Liquid Crystals and the Origin of Life

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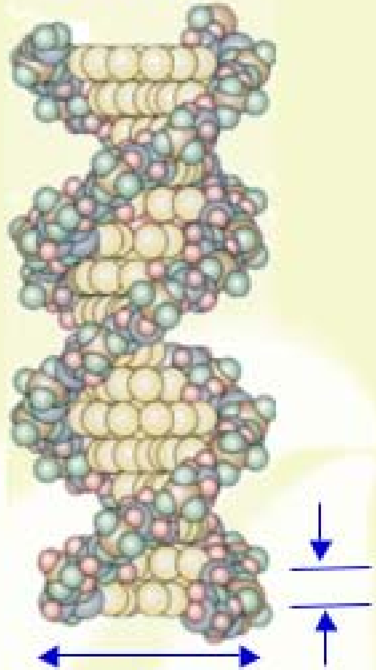
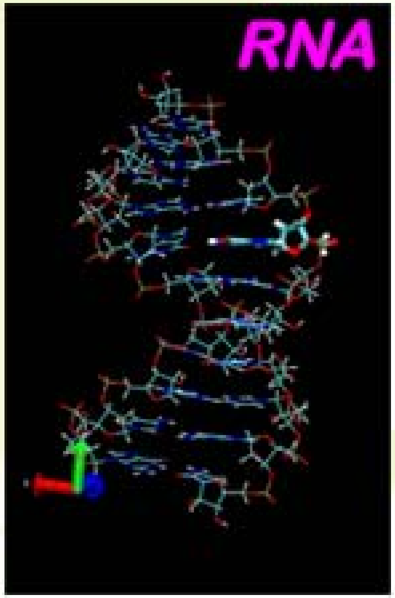
Michi Nakata (1975-2006)

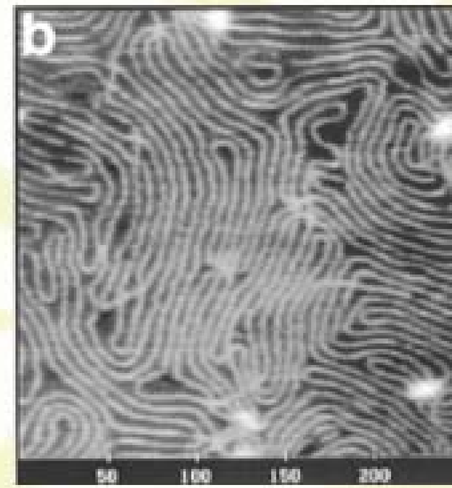
DNA & RNA



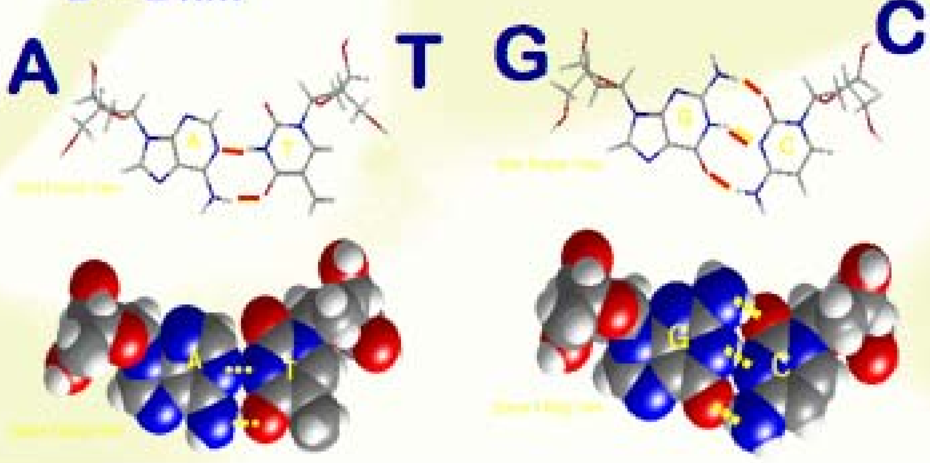


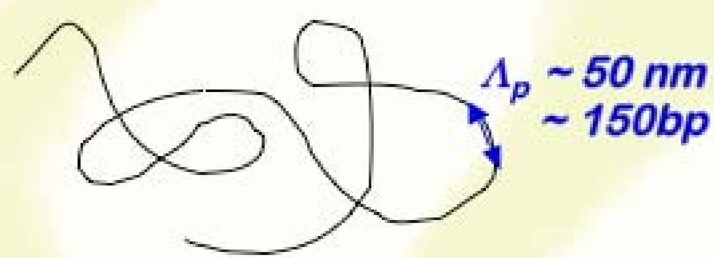
3'-CGCGAAAATTTTCGCG-5'
3'-CGCGAAAATTTTCGCG-5'

self-complementary 16-mer palindromes



Y. Fang, J. Phys. Chem B (1997)



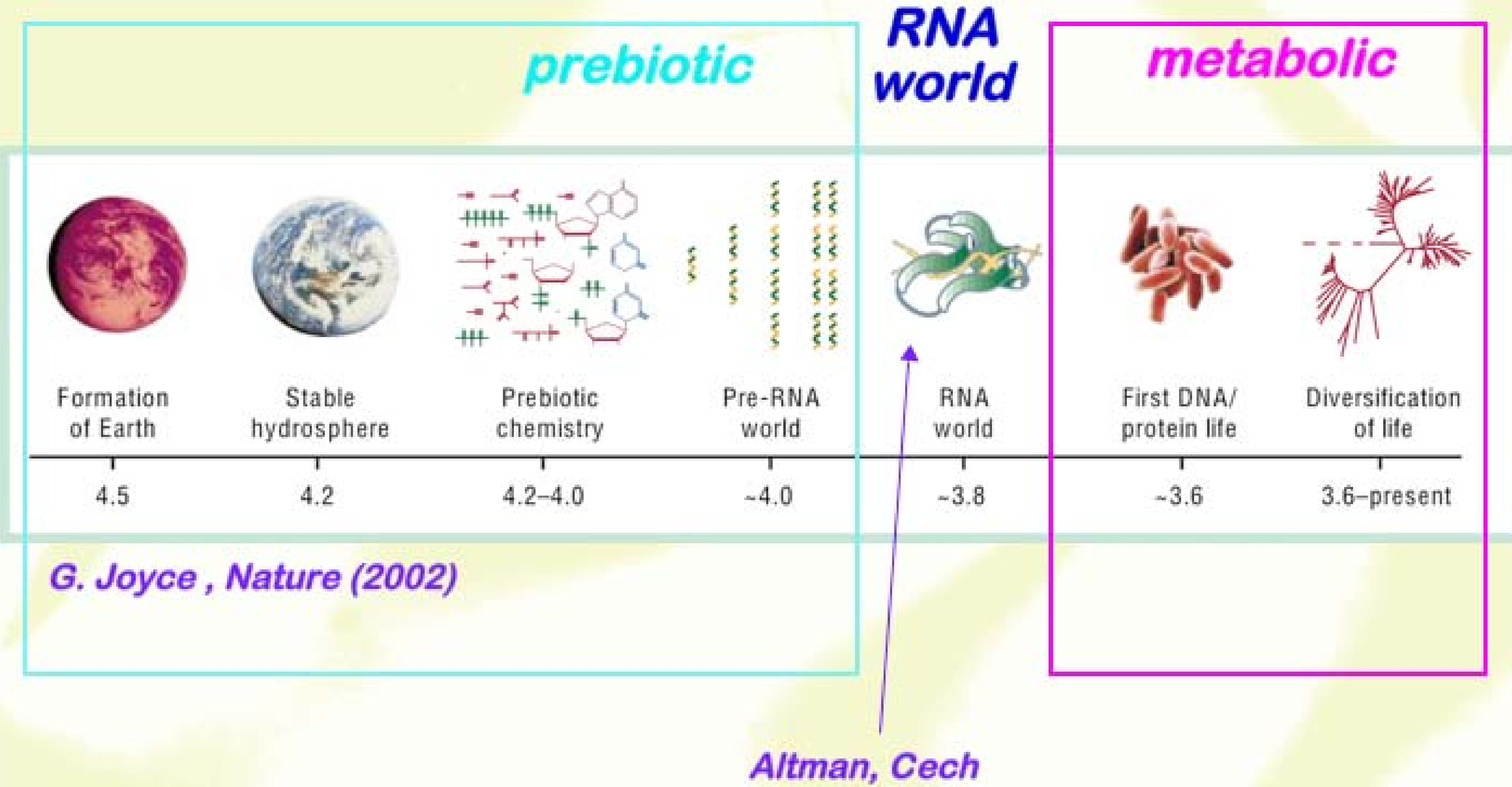


Why are life's

information carrying molecules

linear polymers?

timeline

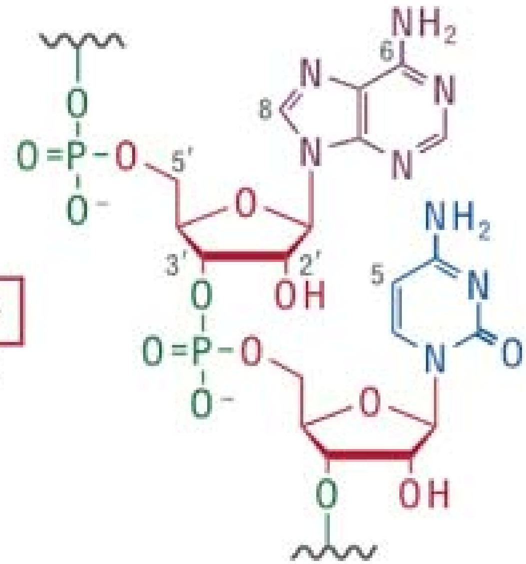


prebiotic
RNA world
metabolic
Formation of Earth
Stable hydrosphere
Prebiotic chemistry
Pre-RNA world
RNA world
First DNA/ protein life
Diversification of life
4.5
4.2
4.2–4.0
~4.0
~3.8
~3.6
3.6–present
G. Joyce , Nature (2002)
Altman, Cech

"cluttered path to RNA"

3′,5′	**Phosphate**
2′,5′	Pyrophosphate
2′,2′	Polyphosphate
3′,3′	Alkylphosphate
5′,5′	

β	**D**	**Ribo**	**furanose**
α	L	Lyxo	pyranose
		Xylo	
		Arabino	
		Tetroses	
		Hexoses	
		Branched sugars	



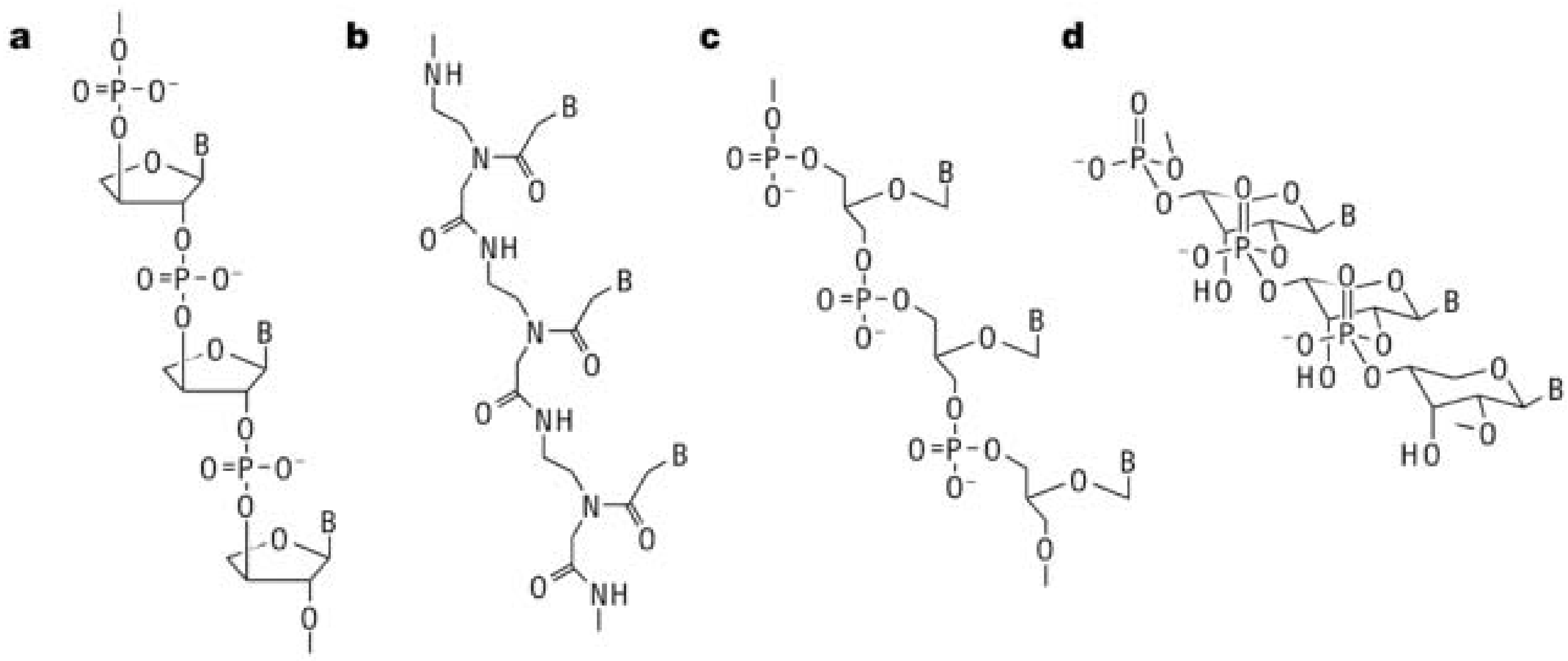
Adenine, guanine

Diaminopurine
Hypoxanthine
Xanthine
Isoguanine
N6-substituted purines
C8-substituted purines

