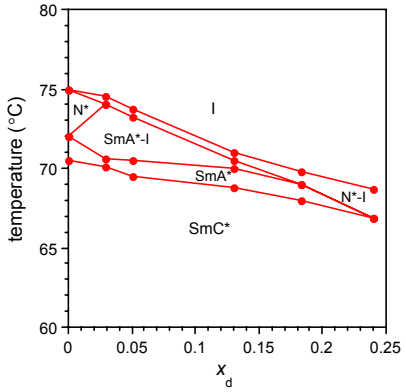
NCB76

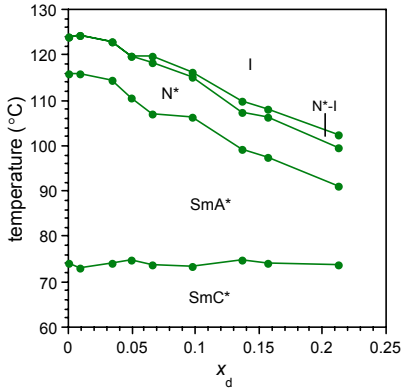


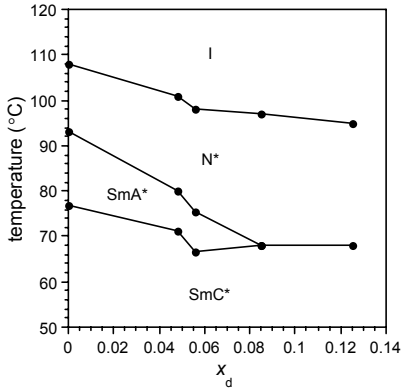
DFT

5,5’

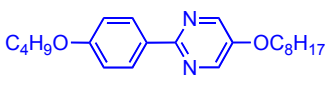




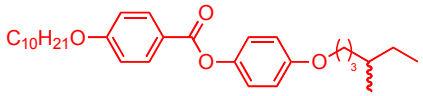




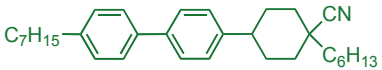
Dopant-Host Compatibility



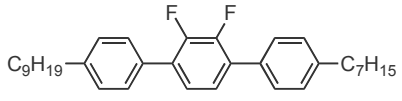
PhP1



PhB

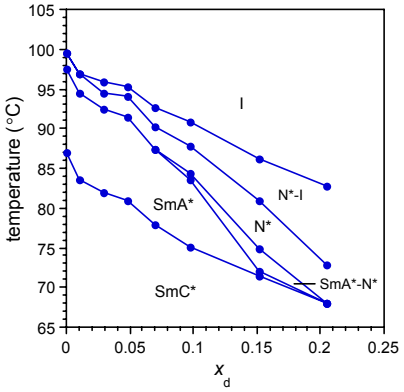


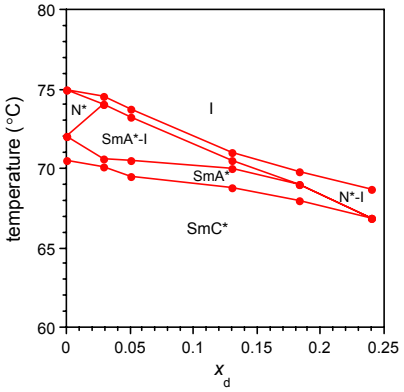
NCB76

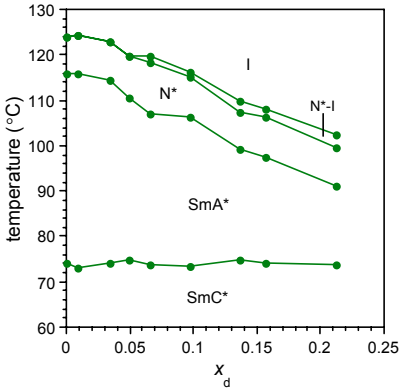


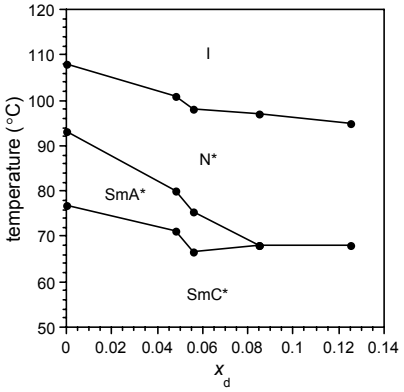
DFT

5,5'





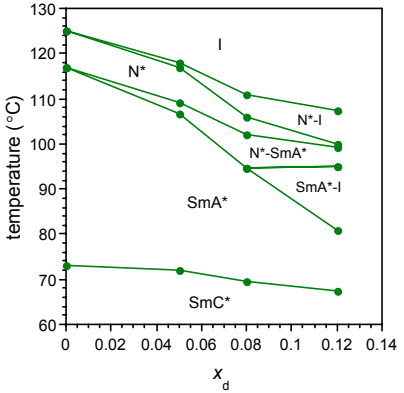




6,6'

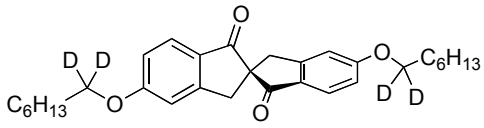
SmC*/I biphasic at x_d > 0.03

SmC*/I biphasic at x_d > 0.05

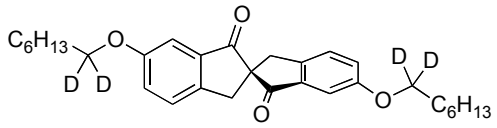


SmC*/I biphasic at x_d > 0.05

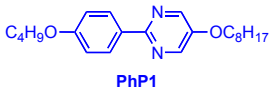
^{2}H NMR @ T–T_C = –10 K



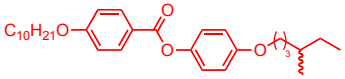
(±)-5,5'



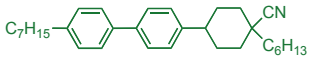
(±)-6,6'



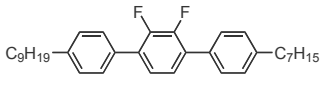
PhP1



PhB

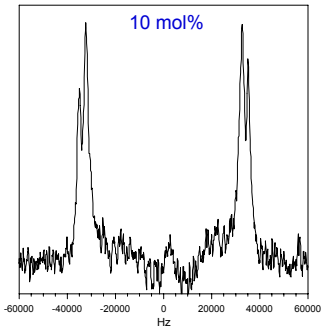


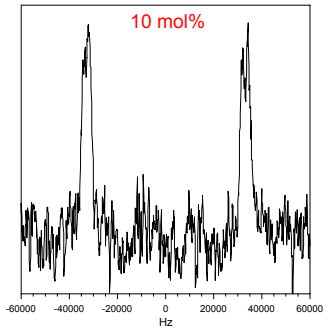
NCB76

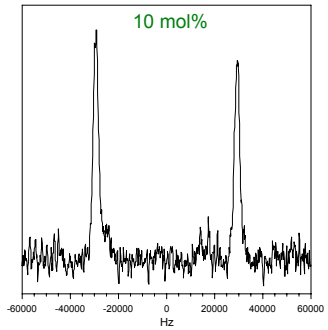


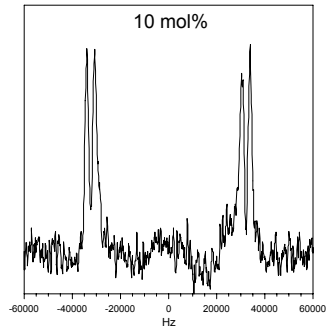
DFT

5,5’

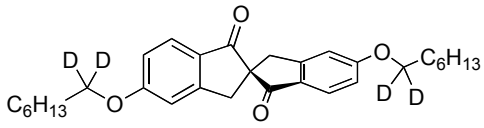




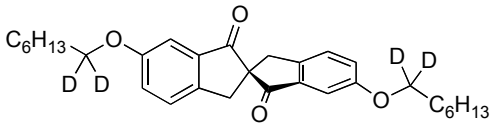




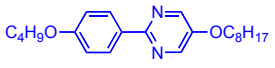
^{2}H NMR @ T–T_C = –10 K



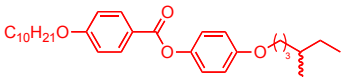
(±)-5,5'



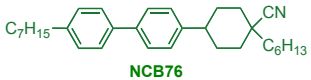
(±)-6,6'



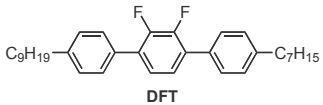
PhP1



PhB

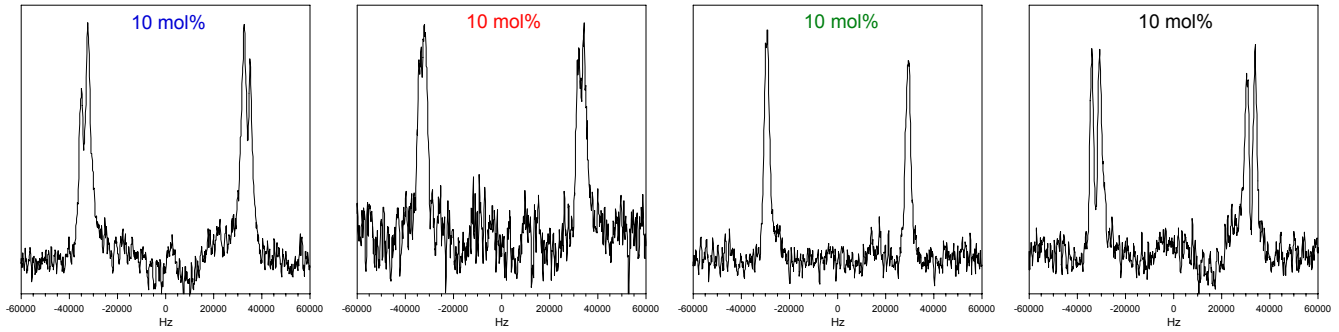


NCB76

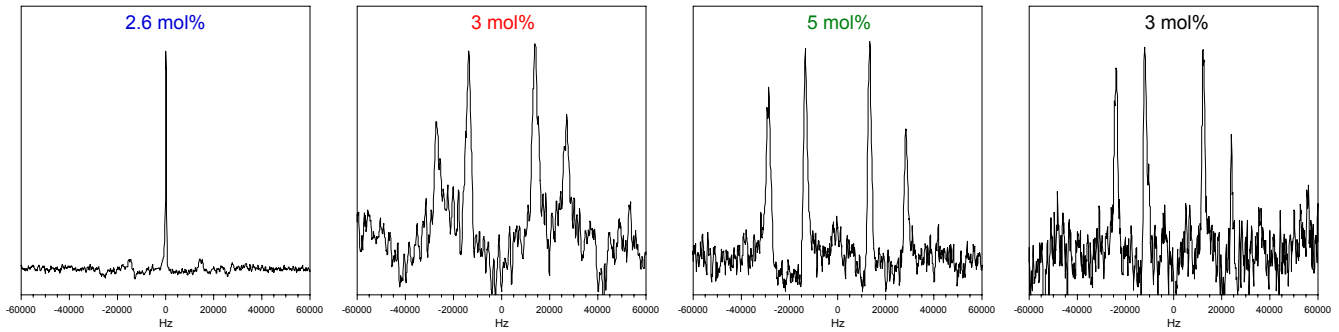


DFT

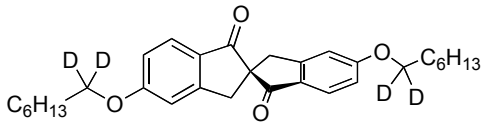
5,5’



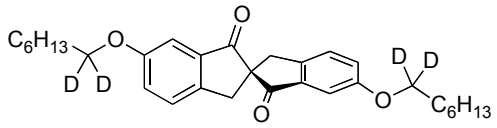
6,6’



