Glossy Liquid Crystalline Cyclic and Monodisperse π-Conjugated Oligomers:

Self-Organized Solid Films for Optoelectronics

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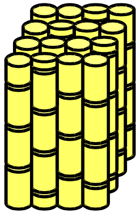
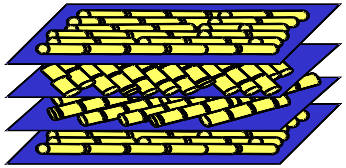
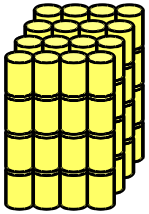
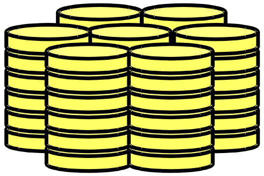
What is Glass Transition?

Solidification of a liquid upon cooling through its T_g without altering morphology

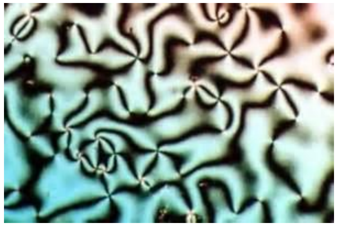
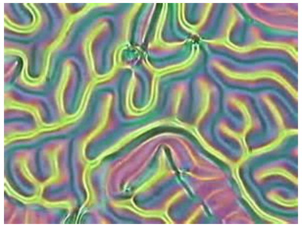
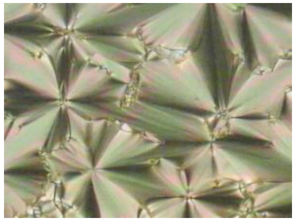
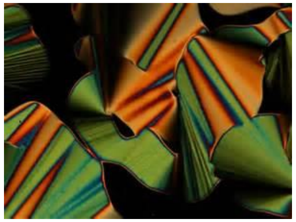
"The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition. This could be the next breakthrough in the coming decade. The solution of the problem of spin glass in the late 1970s had broad implications in unexpected fields like neural networks, computer algorithms, evolution, and computational complexity. The solution of the more important and puzzling glass problem may also have a substantial intellectual spin-off. Whether it will help make better glass is questionable."—P. W. Anderson [*Science* **1995**, *267*, 1615]

Philip W. Anderson, Nobel Laureate in condensed matter physics, 1977. These statements still hold true today.

Liquid Crystals Identified with Optical Textures

Nematic ***Cholesteric*** ***Smectic*** ***Columnar***

I. Dierking, *Textures of Liquid Crystals*, Wiley-VCH Verlag: Weinheim, 2003.

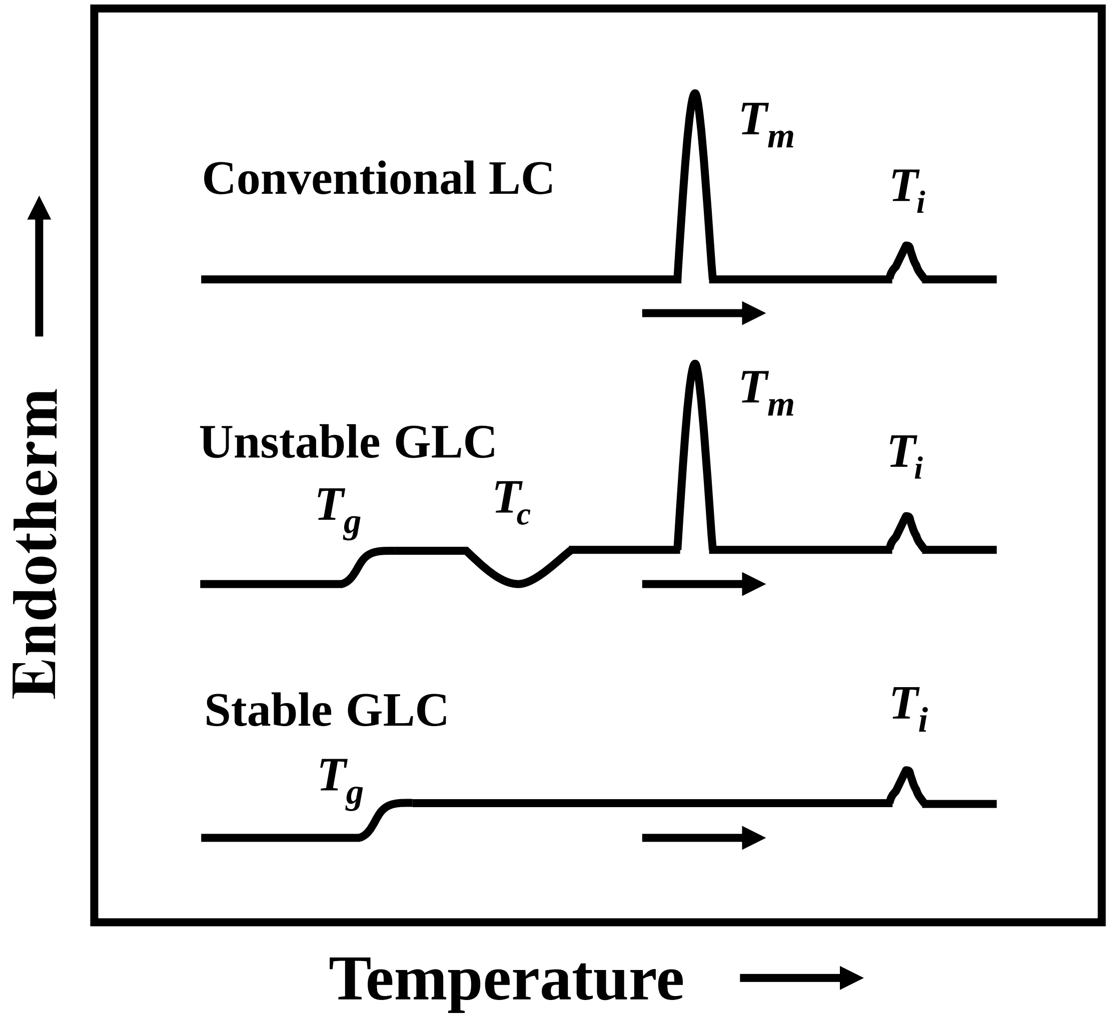
Glassy Liquid Crystals, GLCs

- **Crystals: positional order in a three-dimensional lattice**
- **Liquid Crystals: orientational order, positional order in 1- or 2-D**
- **GLCs: liquid crystals frozen into solid state without crystallization, a three-way oxymoron**
- **All liquids expected to form glass at a sufficiently rapid cooling rate**
- **Most organics, *e.g.* liquid crystals, will crystallize on cooling from melt**
- **GLCs as an approach to self-organized solid films across a large area**

Unique Features of Glassy Liquid Crystals

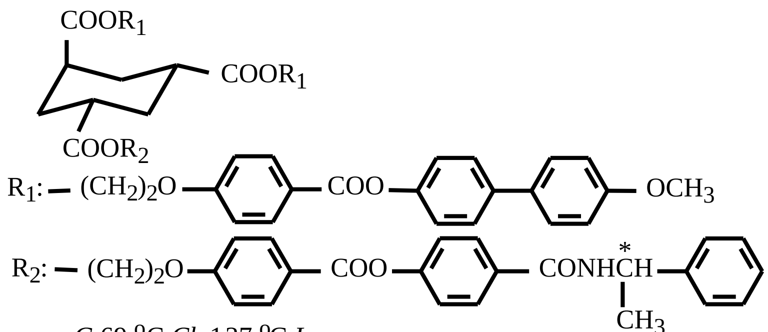
- **Glassy Liquid Crystals (GLCs): three-way oxymoron**
- **Glass formation over crystallization of liquid crystals is an exception rather than a rule**
- **The nature of glass and glass transition has remained one of the most challenging problems in solid-state physics**
- **No theory or computation has been demonstrated for molecular design of organic glasses, especially GLCs**
- **Our modular approach has produced multifunctional GLCs with record high glass transition and clearing temperatures while resisting crystallization for over two decades and counting**
- **Monodomain solid films can be fabricated via solvent-vapor annealing at room temperature**

DSC Thermograms of Single-Component Liquid Crystals



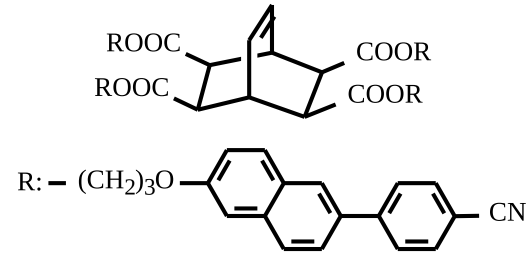
First-Generation Core-and-Pendant Glassy Liquid Crystals

Cyclohexane core:



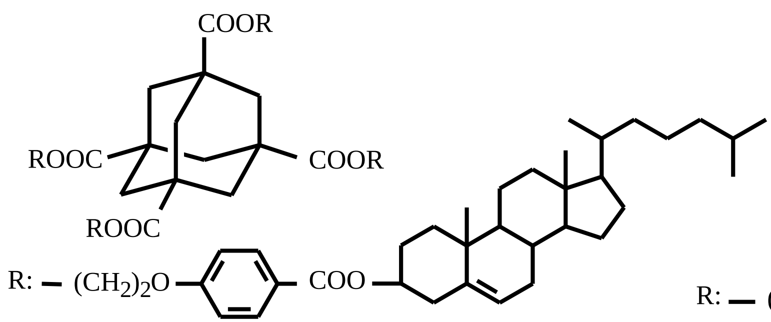
G 69 °C *Ch* 137 °C *I*

Bicyclooctene core:

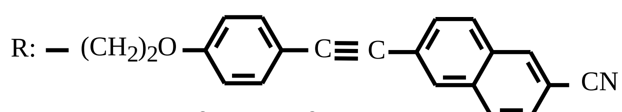


G 84 °C *N* 222 °C *I*

Adamantane core:

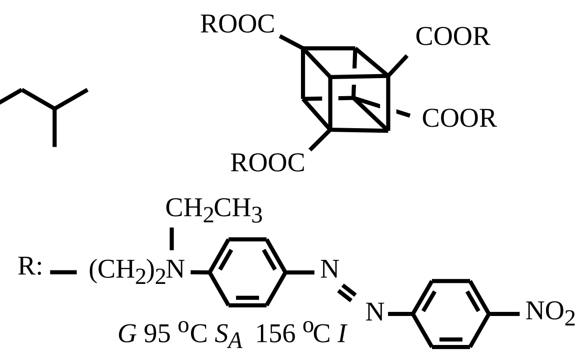


G 86 °C S_A 236 °C *I*

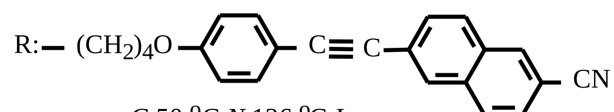


G 77 °C *N* 190 °C *I*

Cubane core:



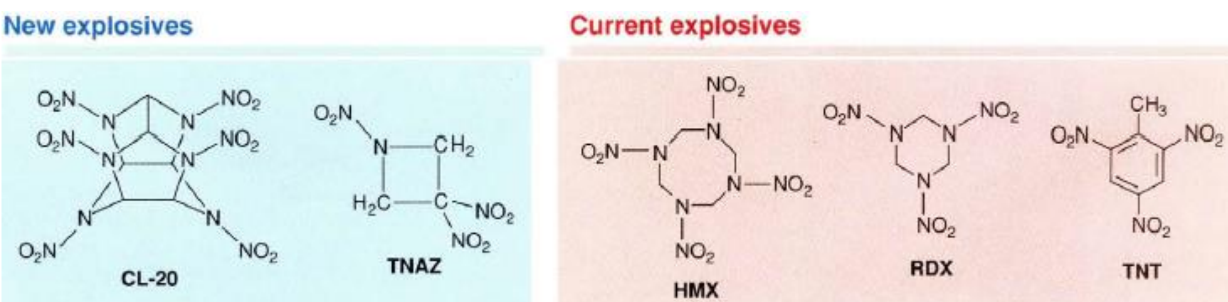
G 95 °C S_A 156 °C *I*



G 50 °C *N* 126 °C *I*

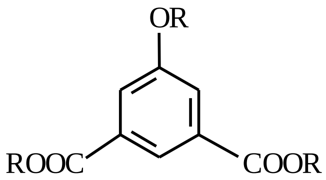
Adv. Mater. **1996**, *8*, 998.

C&E News, 17 January 1994: Cover Story on Advanced Energetic Materials

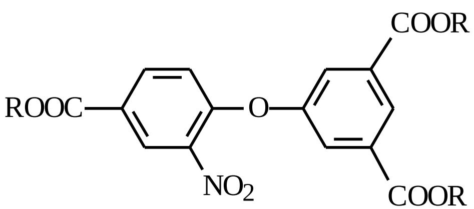


Advanced explosives serving as the cores for GLCs

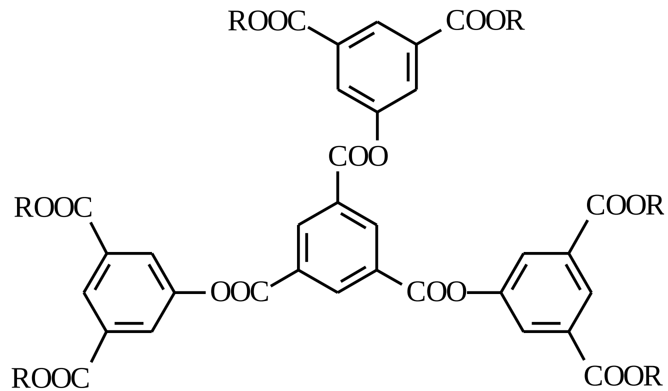
High-Temperature Nematic GLCs



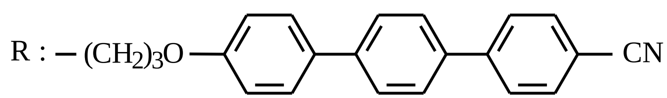
(**12**) *G* 82°C *N* 347°C *I*



(**13**) *G* 86°C *N* 288°C *I*



(**14**) *G* 127°C *N* 308°C *I*



Chem. Mater. **2001**, *15*, 4584.

Morphological Stability of Liquid-Crystal and Amorphous Glasses Quantified by Maximum Crystallization Velocity, MCV

$T_{c,max}/T_m$=0.93 ± 0.01 | CV=0 at T_m for all | $T_{c,max}/T_m$=0.92 ± 0.03; T_g/T_m≈2/3

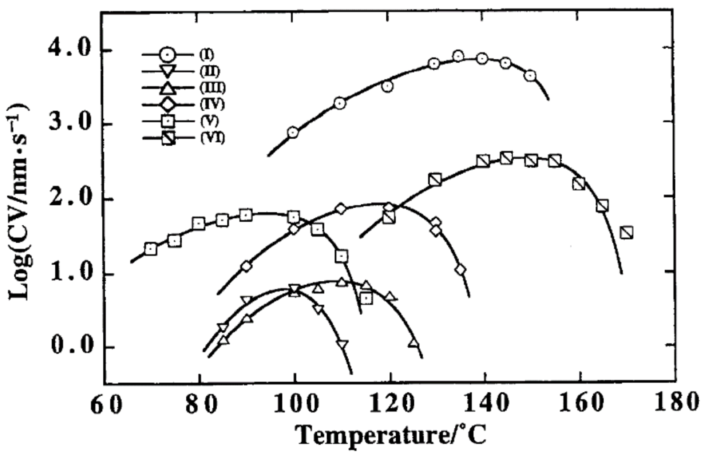


Figure 9. Crystallization velocity, CV, as a function of temperature for all six model GLMLCs to display the effects of stereochemistry, mesogenic core structure, and spacer length.

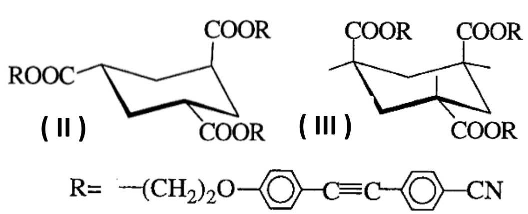
compound	T_m (K)	$T_{c,max}$ (K)	N	log(*MCV*) (m/s)
naphthalene	351		10	−0.2
p-dichlorobenzene	326	306	8	−0.4
p-dinitrobenzene	447	406	12	−0.6
p-dibromobenzene	359	332	8	−0.9
diphenyl	343	327	12	−0.9
1,3,5-trichlorobenzene	337	312	9	−1.0
o-dichlorobenzene	256	237	8	−1.5
azobenzene	340	310	14	−2.0
1,2-diphenylethane	324	294	14	−2.0
diphenylmethane	298	275	13	−2.1
benzil	368	333	16	−2.2
o-cresol	303	273	8	−2.4
benzophenone	308	280	14	−3.0
triphenylmethane	366	341	19	−3.4
piperonal	310	290	11	−4.0
chalcone	328	303	13	−4.1
phenyl saliciate	315	295	16	−4.3
o-terphenyl	329	314	18	−4.7
1,1-diphenylethane	255	228	14	−4.8

(II) and (III) at 6 nm/s, comparable to slowly crystallizing isotactic polystyrene

Top to bottom: 6.3×10^8 to 1.6×10^4 nm/s

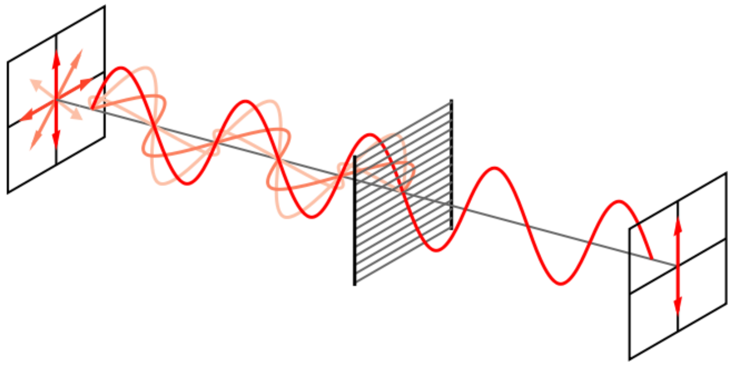
Shi and Chen, *Liq. Cryst.*, 1995, *12*, 785-790.