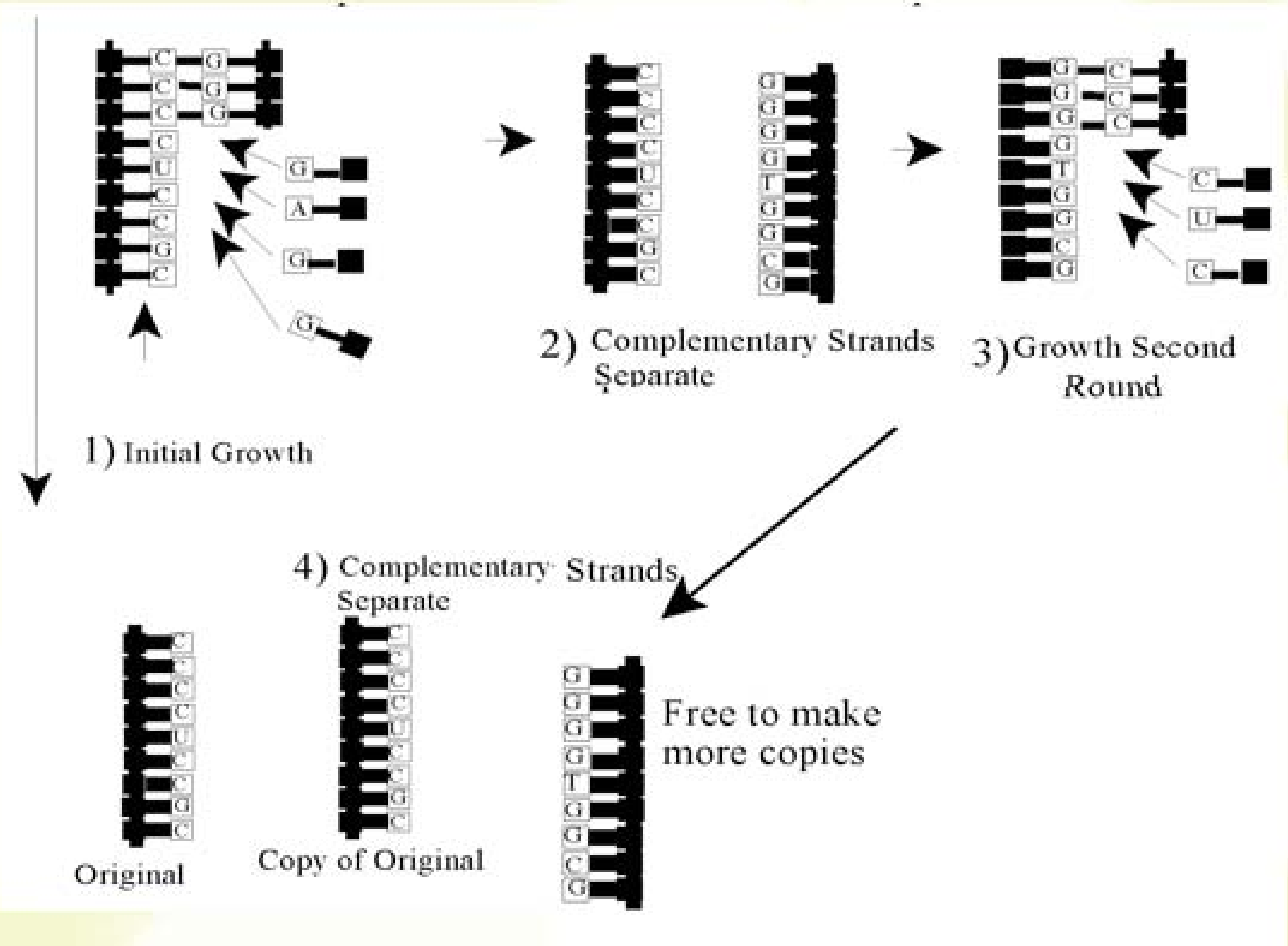
Cytosine, uracil

Diaminopyrimidine
Dihydrouracil
Orotic acid
C5-substituted pyrimidines

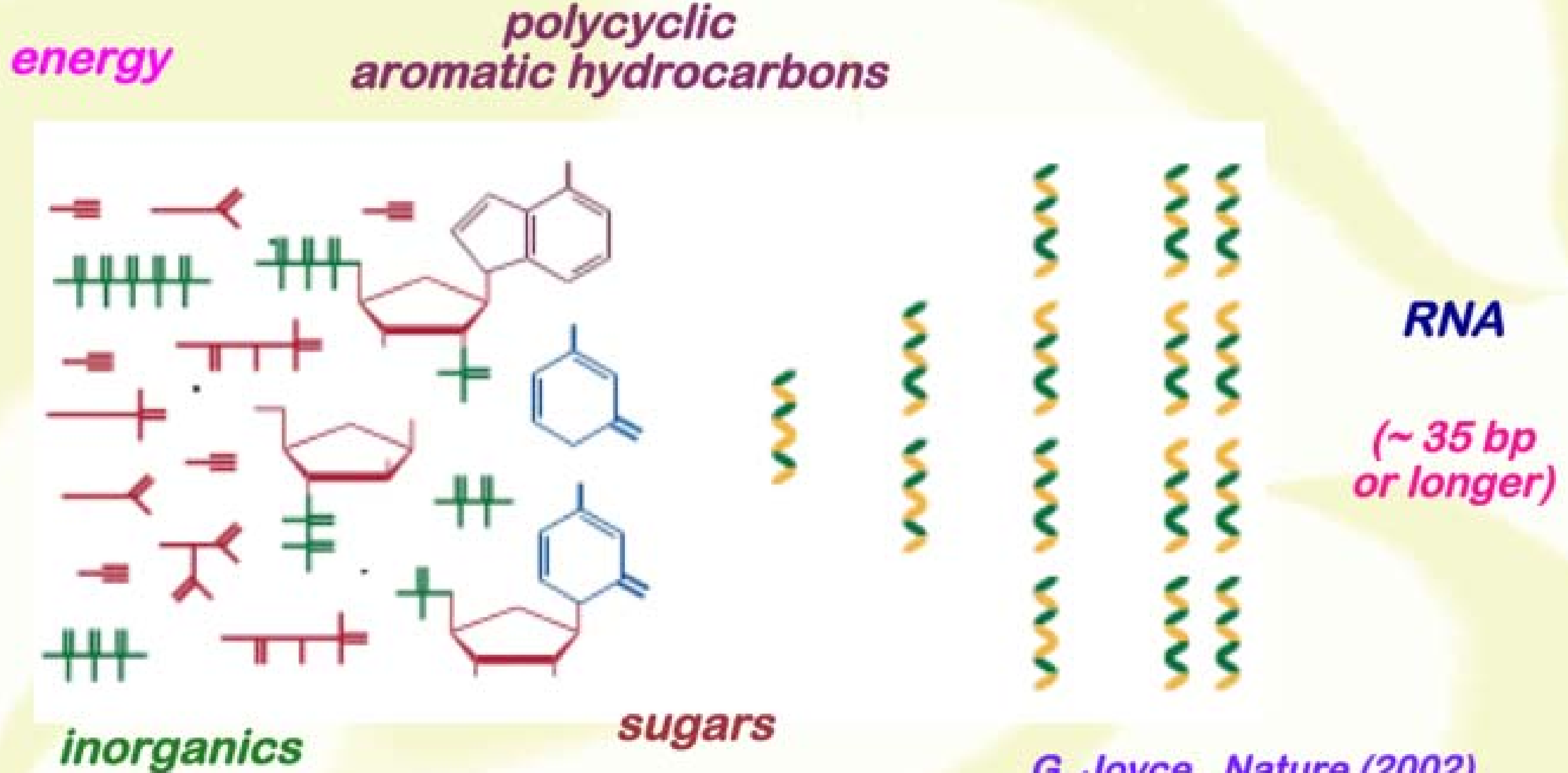
possible RNA precursors



templated replication of RNA

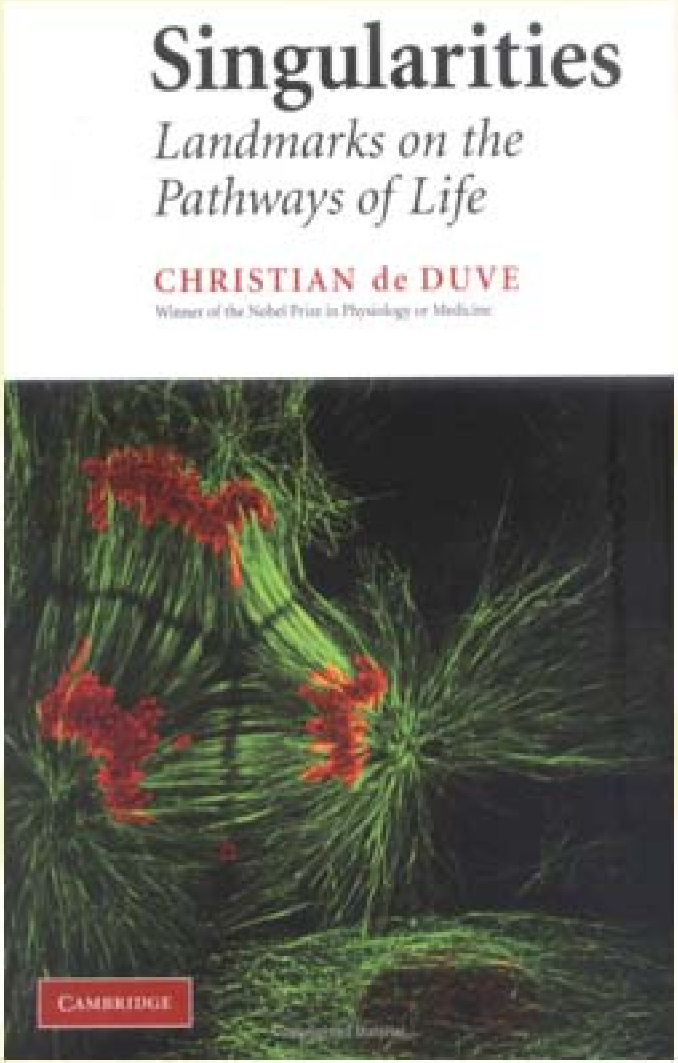


“cluttered path to RNA”



G. Joyce , Nature (2002)

selection and replication of RNA



"How RNA could possibly have emerged from the clutter without a "guiding hand" would baffle any chemist.

It seems possible only by selection, a process that presupposes replication"

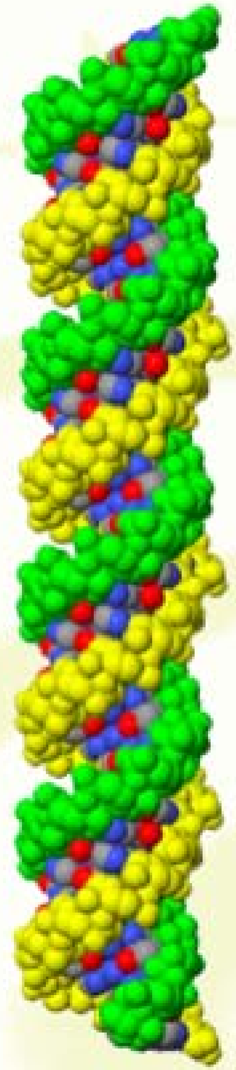
"The need seems inescapable for some autocatalytic process such that each lengthening step favors subsequent lengthening.

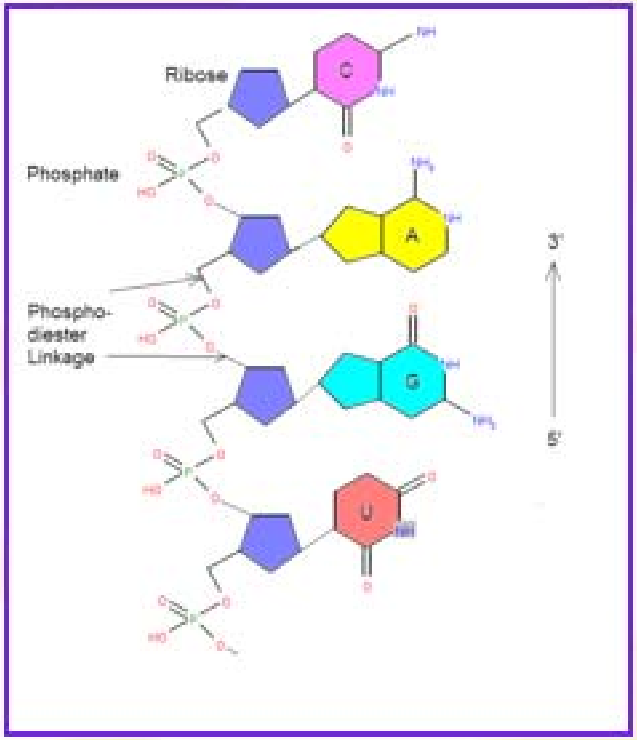
Only in this way could the enormous kinetic obstacle to chain elongation be surmounted."

RNA: what is the organizing principle?

"…any invoked catalytic mechanism must accom-modate the participation of a template, for there can have been no emergence of true RNA molecules without replication"

Christian de Duve





A-RNA

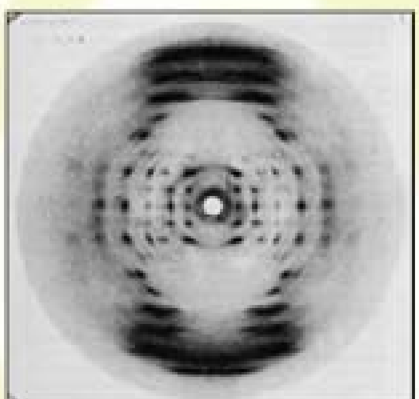
35mer

liquid crystals and DNA

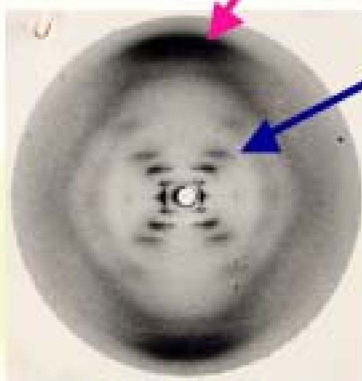
Crick, Watson

Wilkins

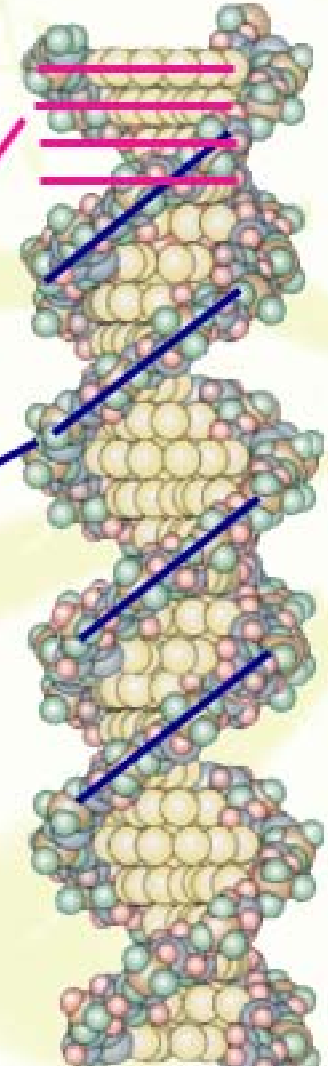
Franklin

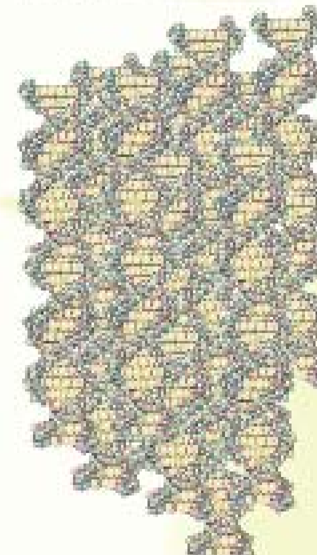


dehydrated



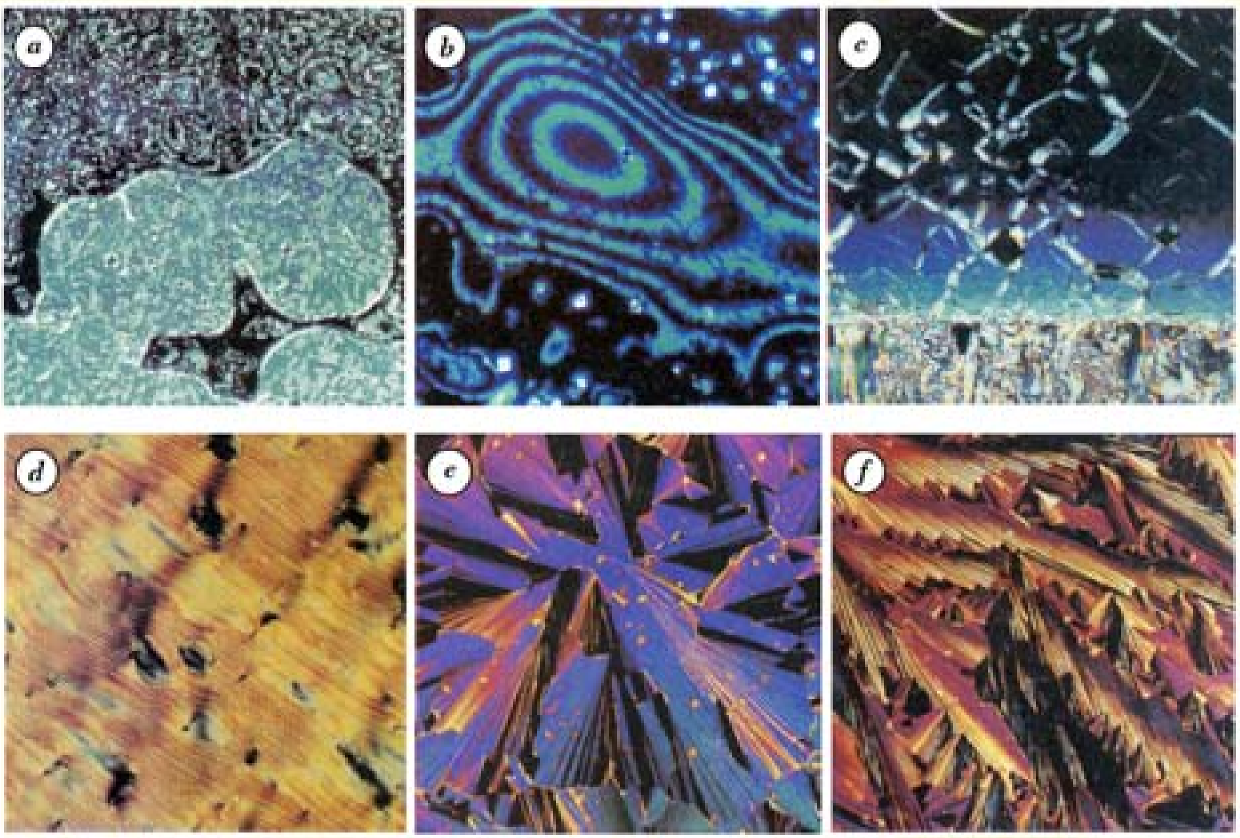
hydrated
(photo 51)



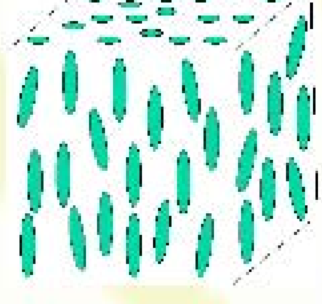


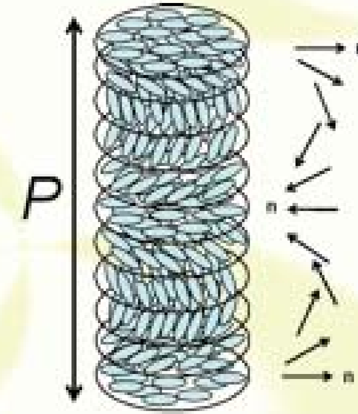
no interchain
correlations:
a DNA liquid
crystal!