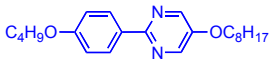
^{2}H NMR @ T–T_C = –10 K



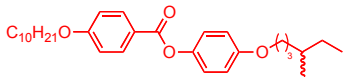
(±)-5,5'



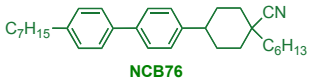
(±)-6,6'



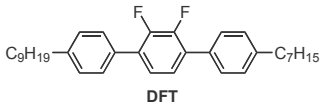
PhP1



PhB

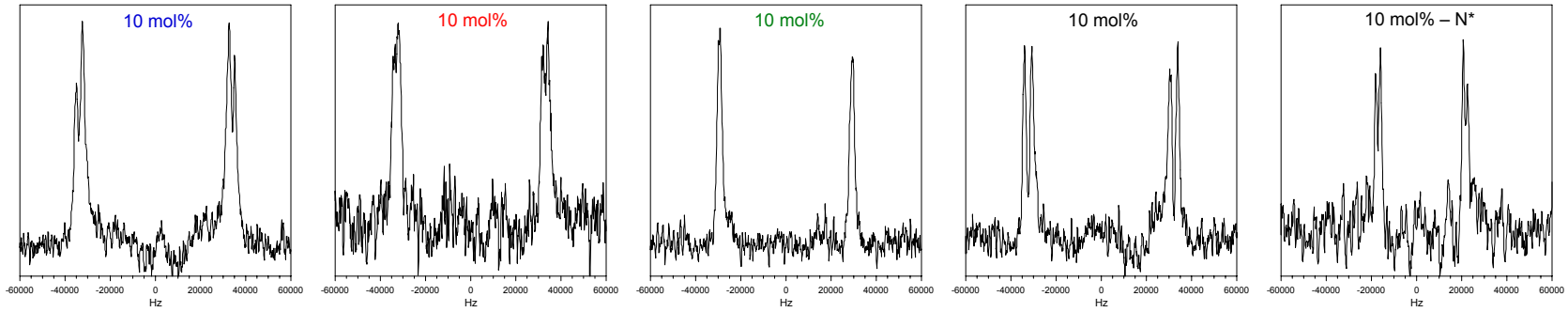


NCB76

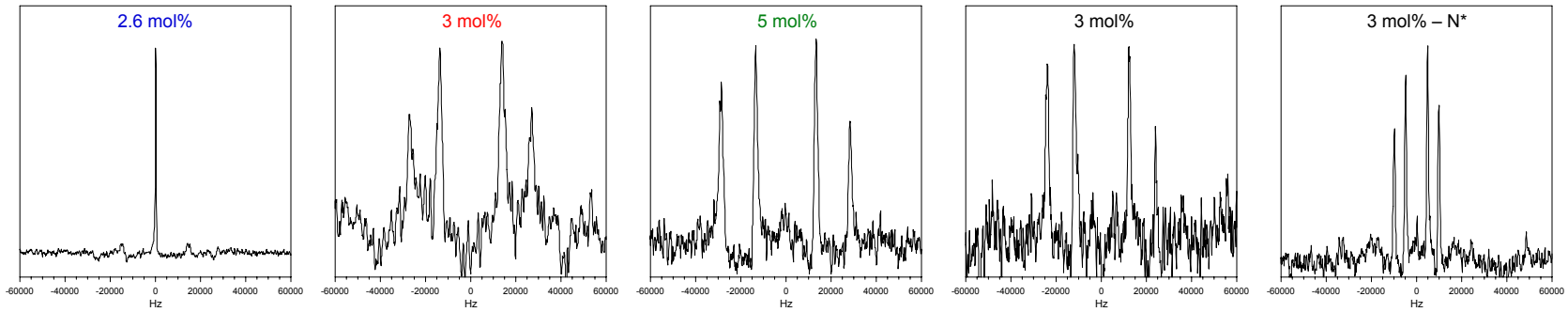


DFT

5,5'



6,6'



^{2}H NMR in a Chiral Nematic Host: Poly-γ-Benzyl-L-Glutamate

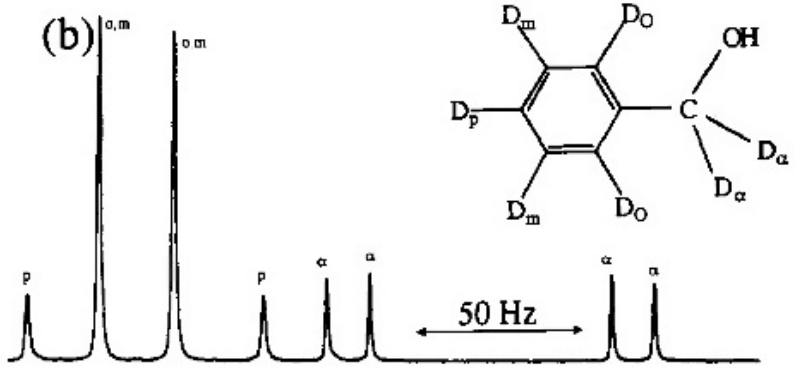


Figure 4. Proton-decoupled ^{2}H NMR spectra in PBLG/CH_2Cl_2 solvent of (a) racemic C_6D_5–CHD–OH at T = 300 K, and (b) nonchiral C_6D_5–CD_2–OH at T = 306 K.

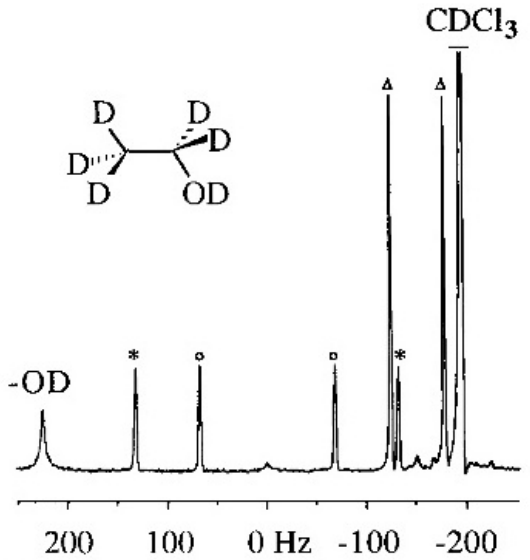


Figure 2. ^{2}H−{^{1}H} partial spectrum of perdeuterated ethanol dissolved in the PBLG/$CDCl_3$ phase. A Gaussian filtering and zero filling to 8K data points were used to improve the spectral appearance and the digital resolution. (*, o) Components of doublets belonging to the methylene group. (△) Components of the doublet belonging to the methyl group. The measured quadrupolar splittings for the −OD group and $CDCl_3$ were 765.8 and 841.3 Hz, respectively. Only the shielded component of each doublet is shown in the figure.

Czarniecka, K.; Samulski, E.T. *Mol. Cryst. Liq. Cryst.* **1981**, *63*, 205.
Meddour, A.; Canet, I.; Loewenstein, A.; Péchiné, J.M.; Courtieu, J. *J. Am. Chem. Soc.* **1994**, *116*, 9652.
Merlet, D.; Loewenstein, A.; Smadja, W.; Courtieu, J.; Lesot, P. *J. Am. Chem. Soc.* **1998**, *120*, 963.

^{2}H NMR in a Chiral Nematic Host: Poly-γ-Benzyl-L-Glutamate

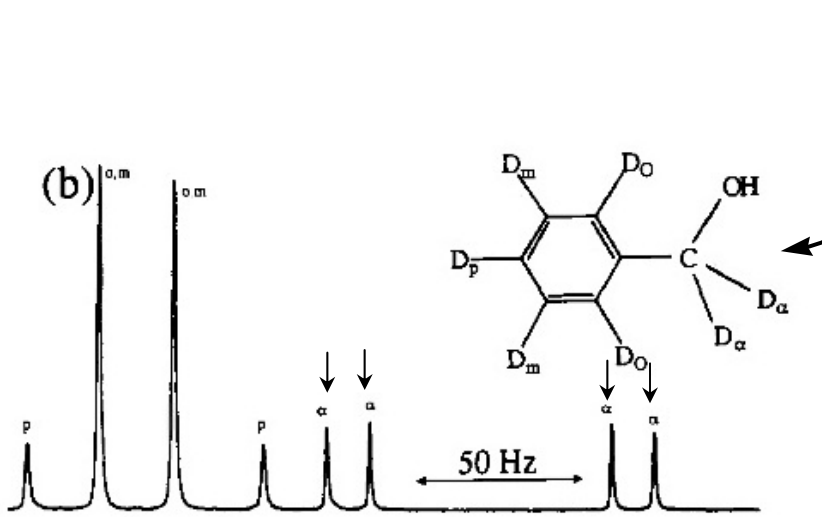


Figure 4. Proton-decoupled ^{2}H NMR spectra in PBLG/CH_2Cl_2 solvent of (a) racemic C_6D_5–CHD–OH at T = 300 K, and (b) nonchiral C_6D_5–CD_2–OH at T = 306 K.

diastereotopic in PBLG

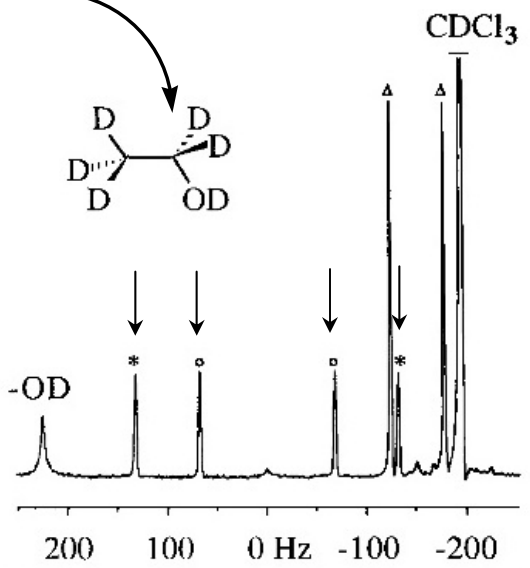
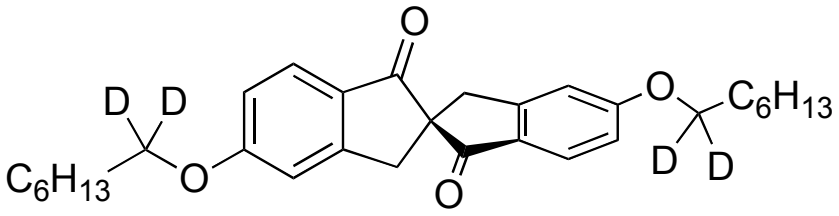


Figure 2. ^{2}H−{^{1}H} partial spectrum of perdeuterated ethanol dissolved in the PBLG/$CDCl_3$ phase. A Gaussian filtering and zero filling to 8K data points were used to improve the spectral appearance and the digital resolution. (*, o) Components of doublets belonging to the methylene group. (△) Components of the doublet belonging to the methyl group. The measured quadrupolar splittings for the −OD group and $CDCl_3$ were 765.8 and 841.3 Hz, respectively. Only the shielded component of each doublet is shown in the figure.