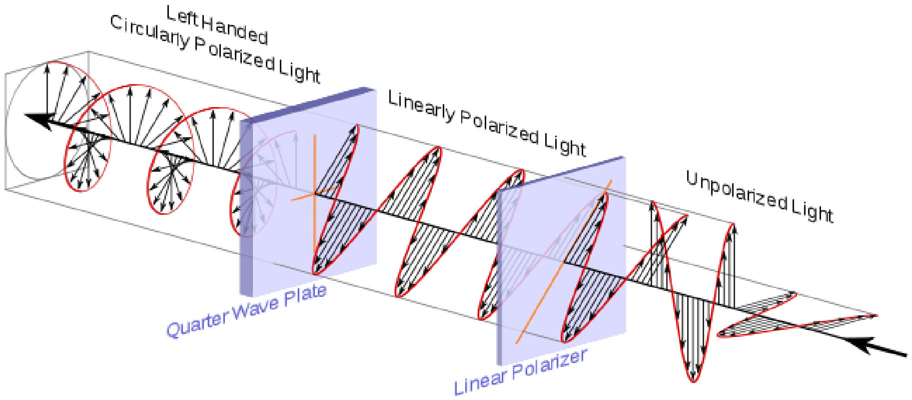
Naito and Miura, *J. Phys. Chem.* 1993, *97*, 6240-6248.



Thermally processed GLC films have remained intact left at 25 °C for 22 years and counting

Linear and Circular Polarization of Light

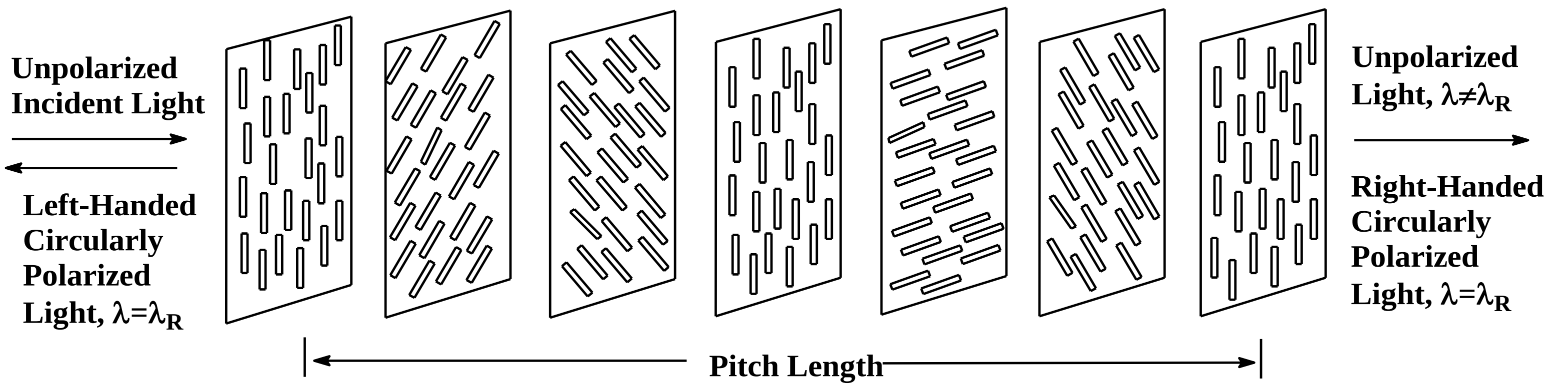




Wire-grid linear polarizer allows incident waves with electric fields perpendicular to wires to pass through without attenuation. The vertical components of waves with other orientations will be allowed as well.

A linear polarizer and a quarter wave plate combine to form a circular polarizer, converting an unpolarized incident to circularly polarized light with handedness determined by the nature of quarter wave plate.

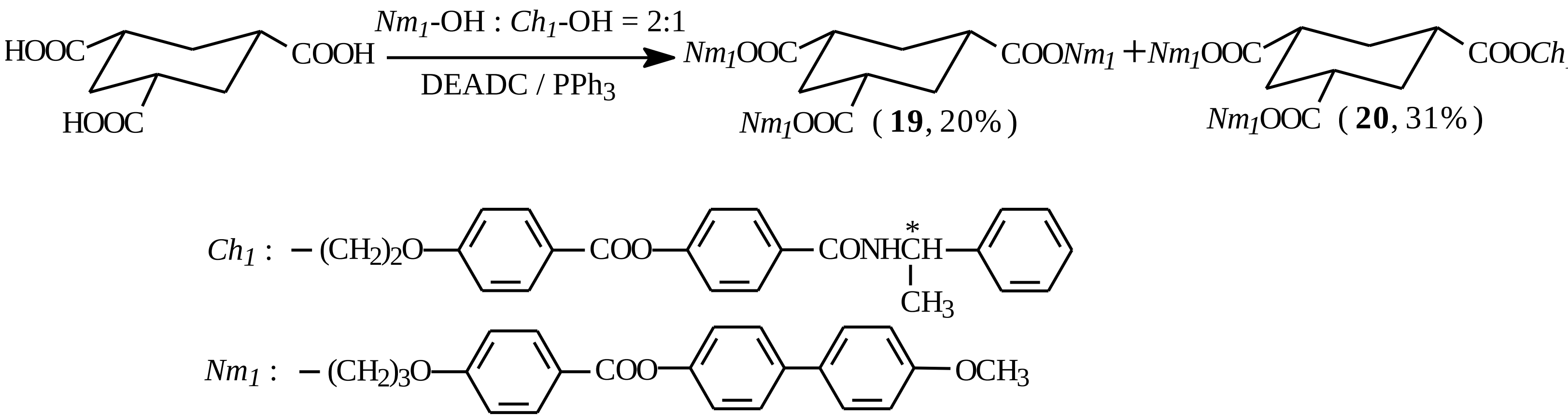
Selective Wavelength Reflection by a Left-Handed Cholesteric Film
One Dimensional Photonic Band-Gap



- **Cholesteric film as a helical stack of quasinematic layers**
- **Three parameters governing optical properties: helical sense, pitch length, *p*, and average refractive index, n_{avg}; selective reflection wavelength, $\lambda_R = p\, n_{avg}$**
- **Unpolarized light with $\lambda=\lambda_R$ on a left-handed film: left-handed circularly polarized component reflected, right-handed transmitted**
- **Complete reflection of unpolarized light with $\lambda=\lambda_R$ by a stack of left- and right-handed films with otherwise identical properties**
- **Incident light with $\lambda\neq\lambda_R$ and any polarization state, transmitted through left- or right-handed film**

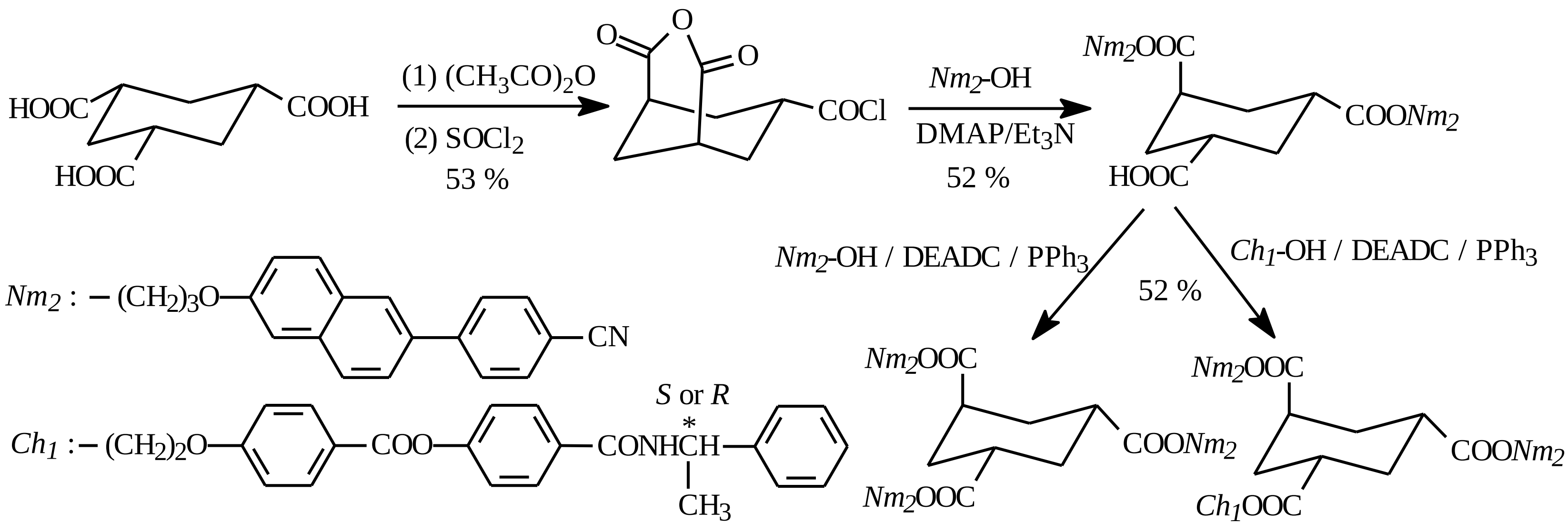
Examples of Reflective Coloration in Nature

Statistical Synthesis of Cholesteric GLCs



Chem. Mater. **1999**, *11*, 1590.

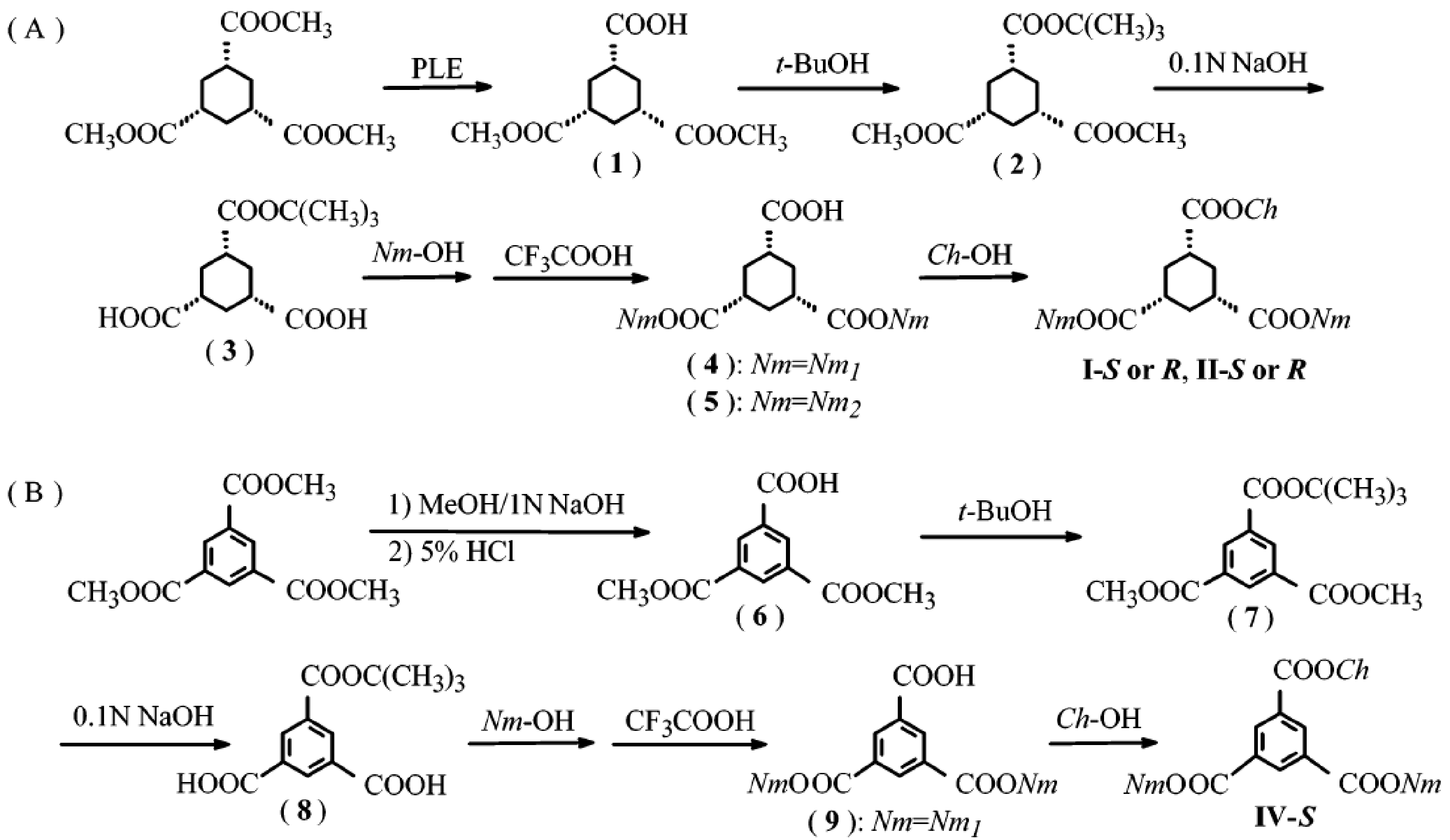
Deterministic Synthesis of Cholesteric GLCs - I



(**21**) *G* 63°C *N* 183°C *I* (***22-S* or *R***) *G* 75°C *I*

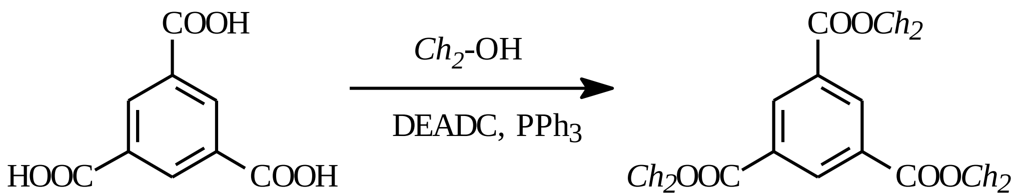
Adv. Mater. **2000**, *12*, 1283.

Deterministic Synthesis of Cholesteric GLCs – II and III

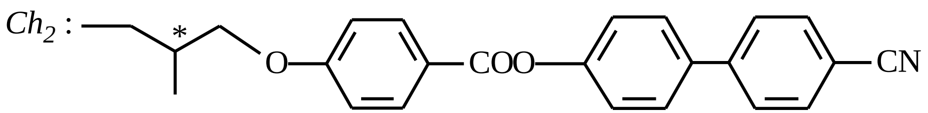


Chem. Mater. **2003**, *15*, 2534.

Deterministic Synthesis of Cholesteric GLCs - IV

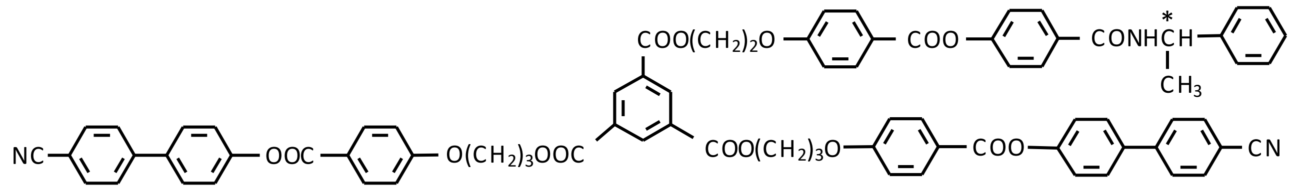


(**26**) *G* 73°C *Ch* 295°C *I*

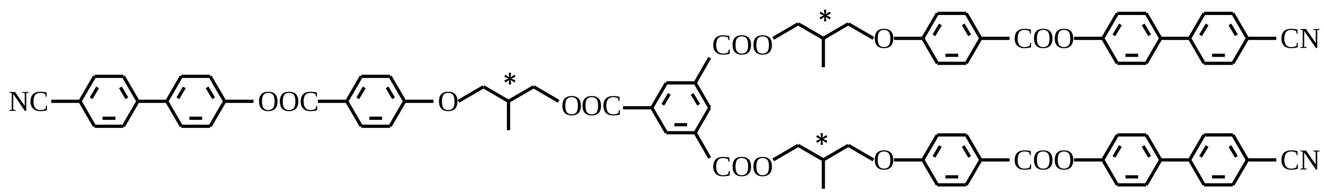


Chem. Mater. **2008**, *20*, 5859.

Cholesteric Glassy Liquid Crystals



G 85ºC *Ch* 216ºC *I*



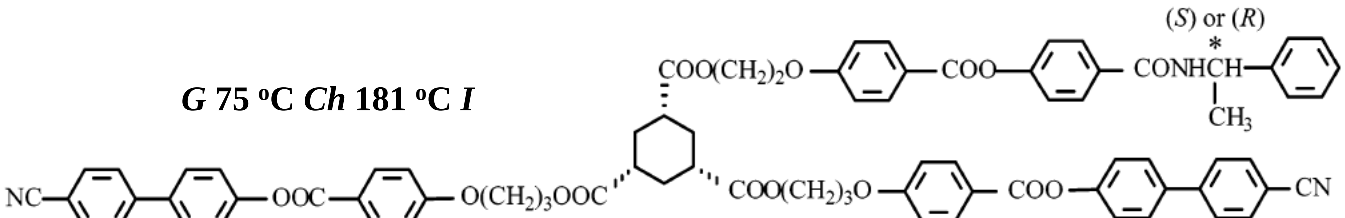
G 73ºC *Ch* 295ºC *I*

Enantiomeric chiral-nematic GLCs yield opposite handedness and selective reflection in UV-region

Chem. Mater. **2003**, *15*, 2534.

