

Controlling Where the Chips Fall: Novel Nanomaterials from Molecular Disks

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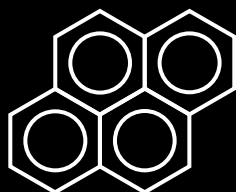
"Let the chips fall where they may"

Disk-like molecular building blocks

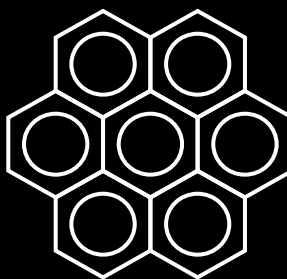
naphthalene



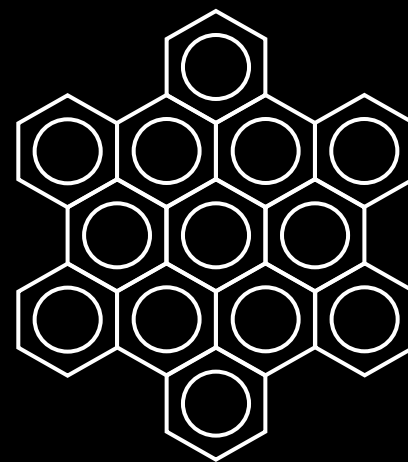
pyrene



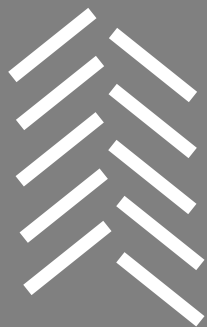
coronene



hexabenzocoronene



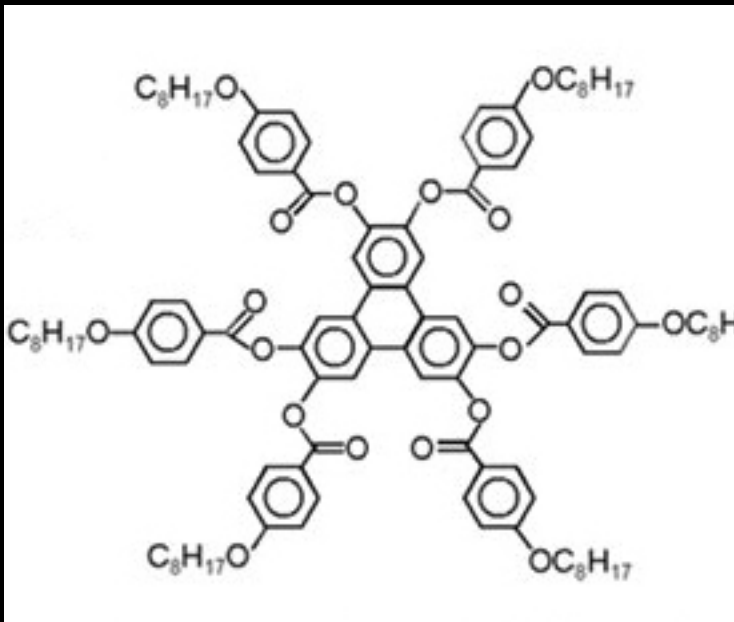
typical crystal
structure (herringbone)