DNA liquid crystals: chiral nematic phase (N = 146 bp)



Strzelecka, Davidson, Rill, Nature (1988)





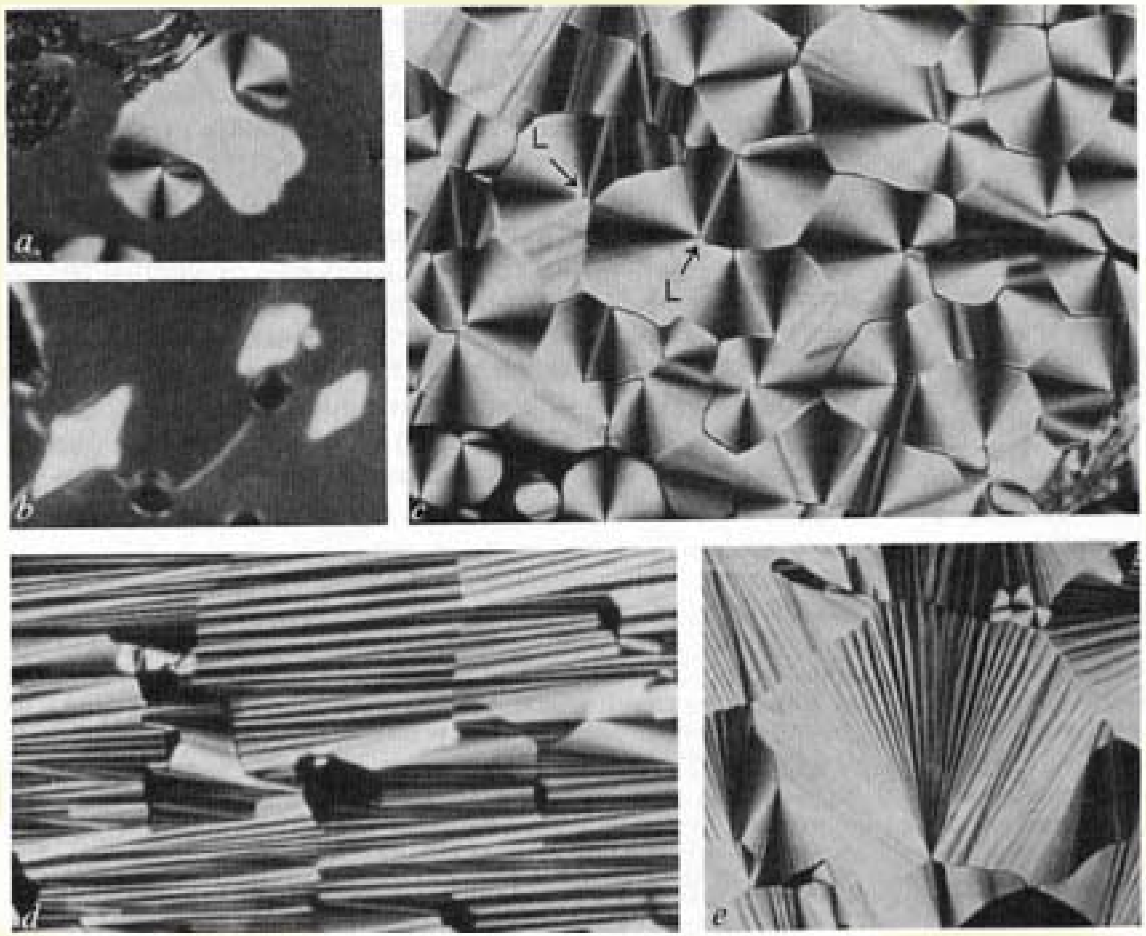
$L = 50$ nm ~ Λ_p

shape:

L/D ~ 25/1

DNA liquid crystals: columnar phase (N = 146 bp)

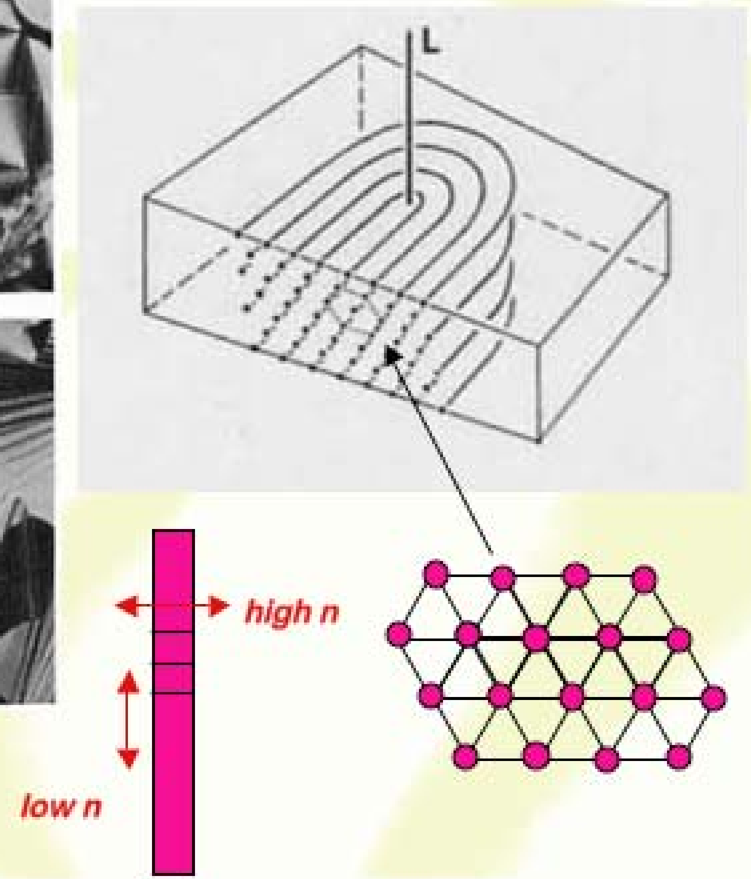
146 bp, L = 50 nm, L/D = 25:1



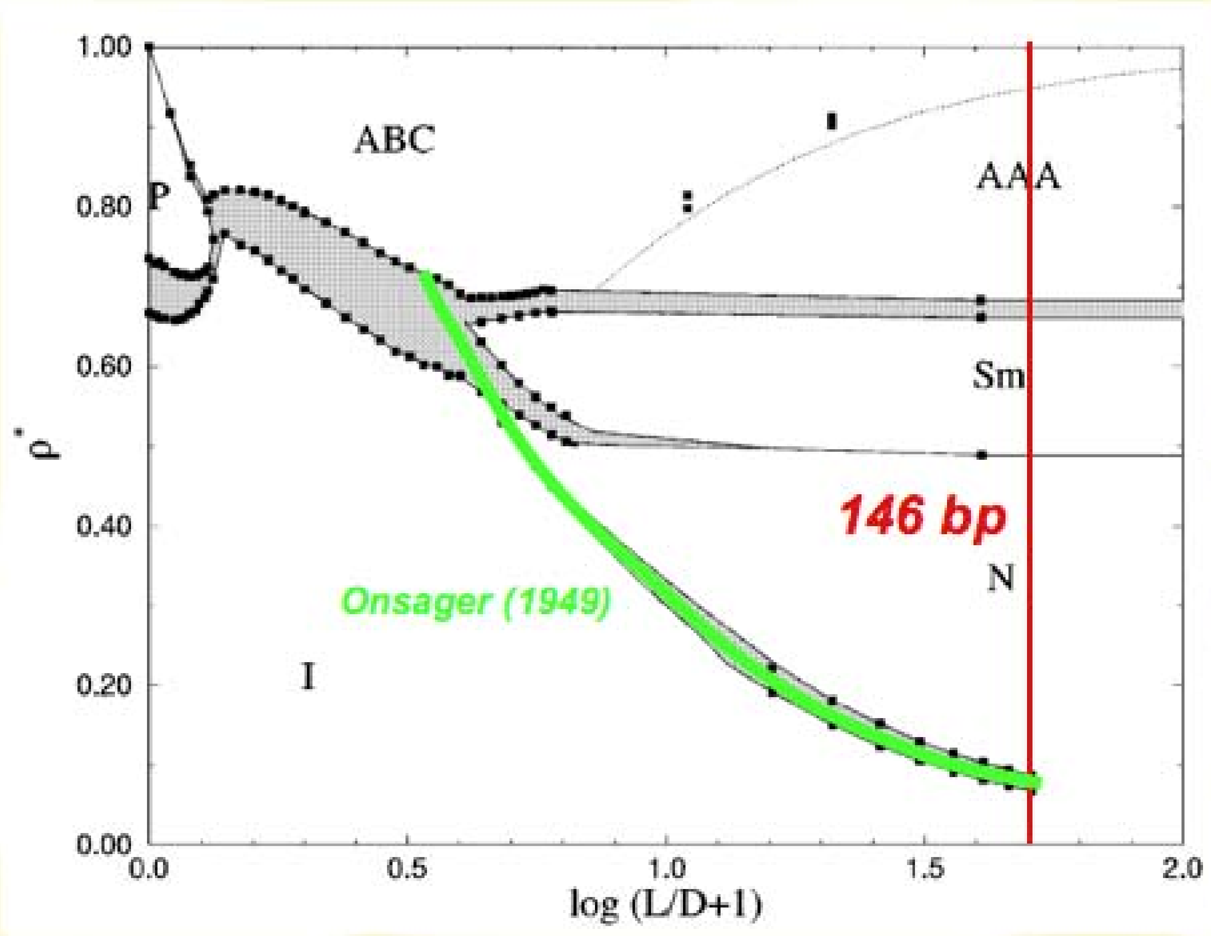
The highly concentrated liquid-crystalline phase of DNA is columnar hexagonal

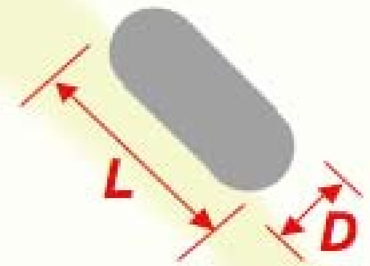
F. Livolant*, A. M. Levelut†, J. Doucet‡† & J. P. Benoit‡

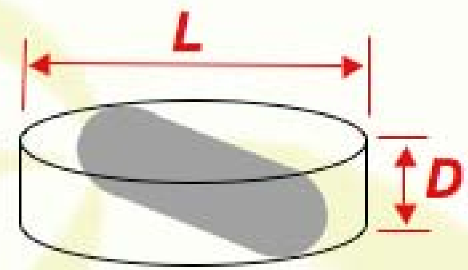
Nature (1989)

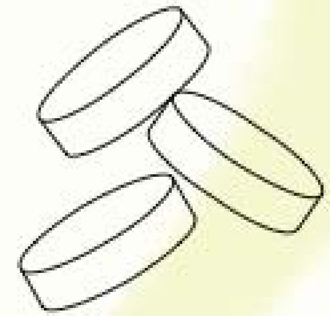


model: hard rods



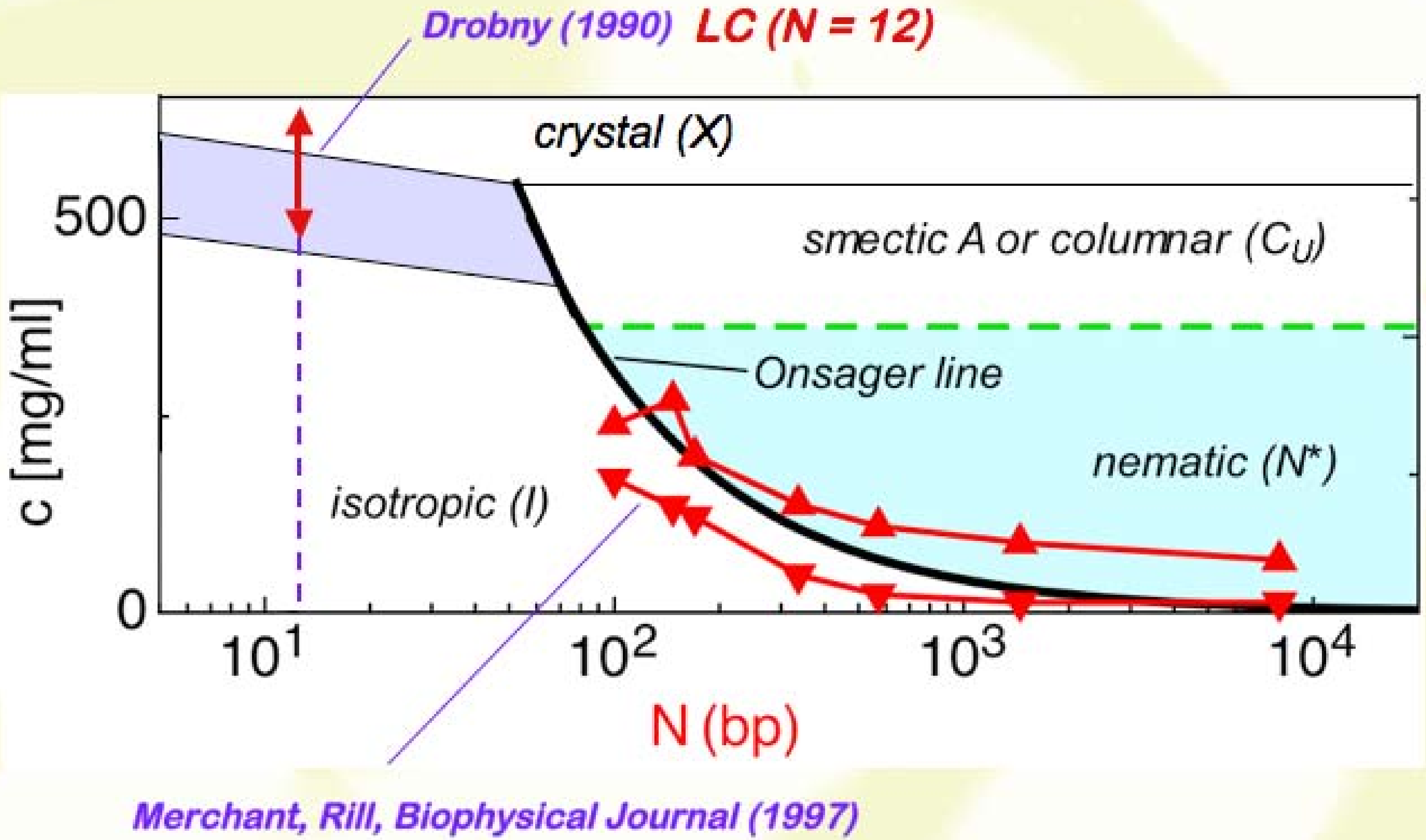






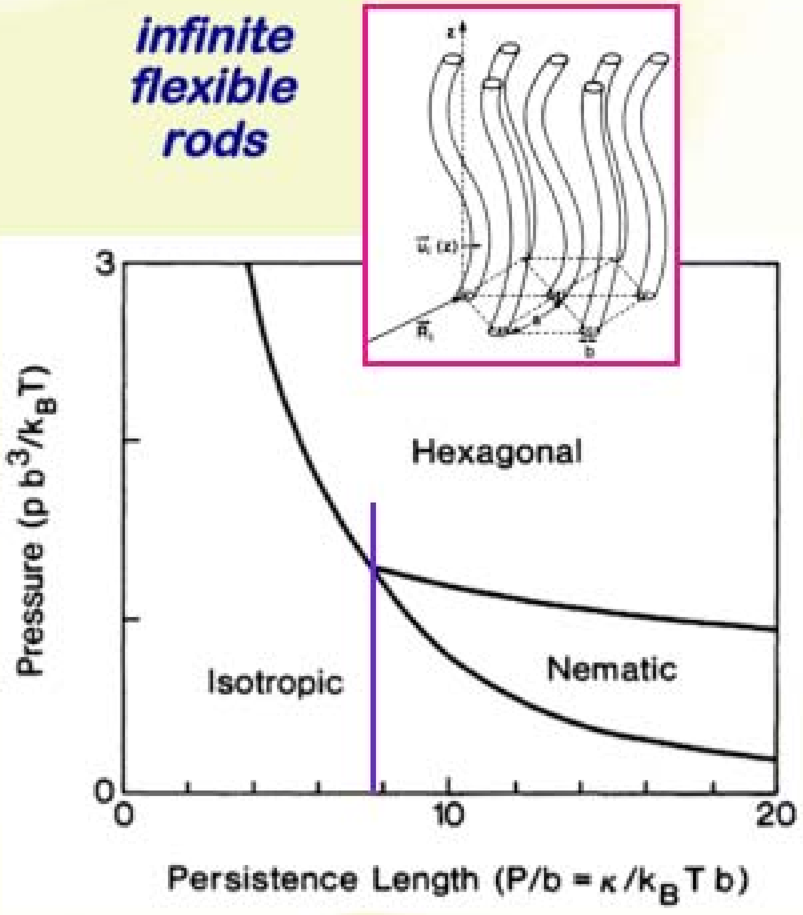
Bolhuis, Frenkel, JCP (1997)