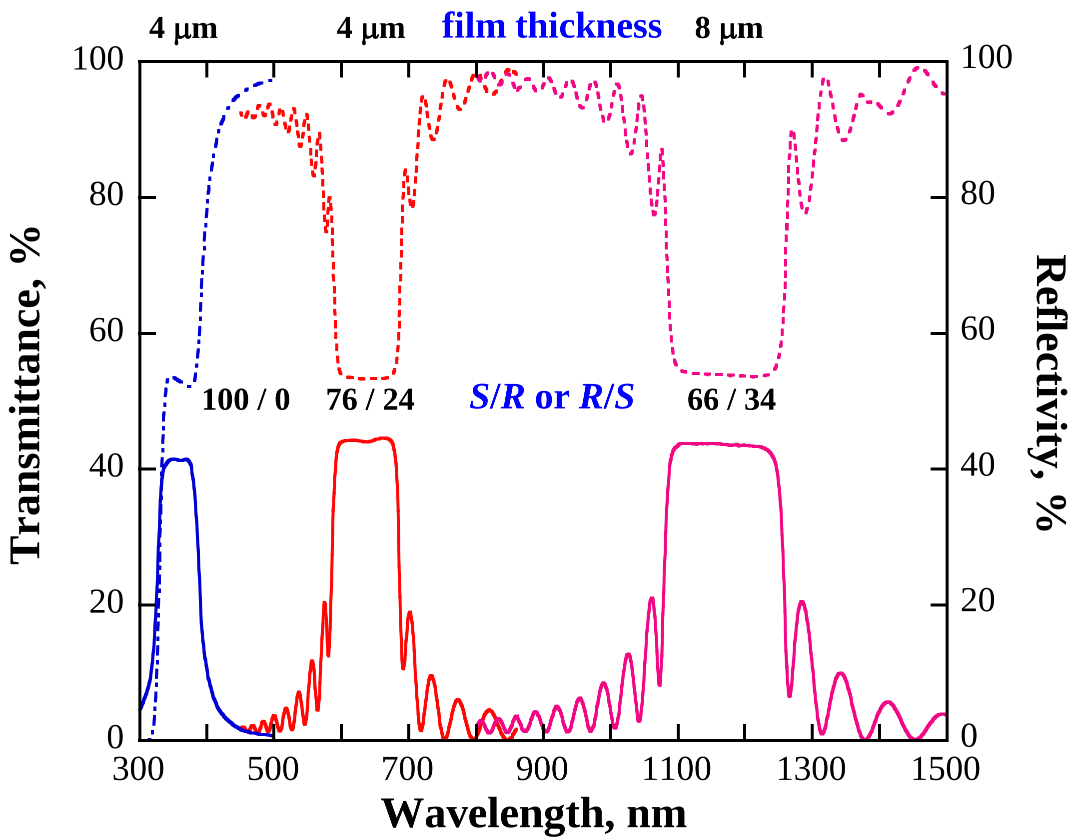
Chem. Mater. **2008**, *20*, 5859.

G 75 ºC *Ch* 181 ºC *I*

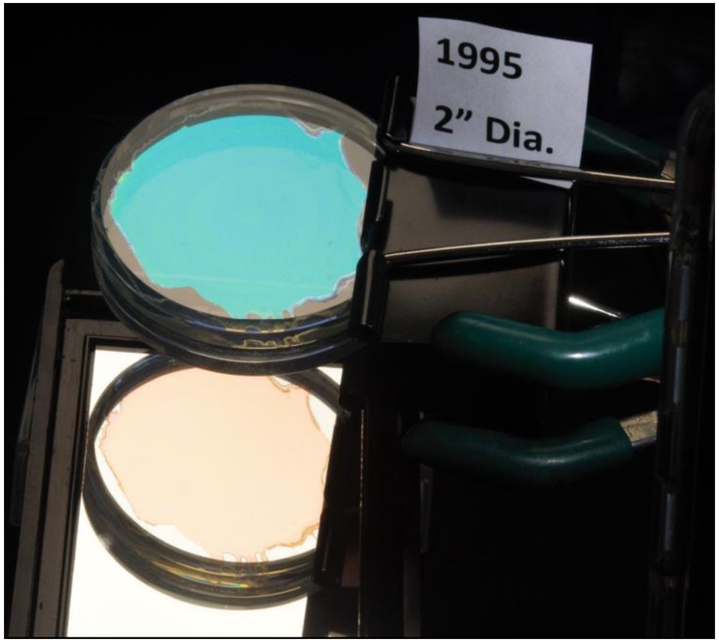


I-*S*, I-*R*

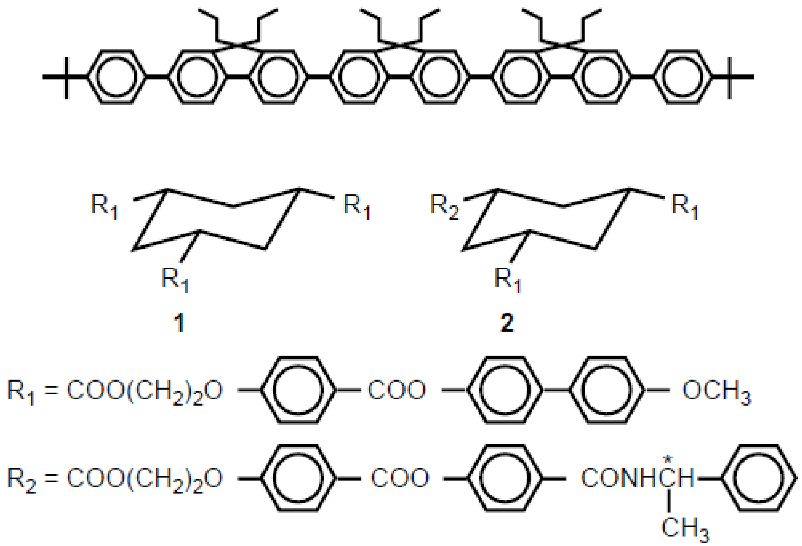
Chem. Mater. **2003**, *15*, 2534−2542



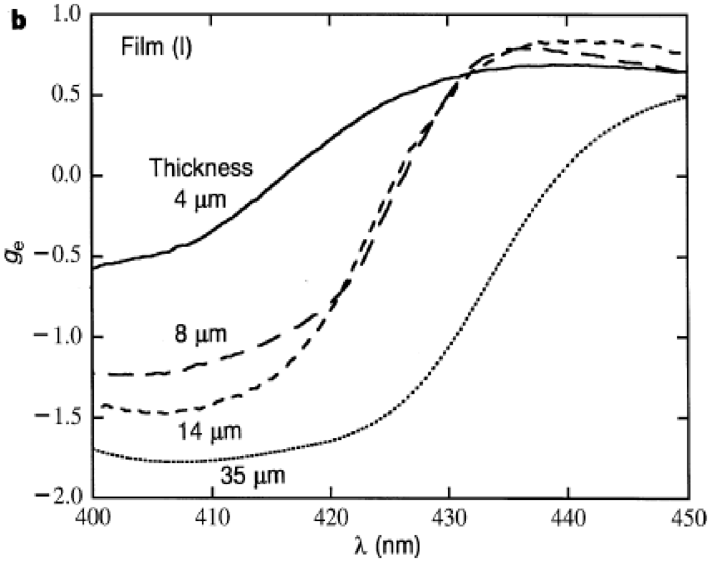
Quality Ch-GLC Film: Fabricated, 1995; Photo, 2020



Highly Circularly Polarized Fluorescence from a Chiral-Nematic GLC Film Doped with a Laser Dye

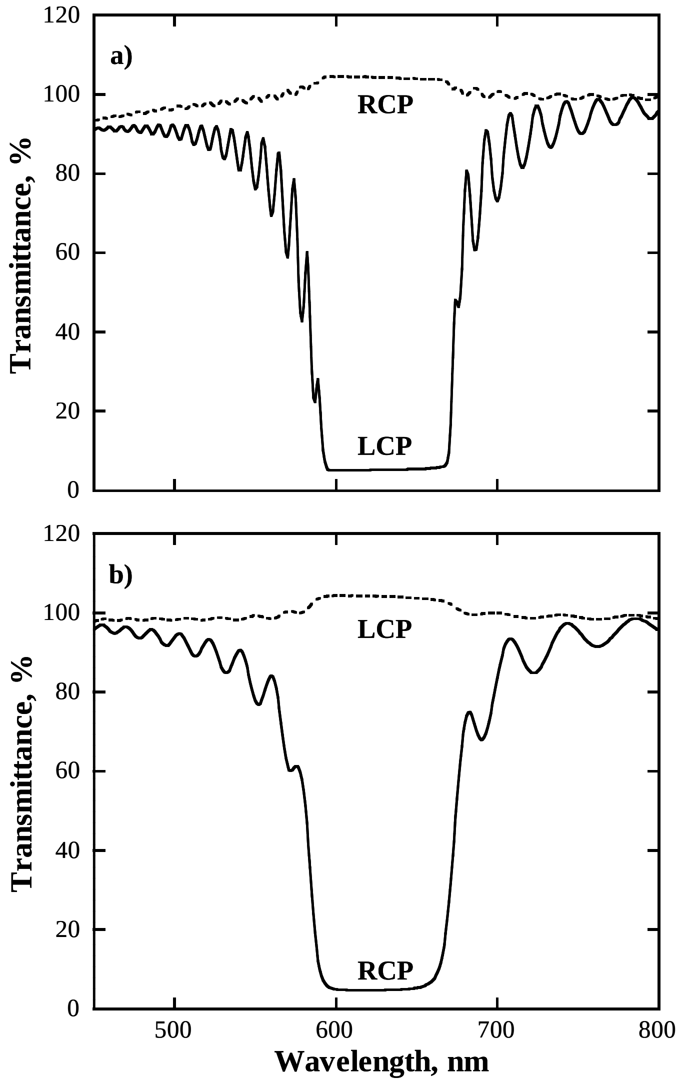


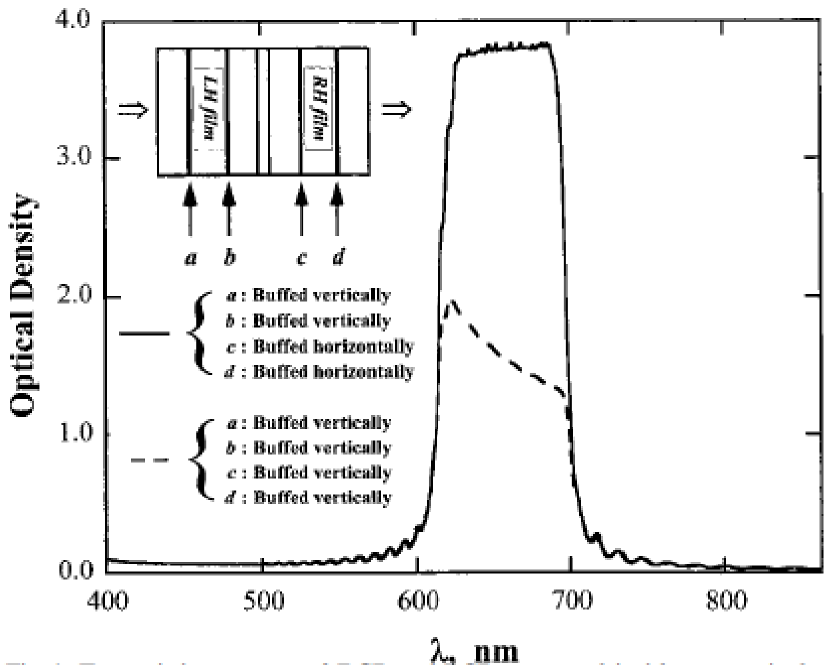
$g_e = 2(I_L - I_R)/(I_L + I_R)$, $|g_e| \le 2$



Nature **1999**, *397*, 506.

Circular Polarizers and Notch Filters with Chiral-Nematic GLCs

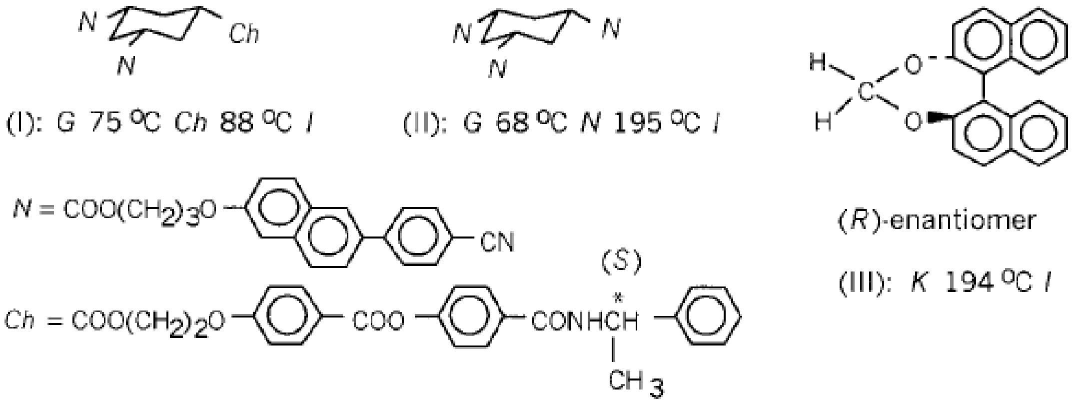




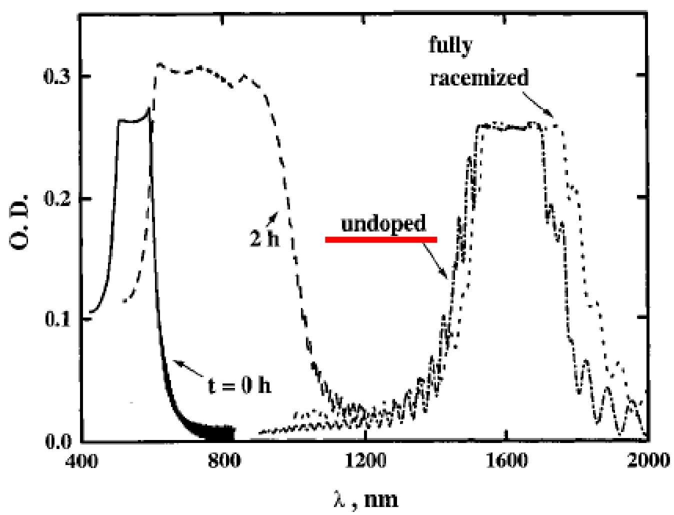
- **Nearly 100% circular polarization**
- **Notch filter with a contrast ratio > 5000:1**
- **Spectral tunability by mixing enantiomeric chiral-nematic GLCs at varying ratios**

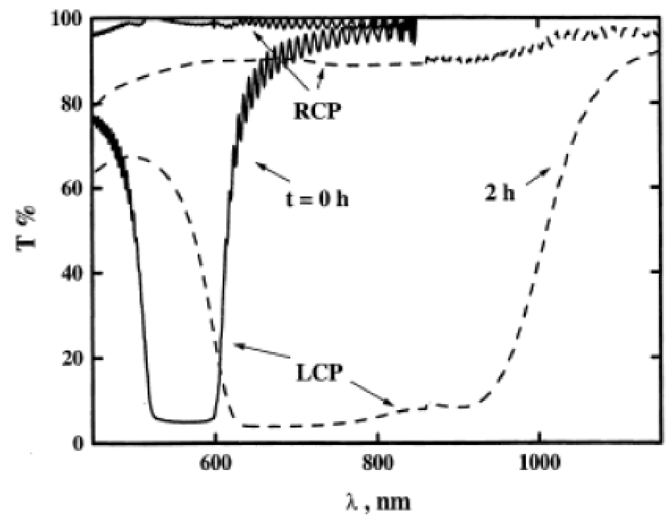
Adv. Mater. **2000**, *12*, 1283.