M.P. 440 C

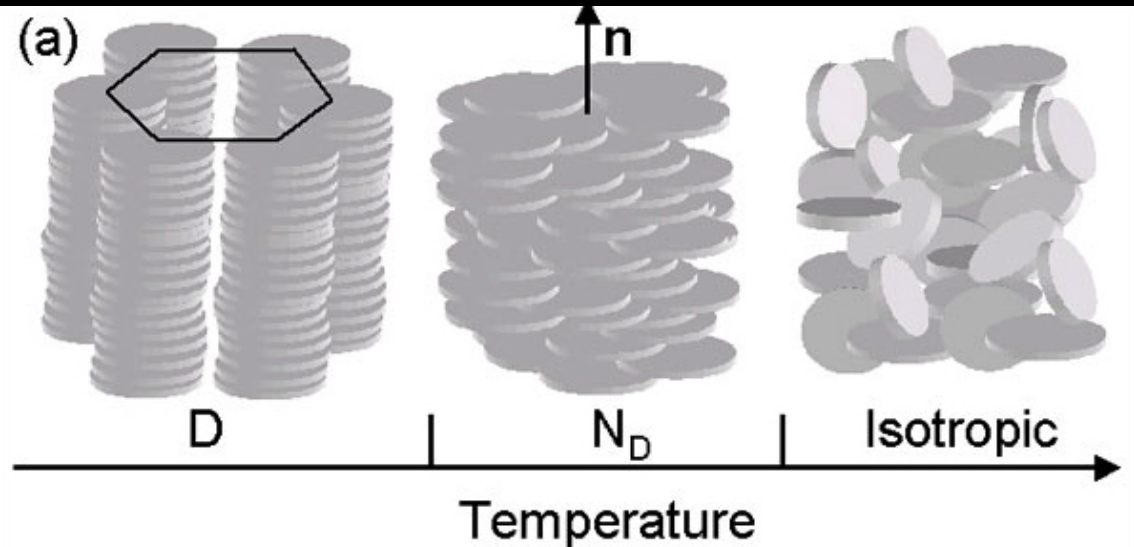
B.P. 525 C

Functionalizing polyaromatic cores leads to liquid crystalline behavior

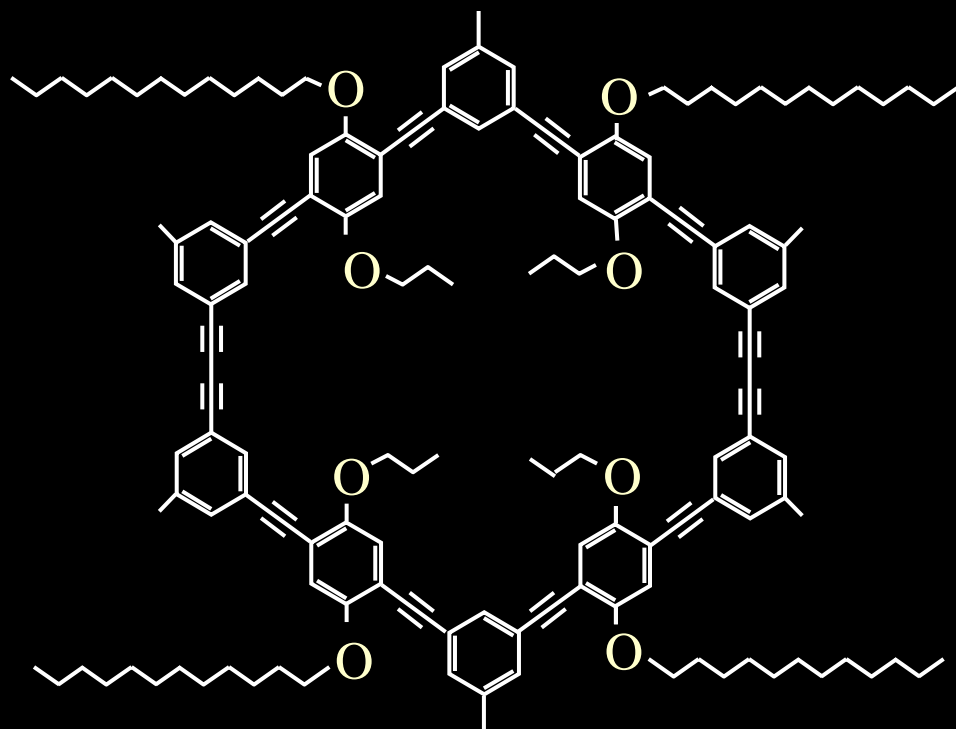


Example discotic LC

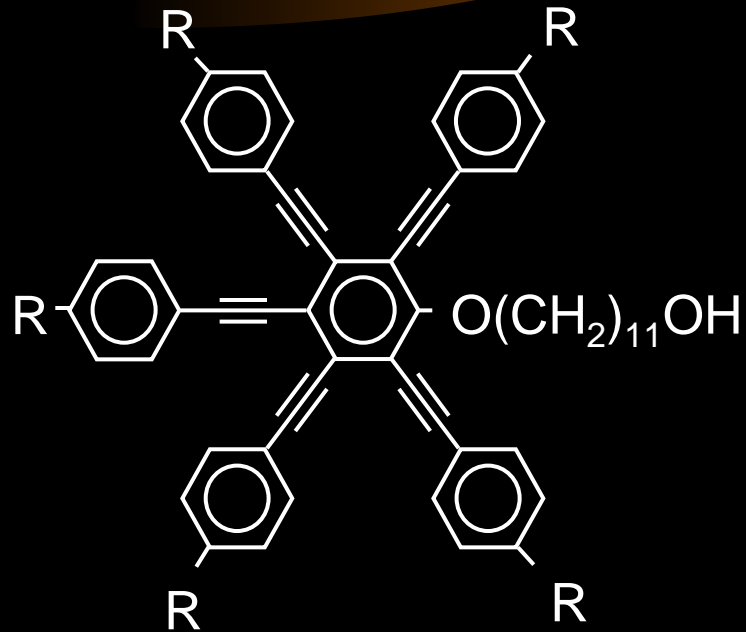
Discotic phases



Unusual discotic forms



Rigid ring and flexible core

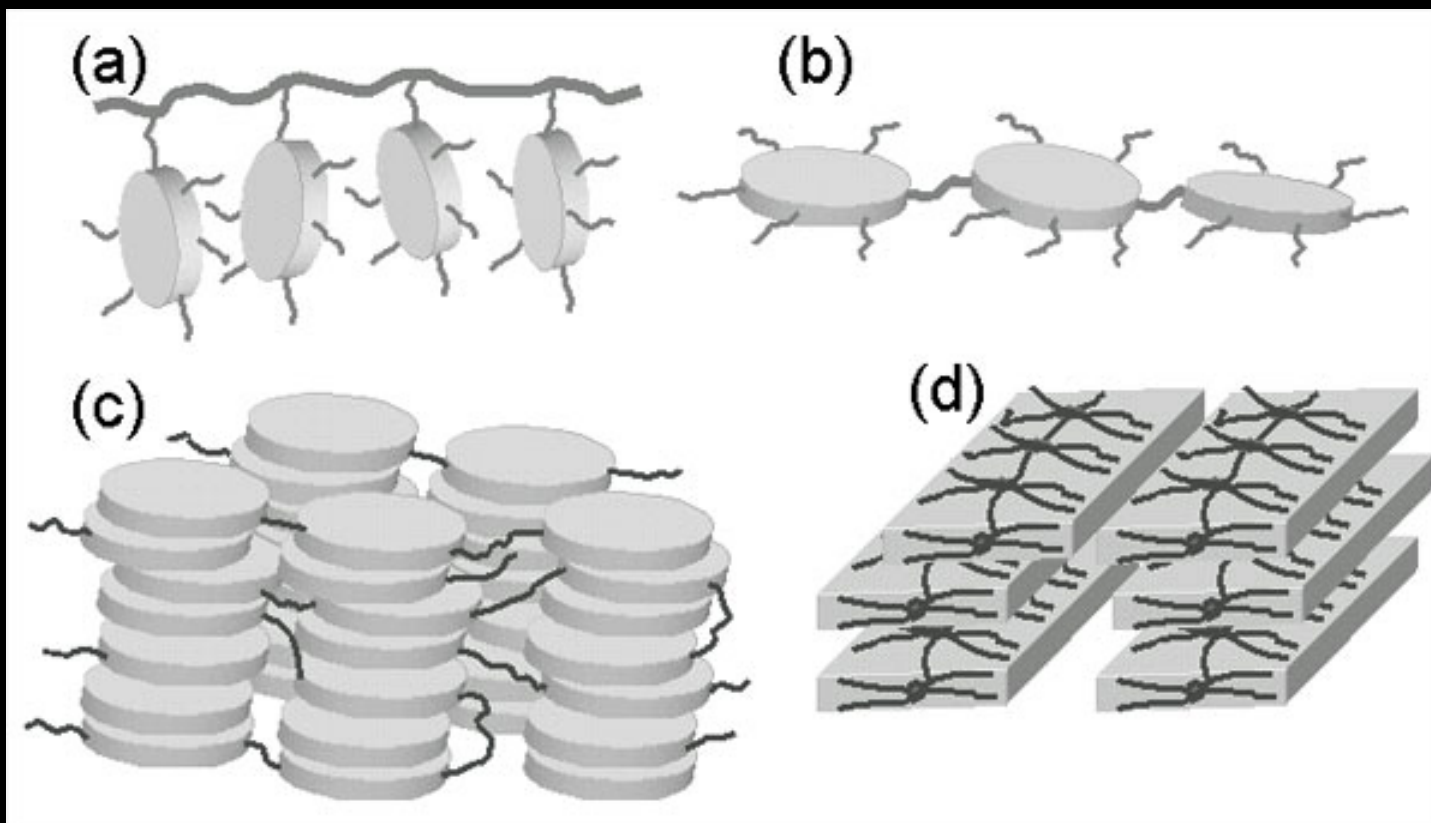