DNA phase diagram



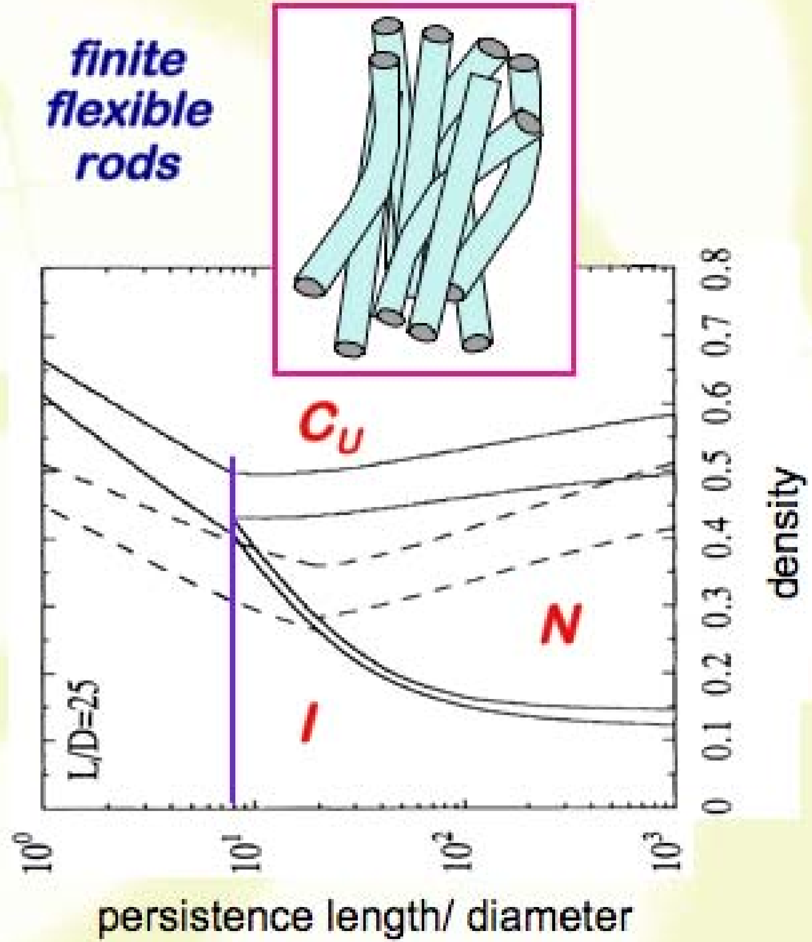
role of rigidity (rods too flexible - no nematic)

infinite flexible rods



Selinger, Bruinsma, PRA (1991)

finite flexible rods



Hentschke, Herzfeld, PRA (1991)

nematic order requires $P/D > 10$ or $P > 60$ bp

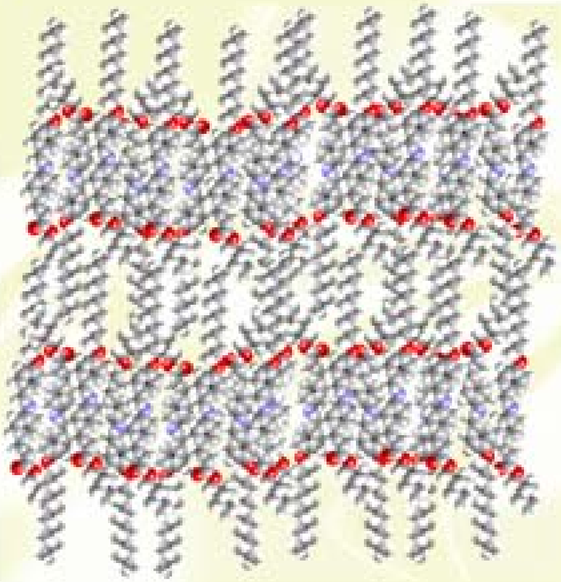
20th century wisdom

Because life's information carriers

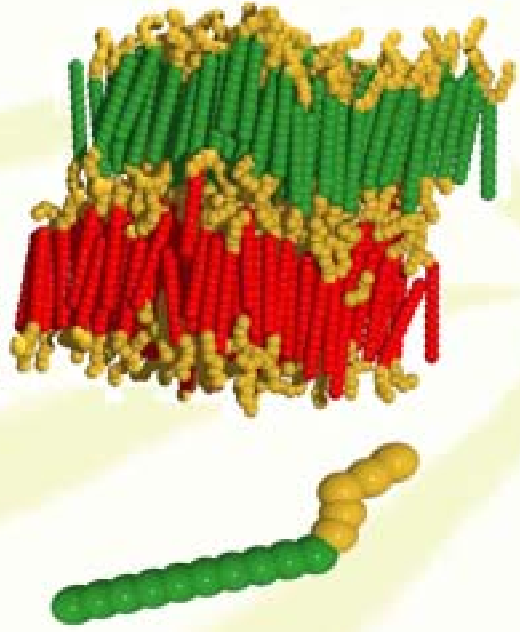
are linear semiflexible polymers

they form liquid crystal phases.

fluid smectic phases

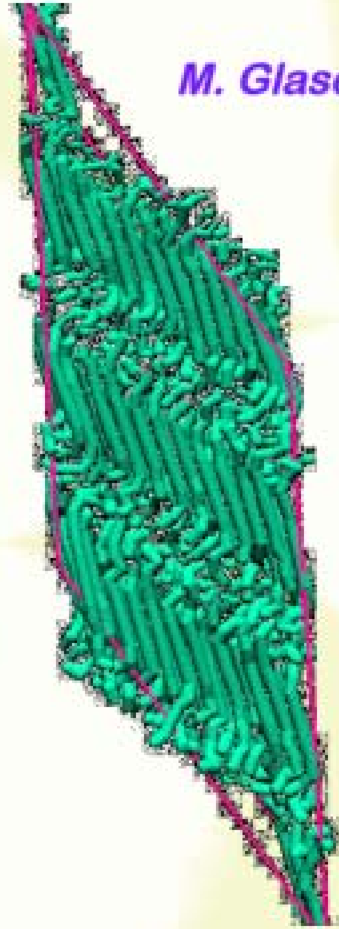


rigid cores
flexible tails



C. McBride JCP (2002)

M. Glaser

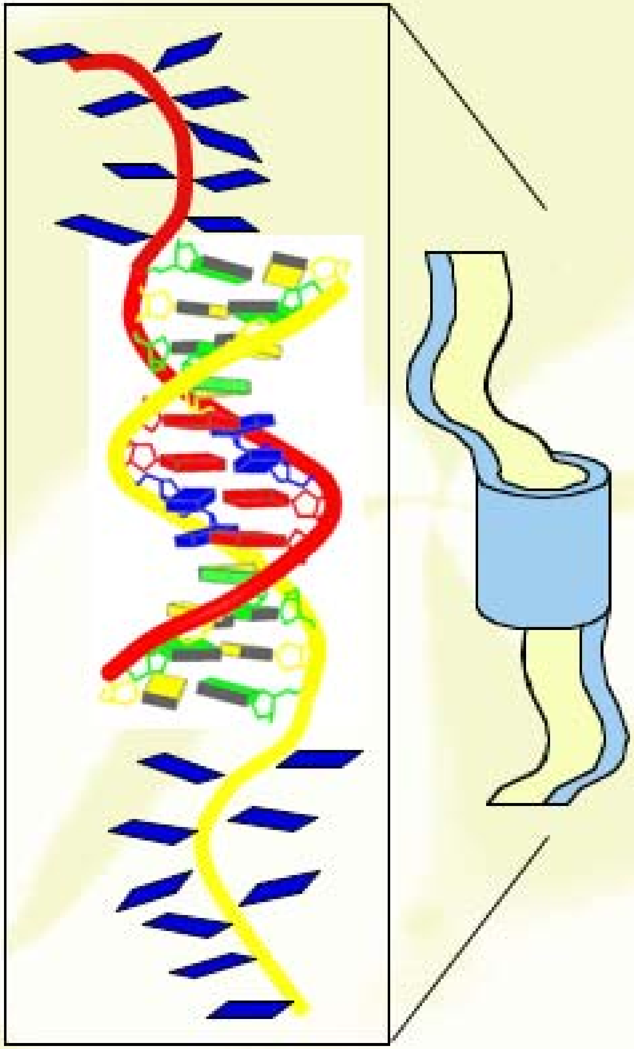


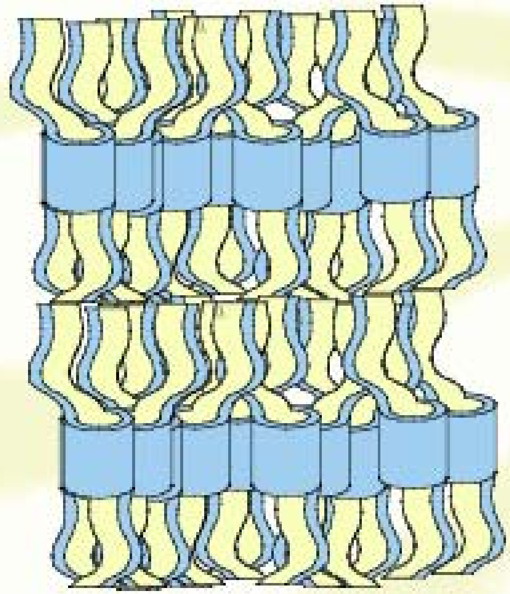
first tries

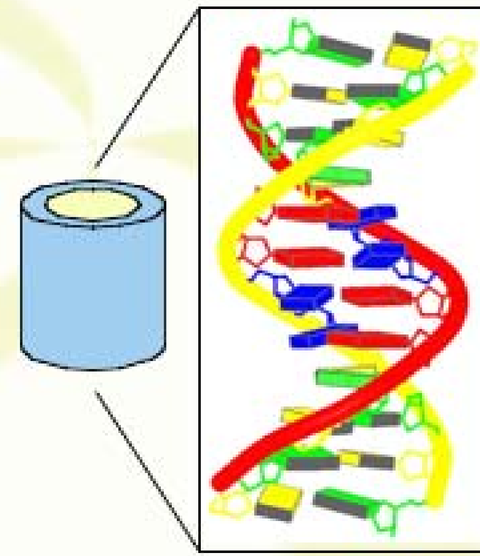
10bp: 5'-CGCAATTGCG-3'

12bp: 5'-CGCGAATTCGCG-3'

"Drew-Dickerson dodecamer"



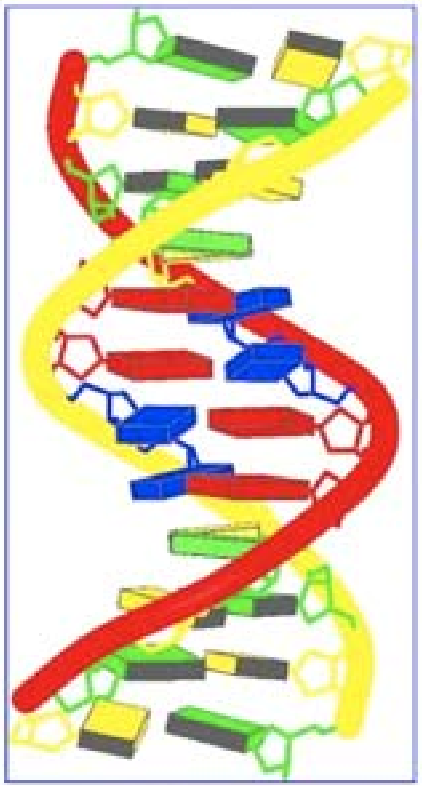




12bp10T: 5'-CGCGAATTCGCGTTTTTTTTTTT-3'

Drew-Dickerson dodecamer (DDd)

12bp > 5'-CGCGAATTCGCG-3'



$T_{melting}$ ~ 55ºC

Crystal structure analysis of a complete turn of B-DNA

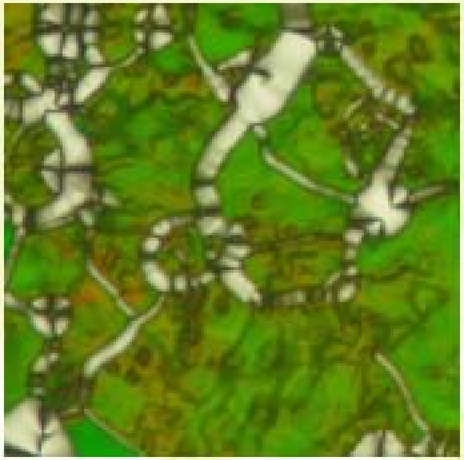
Richard Wing*, Horace Drew, Tsunehiro Takano, Chris Broka, Shoji Tanaka, Keiichi Itakura† & Richard E. Dickerson

Nature 1980

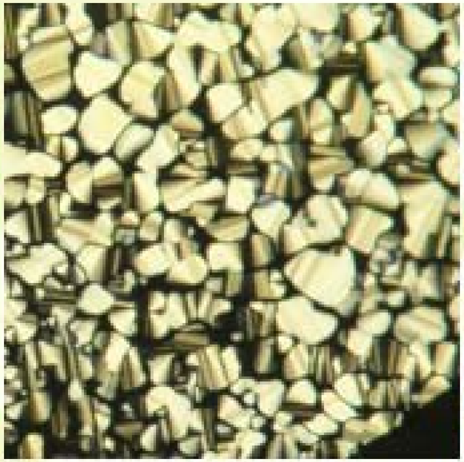
(~750 papers on this molecule)

nanoDNA liquid crystal textures (N=10)

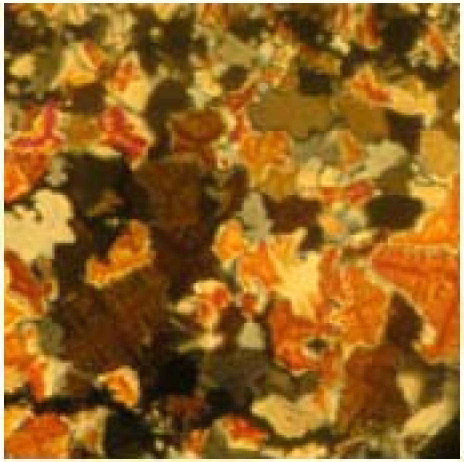
10bp: 5'-CGCAATTGCG-3' (~34.0A)



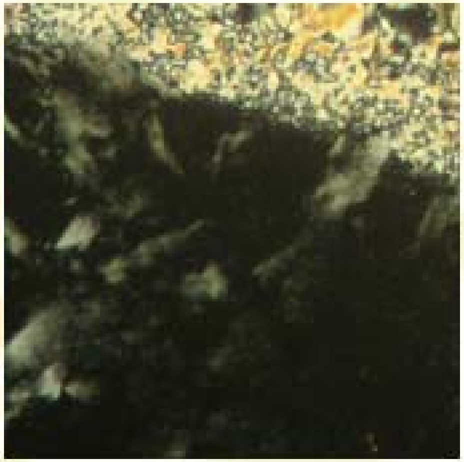
oily-streak texture (N*)