Broadband Reflectors via Racemization of a Chiral Dopant in a Chiral-Nematic GLC Host with 140 μW/cm^2 at 334 nm at 100 ^{o}C



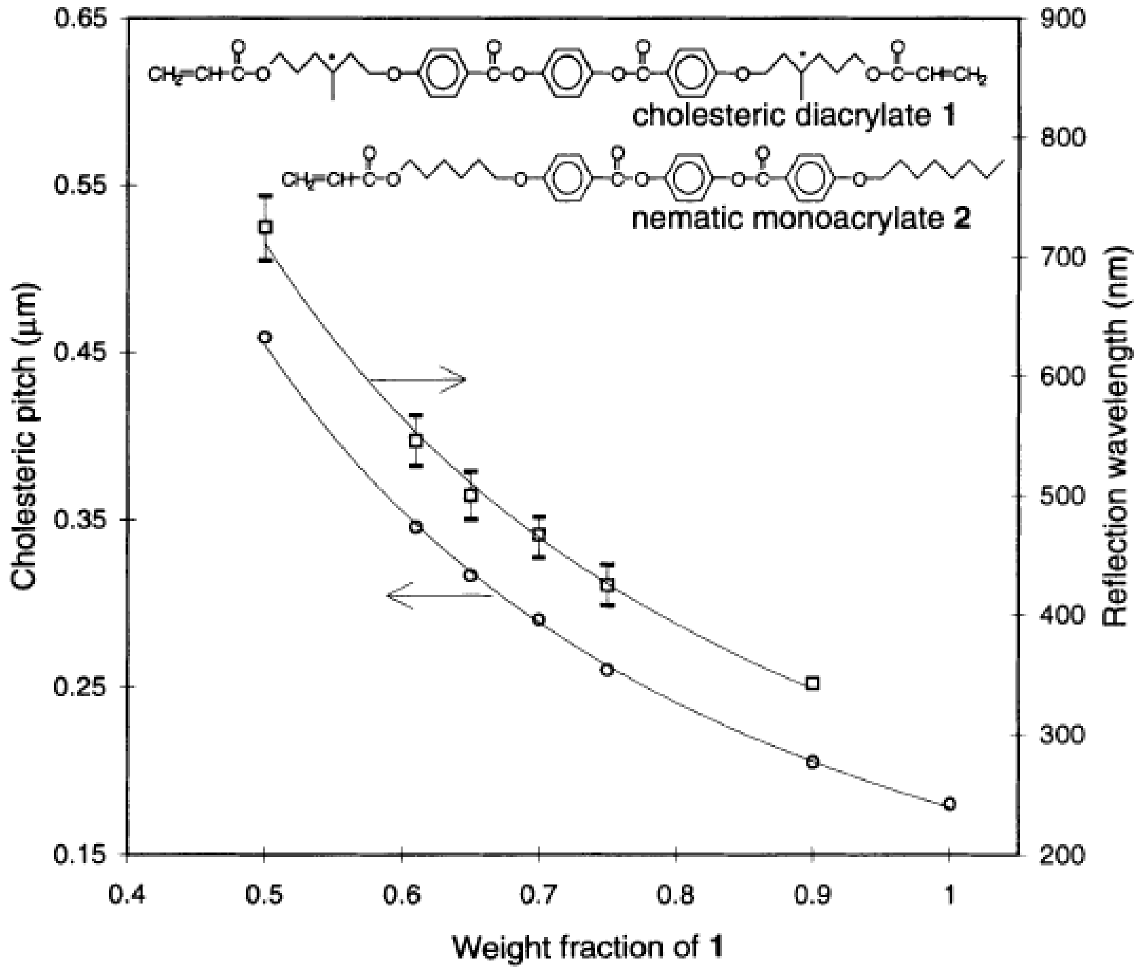
Molar ratio at 1.00:4.36:0.55
T_g= 65, T_c=156 ^{o}C; 22 μm film



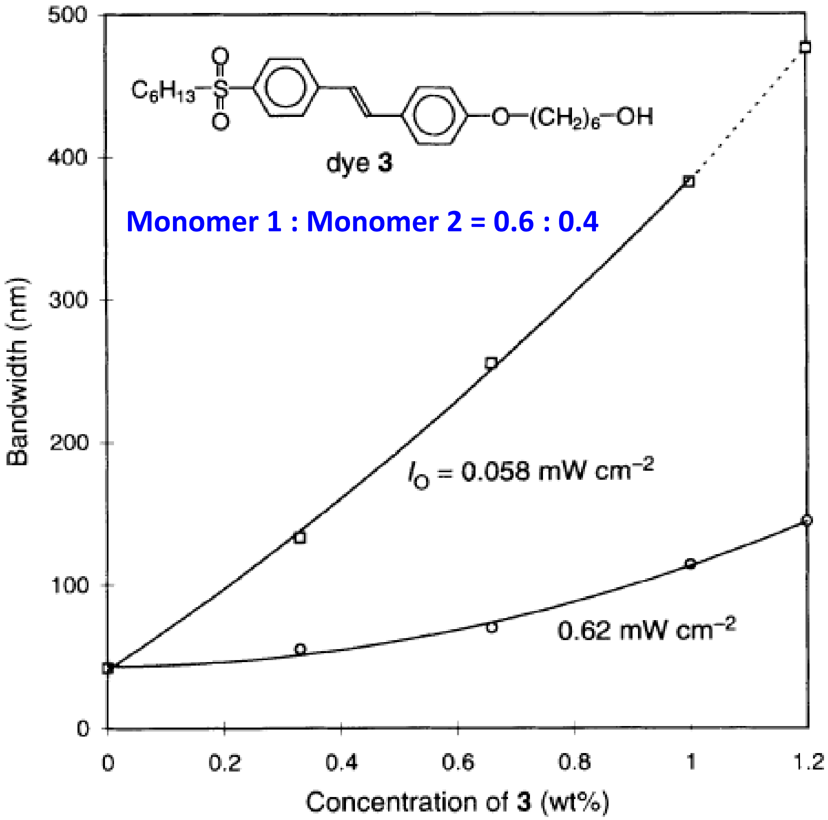


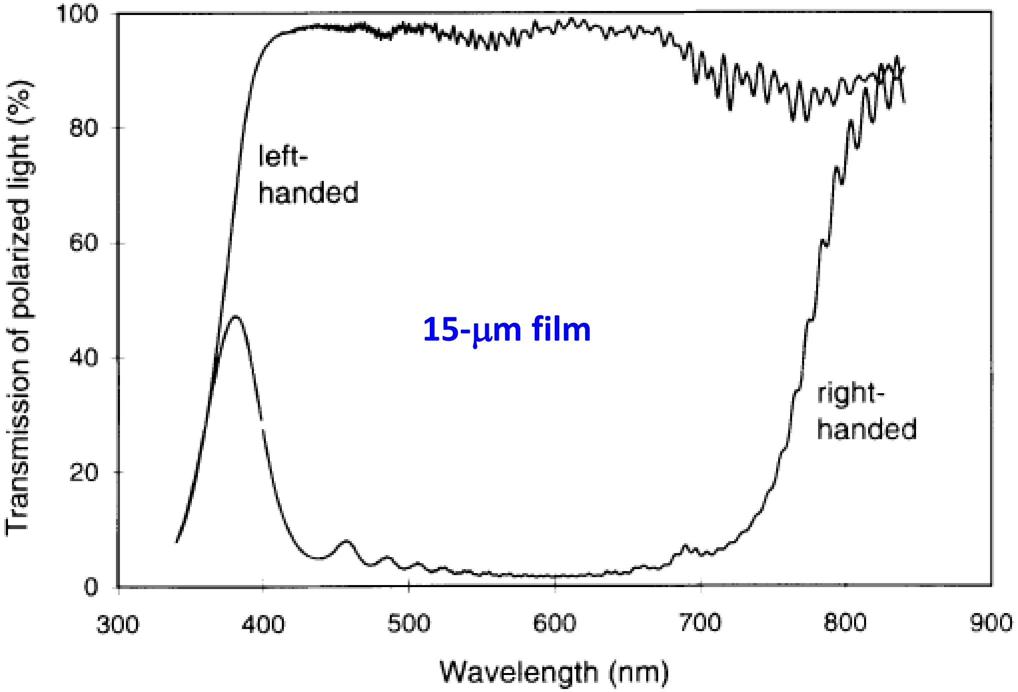
Adv. Mater. **1999**, *11*, 1183.

Photopolymerized Cholesteric Film with Pitch Gradient



Broer et al., *Nature* **1995**, *378*, 467.

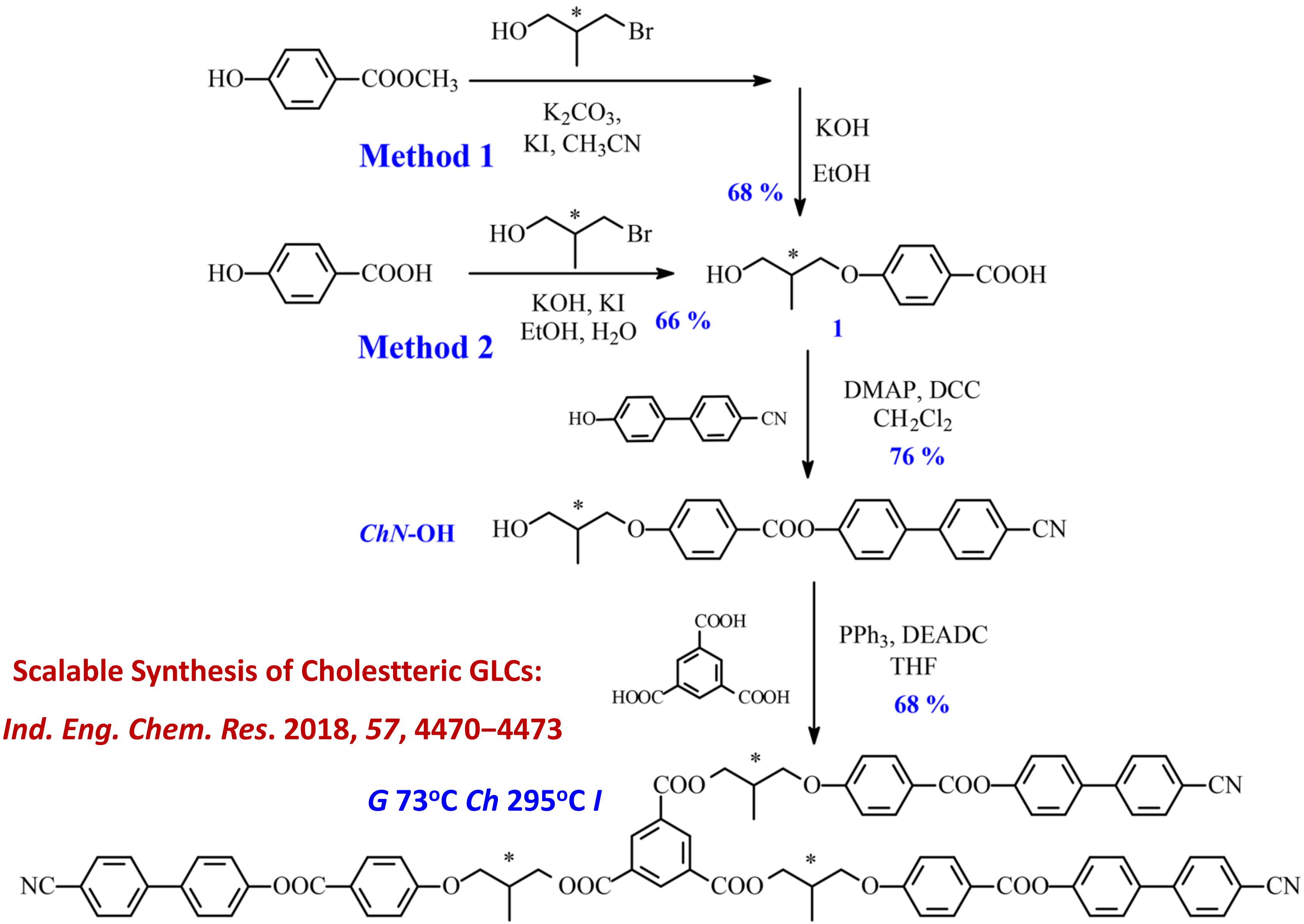




Broer et al., *Nature* **1995**, *378*, 467.

Scalable Synthesis of Cholestteric GLCs:

Ind. Eng. Chem. Res. 2018, *57*, 4470–4473



G 73°C *Ch* 295°C *I*

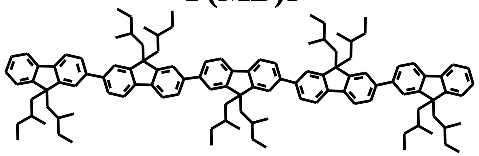
Motivation for Monodisperse π-Conjugated Oligomers

- **Conjugated polymers widely explored for photonics & electronics**
  - **Distributed chain length and composition, kinks, bends**
  - **Purification, processing, alignment can be quite challenging**
- **Monodisperse conjugated oligomers**
  - **Structural uniformity, solubility, purity**
  - **Ease of processing and characterization: understanding of structure-property relationships, conducive to practical applications**
  - **Glass transition? Crystallization? Liquid crystallinity? Synthesis?**
- **"Glass transition is currently regarded as the deepest unsolved problem in solid state theory."** **Freed,** *Acct. Chem. Research*, **2011**, *44,* 194-203.
  - **Referring to glass formation in isotropic polymer fluids, let alone ordered fluids such as liquid crystals, be they small molecules or polymers**

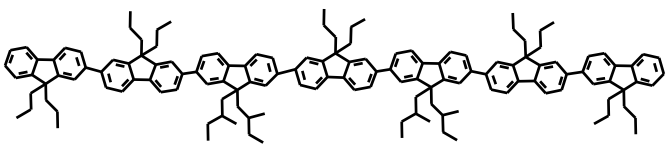
Hairy-Rod Approach to GLC Conjugated Oligomers

- **Rigid rods: high melting point to obscure inherent liquid crystallinity**
- **Aliphatic pendants: meltability and solubility, film preparation by spin-casting from solution**

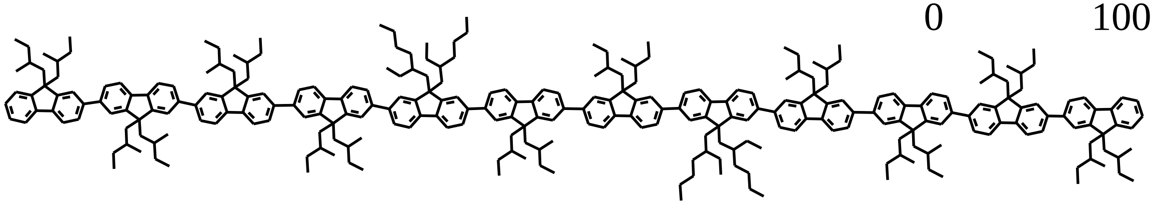
F(MB)5

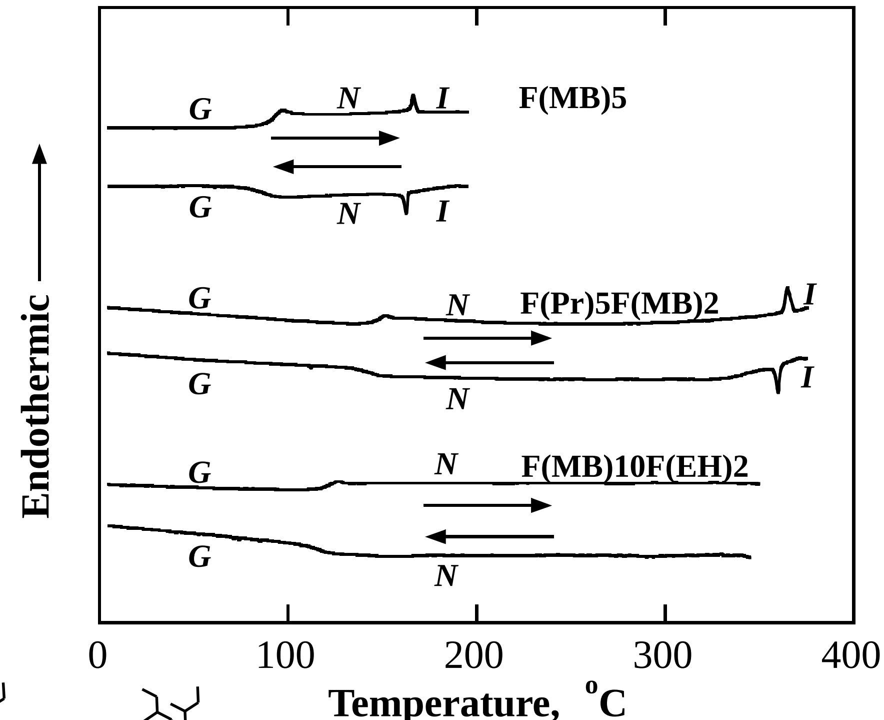


F(Pr)5F(MB)2



F(MB)10F(EH)2

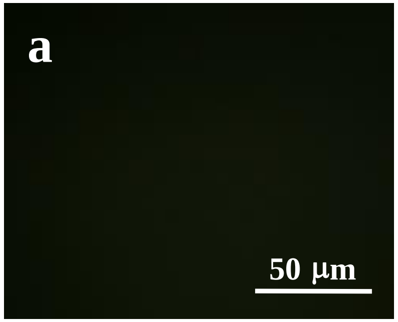




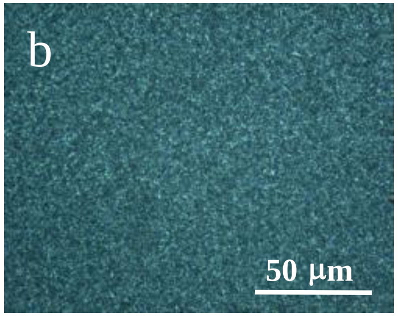
Chem. Mater. **2003** *15*, 542.

Adv. Mater. **2003**, *15*, 1176.