Hub and spoke w/
sp¹-hybridized bonds

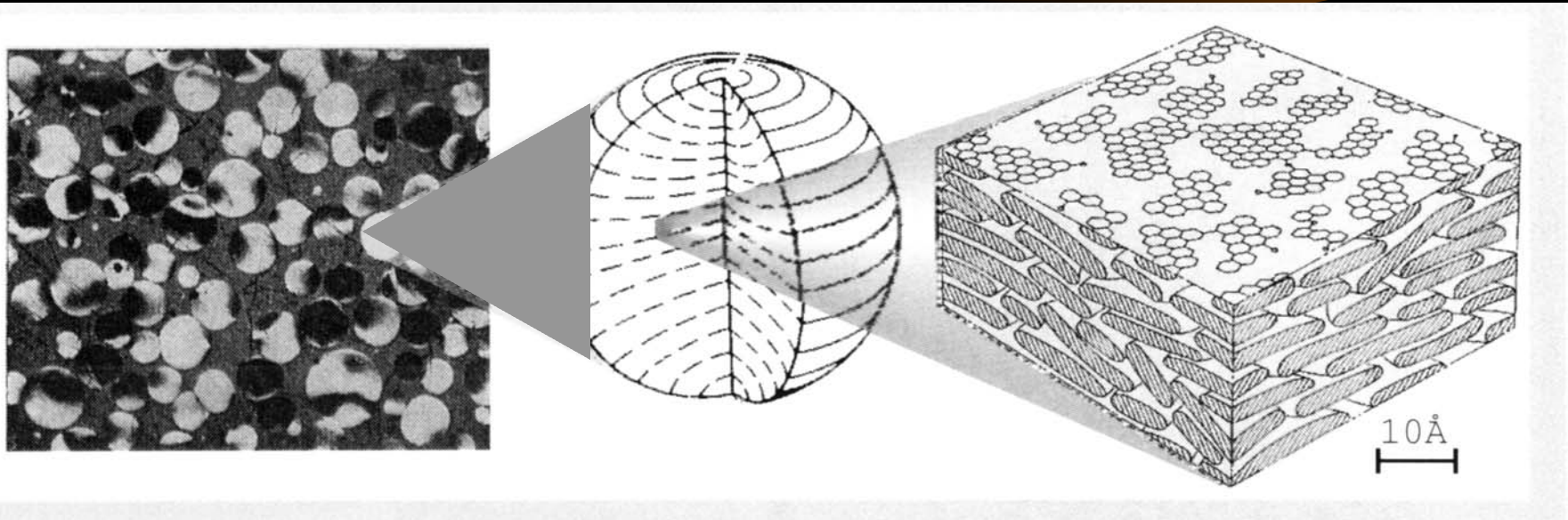
Discotic polymeric liquid crystals

Side chain

Main chain



Carbonaceous mesophase: Nature's discotic liquid crystal



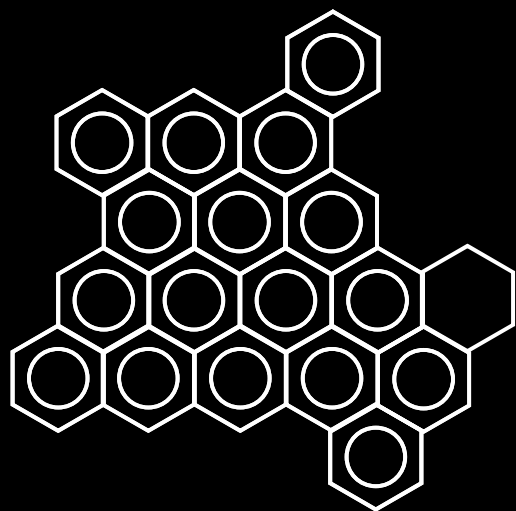
Mesophase spheres
in isotropic matrix

Molecular structure
within mesophase sphere