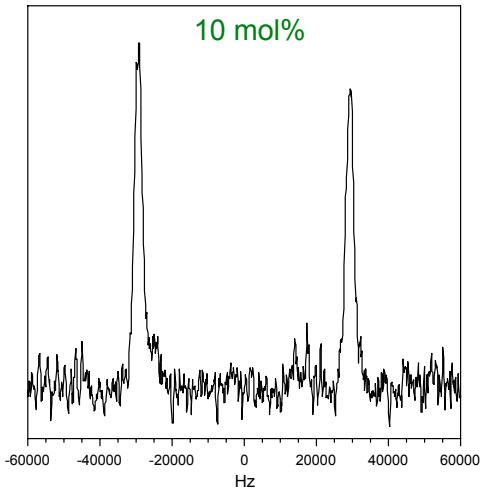
Czarniecka, K.; Samulski, E.T. *Mol. Cryst. Liq. Cryst.* **1981**, *63*, 205.
Meddour, A.; Canet, I.; Loewenstein, A.; Péchiné, J.M.; Courtieu, J. *J. Am. Chem. Soc.* **1994**, *116*, 9652.
Merlet, D.; Loewenstein, A.; Smadja, W.; Courtieu, J.; Lesot, P. *J. Am. Chem. Soc.* **1998**, *120*, 963.

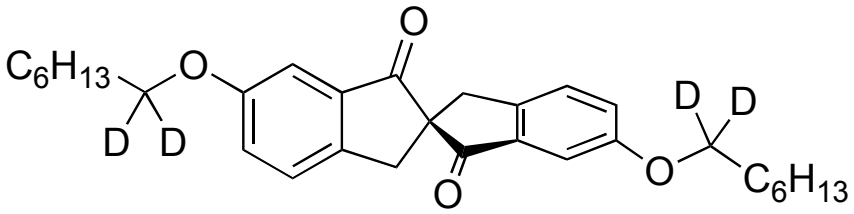
Evidence of Chirality Transfer ?



(±)-5,5'

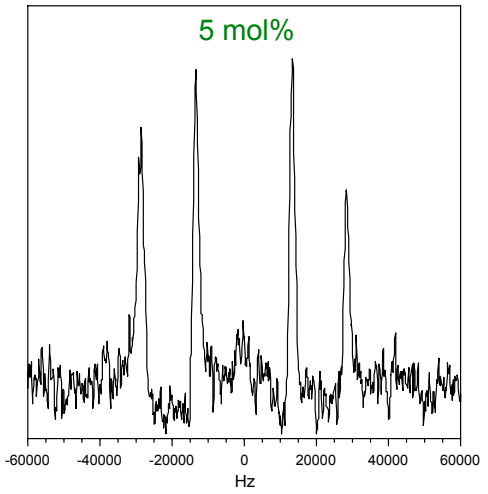
no chirality transfer



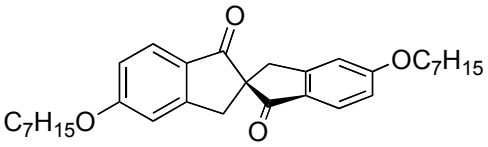


(±)-6,6'

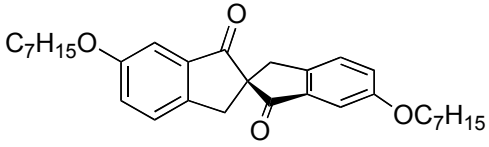
diastereotopic in the SmC* phase
due to chirality transfer ??



Polarization Power @ $T–T_C$ = –10 K



(*R*)-5,5'



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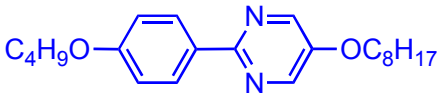
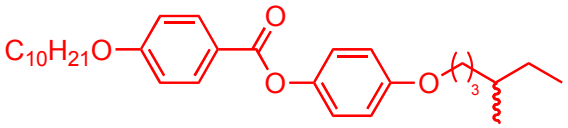
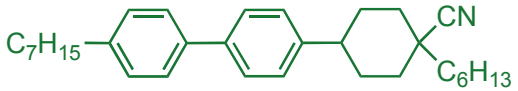


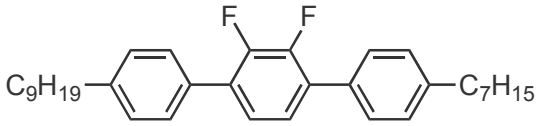
PhP1



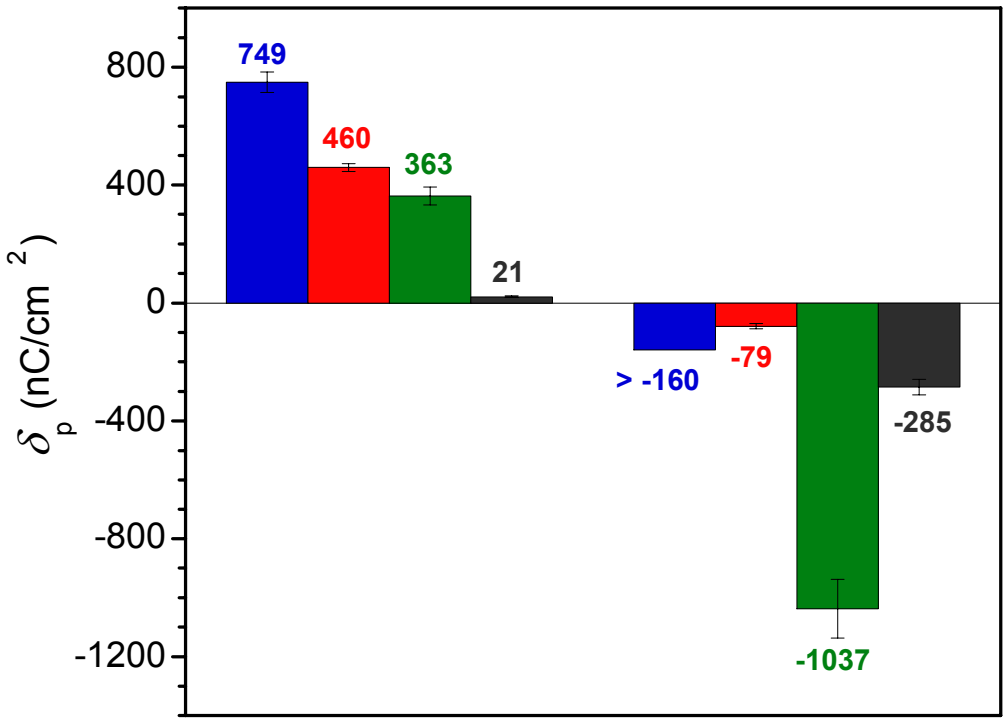
PhB



NCB76

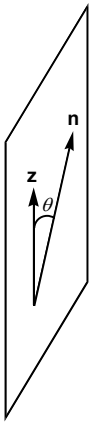


DFT

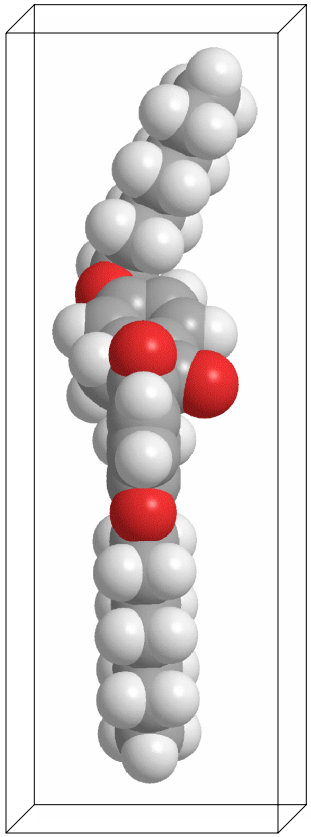


(*R*)-**5,5'** (*R*)-**6,6'**

Conformational Analysis: 5,5’ vs 6,6’

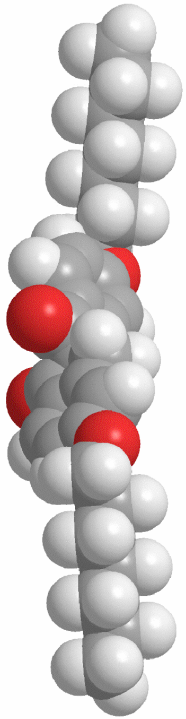


(*R*)-5,5’



P

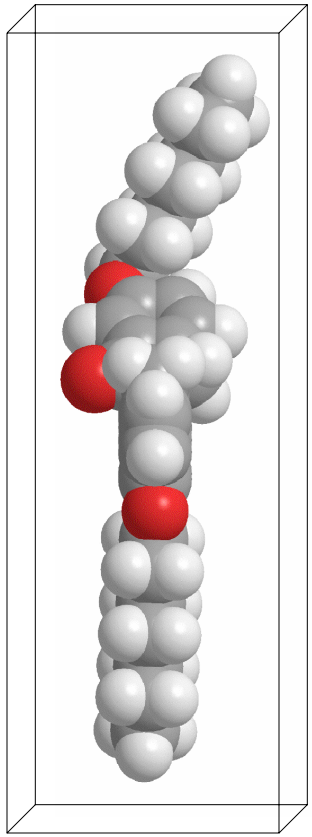
⊕ ← ⊖



C_2

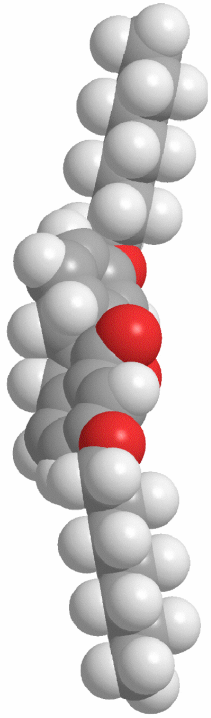
⊖ → ⊕

(*R*)-6,6’



P

⊖ → ⊕

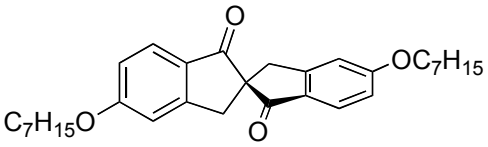


C_2

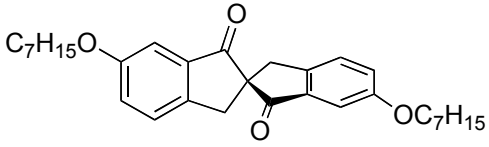
⊕ ← ⊖

$\mu_\perp$	**+1.61**	**–2.70**	**–3.52**	**+4.30**	(D)
ΔH_f	**–162.17**	**–162.31**	**–159.68**	**–159.44**	(kcal/mol)

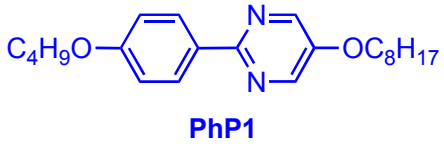
Polarization Power @ $T–T_C$ = –10 K



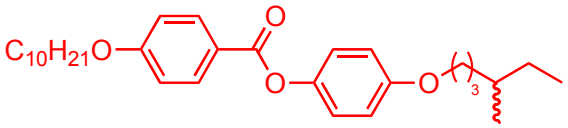
(*R*)-5,5'



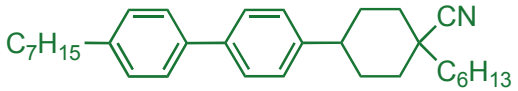
(*R*)-6,6'