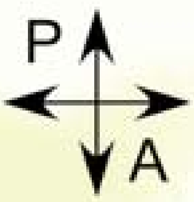
developable domain texture (C_U)



mosaic texture (C_2)



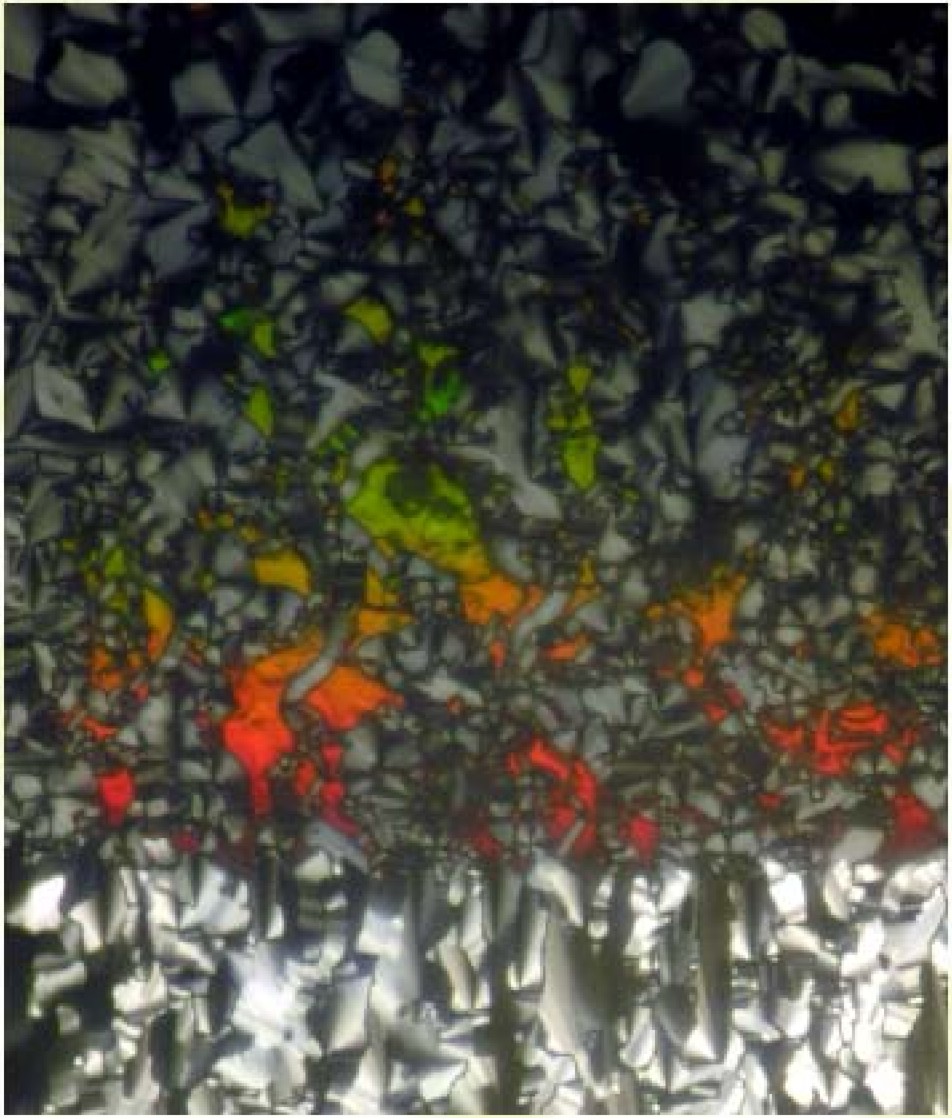
high density (crystal?, glass?)



incresing density

gradient cells

10bp: 5'-CGCAATTGCG-3' (~34.0A)

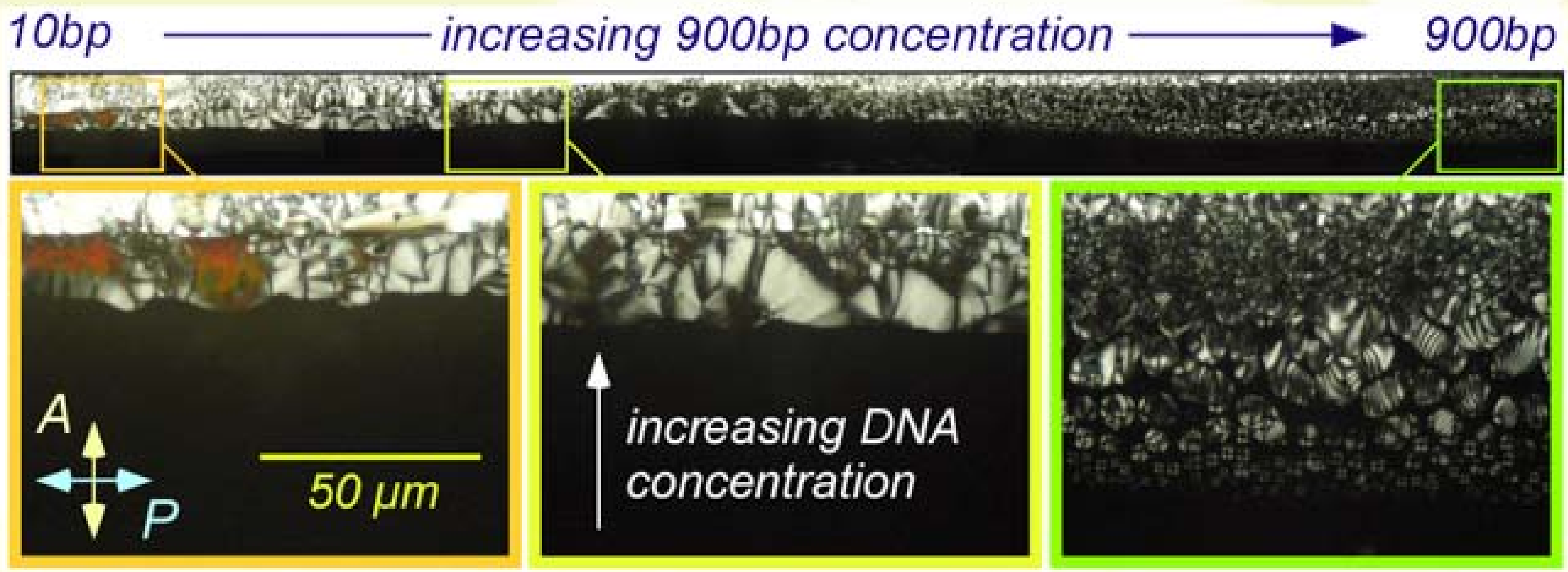


increasing concentration

N^*

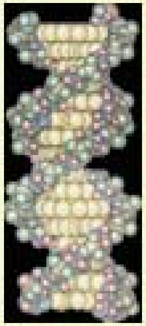
C_U

contact (dual gradient) cell

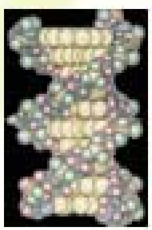


liquid crystals of nanoDNA

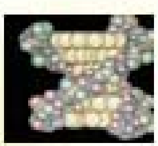
16 bp

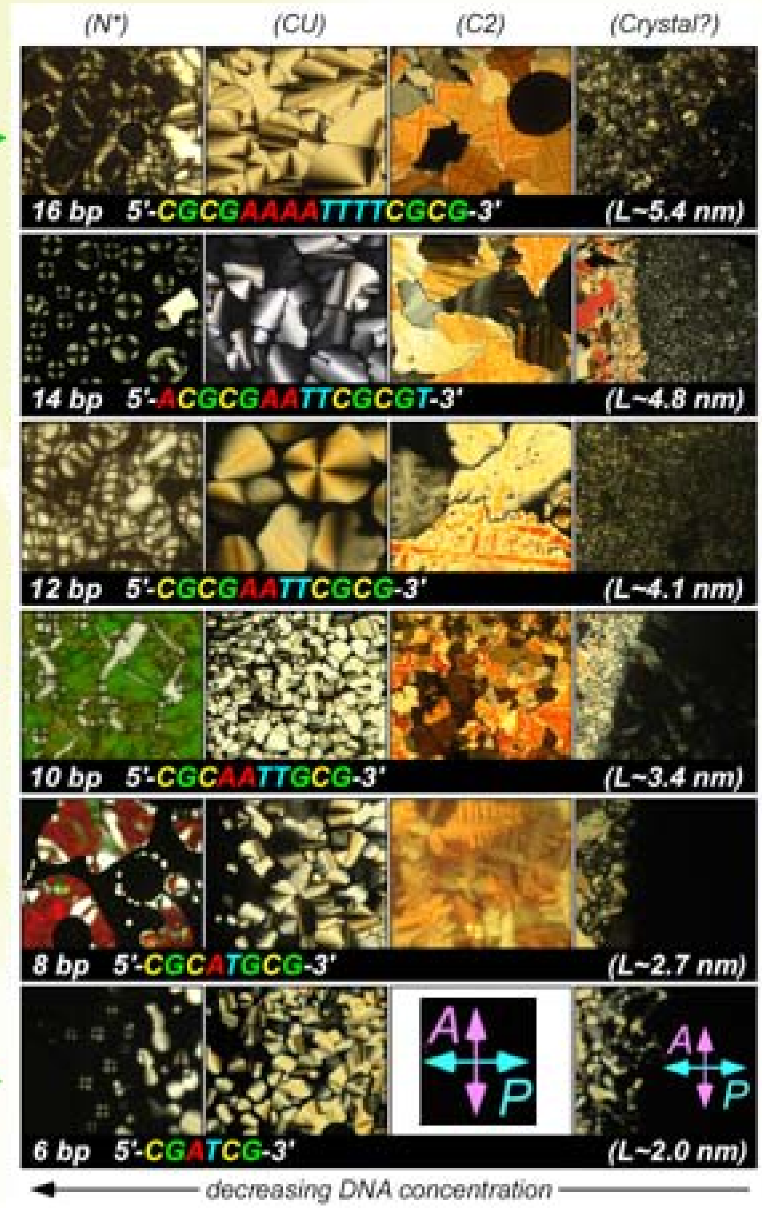


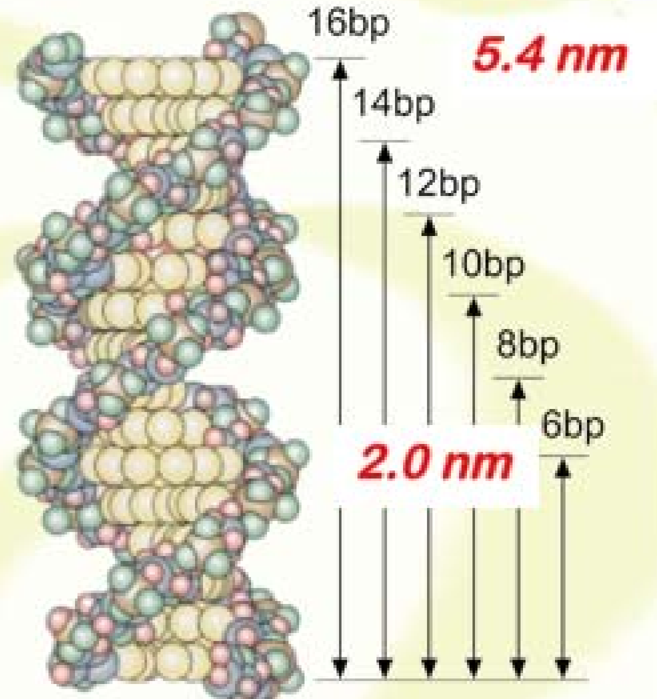
10 bp



6 bp



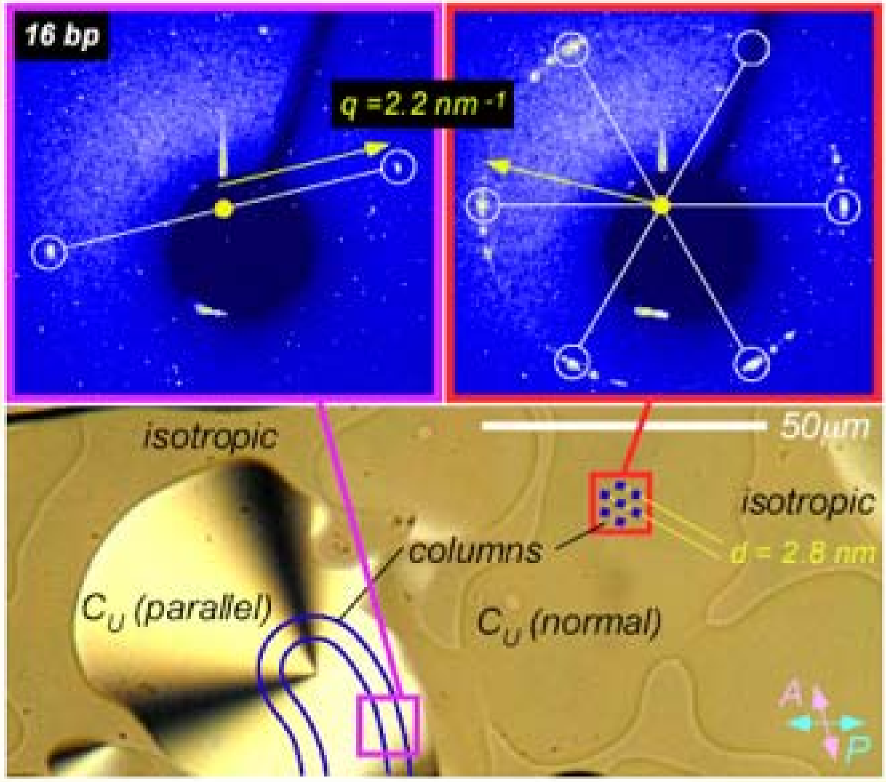


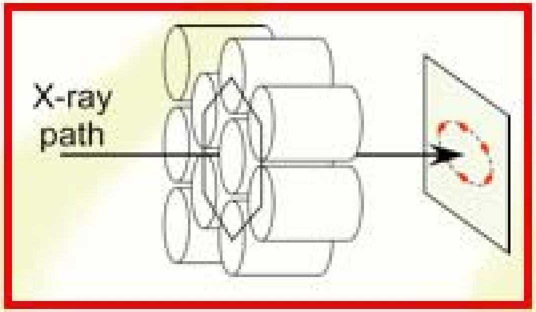


structure of the C_U phase

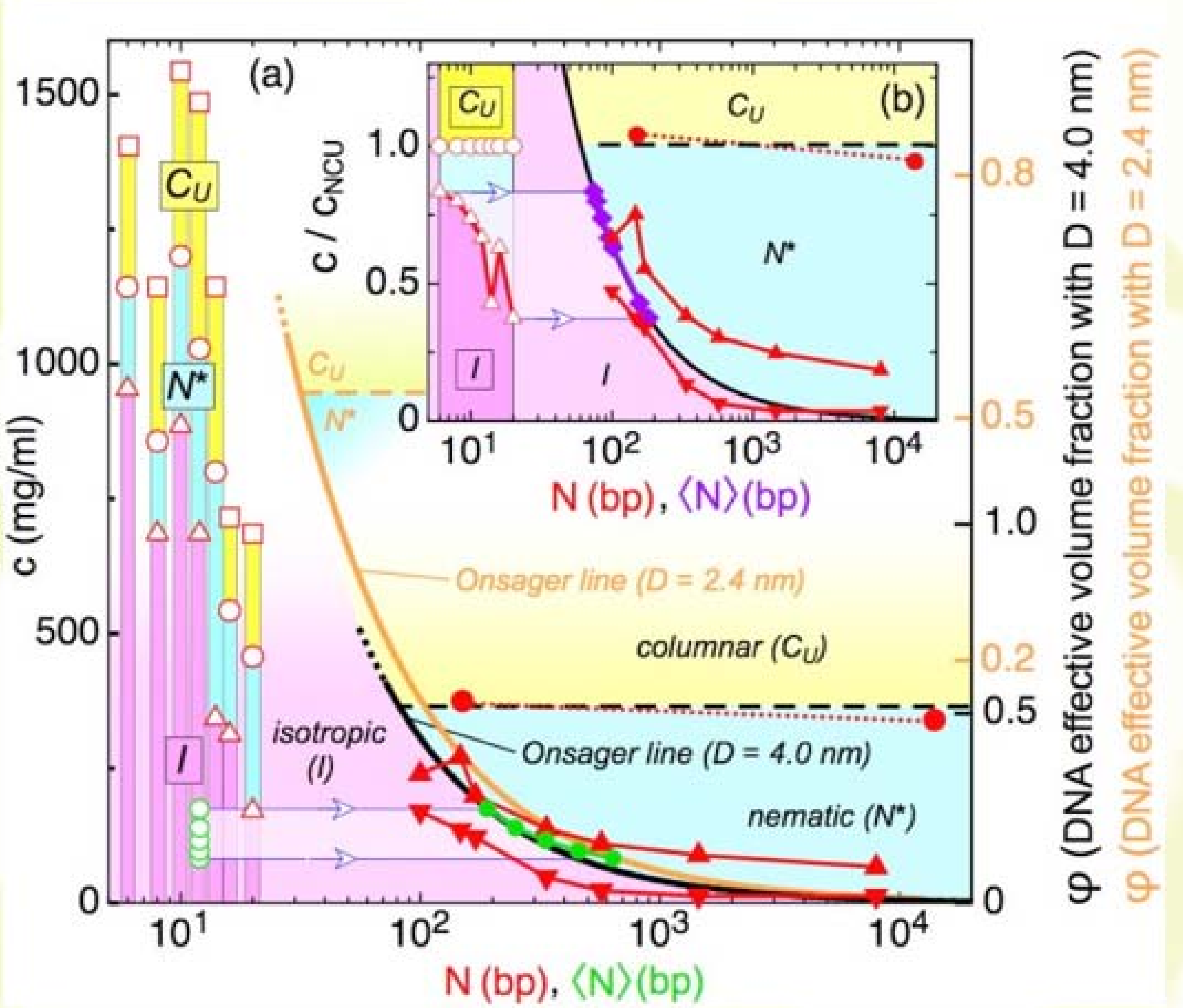
x-ray microbeam diffraction patterns in the C_U phase of 16bp (APS)