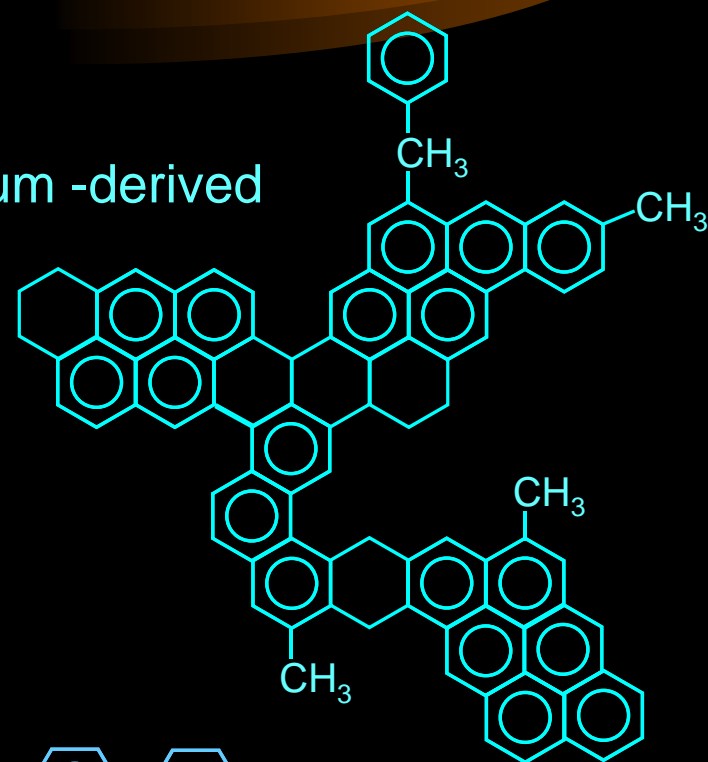
Close-up of polyaromatic
molecules in discotic
liquid crystalline phase

Representative molecular structures in carbonaceous mesophase

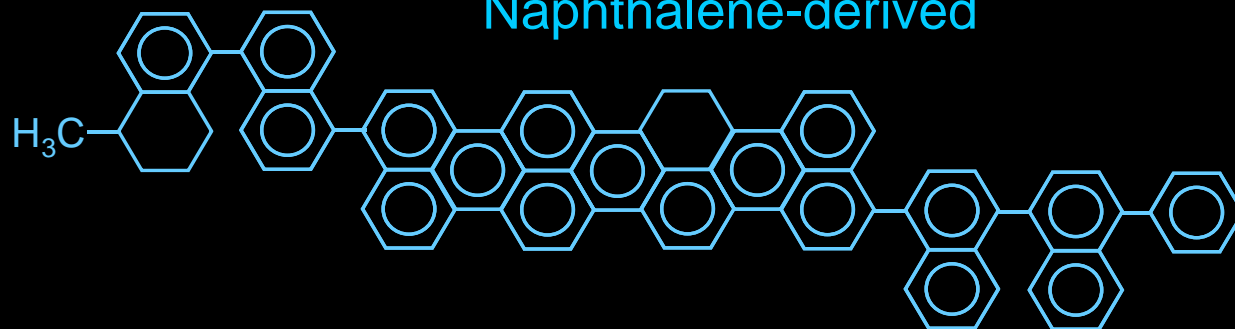
Coal-tar
derived



Petroleum -derived



Naphthalene-derived

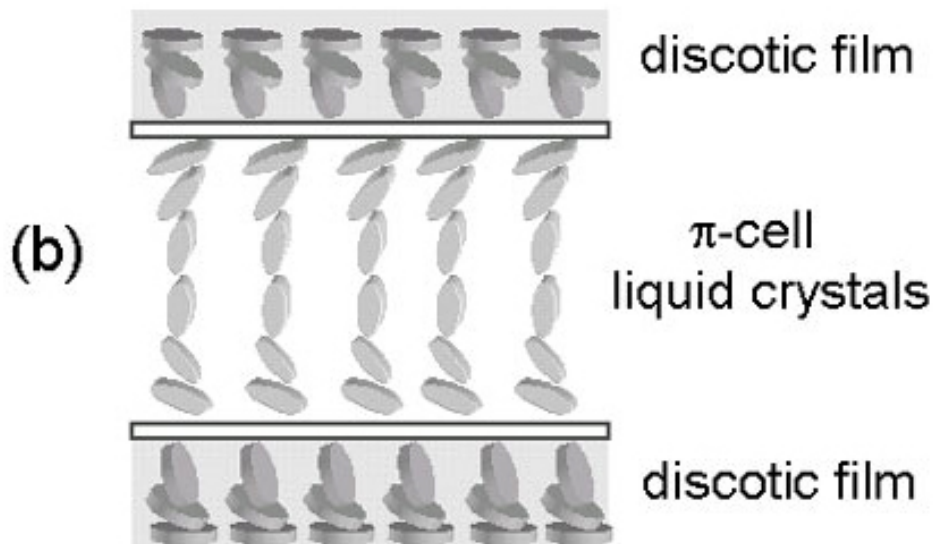
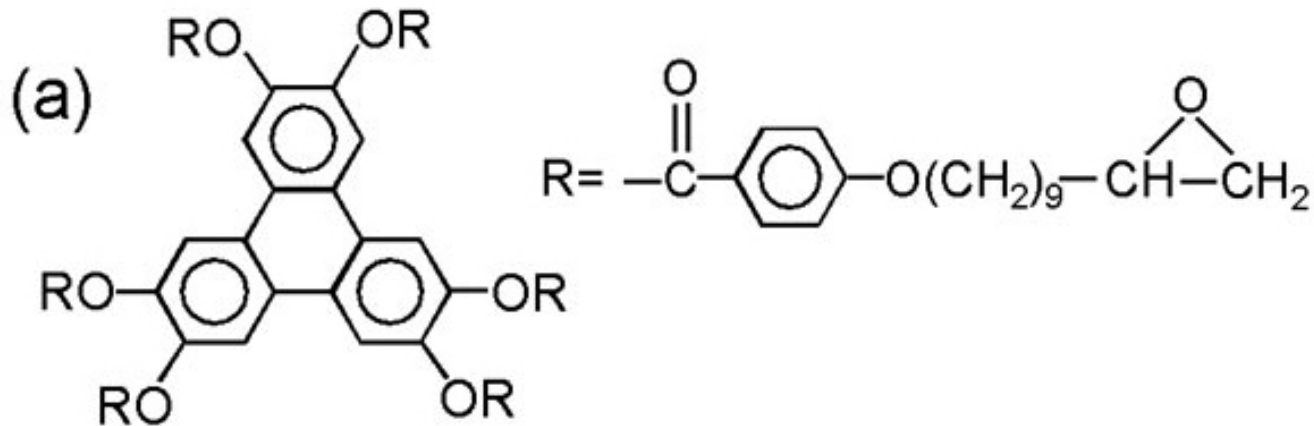