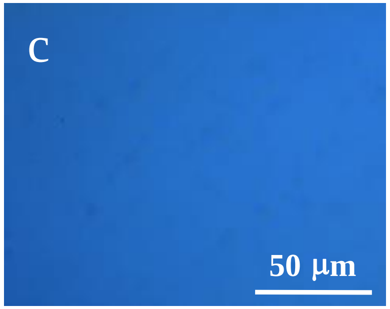
Film Morphology and Polarized OLED Device Structure



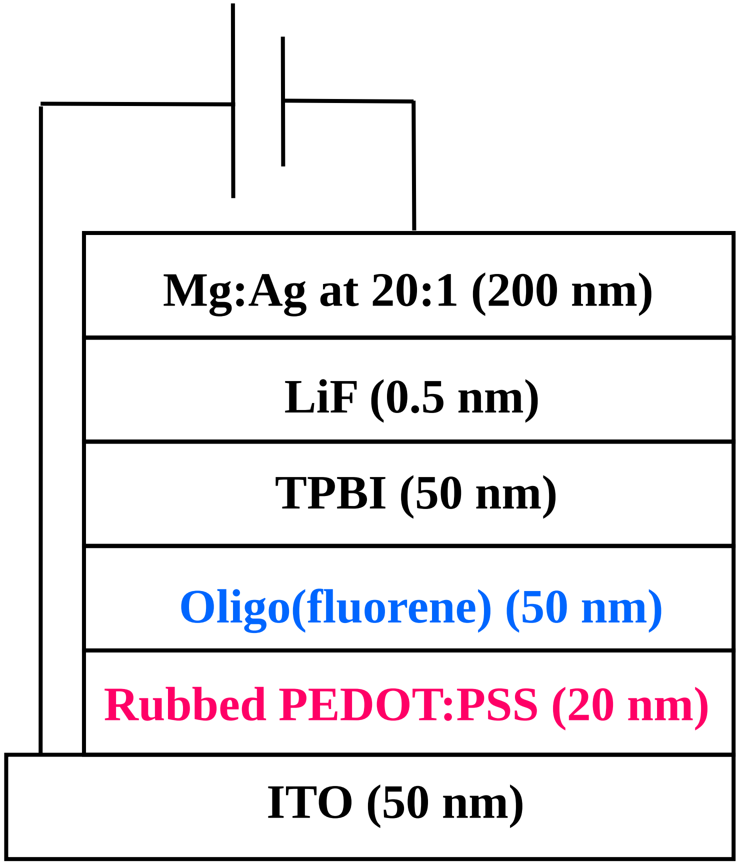
Glassy-Amorphous



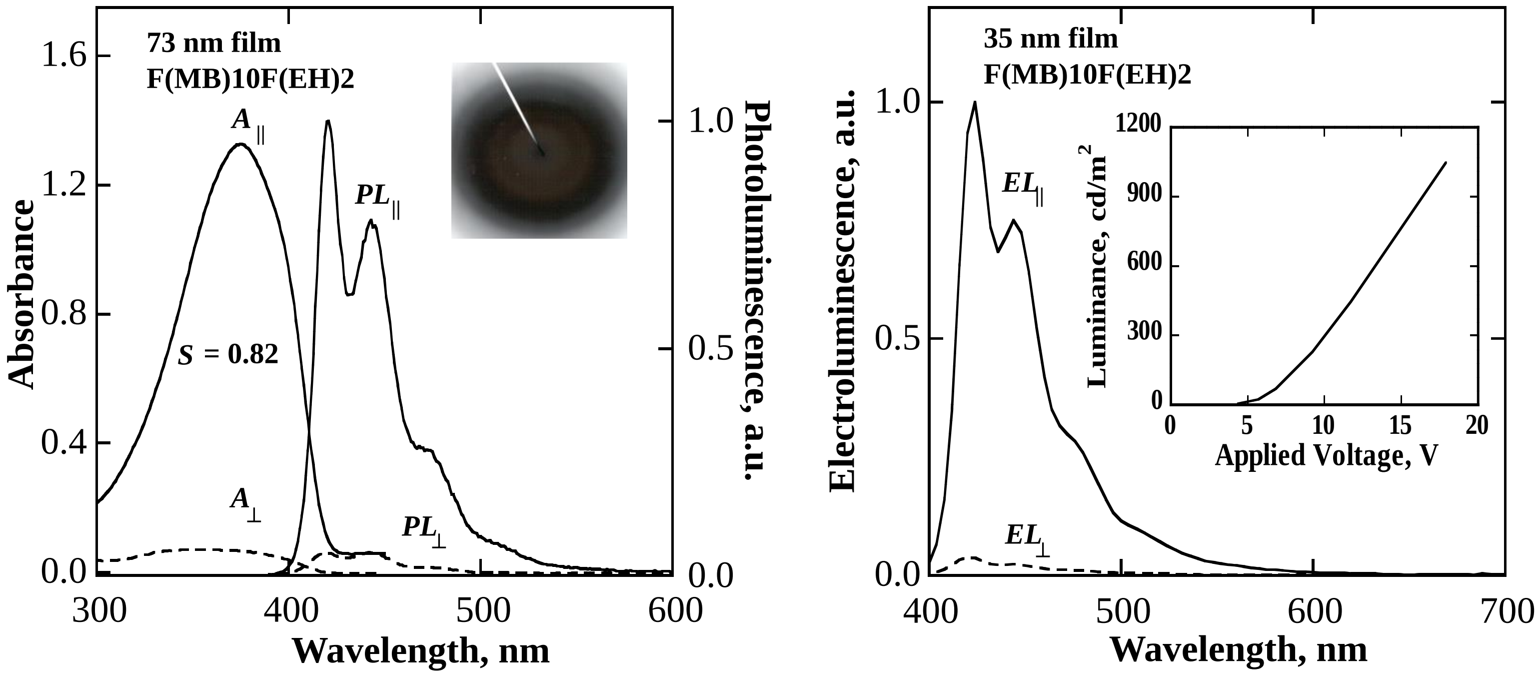
Polydomain Glassy-Nematic



Monodomain Glassy-Nematic

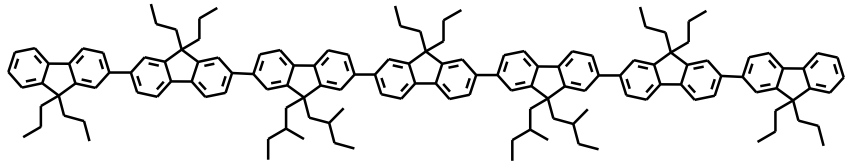


Polarized Absorption and Emission of Monodomain Films on Rubbed PEDOT/PSS

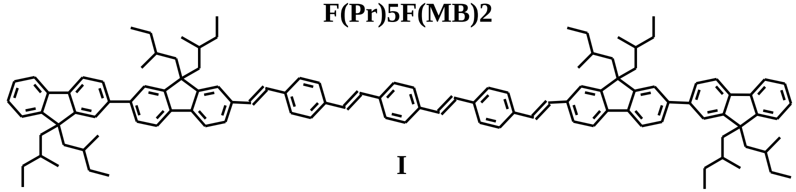


Adv. Mater. **2003**, *15*, 1176.

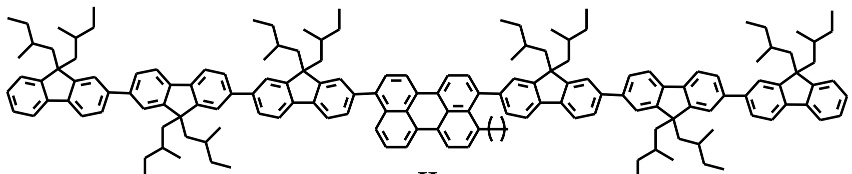
Molecular Structures of Donors and Acceptors for Polarized OLEDs



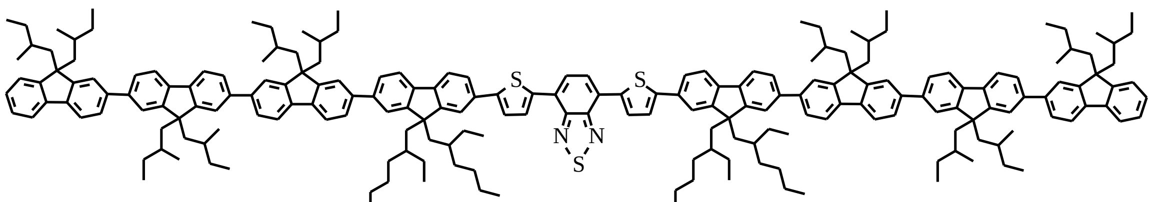
F(Pr)5F(MB)2



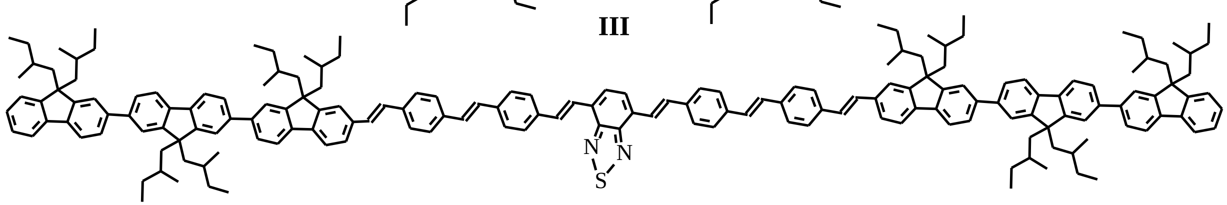
I



II



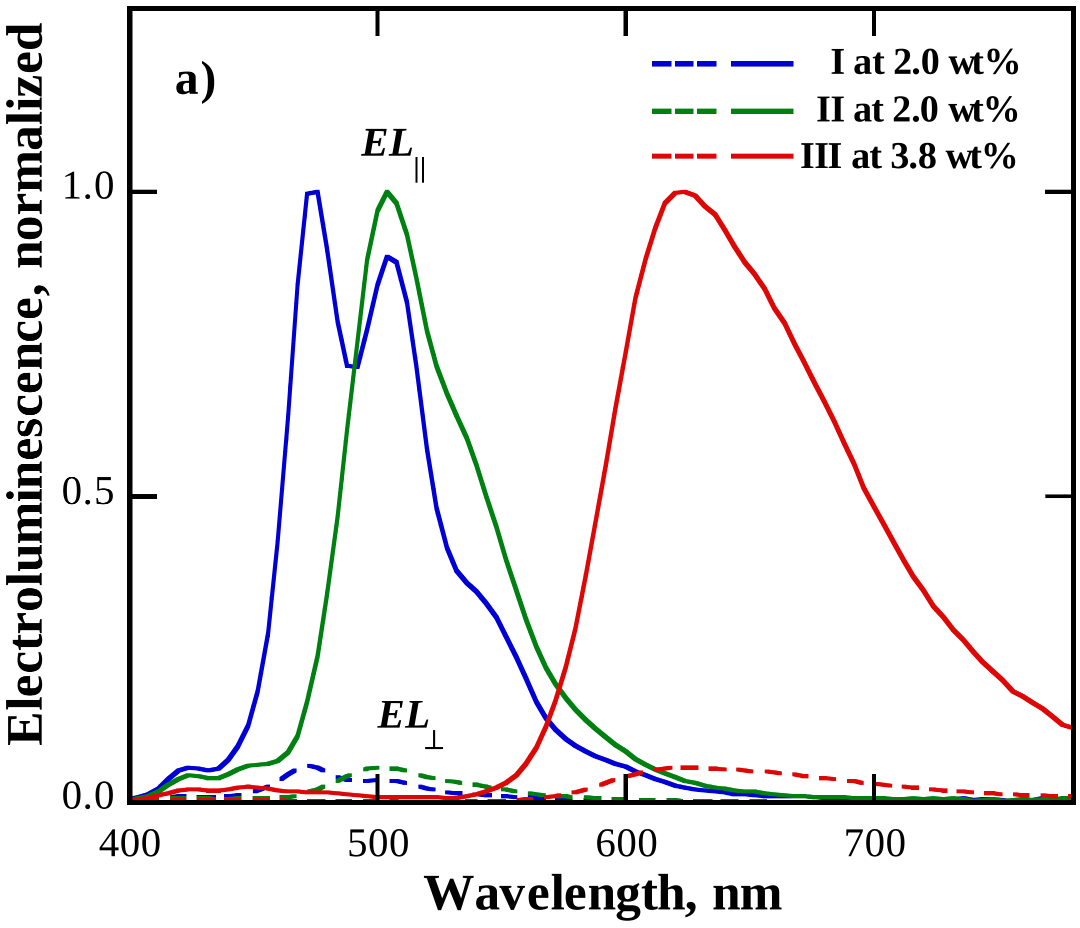
III



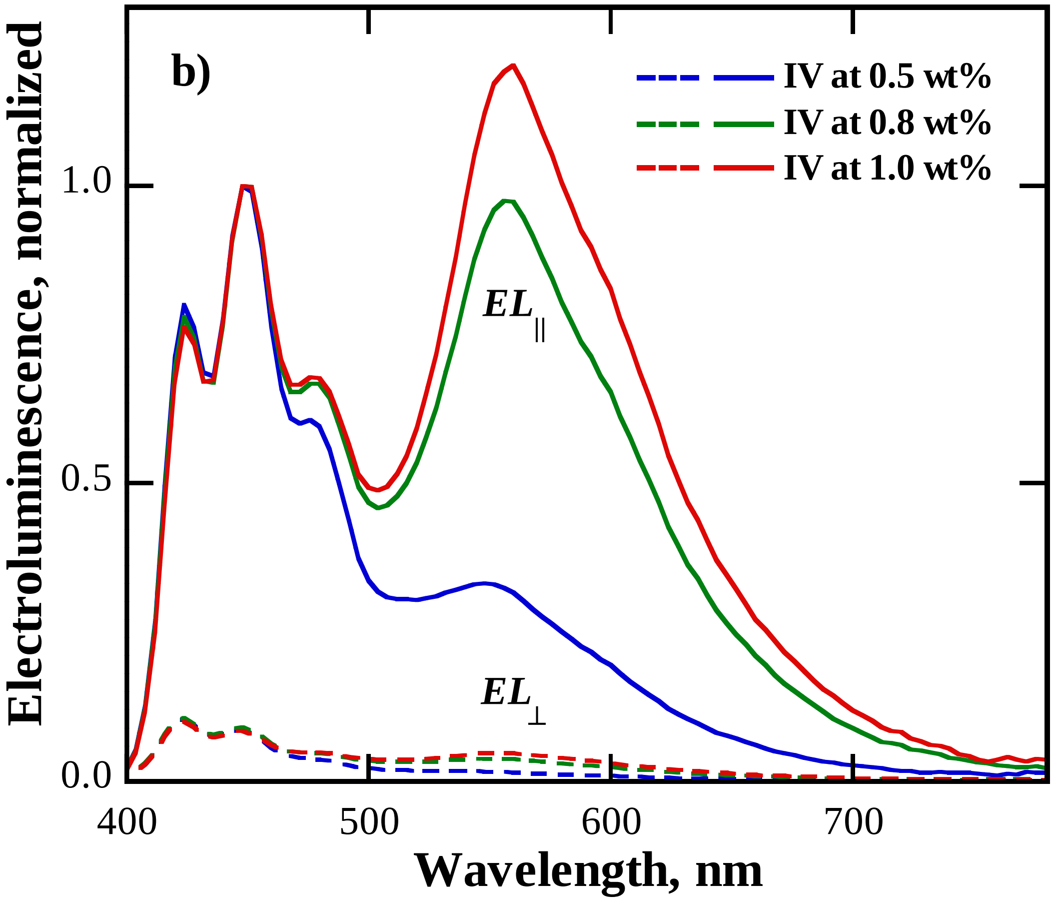
IV

Chem. Mater. **2003**, *15*, 4352.

Linearly Polarized Fluorescent OLEDs via Förster Energy Transfer from Heptafluorene



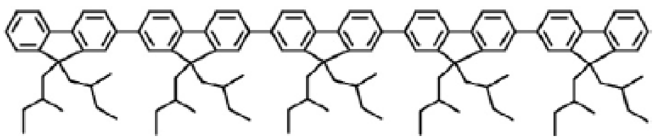
Linearly Polarized White-Light Fluorescent OLEDs



Adv. Mater. **2004**, *16*, 783.

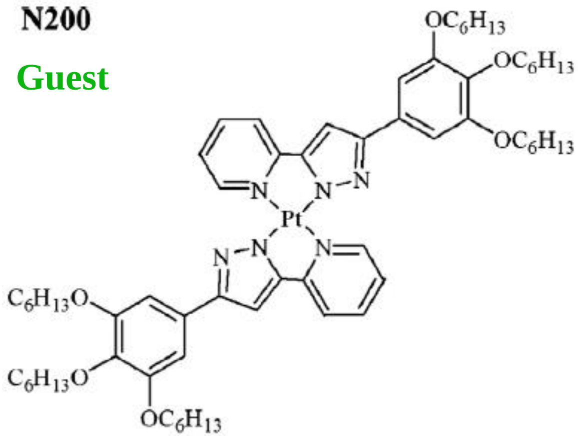
Linearly Polarized Phosphorescent OLEDs

F(MB)5 **Host**

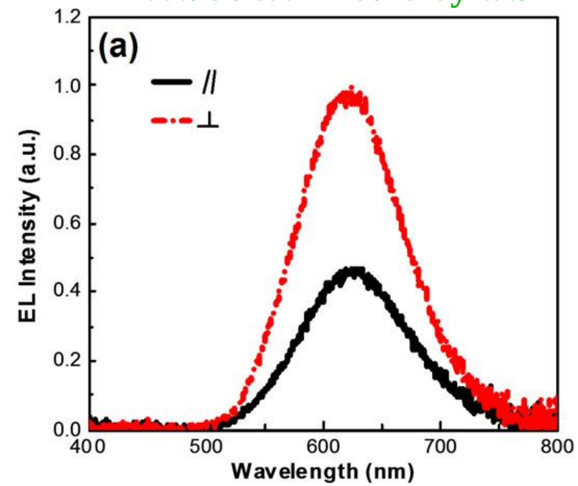


N200

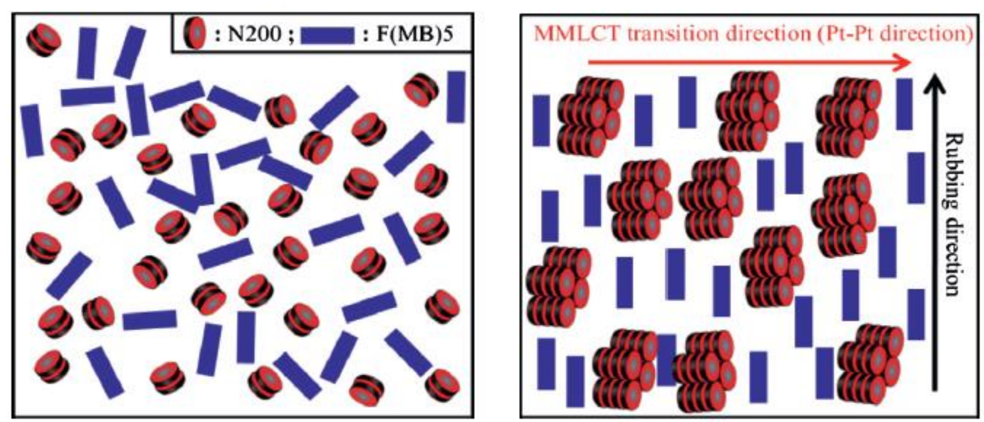
Guest



Host:Guest = 75:25 by wt.