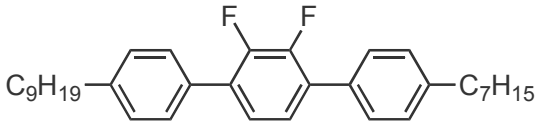
PhP1



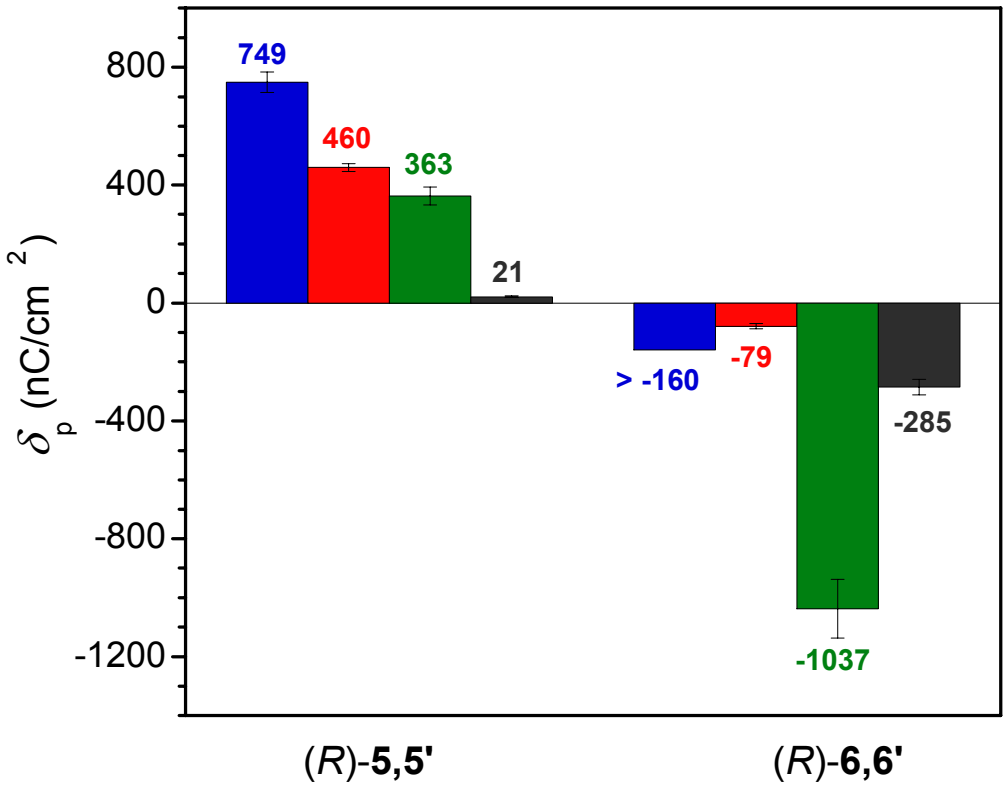
PhB



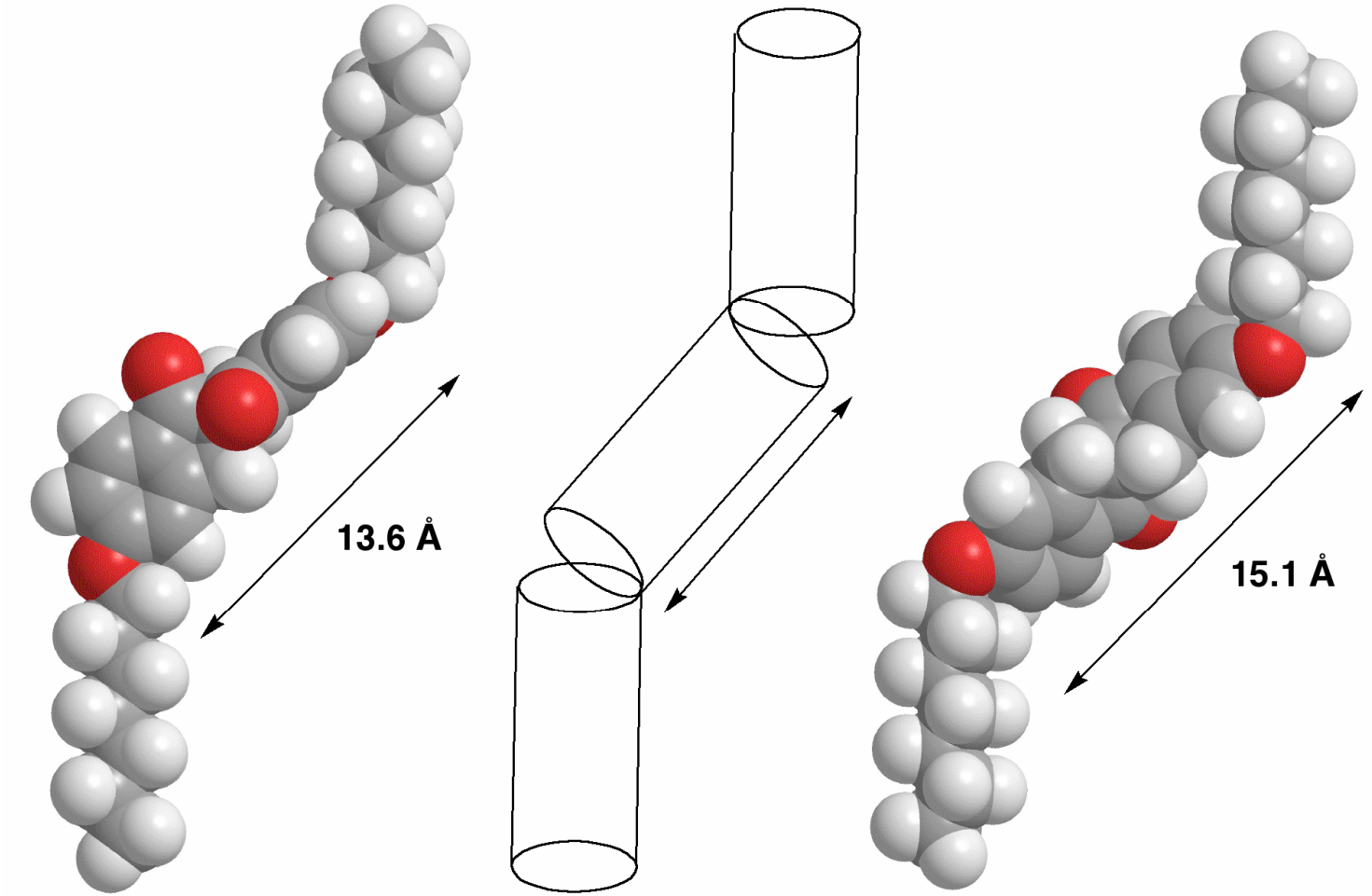
NCB76



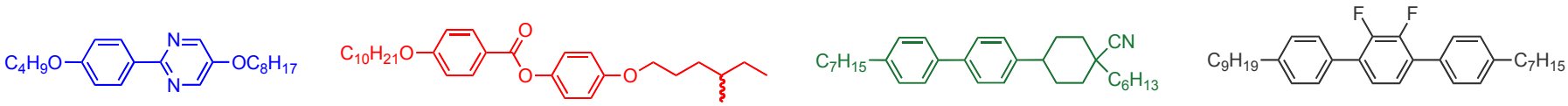
DFT

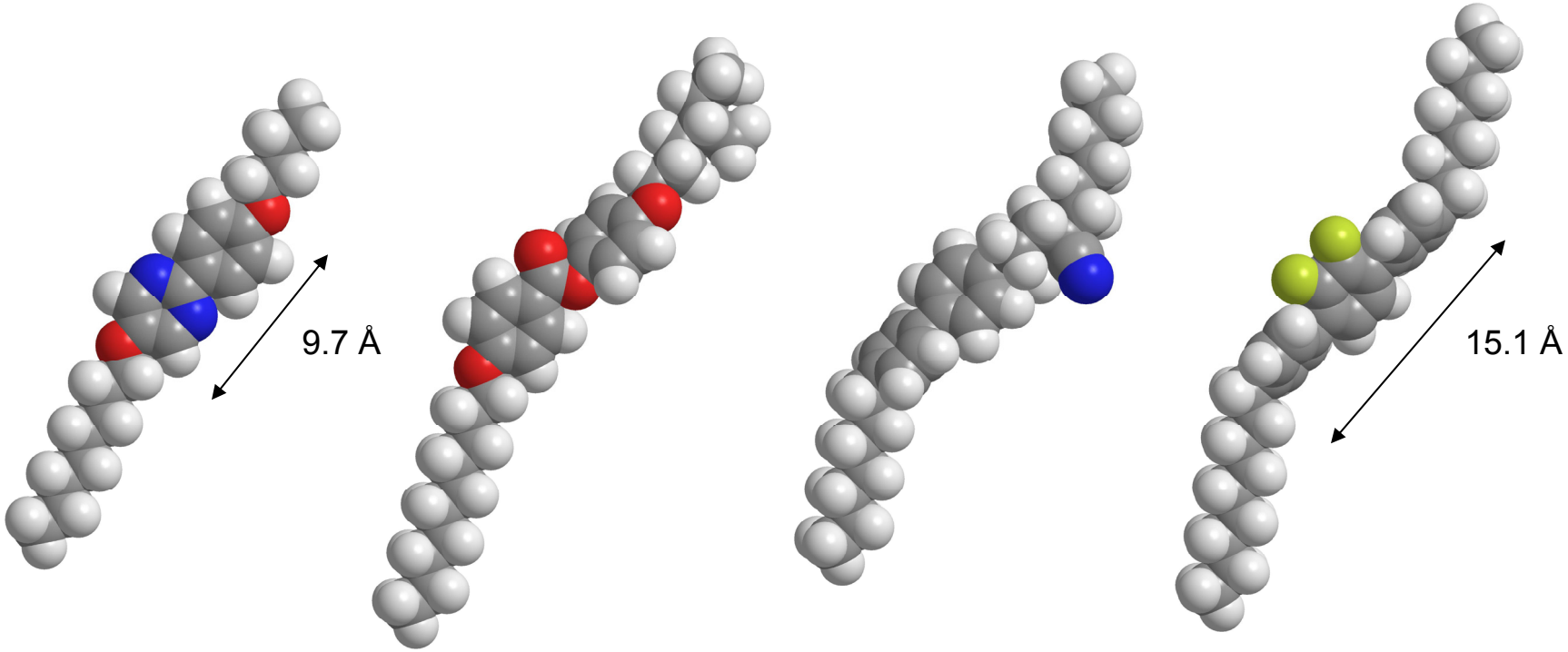


Conformational Steric Demand



Conformational Steric Demand

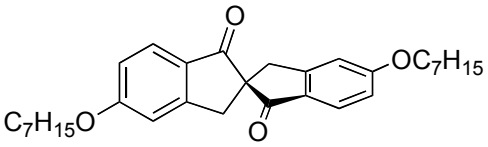




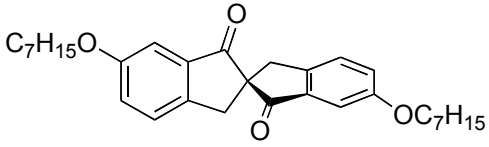
shift towards **P**

shift towards **C_2**

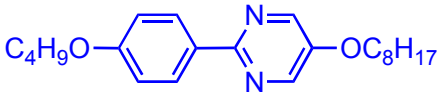
Polarization Power @ $T–T_C$ = –10 K



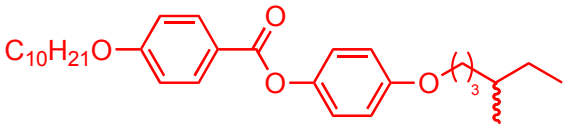
(*R*)-5,5'



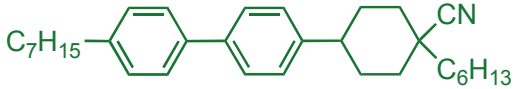
(*R*)-6,6'