Applications of discotic materials

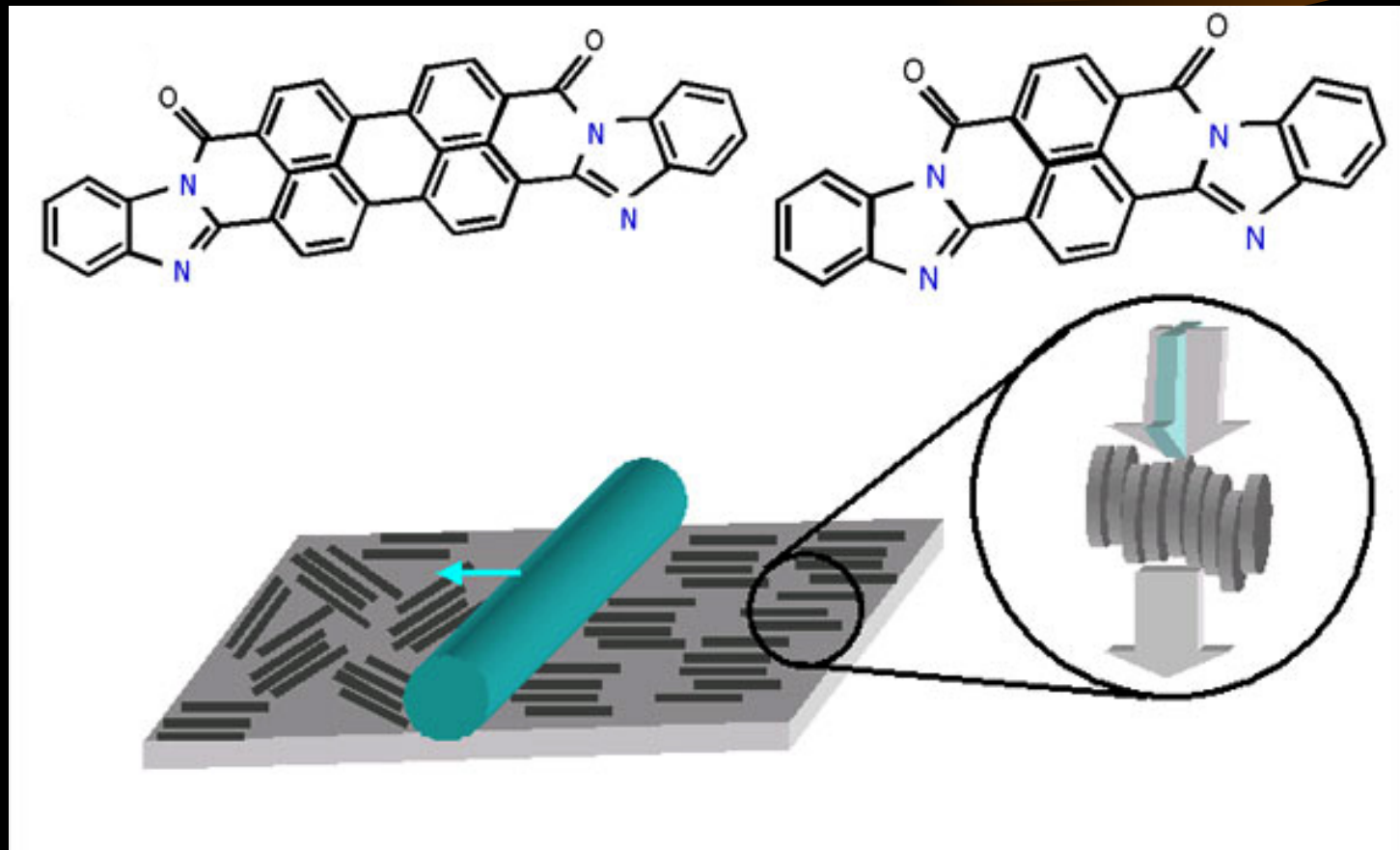


- thin film polarizers
- compensation films for LC displays
- precursors for carbon materials
(high modulus fibers, microbeads)
and carbon nanomaterials
(nanofibers, tubes, films)
- photovoltaics
- organic LEDs
- molecular wires
(as columns)
- thin films