(Ron Pindak, Brandon Chapman, Julie Cross, Chris Jones)

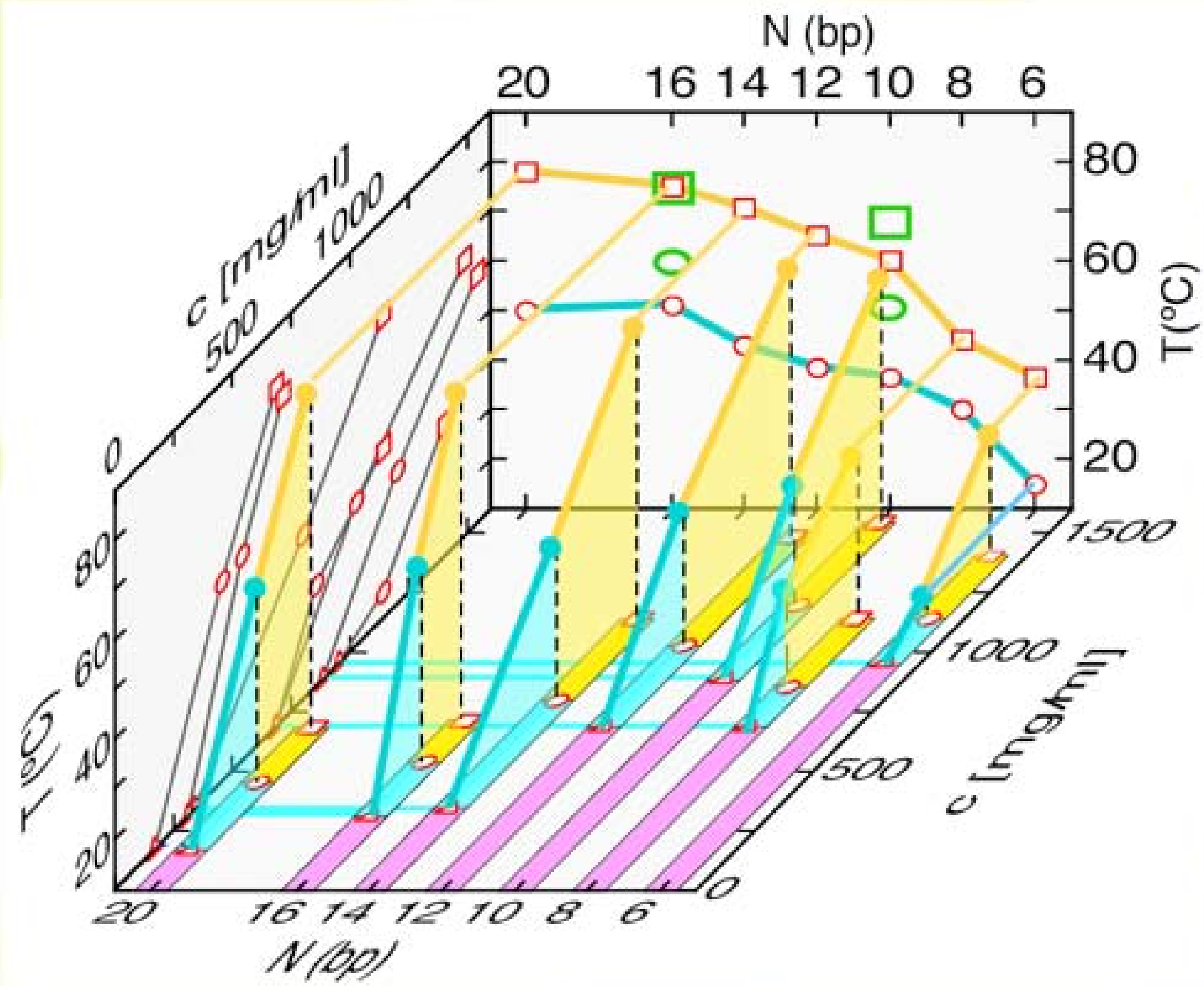




nanoDNA (c-N) phase diagram @ T = 25ºC



nanoDNA (c-N-T) phase diagram



effect of DNA oligomer termination

12bp

OH-CGCGAAAATTTTCGCG-OH

OH-CGCGAAAATTTTCGCG-PO_4

} ***N*, CU, C2 LC phases***

PO_4-CGCGAAAATTTTCGCG-PO_4 ***No LC phases***

12bp-T, 12bp-TT

3'-TTCGCGAAAATTTTCGCG-5'
3'-TTCGCGAAAATTTTCGCG-5'

C1 and C2 phase

No nematic phase

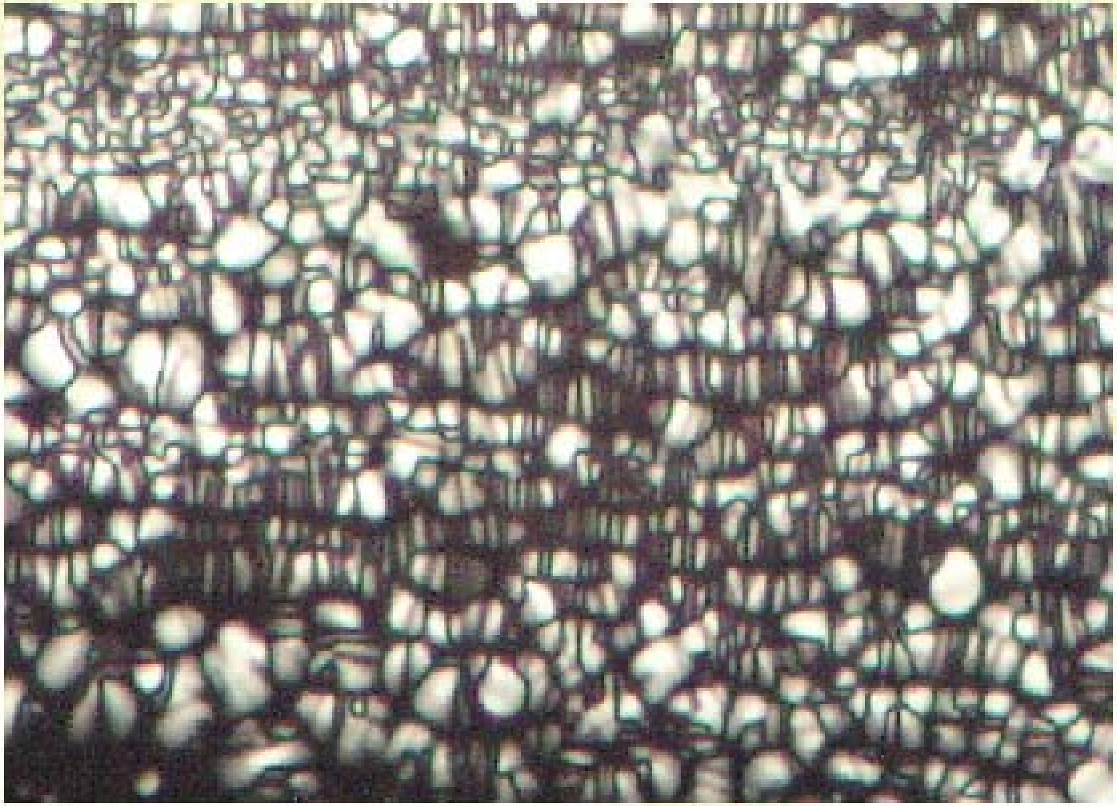
10bp-TTTTTTTTTT

3'-TTTTTTTTTTCGCGAAAATTTTCGCG-5'
3'-TTTTTTTTTTCGCGAAAATTTTCGCG-5'

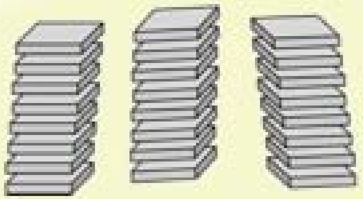
No LC phases

- ***termination matters***
- ***tails destabilize LC phases!!***

18bp and 2 x 9bp - columnar phase

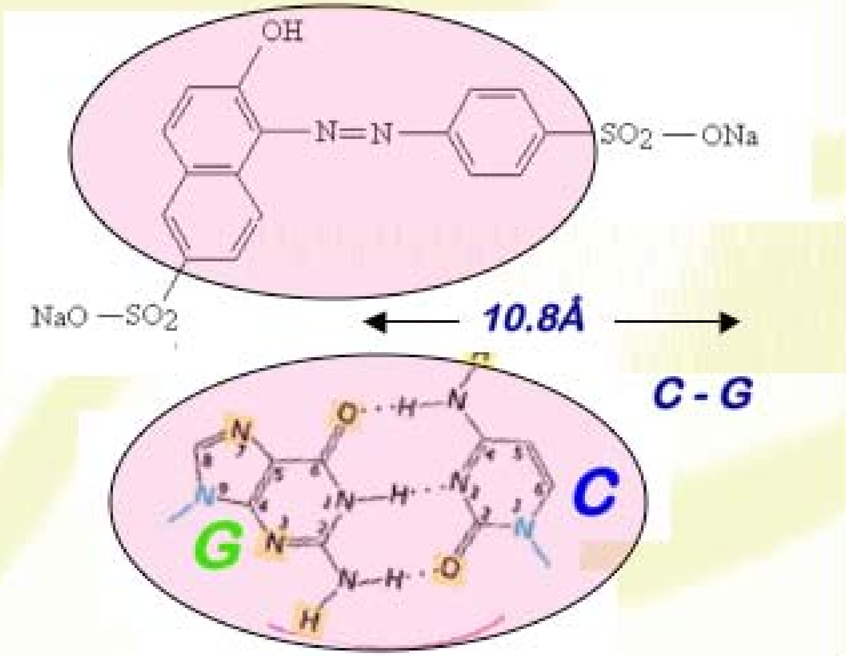


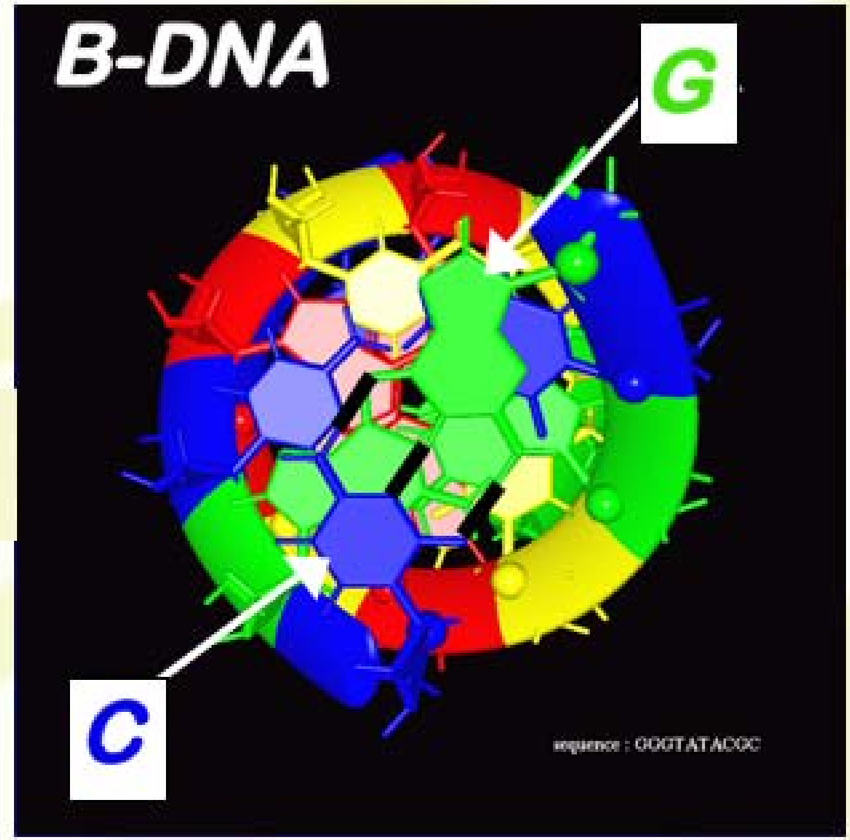
the end of DNA

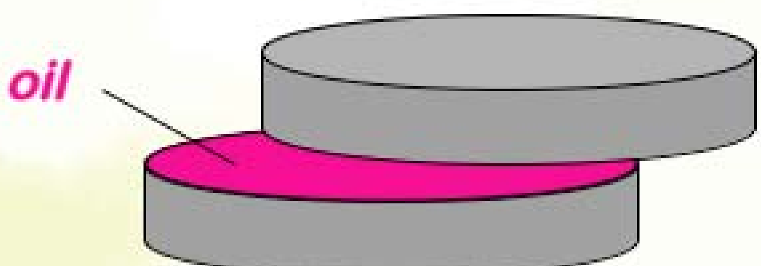


sunset yellow

(chromonic LC)