PhP1



PhB



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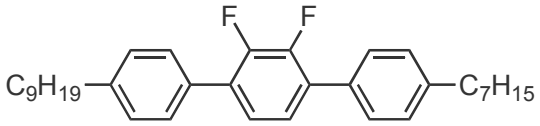
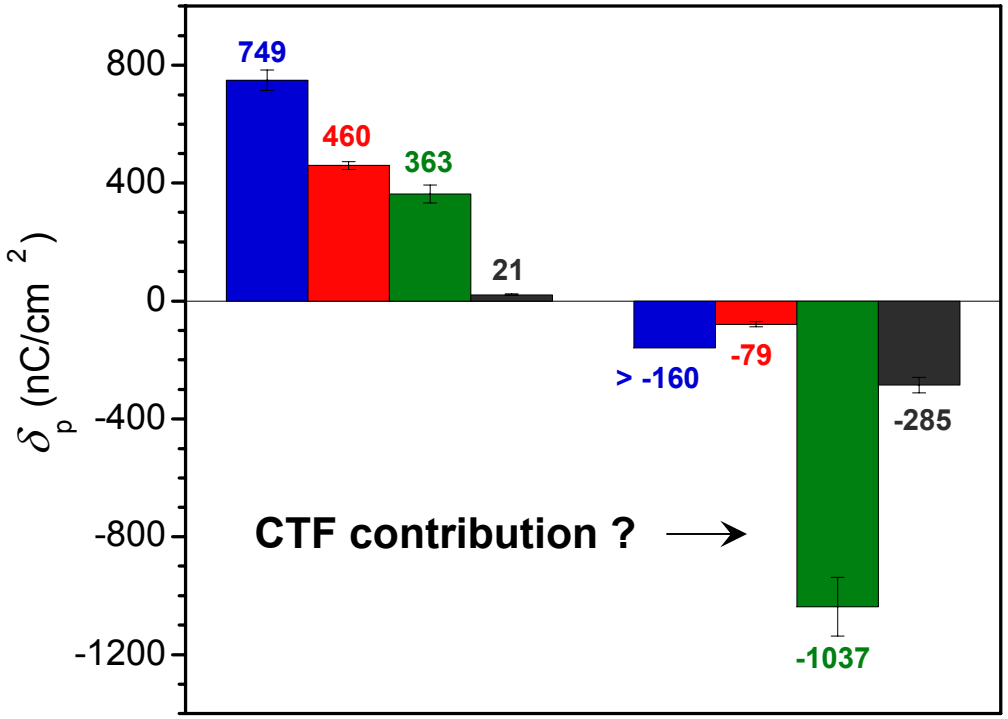
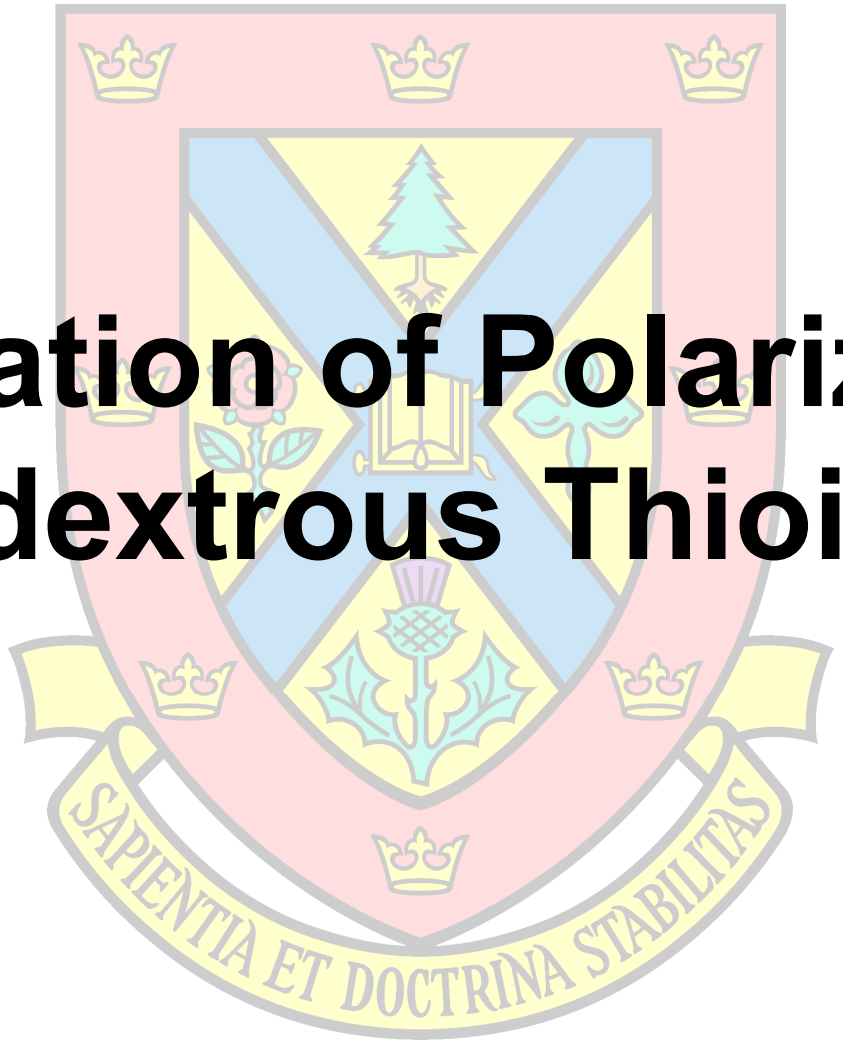


DFT

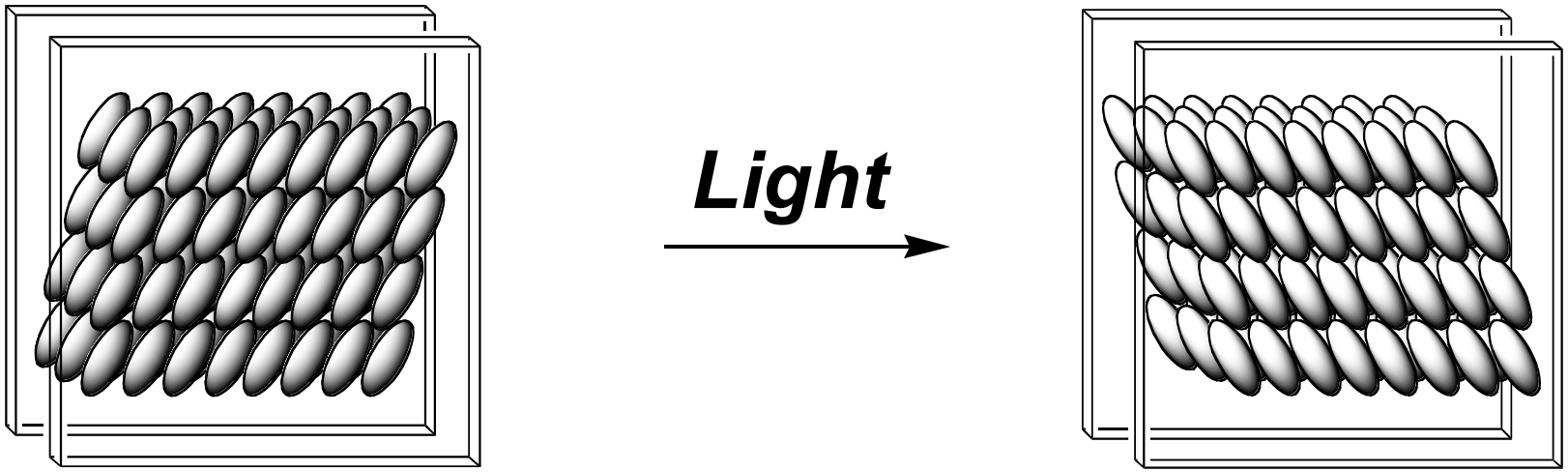


(*R*)-**5,5'** (*R*)-**6,6'**



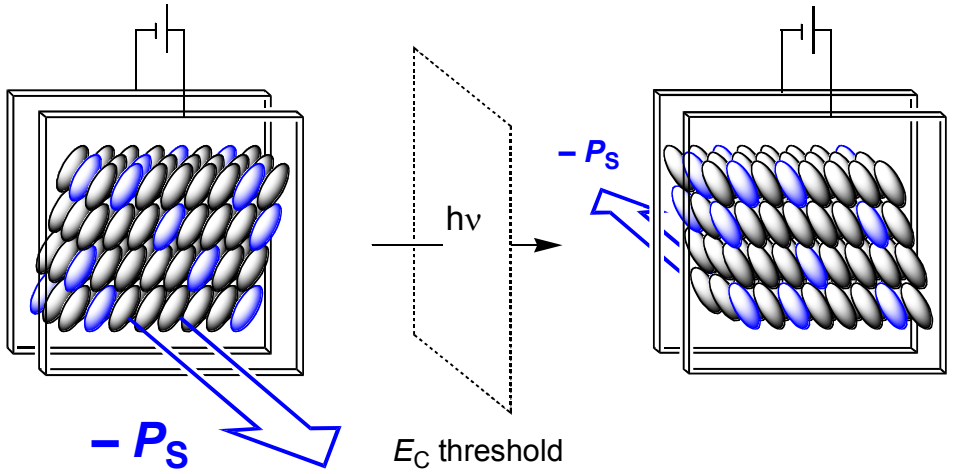
Modulation of Polarization: Ambidextrous Thioindigo