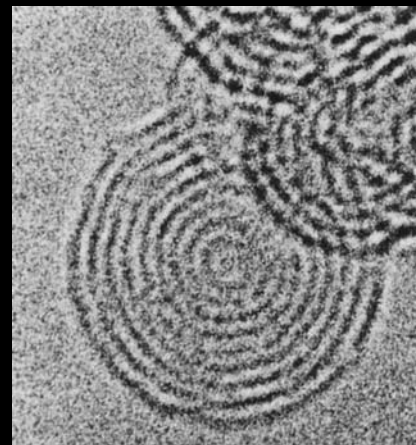
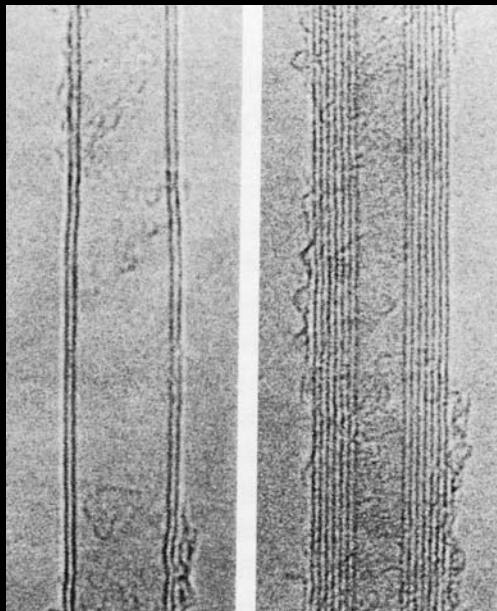
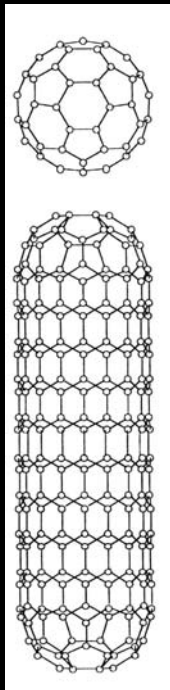
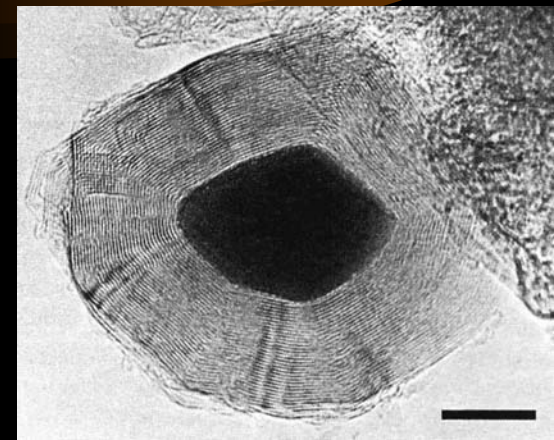
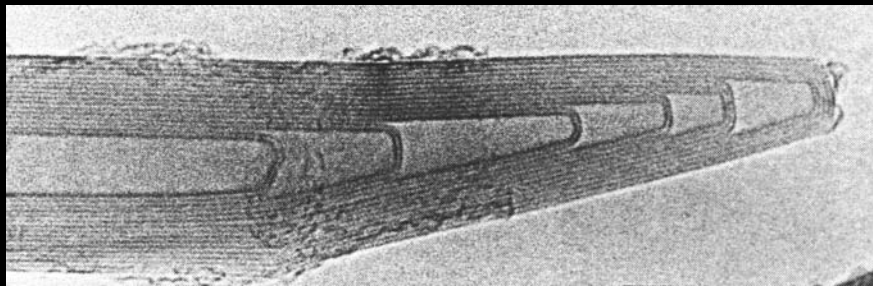
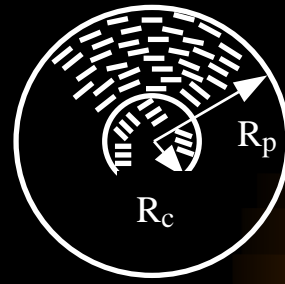
*Application:
Compensation films in π -cell LC displays*



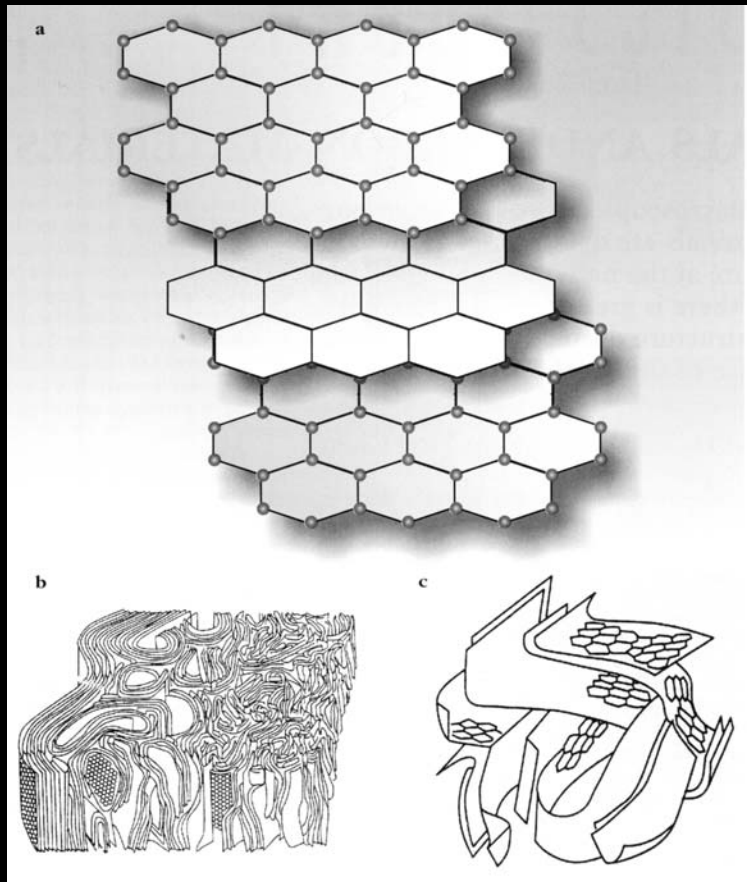
*Application:
Thin film polarizers*



Carbon Nanomaterials



Bonding and anisotropy in graphite



In-plane

- covalent bonding
- high thermal/e-conductivity
- high strength/stiffness
- low reactivity

Between-planes

- Van der Waals bonding
- low thermal/e-conductivity
- low strength/stiffness
- high reactivity (on edge-sites)

Liquid crystal surface anchoring of mesophase pitch

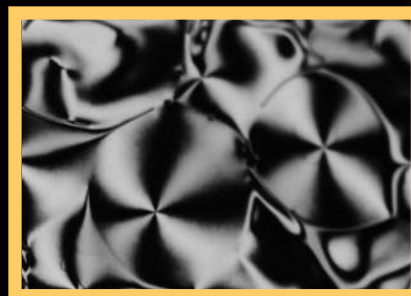
[Hurt et al., *Chemistry of Materials*, 14 4558 (2002)]

[Jian et al., *Carbon*, in press]

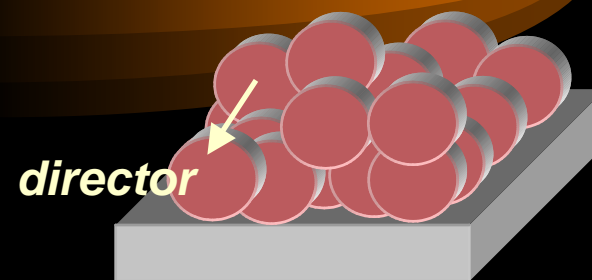
SUBSTRATE

Gas (free surface)