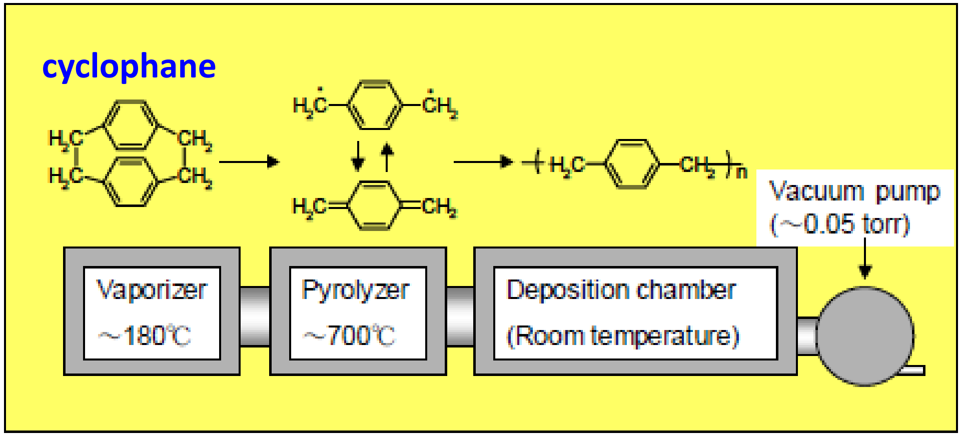
(c) F(MB)5:N200, no treatments (d) F(MB)5:N200, with treatments

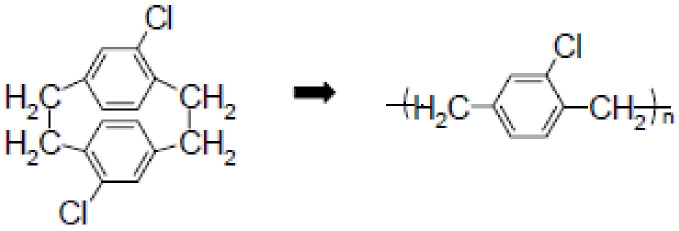


Grazing incident X-Ray scattering
Confocal laser scattering microscopy

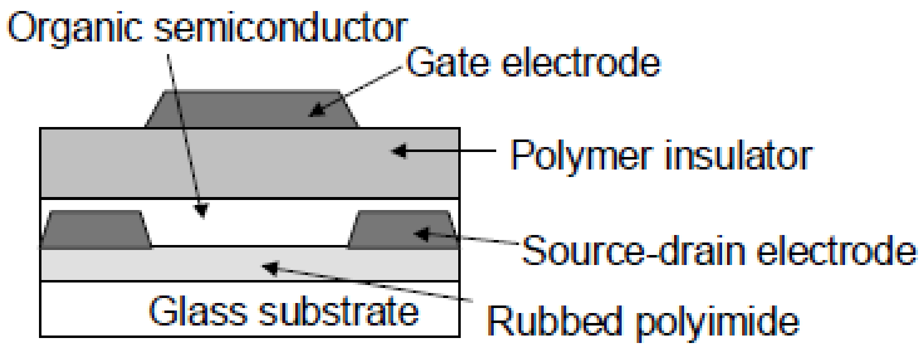
Organic Electronics **2011**, *12*, 15-21; *Ibid.* **2014**, *15*, 311-321.

Organic Insulator Formed by Chemical Vapor Deposition





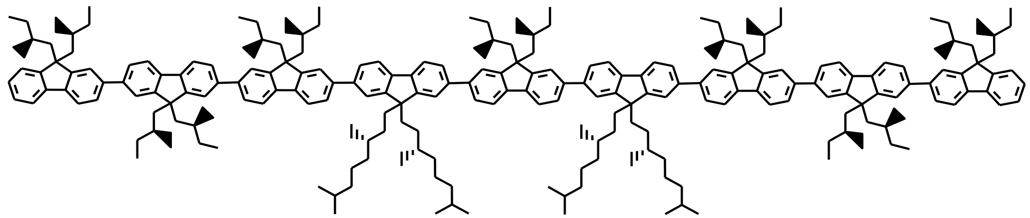
Device Structure and Mobility Data



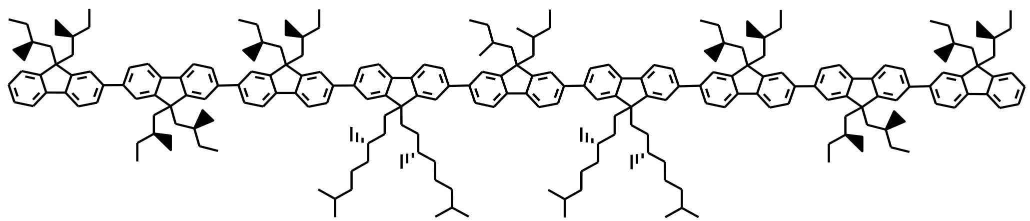
	Hole mobility in OFETs (cm^2/Vs)			
	$\mu_{\parallel}$	$\mu_{\times}$	$\mu_{\perp}$	μ_{a}
F(MB)10F(EH)2	$1.2 \pm 0.2 \times 10^{-2}$	$5.1 \pm 0.3 \times 10^{-3}$	$1.9 \pm 0.1 \times 10^{-3}$	$1.5 \pm 0.3 \times 10^{-5}$
F(Pr)5F(MB)2	$1.7 \pm 0.4 \times 10^{-3}$	$7.8 \pm 1.8 \times 10^{-4}$	$1.9 \pm 0.1 \times 10^{-4}$	$2.1 \pm 1.1 \times 10^{-5}$
PFO	$5.8 \pm 0.7 \times 10^{-3}$	$2.2 \pm 0.3 \times 10^{-3}$	$5.2 \pm 0.5 \times 10^{-4}$	$3.3 \pm 0.5 \times 10^{-4}$

Chem. Mater. **2005**, *17*, 164.

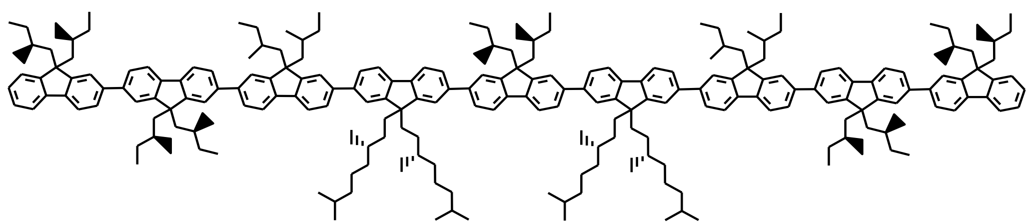
Monodisperse Oligofluorenes with a Varying Degree of Pendant Chirality



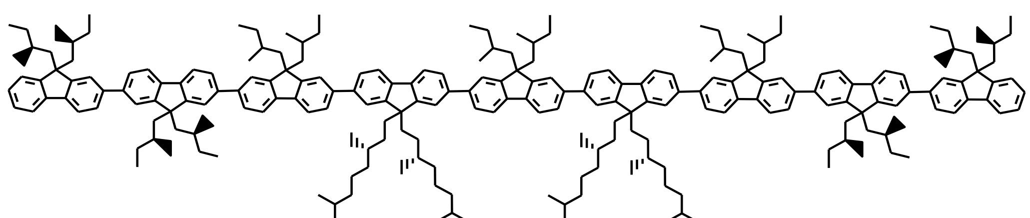
C-702



C-612



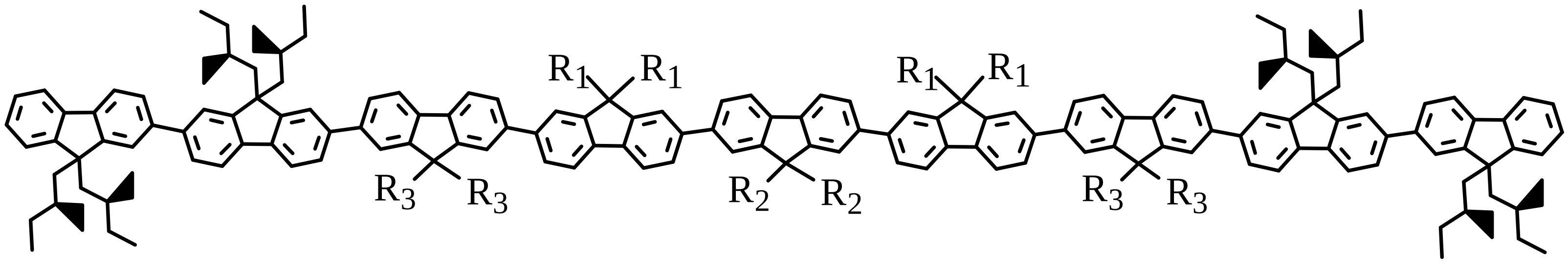
C-522

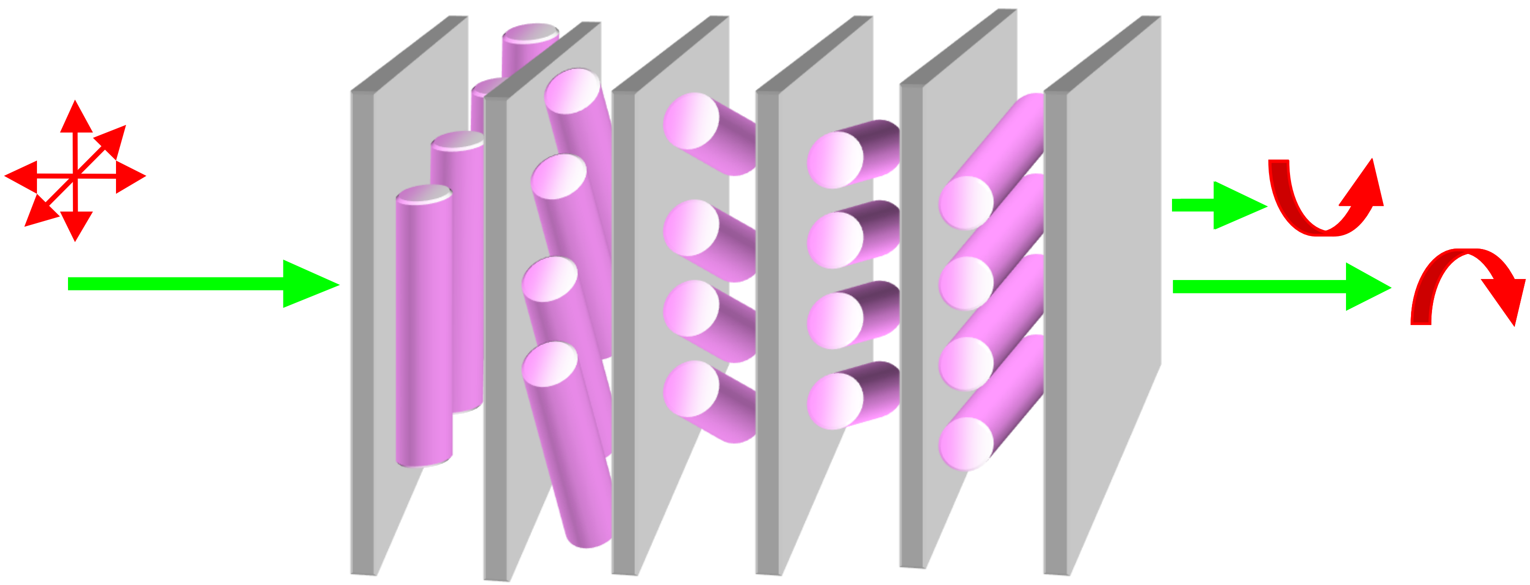


C-432

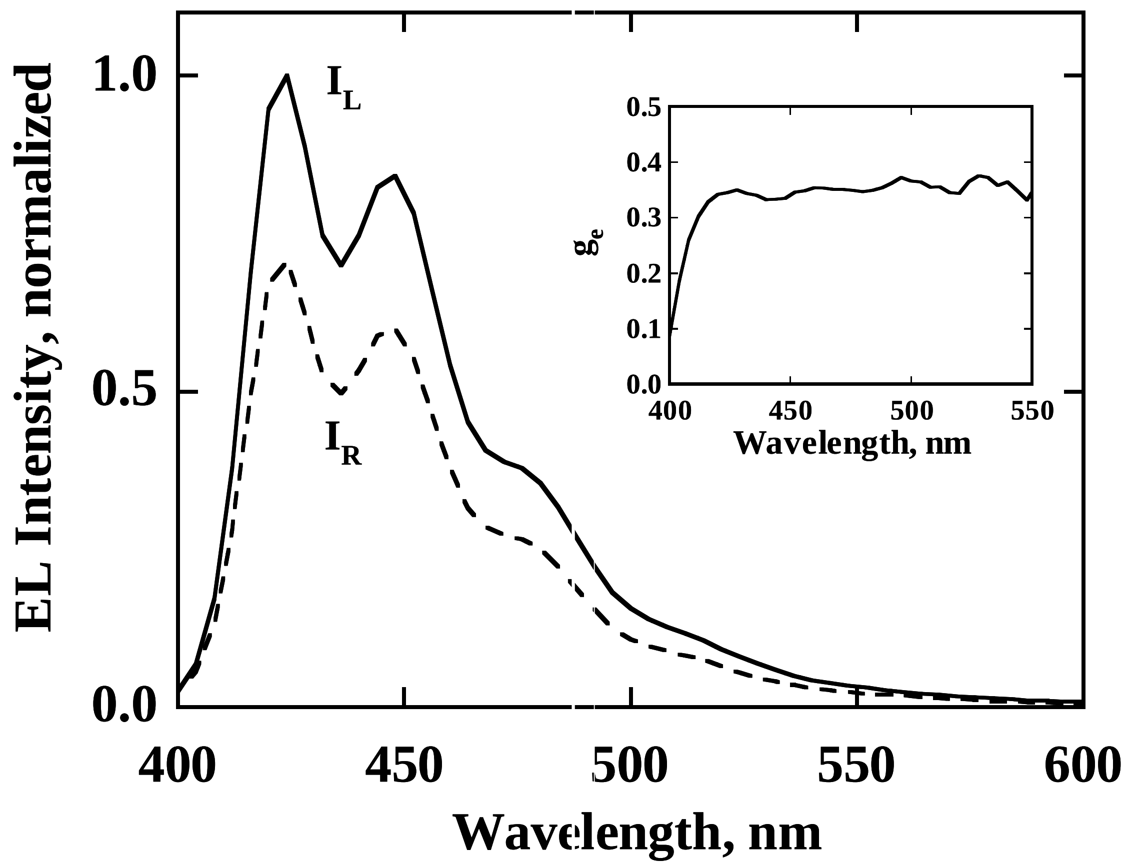
JACS, **2002**, *124*, 8338;
Ibid. **2003,** *125***,** 14032.