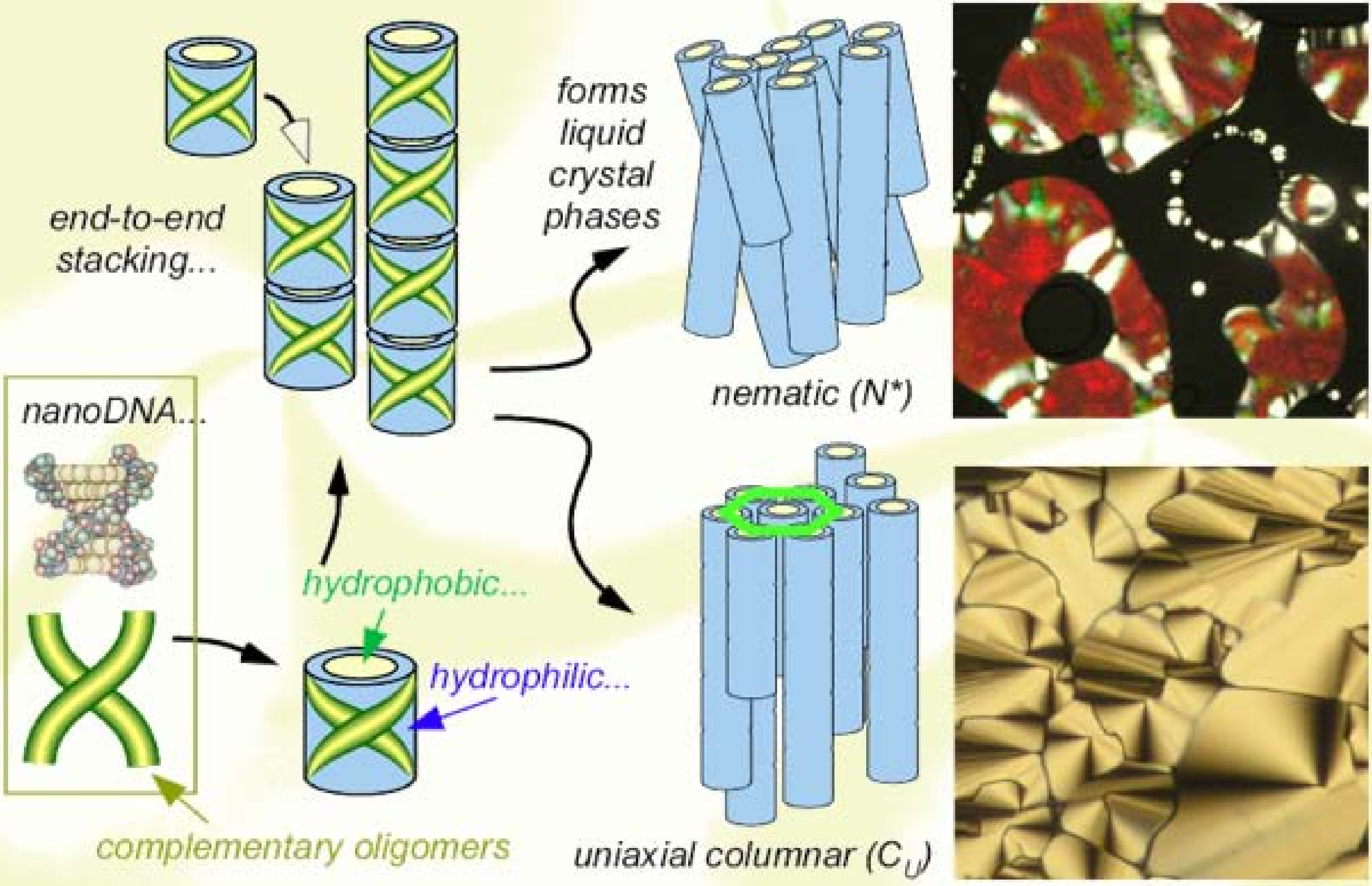






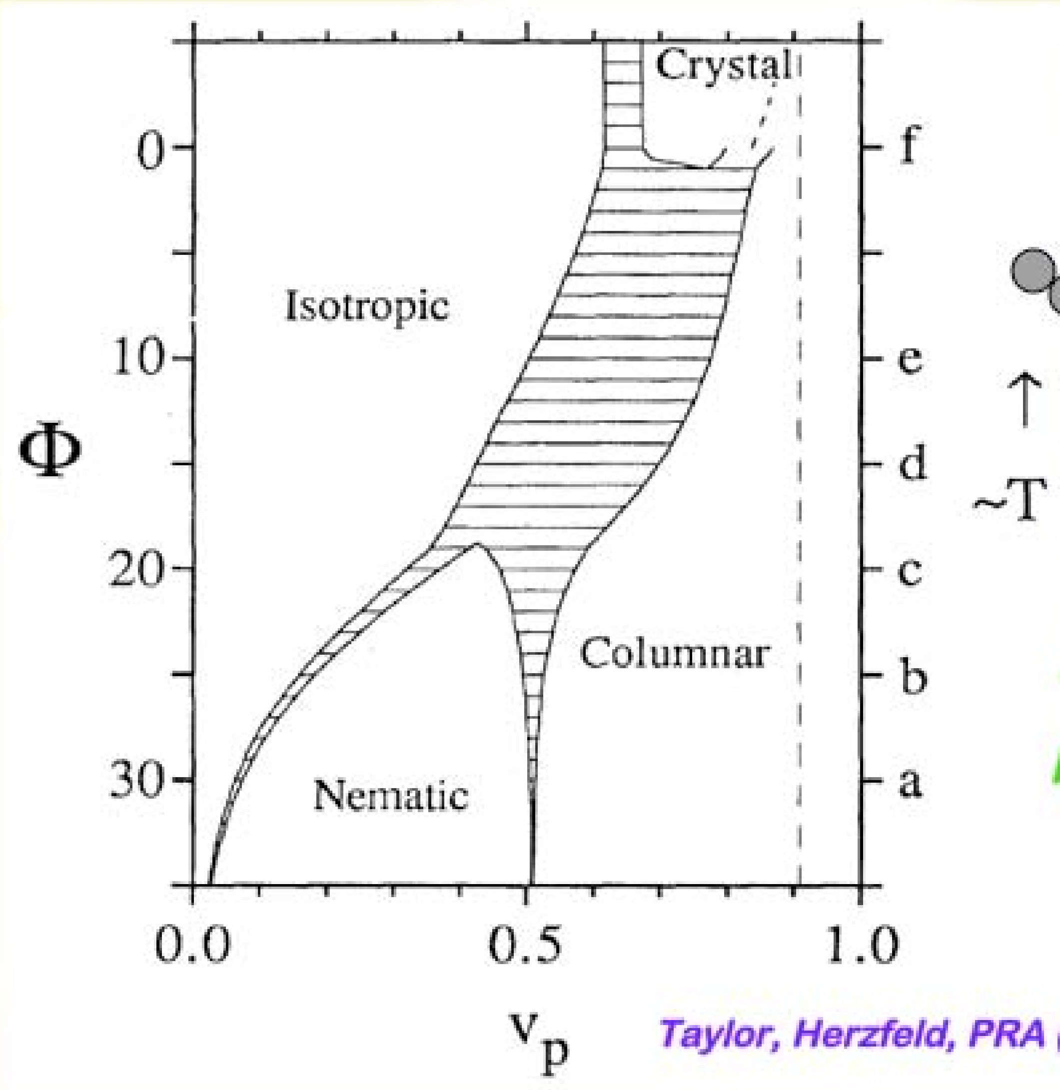
$\varepsilon \sim 2kT\,/\,10\text{Å}^2$

end-to-end adhesion

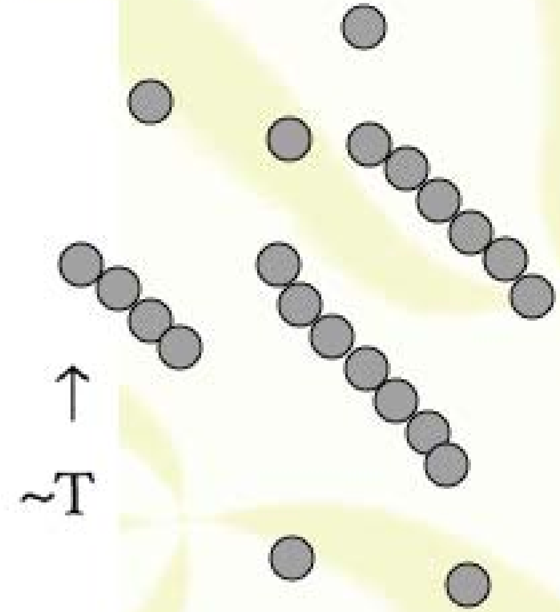


sticky ends → nematic & columnar phases

ε / kT

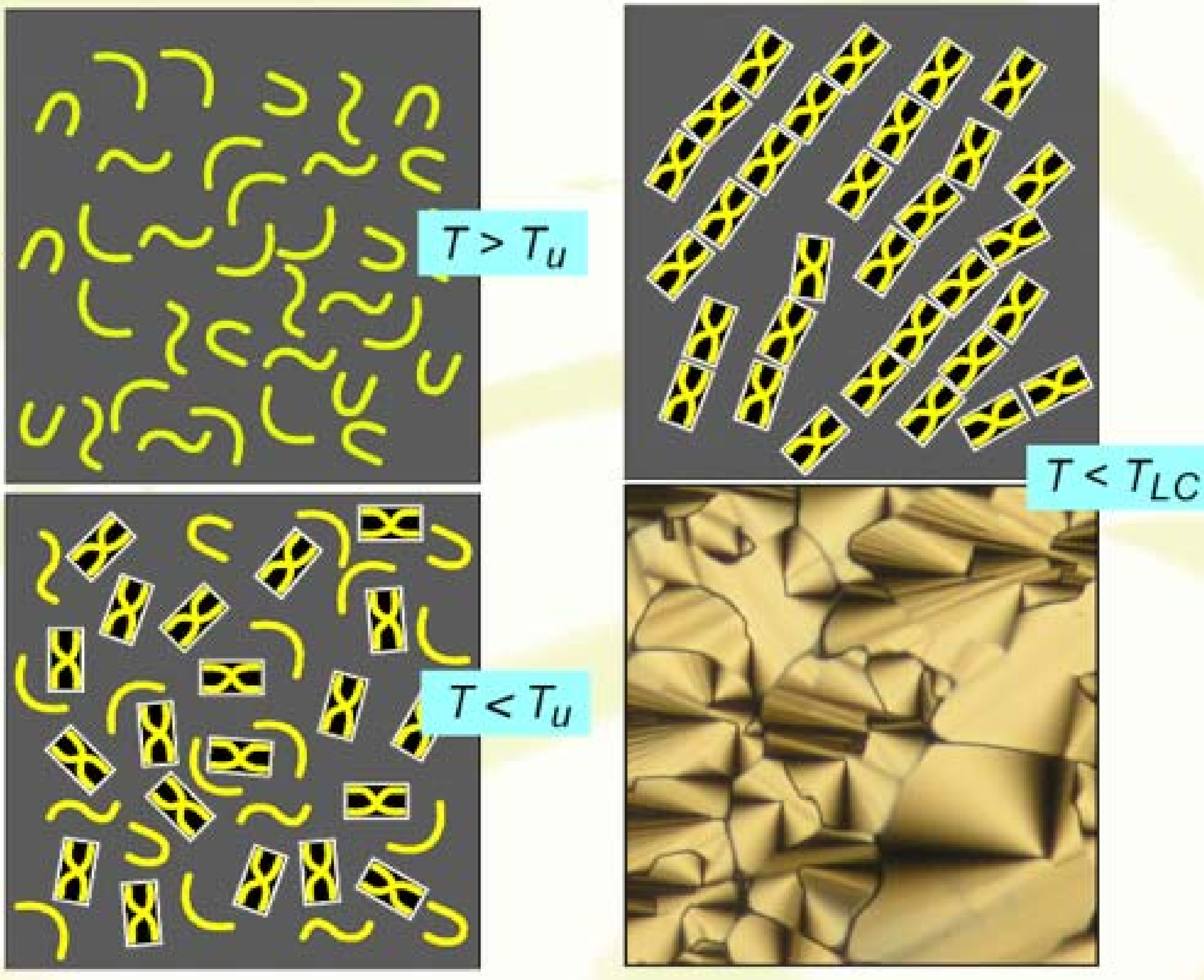


Taylor, Herzfeld, PRA (1990)

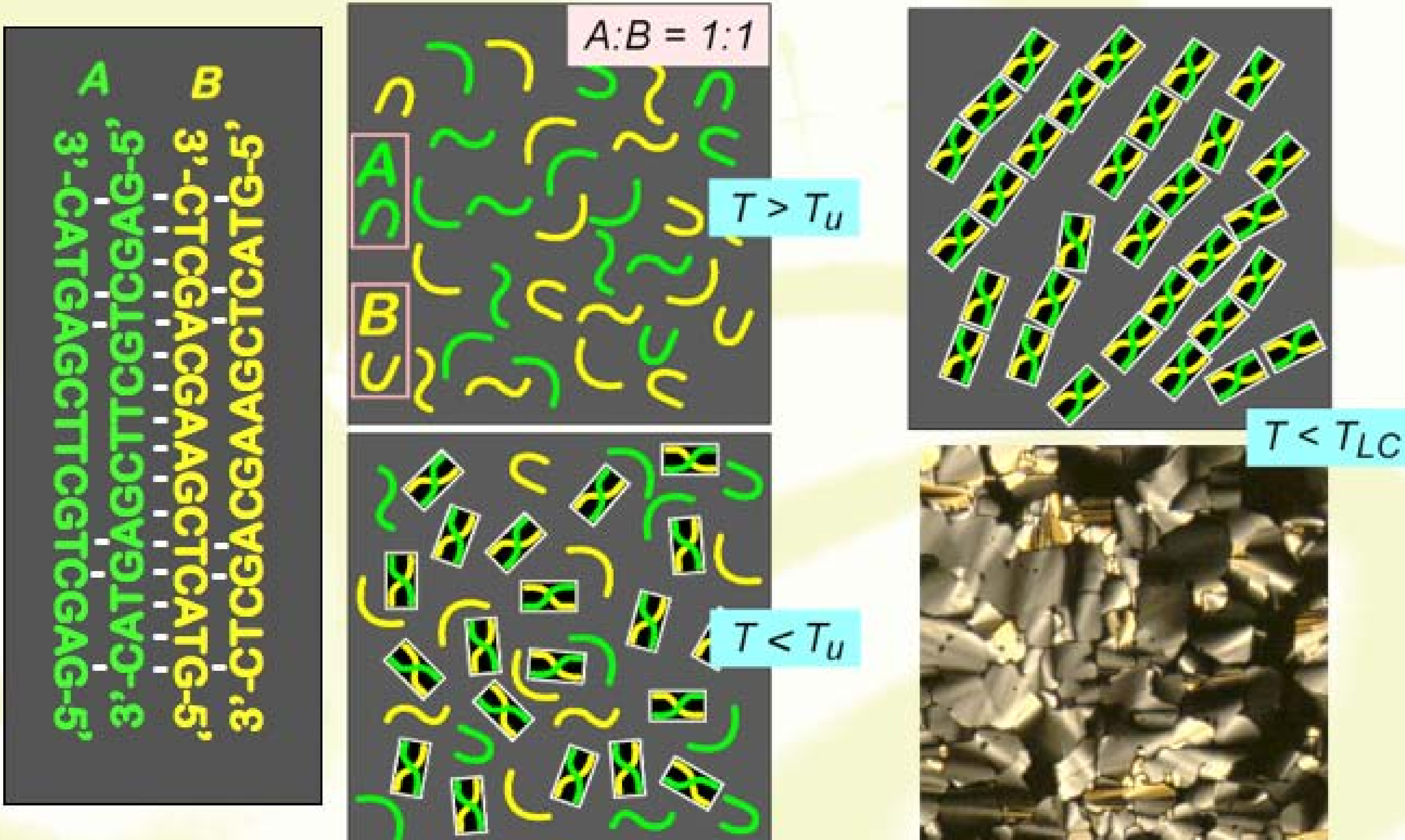


"living polymerization"