Alumina
Borosil. glass, quartz
PTFE
Cu, Al, Zn



edge-on (planar)



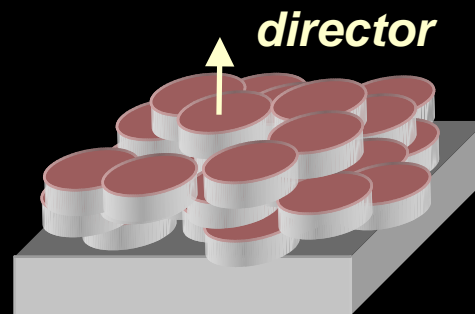
View

Interfacial plane is anisotropic (LC texture)

Graphite basal plane

Mica
Pt
Ag
Glassy carbon

face-on (homeotropic)



View

Interfacial plane is isotropic

Orientationally patterned carbon surfaces

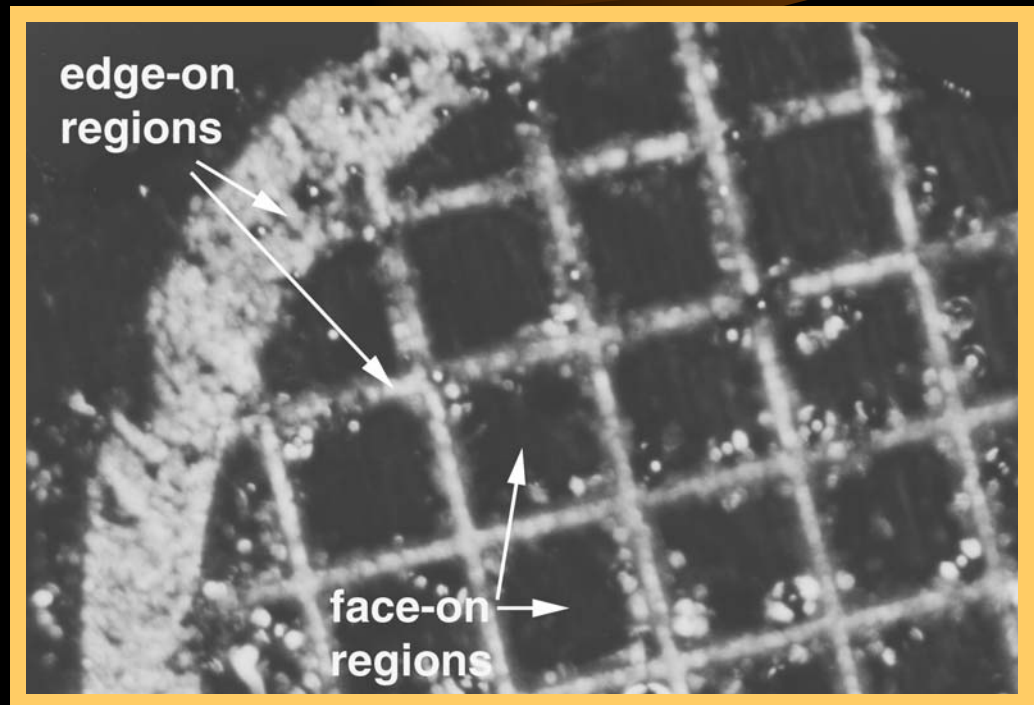
[Hurt et al., *Chemistry of Materials*, 14 4558 (2002)]

Quenched AR mesophase
formed on composite
anchoring template:

Cu TEM grid
(promotes edge-on)