Optical Switching of SSFLC

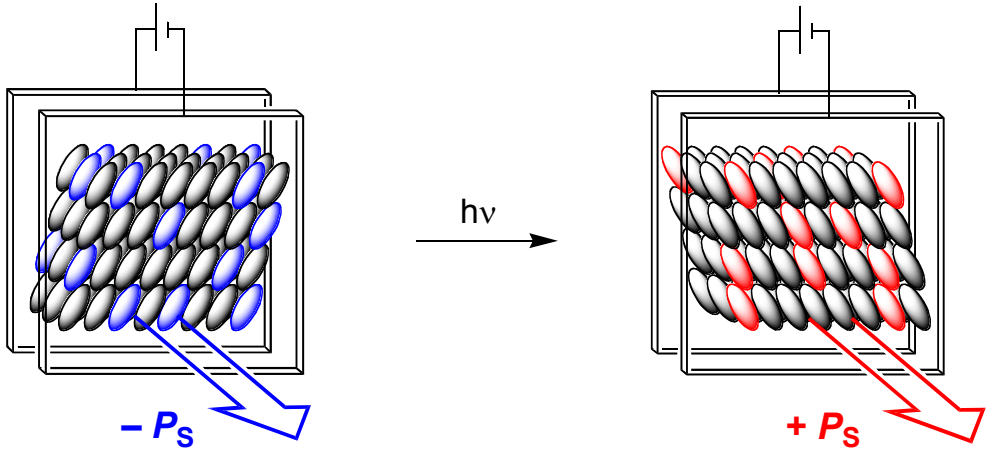


Optical Switching of SSFLC

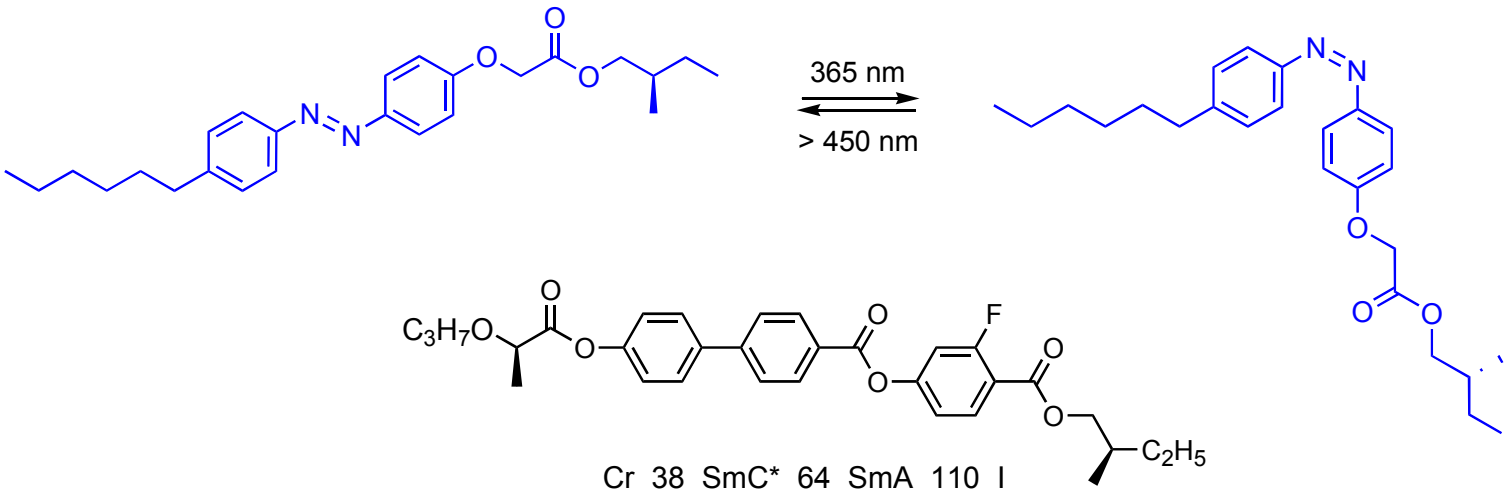
A) Polarization Modulation

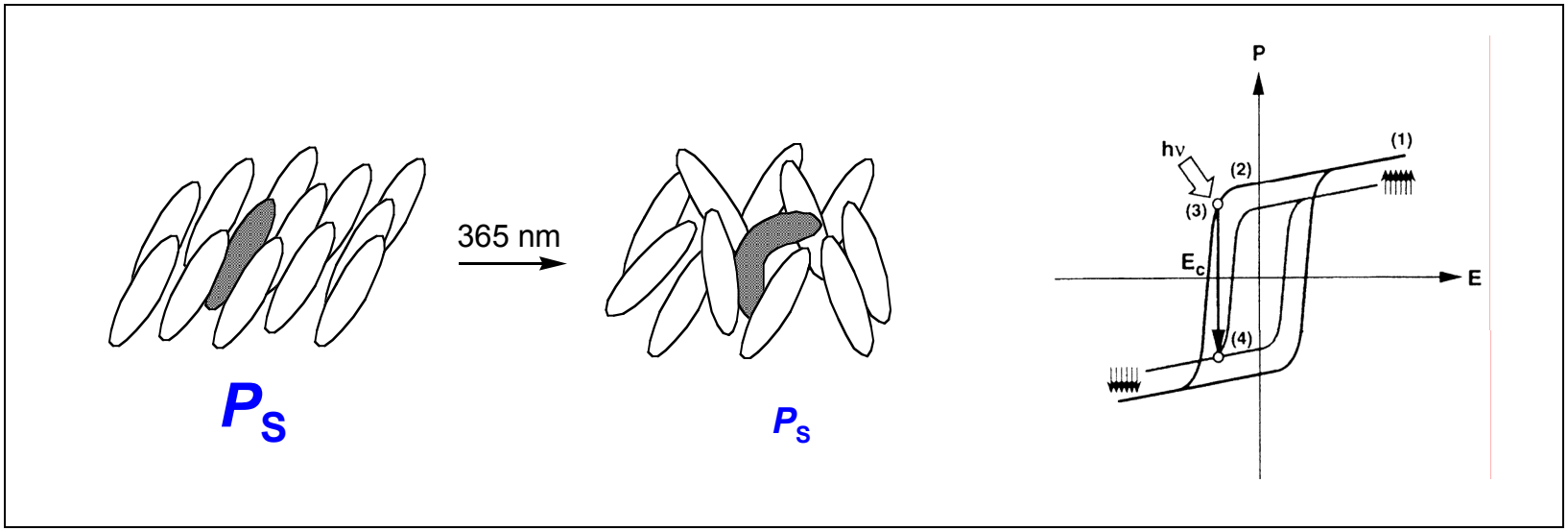


B) Polarization Inversion



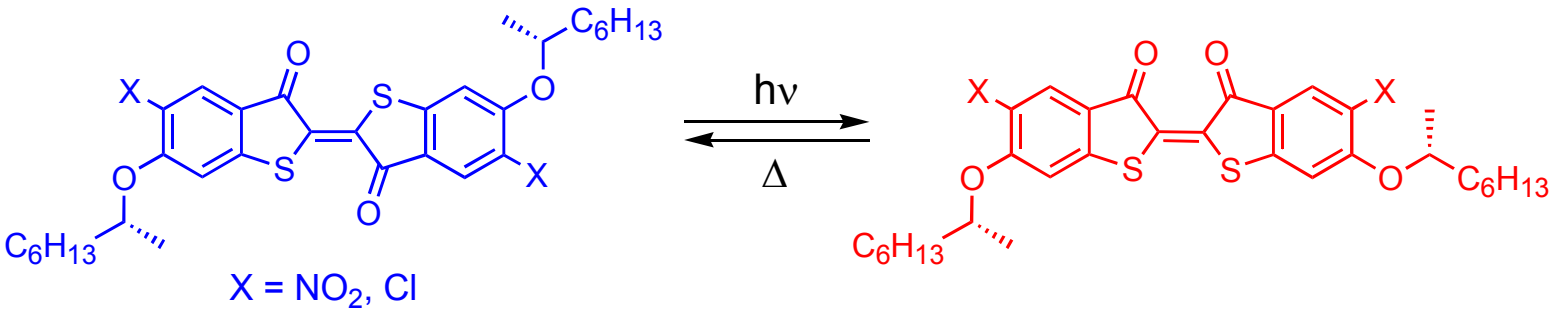
Photomechanical Effect

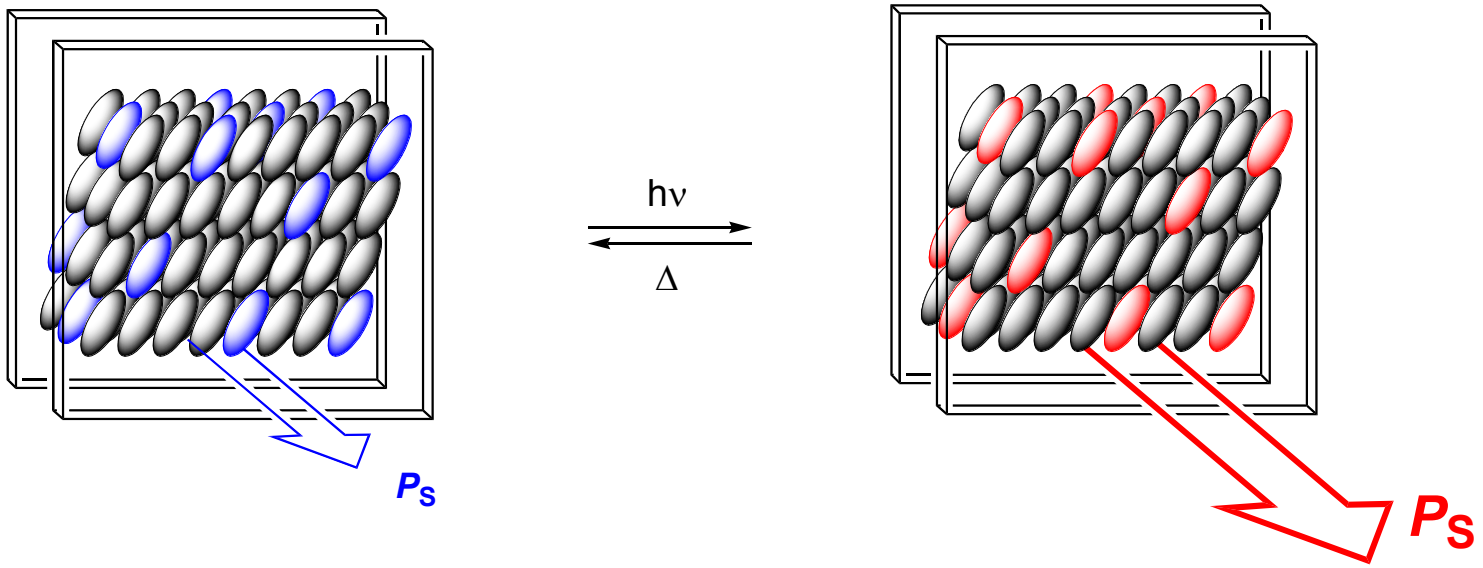




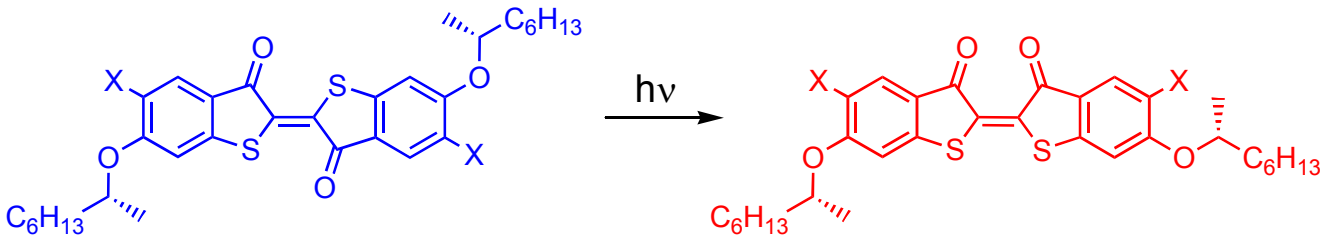
Ikeda, T.; Sasaki, T.; Ichimura, K. *Nature* **1993**, *361*, 428