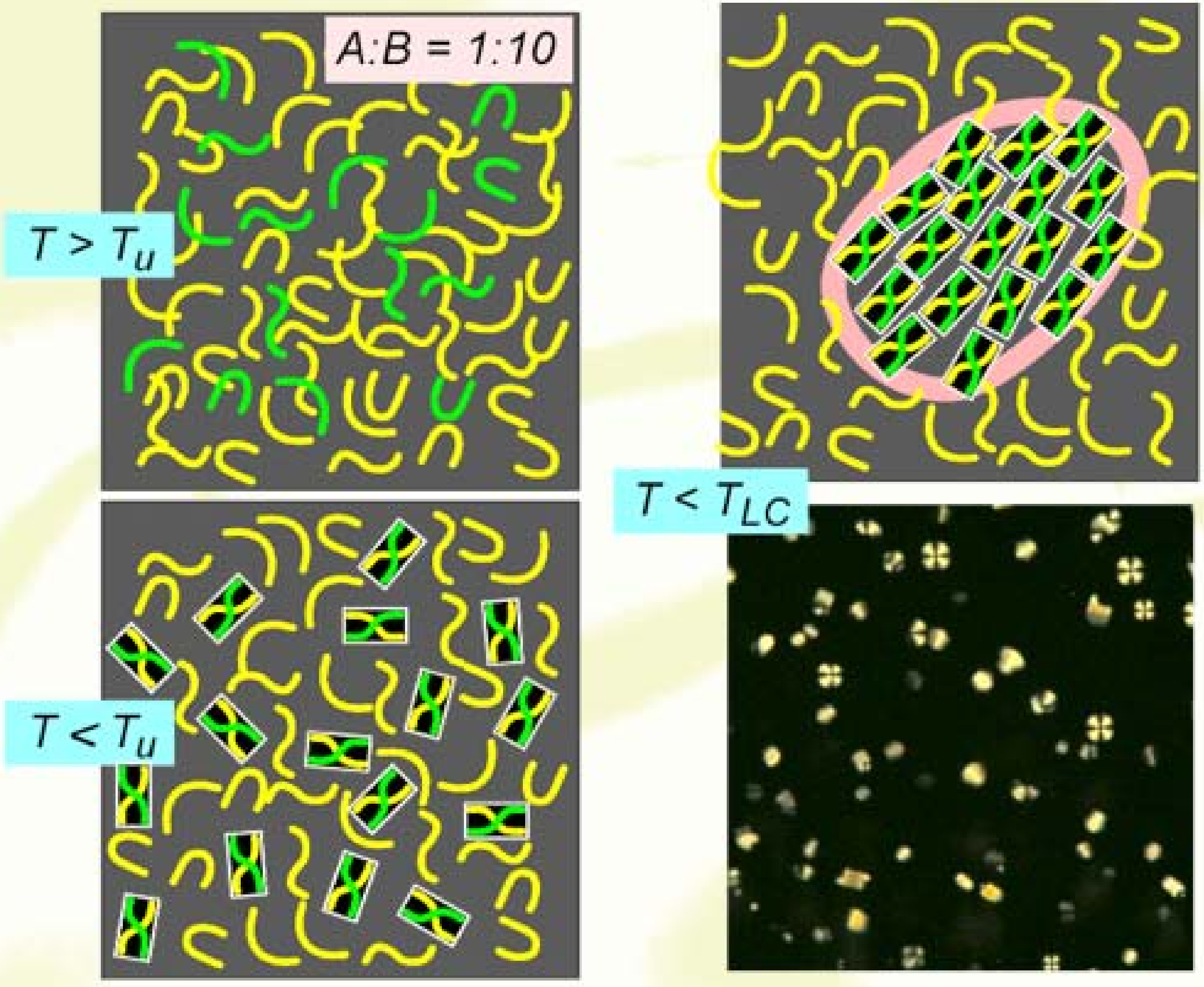
self-complementary pairs



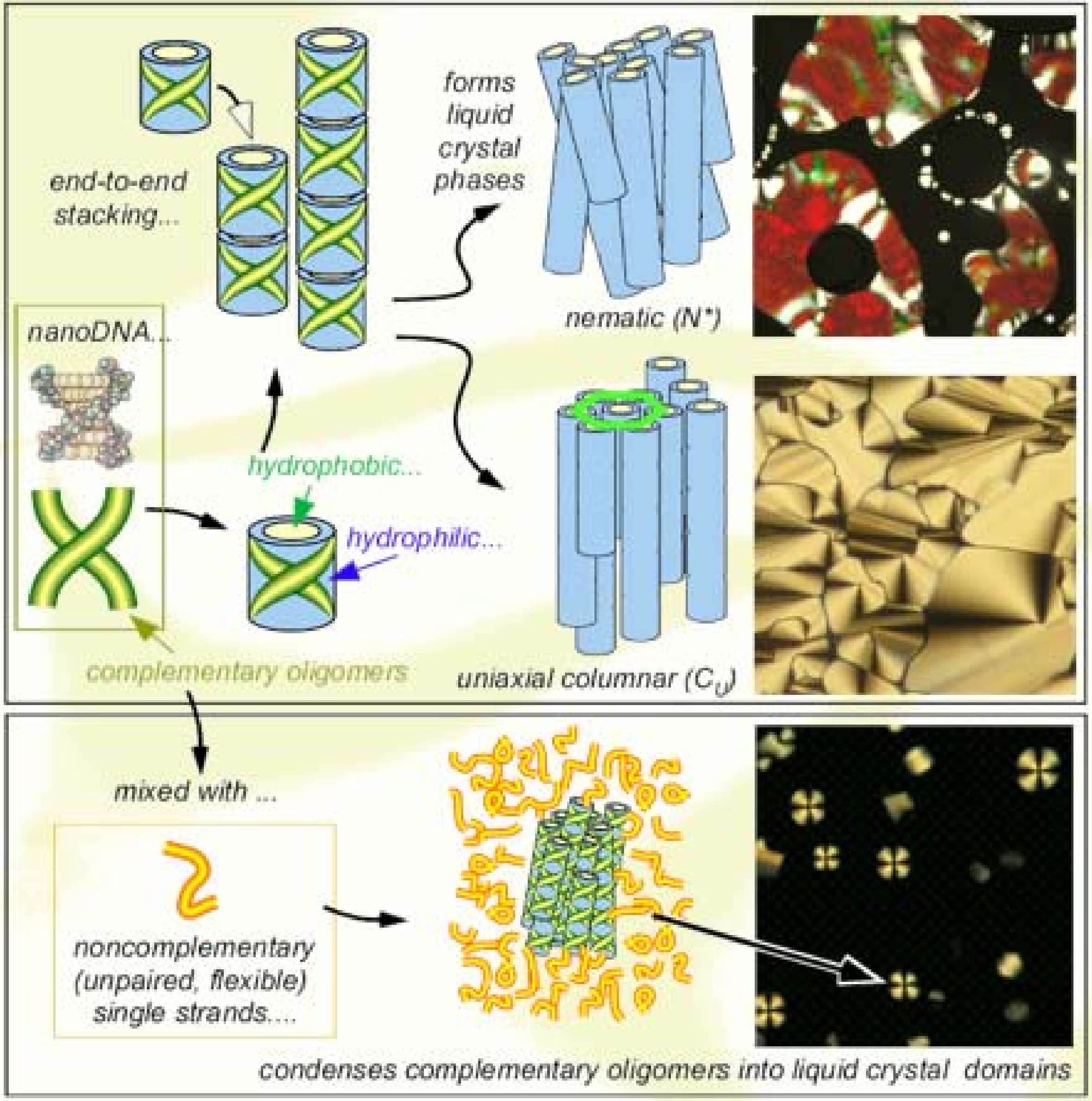
equimolar complementary pairs



liquid crystal condensation of complementary strands

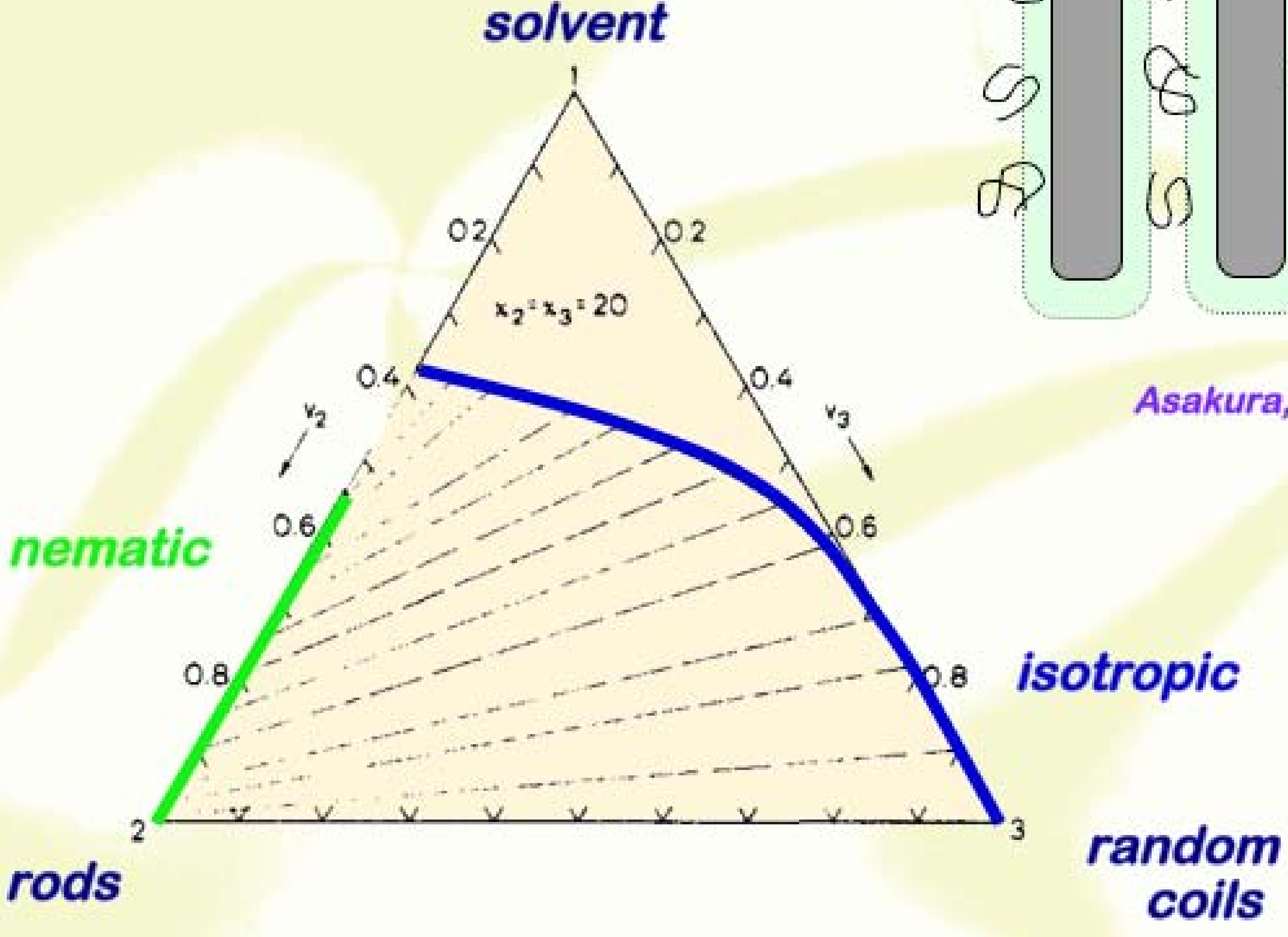


flexible and rigid won't mix

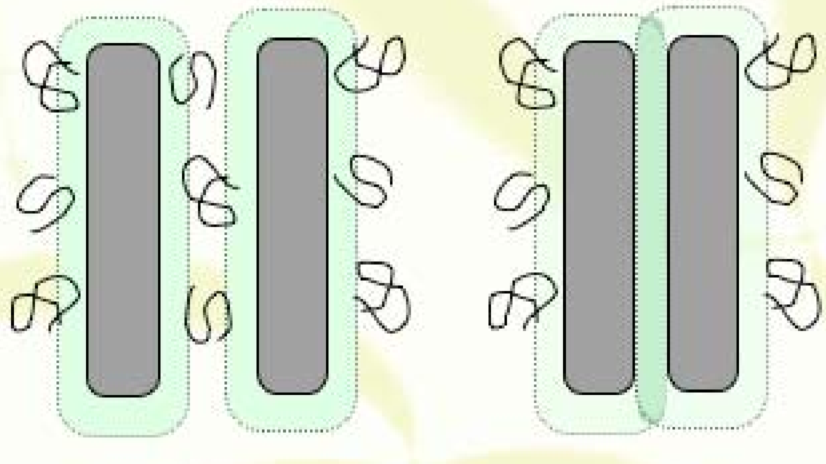


condensation mechanisms

Flory, Macromolecules (1978)

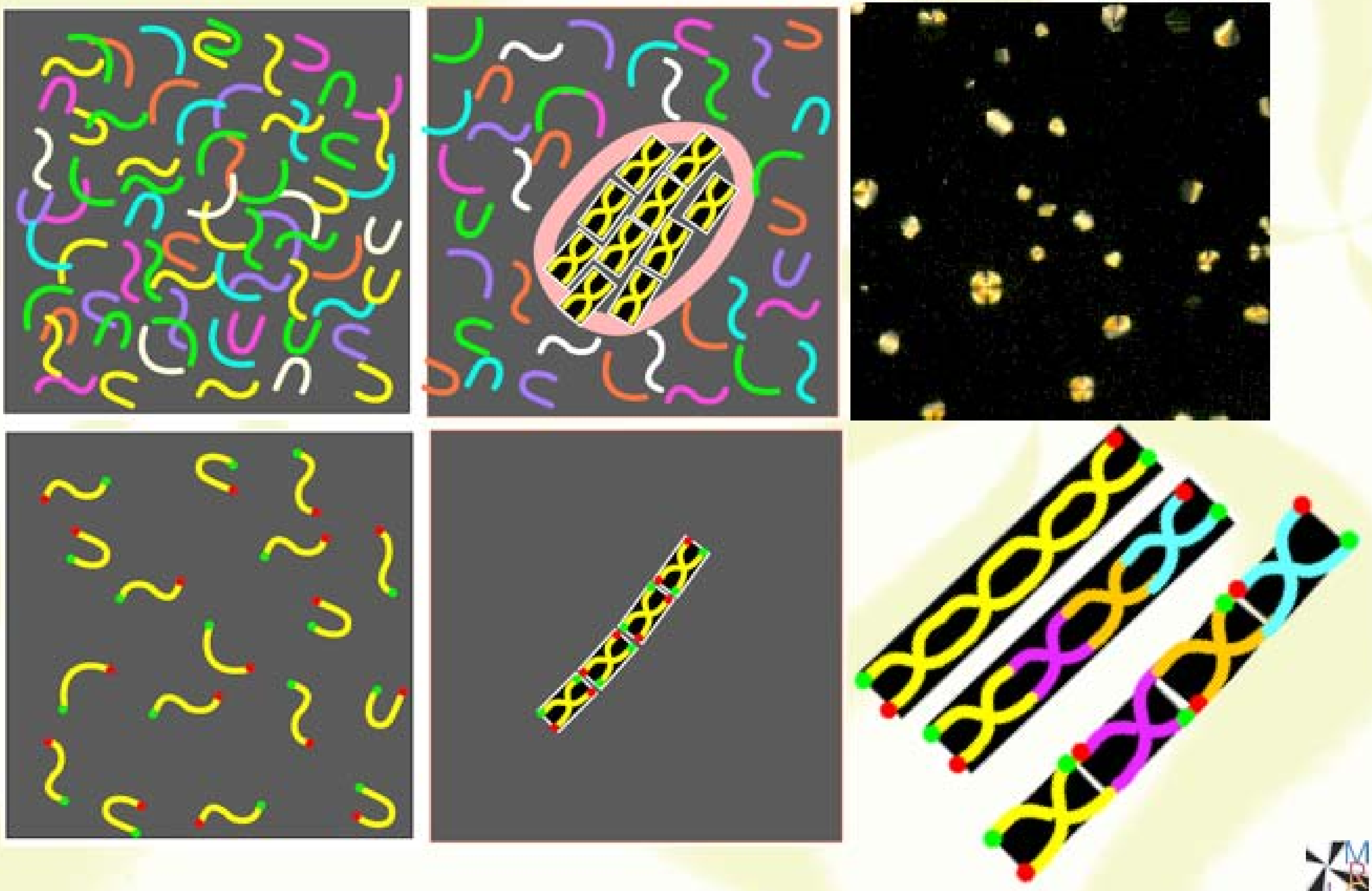


depletion attraction



Asakura, Oosawa, JCP (1954)

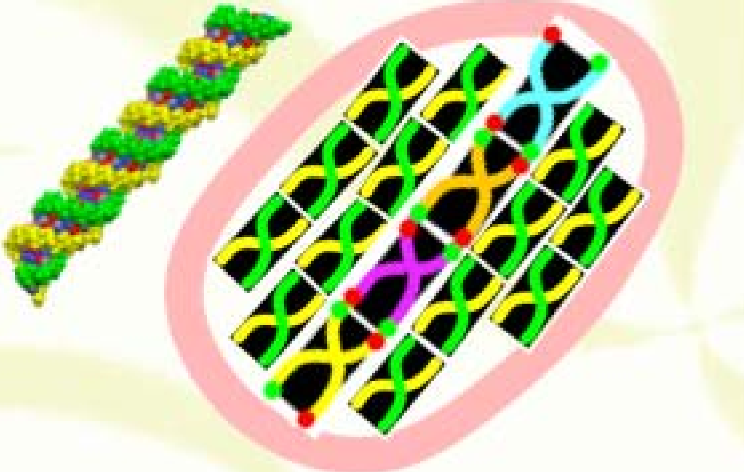
liquid crystal condensation of complementary strands



liquid crystal autocatalysis

Wickepedia:

- A chemical reaction is autocatalytic if the reaction product is itself the catalyst for that reaction…



…leads to the notion of

liquid crystal
autocatalysis / autotemplating

the catalyst establishes the structural paradigm…

and, in this case,

the liquid crystal is the catalyst , and the template

<u>selection</u> - three cascaded stages of self assembly

What is the purpose of life?

…to make liquid crystals.

20th century wisdom

Because life's information carriers

are linear semiflexible polymers

they form liquid crystal phases.

We would suggest…

Because they form liquid crystal phases

life's information carriers

are linear semiflexible polymers.