Right-Handed Helical Stacking of Chiral Oligofluorenes





Circularly Polarized Fluorescent OLED Comprising a 70-nm-thick C-522 Film [turn-on voltage less than 5V; luminance yield, 0.94 cd/A at 20 mA/cm^2]

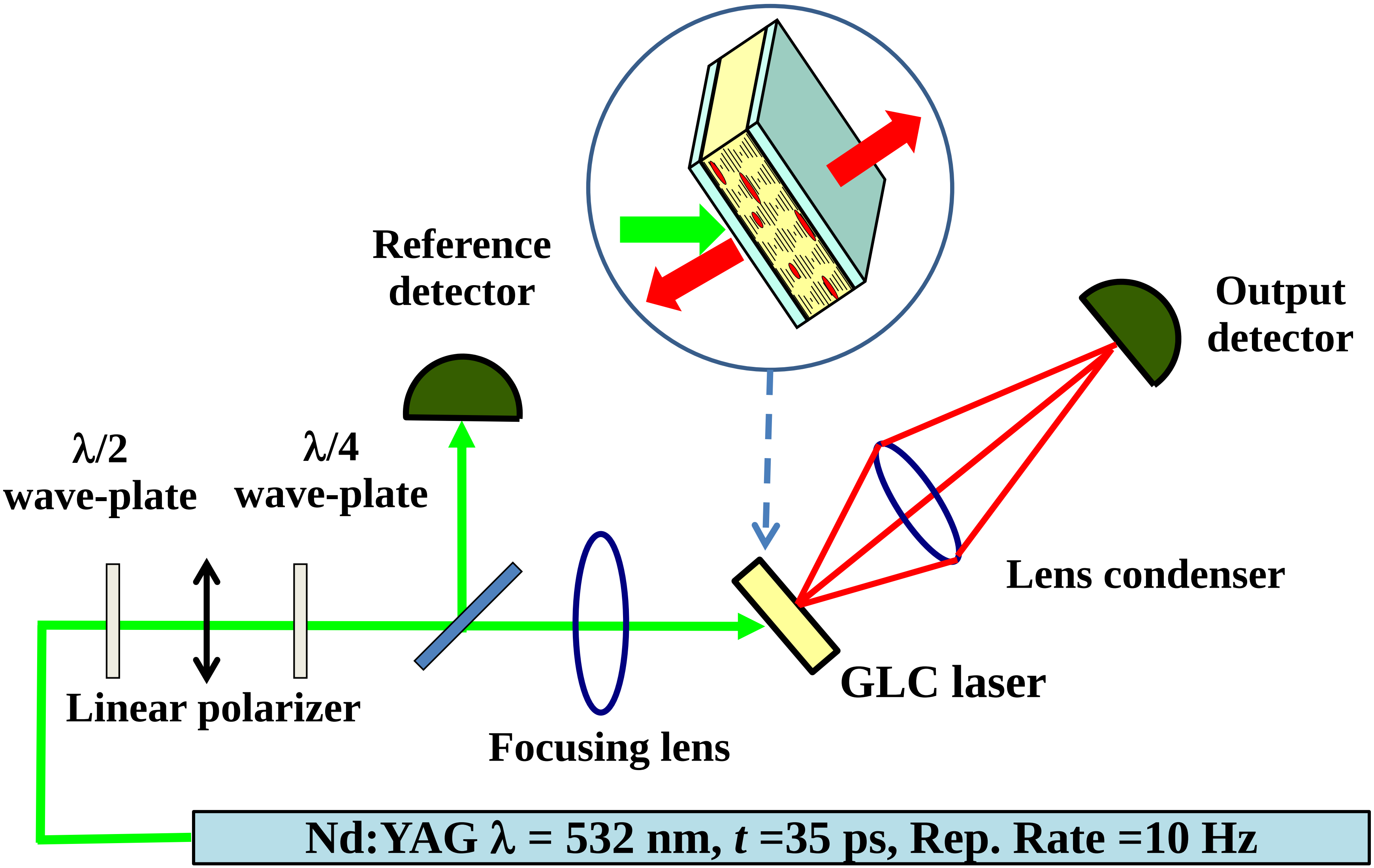


Light Amplification by Stimulated Emission of Radiation

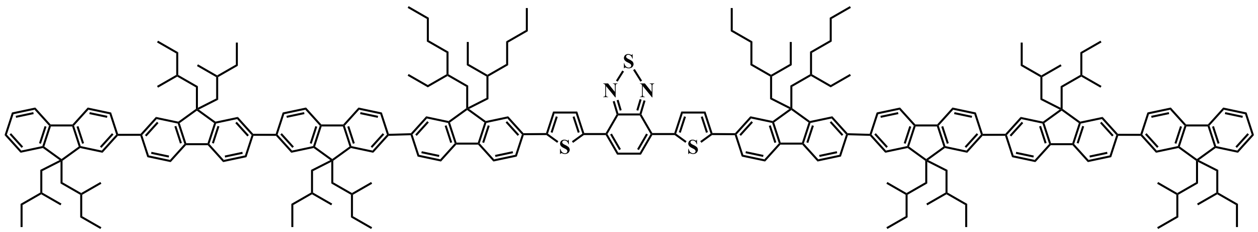
Lasing Identified by Five Criteria

- **Clear evidence of threshold in output energy as a function of pump energy with a greater slope above threshold than below**
- **Spatial and temporal coherence, highly directional, and sharply focused**
- **Significant spectral line narrowing, less than 1 to several nm**
- **Existence of laser cavity resonance, including mirrorless cavity presented by a cholesteric liquid crystal film**
- **Strong output beam regardless of polarization state**

Apparatus for Characterization of GLC Lasers

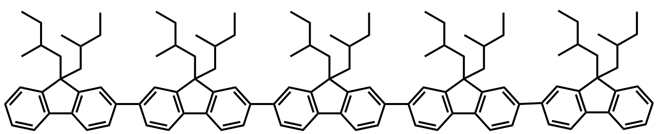


Host and Guest Molecules for Fabrication of Lasers



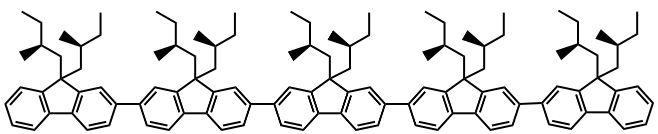
OF-r *G* 104 ^{o}C *N* 304 ^{o}C *I*

Chem. Mater. **2003,** *15*, 4352; *Adv. Mater*. **2004**, *16*, 783.



F(MB)5-N *G* 92 ^{o}C *N* 171 ^{o}C *I*

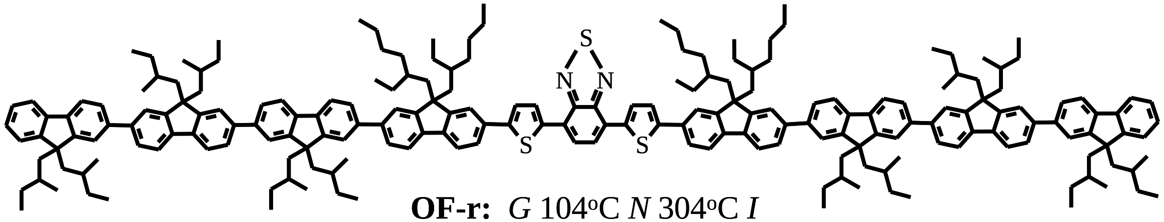
Chem. Mater. **2003,** *15*, 542.



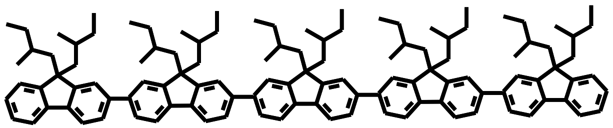
F(MB)5-Ch *G* 91 ^{o}C *Ch* 173 ^{o}C *I*

J. Am. Chem. Soc. **2002,** *124*, 8337.

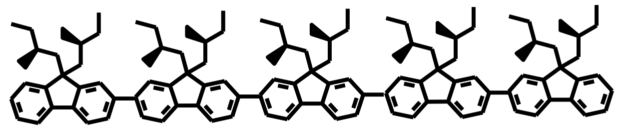
Robust Circularly Polarized Lasers



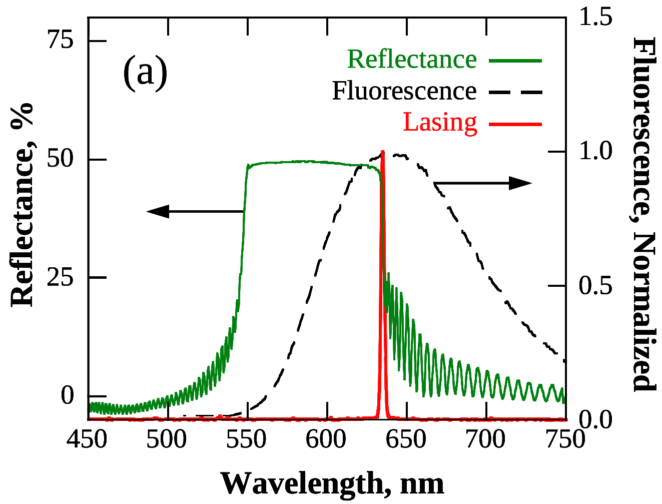
OF-r: *G* 104°C *N* 304°C *I*

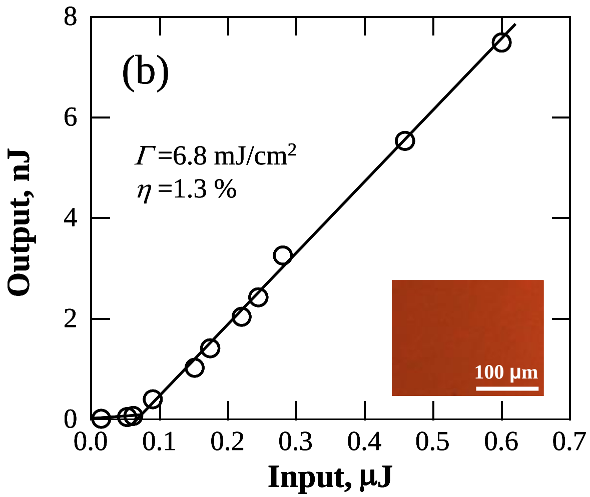


F(MB)5-N: *G* 92°C *N* 171°C *I*



F(MB)5-Ch: *G* 91°C *Ch* 173°C *I*

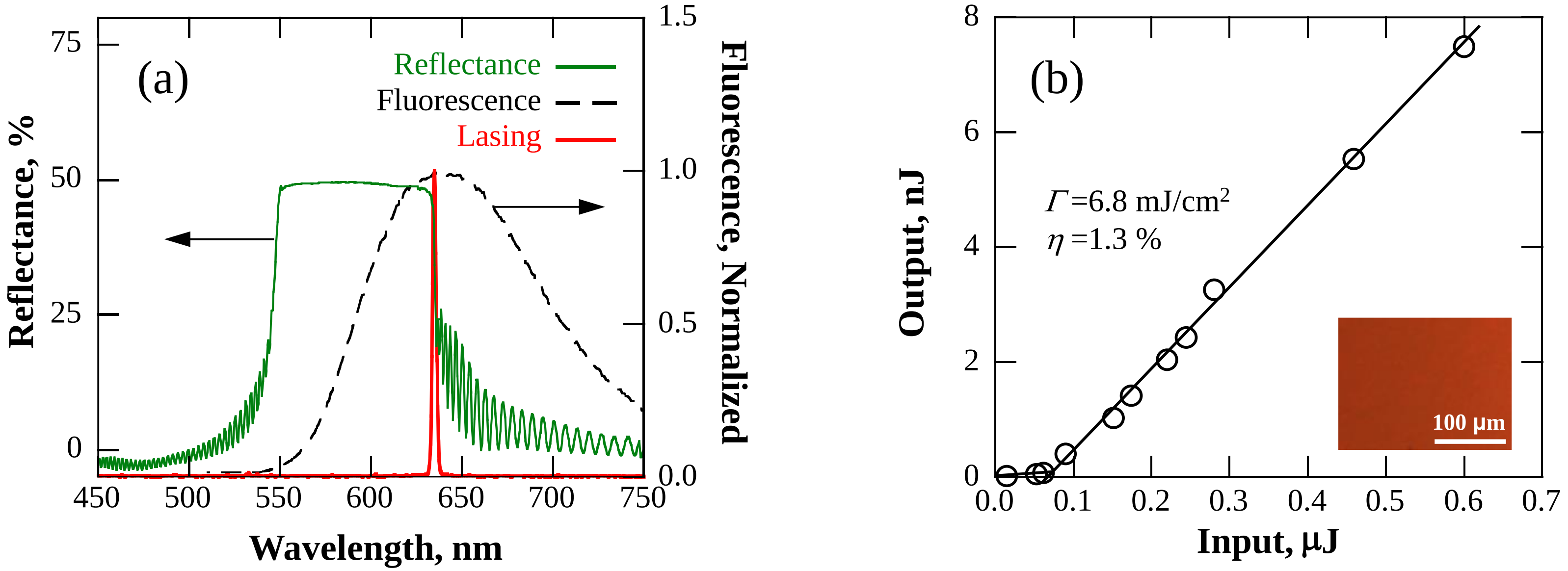




Appl. Phys. Lett. **2009**, *94*, 04111.

Cholesteric GLC Laser

Chemical composition: 1.5 wt% **OF-r** in **F(MB)5-Ch:F(MB)5-N** at a 24.0:76.0 mass ratio

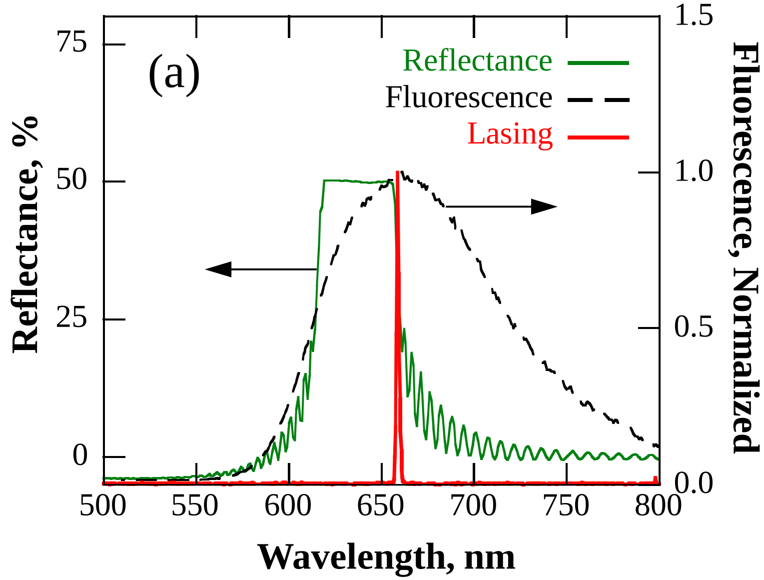


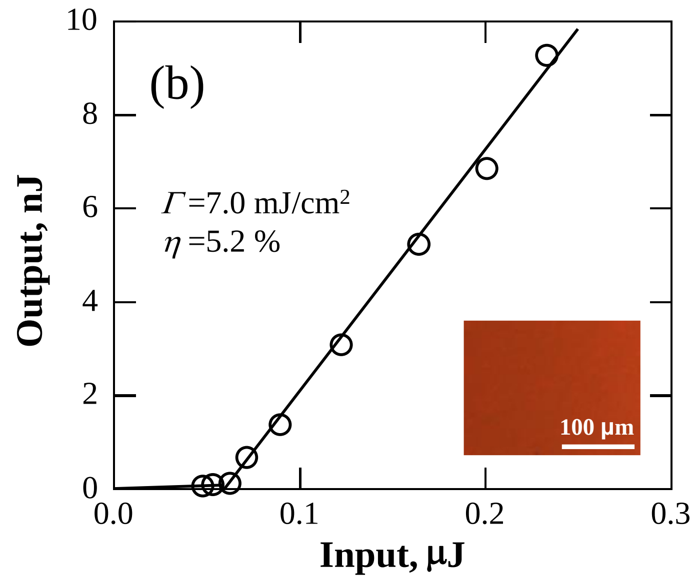
- **Green curve**: Reflection spectrum
- **Black curve**: **OF-r** fluorescence spectrum from nematic GLC **F(MB)5-N** film
- **Red curve**: lasing peak at 635 nm with a pump fluence of 121 mJ/cm^2 at 10 Hz

- Lasing output energy as a function of pump energy
- Monodomain character of the cholesteric GLC film verified with a polarizing optical micrograph included as the inset

Cholesteric Fluid LC Laser

Chemical composition: 2.0 wt% **OF-r** in **CB-15:ZLI-2244-000** at a 35.6:64.4 mass ratio



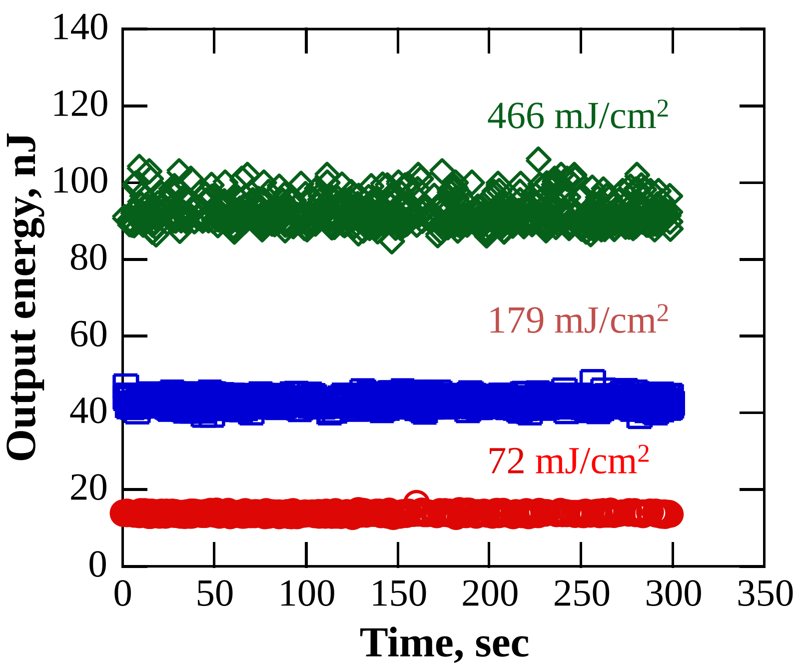


- **Green curve**: Reflection spectrum
- **Black curve**: **OF-r** fluorescence spectrum from nematic LC **ZLI-2244-000** film
- **Red curve**: lasing peak at 658 nm with a pump energy of 30 mJ/cm^2 at 10 Hz

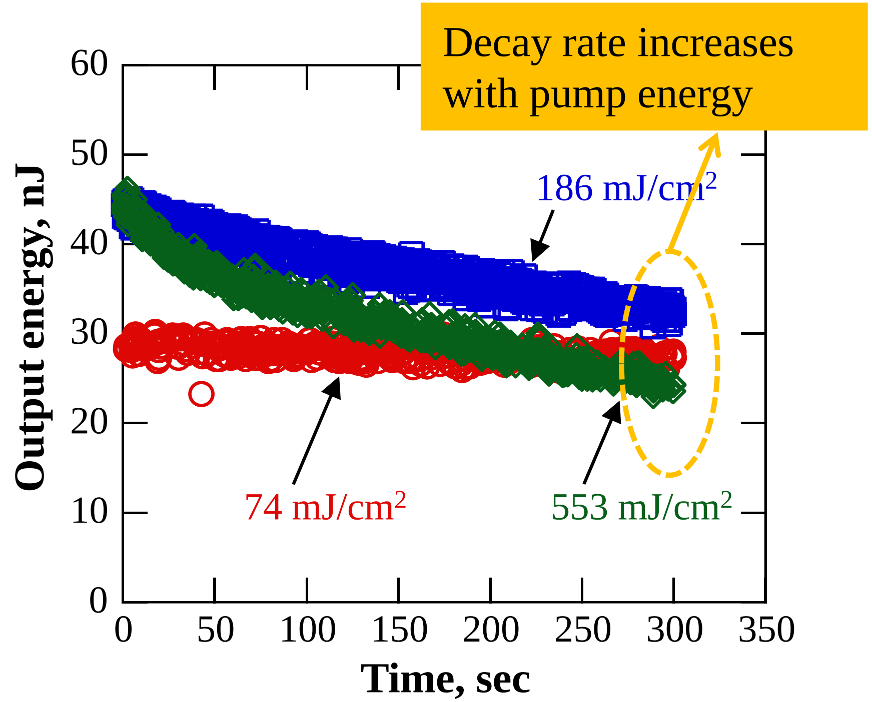
- Lasing output energy as a function of pump energy
- Monodomain character of the fluid CLC film verified with a polarizing optical micrograph included as the inset.