Transverse Dipole Modulation



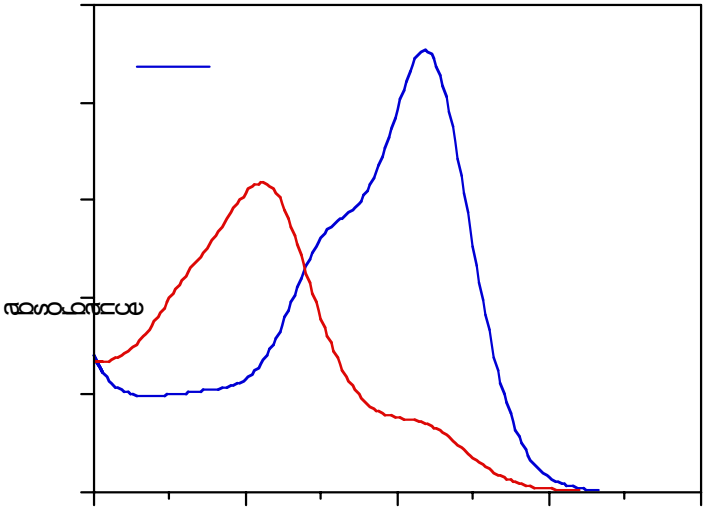


Thioindigo Photochromism

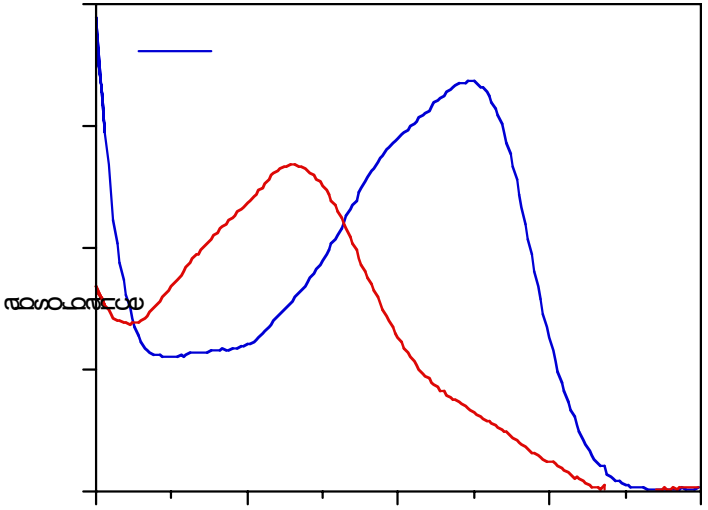


10^{-4}M solution in C_6H_6

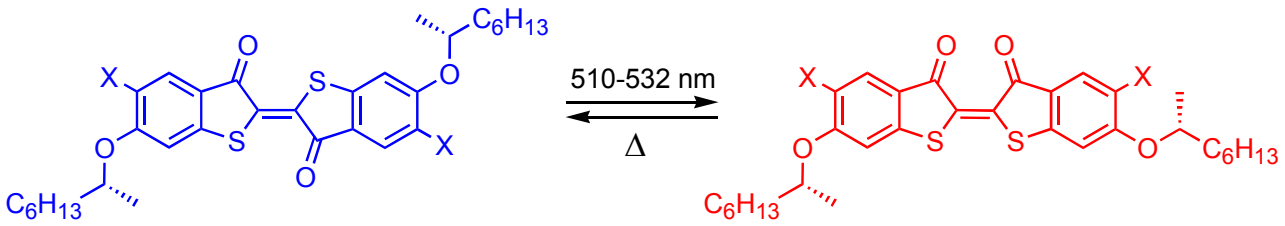
X = NO_2

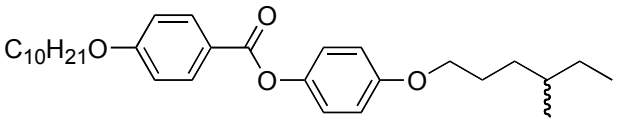


X = Cl



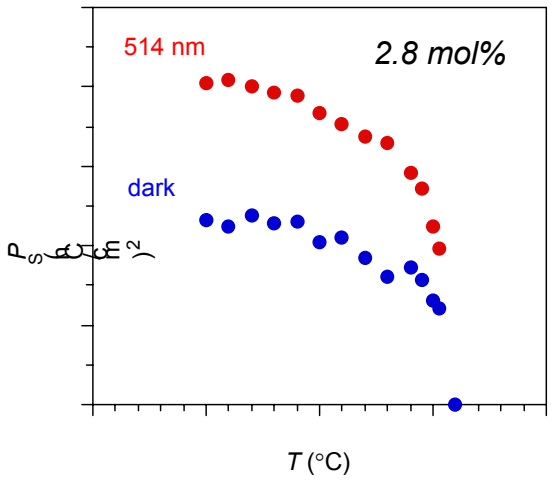
P_S Photomodulation



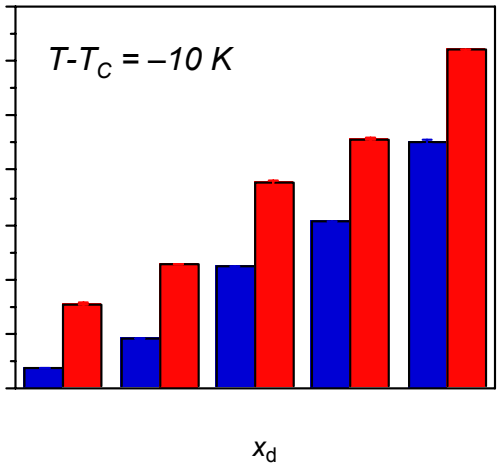


PhB; Cr 35 SmC 70 SmA 72 N 75 I

X = NO₂

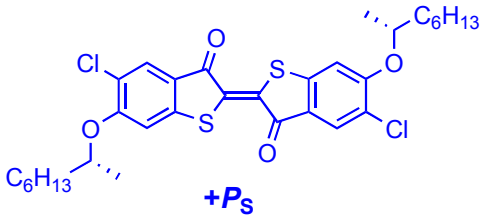


X = Cl



Dinescu, L.; Maly, K. E.; Lemieux, R. P. *J. Mater. Chem.* **1999**, *9*, 1679

Photoinversion of P_S

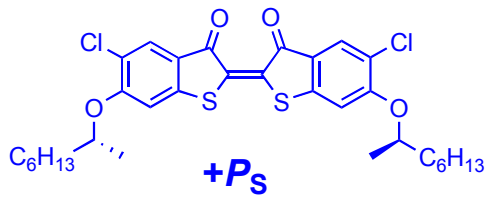


$+P_S$

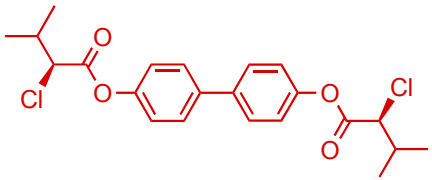
3 mol%

532 nm

Δ

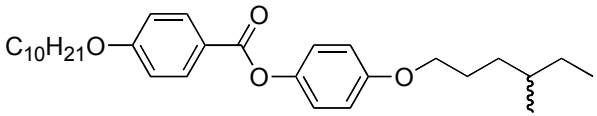


$+P_S$

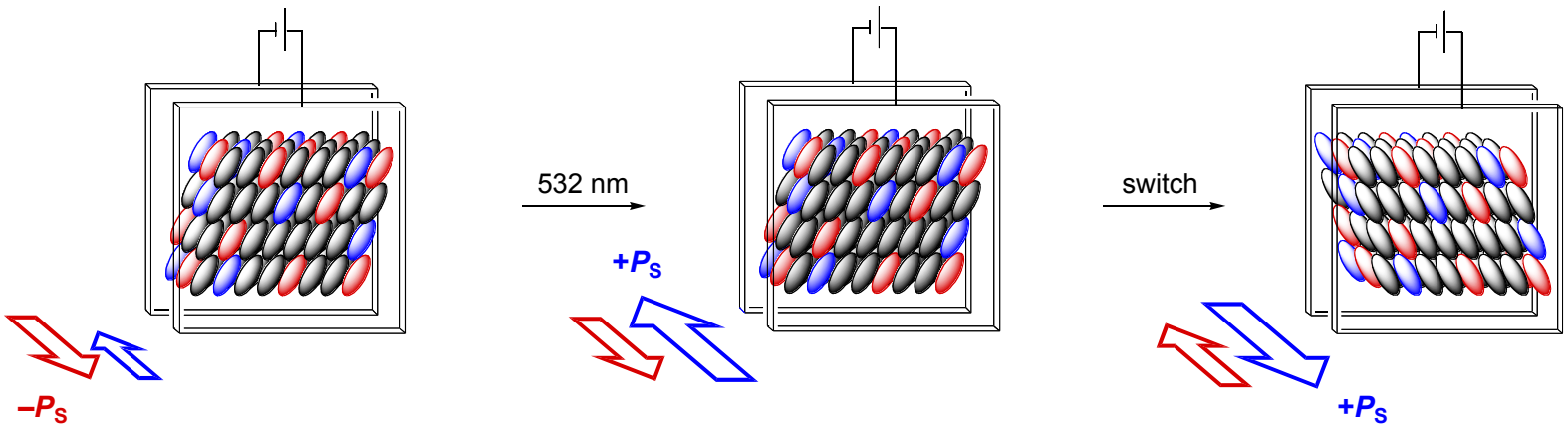


$-P_S$

1.3 mol%

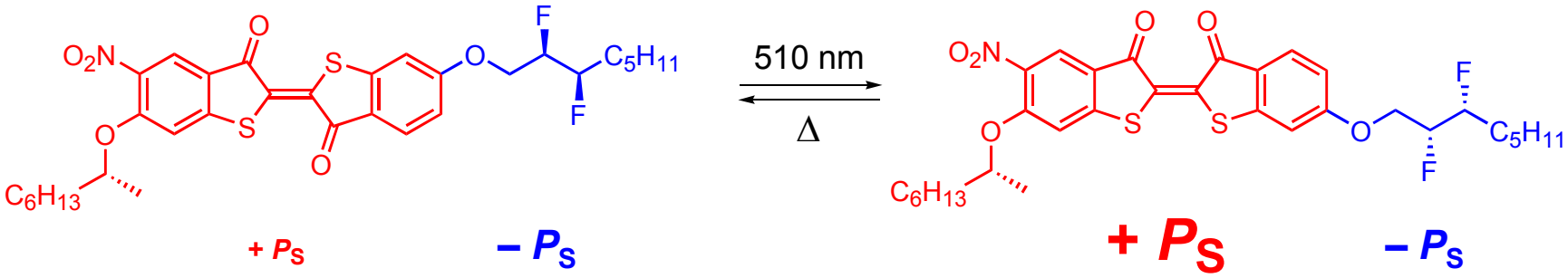


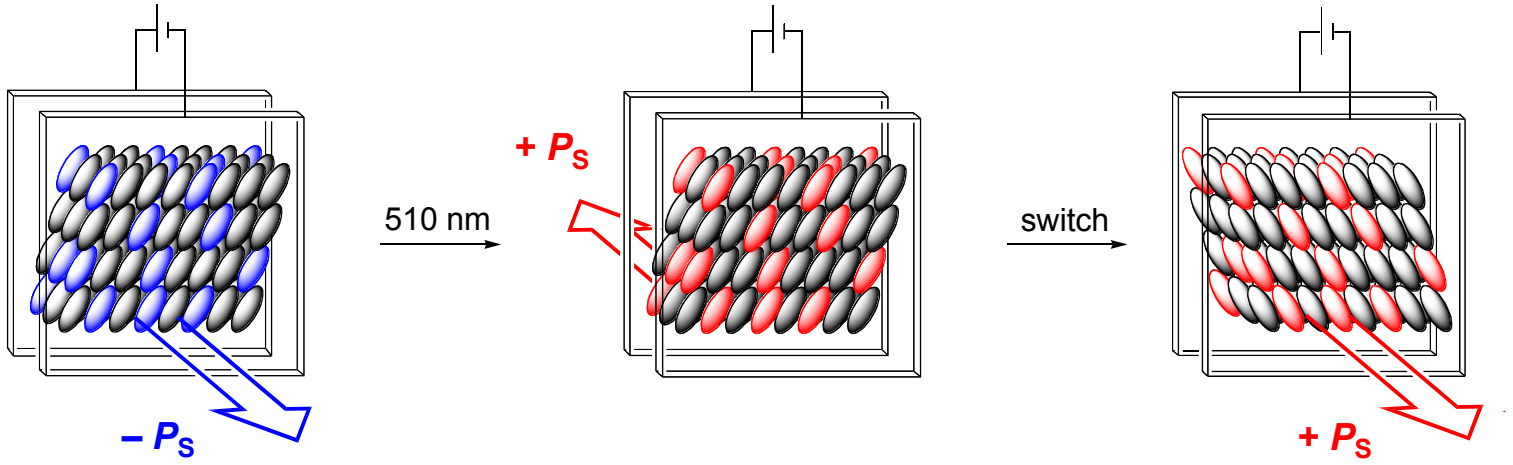
PhB; Cr 35 SmC 70 SmA 72 N 75 I



Dinescu, L.; Lemieux, R. P. *Adv. Mater.* **1999**, *11*, 42

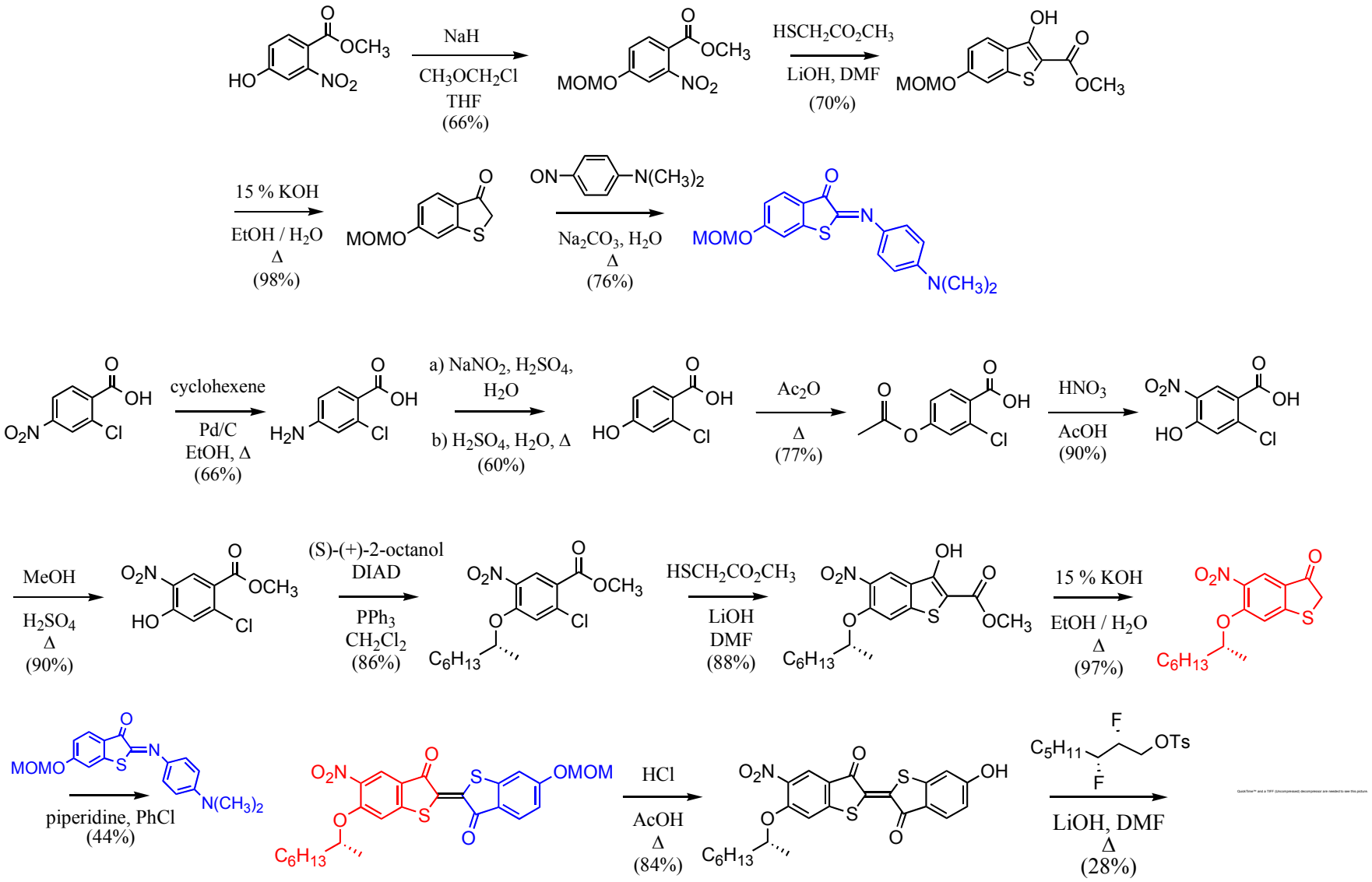
“Ambidextrous” Thioindigo Dopant



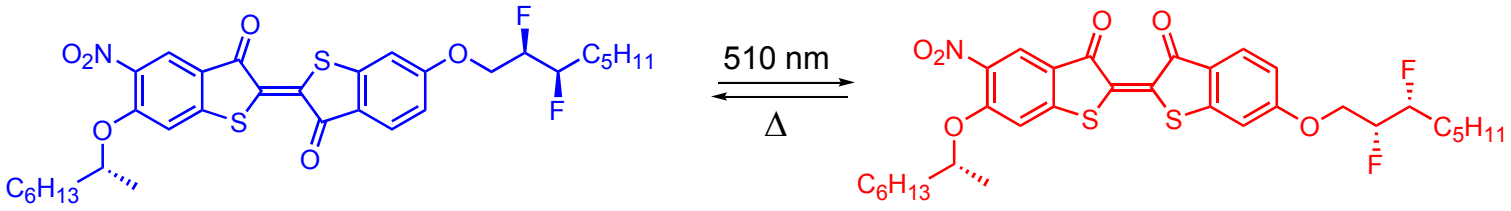


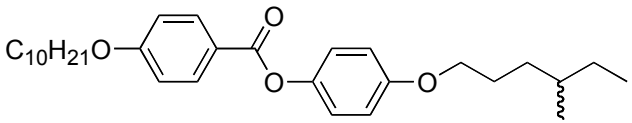
Vlahakis, J. Z.; Wand, M. D.; Lemieux, R. P. *Adv. Funct. Mater.* **2004**, *14*, 637

Synthesis


NaH
CH3OCH2Cl
THF
(66%)
HSCH2CO2CH3
LiOH, DMF
(70%)
15 % KOH
EtOH / H2O
Δ
(98%)
Na2CO3, H2O
Δ
(76%)
cyclohexene
Pd/C
EtOH, Δ
(66%)
a) NaNO2, H2SO4, H2O
b) H2SO4, H2O, Δ
(60%)
Ac2O
Δ
(77%)
HNO3
AcOH
(90%)
MeOH
H2SO4
Δ
(90%)
(S)-(+)-2-octanol
DIAD
PPh3
CH2Cl2
(86%)
HSCH2CO2CH3
LiOH
DMF
(88%)
15 % KOH
EtOH / H2O
Δ
(97%)
piperidine, PhCl
(44%)
HCl
AcOH
Δ
(84%)
LiOH, DMF
Δ
(28%)

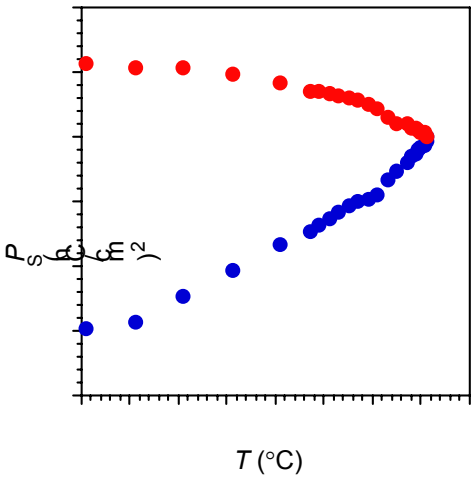
P_S Photoinversion



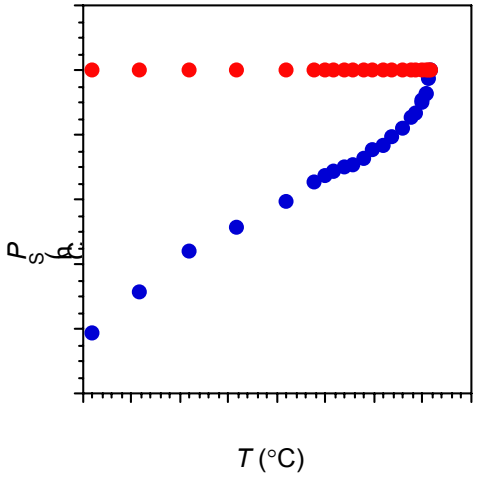


PhB; Cr 35 SmC 70 SmA 72 N 75 I

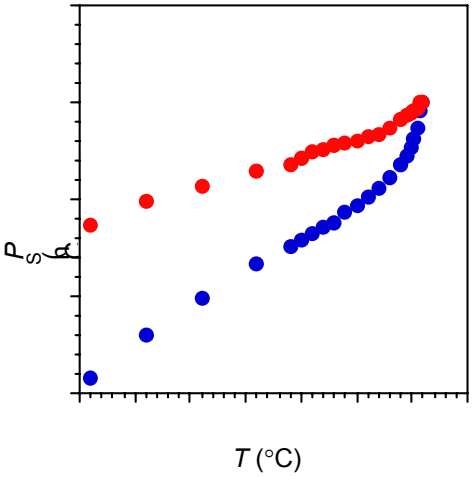
1.0 mol% in **PhB**



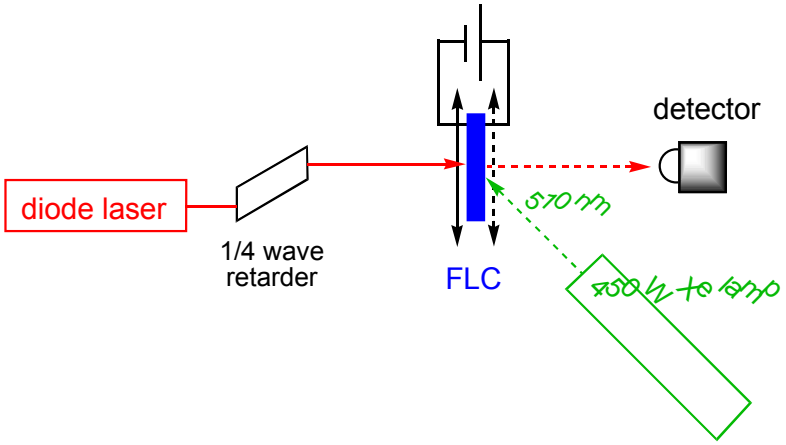
2.0 mol% in **PhB**



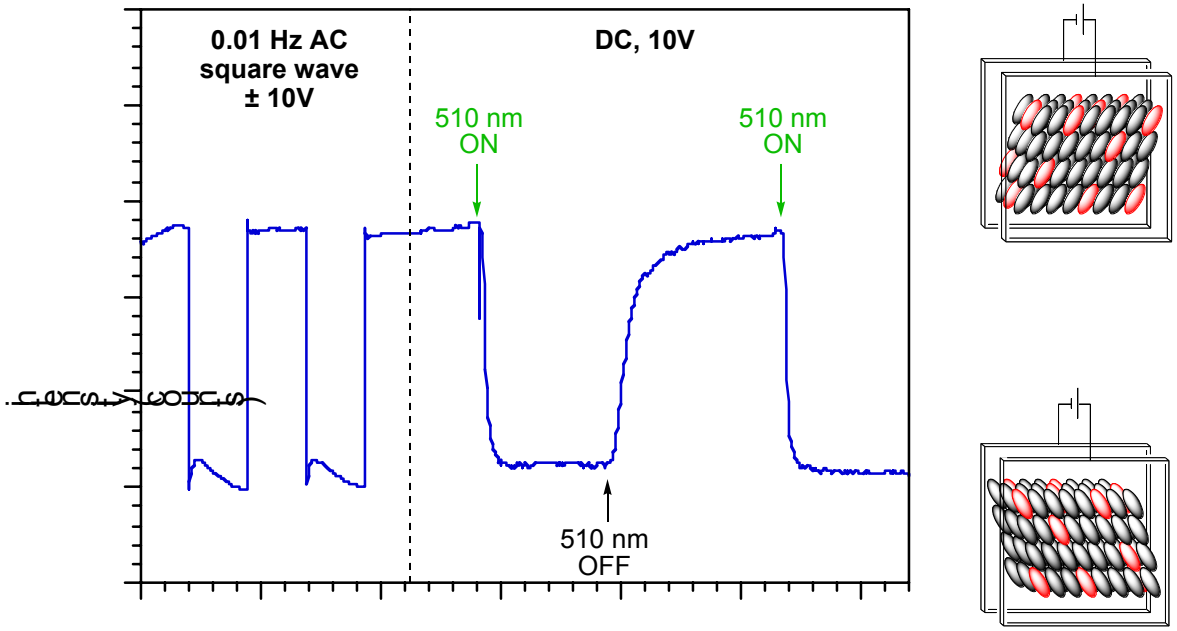
4.0 mol% in **PhB**



Ambidextrous Photoswitch



1 mol% in MX6120 @ 50 °C



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Dr. C. Lazar
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Dr. K. E. Maly
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Dr. A. McCubbin
Dr. S. Swansburg
M. Thompson
Dr. D. Vizitiu
Dr. J. Vlahakis
Prof. V. Williams
E. Yuh
N. Xiao

Postdocs

Prof. T. Hegmann
Dr. S. Mullick
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