Temporal Stability of Lasing Output

Cholesteric GLC Laser: **OF-r** at 2.0 wt% in **F(MB)5-Ch:F(MB)5-N** at 24.1:75.9 mass ratio



Cholesteric fluid LC Laser: **OF-r** at 2.0 wt% in **CB-15:ZLI 2244-000** at 35.6:64.4 mass ratio



- Heating via optical pumping
- Light-induced pitch dilation
- Laser-induced fluid flow

Disruption of fluid LC structure and orientational order of **OF-r** molecules; GLC films remained robust

Appl. Phys. Lett. **2009**, *94*, 04111.

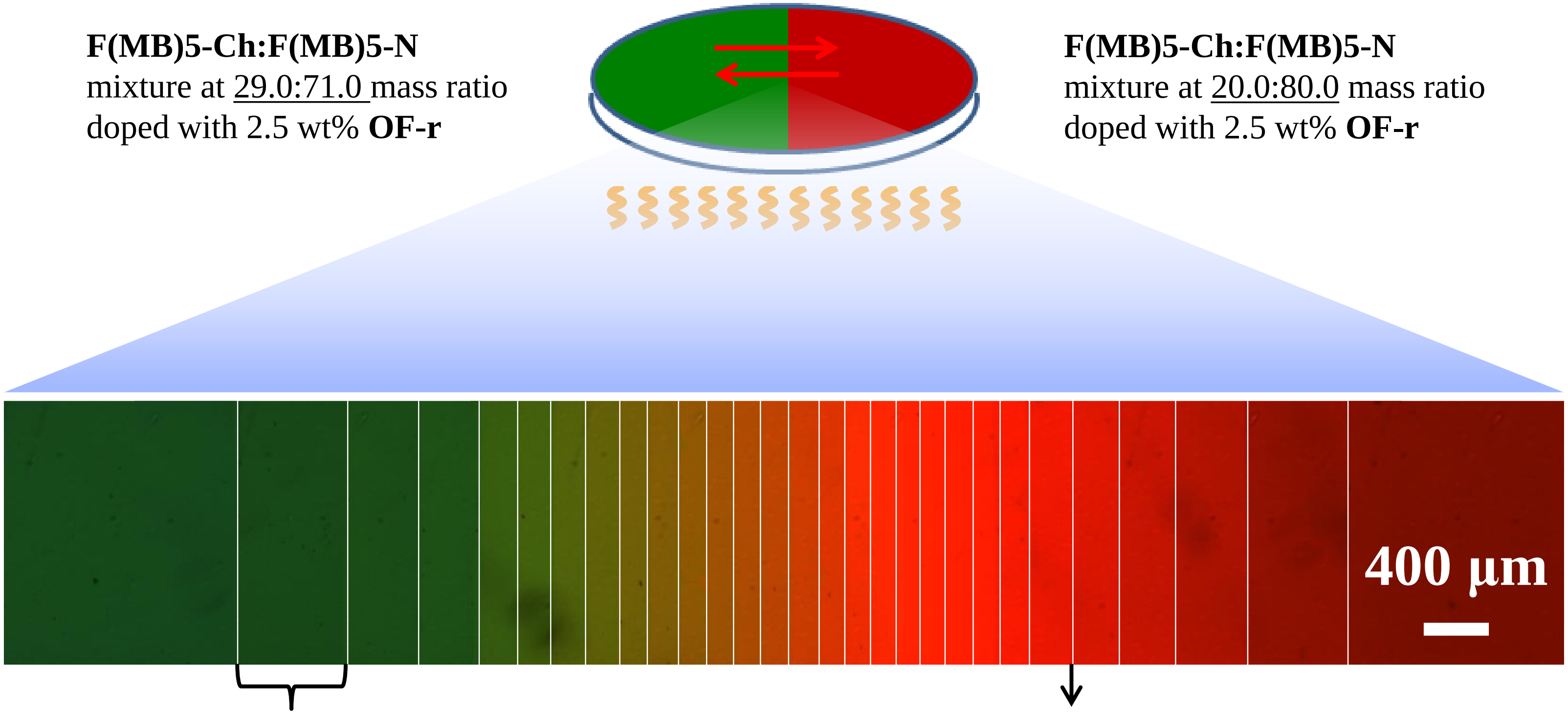
Cholesteric GLC Film with a Lateral Pitch Gradient

Appl. Phys. Lett. **2011**, *98*, 111112

Thermally activated molecular diffusion across interface of 14-μm-thick film at 220 °C for 62 h before cooling to 25 °C

F(MB)5-Ch:F(MB)5-N mixture at 29.0:71.0 mass ratio doped with 2.5 wt% **OF-r**

F(MB)5-Ch:F(MB)5-N mixture at 20.0:80.0 mass ratio doped with 2.5 wt% **OF-r**

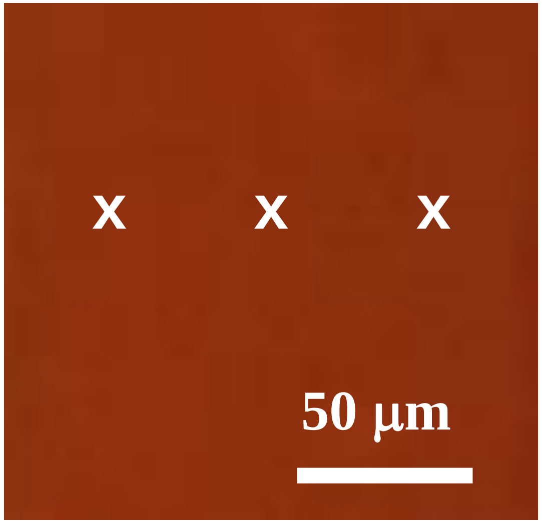


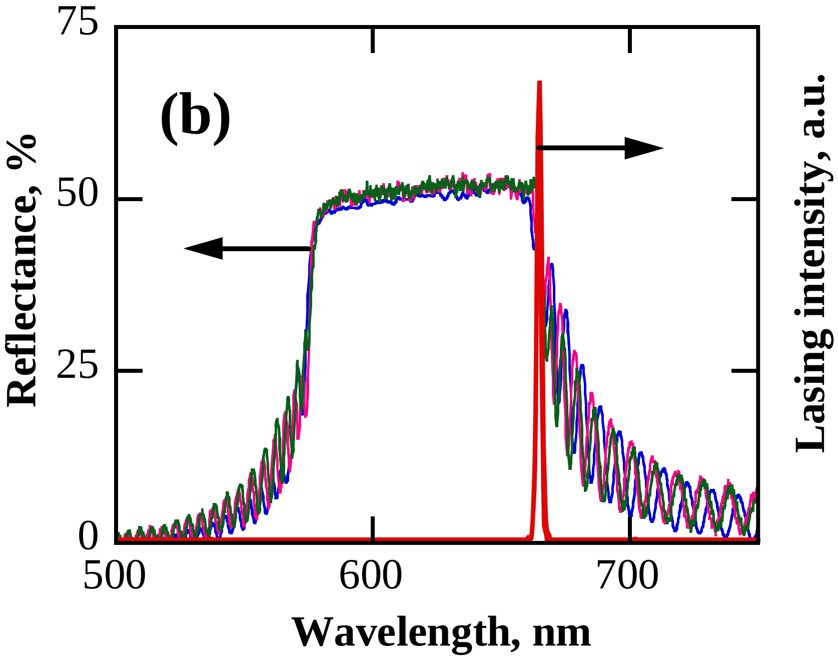
Grandjean-Cano band

Grandjean-Cano line

Stop-Bands and Lasing Spectra in an Arbitrary Grandjean-Cano Band

(a)

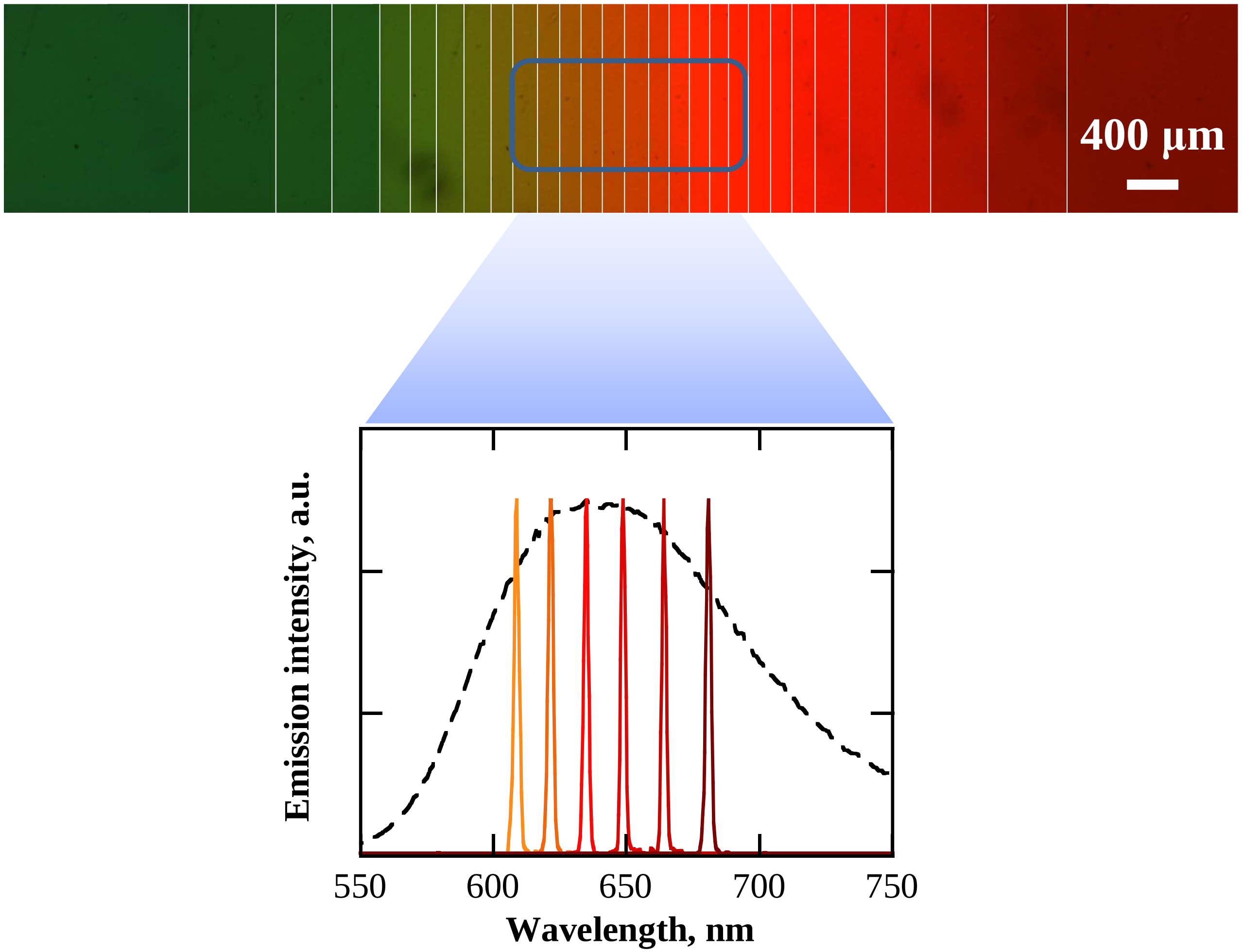




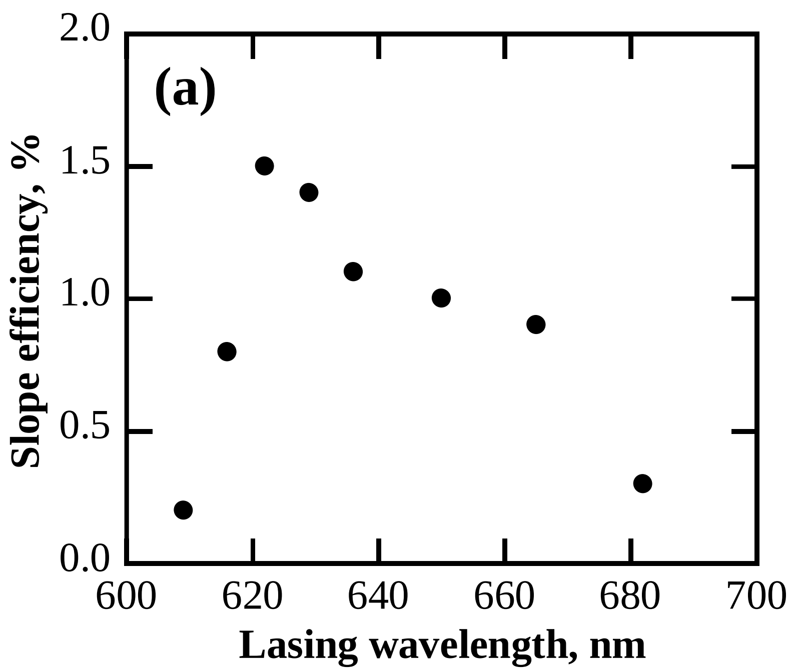
- Each Grandjean-Cano band is characterized by a constant value of an apparent helical pitch length, as evidenced by
  - Three reflection spectra in (b) correspond to the three positions identified as X's in (a)
  - Three overlapping lasing peaks

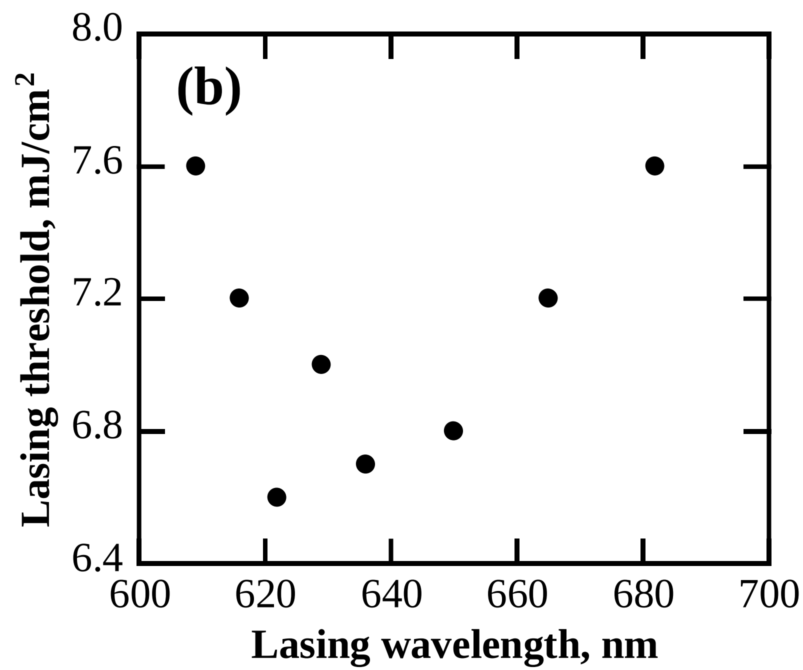
A Cholesteric GLC Film with Lateral Pitch Gradient Capable of Multiple Lasing Wavelengths on Demand within a Single Film

$$g_e = 2(I_L - I_R)/(I_L + I_R) = -1.6 \text{ to } -1.7$$



Slope Efficiency and Lasing Threshold of Spatially Resolved Lasers





- **Maximum slope efficiency at 1.5% superior to the best value of 0.5% reported to date for gradient-pitch cholesteric fluid LC lasers**
- **Observed thresholds, *G*, are the lowest of all gradient-pitch cholesteric fluid and glassy liquid crystal lasers reported to date**
- **The slope efficiency profile largely tracks fluorescence spectrum of OF-r**

Conclusions

- **Absent physical understanding of glass transition, *core-pendant* and *hairy-rod* approaches to the highest T_g and T_c with superior stability against crystallization ever reported**
- **Conformational multiplicity underpinning versatile molecular design concepts, resulting in self-organized solid films for robust optoelectronic devises**
- **Cholesteric and Nematic GLC films demonstrated for**
  - **Non-absorbing circular polarizers, optical notch filters, reflectors**
  - **Polarized fluorescent and phosphorescent OLEDs**
  - **Anisotropic organic field-Effect transistors**
  - **Robust solid-state lasers with temporally stable output**
  - **A lateral gradient-pitch GCLC film renders multiple lasing wavelengths on demand**

Comprehensive book chapter @ http://www.che.rochest/~shc/HP_5.pdf

Acknowledgments

Post-doctoral research associates and doctoral students: Drs. H. P. Chen, Y. Geng, D. Katsis, J. J. Ou, J. U. Wallace, A. Trajkovska, S. W. Culligan, A. C. Chen, C. Kim, L. Zeng, S. K. Wei, H. Shi, J. C. Mastrangelo, and B. M. Conger.

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