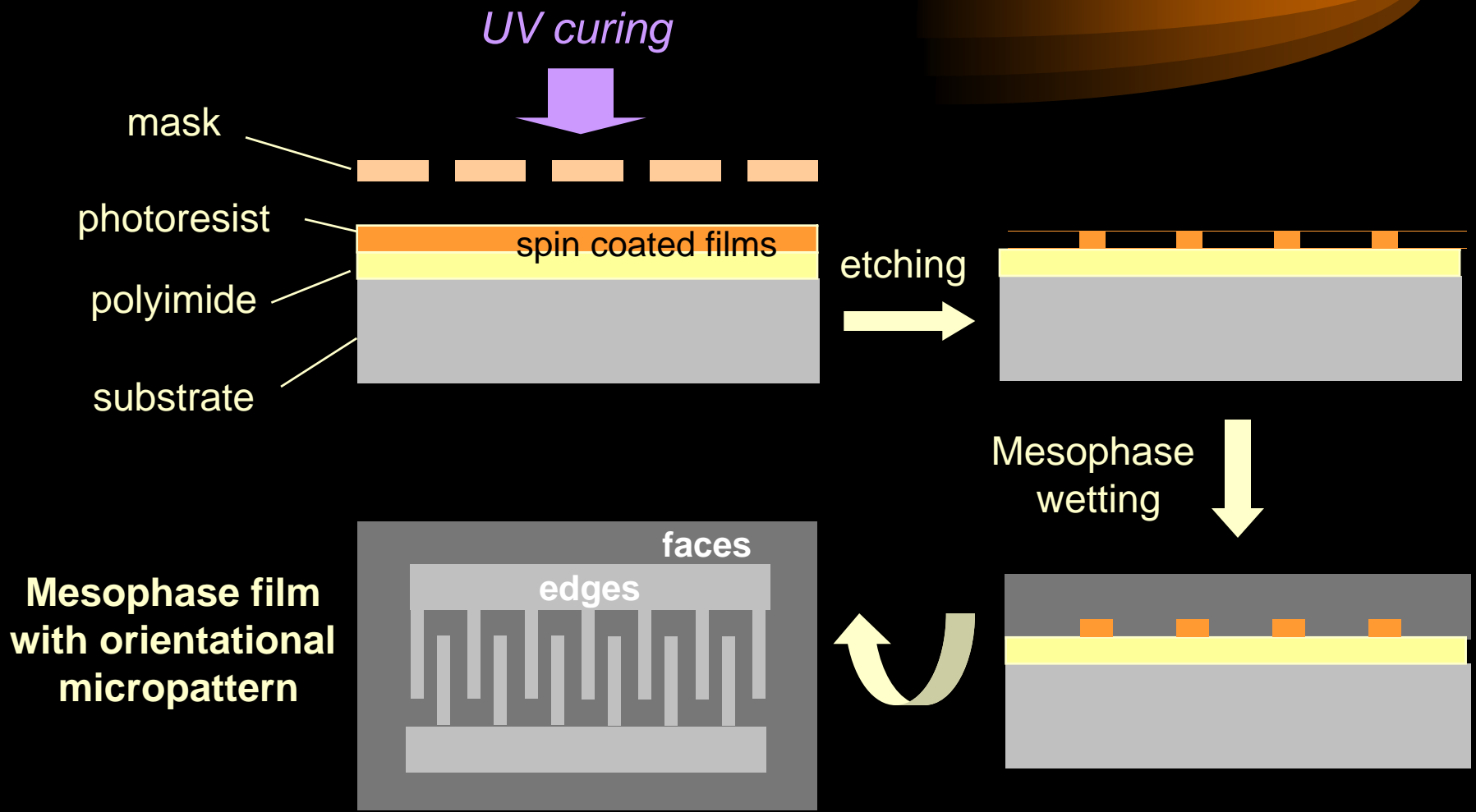
plus

HOPG, graphite basal
(promotes face-on)

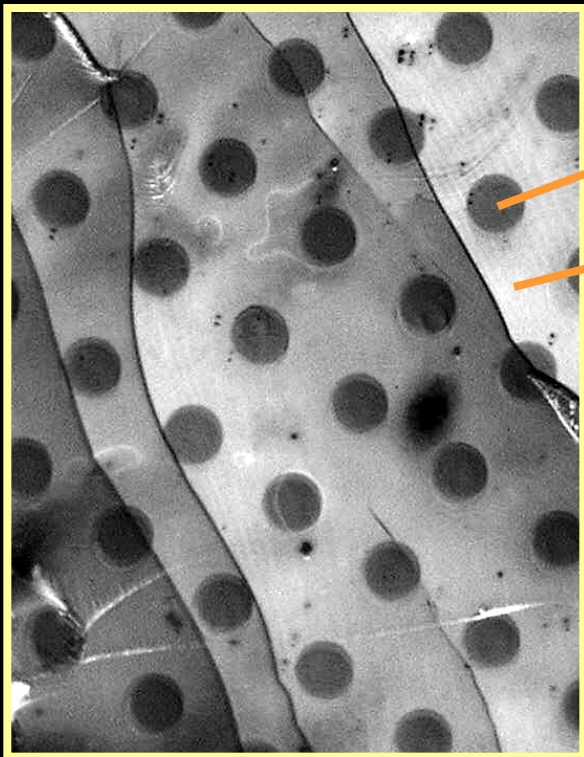


Polarized light micrograph: crossed nichols

Lithographic patterning of discotic films



Lithographically patterned discotic films



Polyaromatic

Faces

Edges

Dot pattern
(crossed polars)

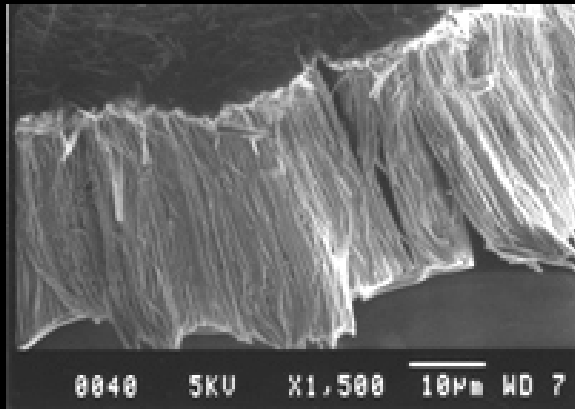
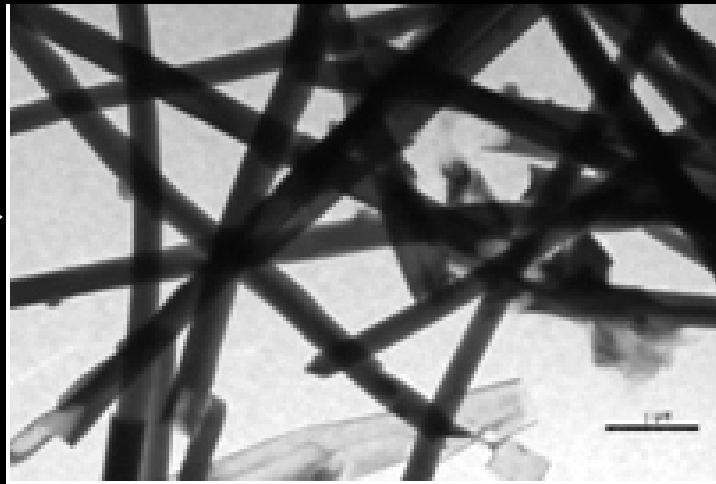
Interdigitated lines
(crossed polars)



"Orthogonal Carbon Nanofibers"

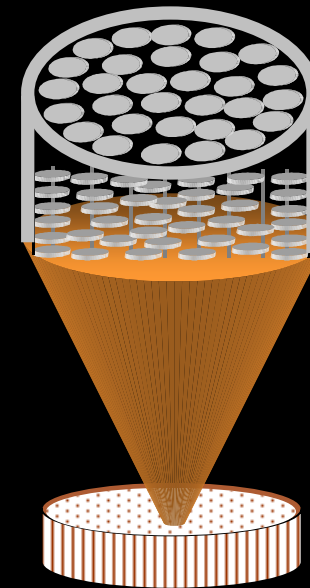
[Jian et al., *Advanced Materials*, 15(2)164-167 (2003)]

dispersion



carbonization

template removal



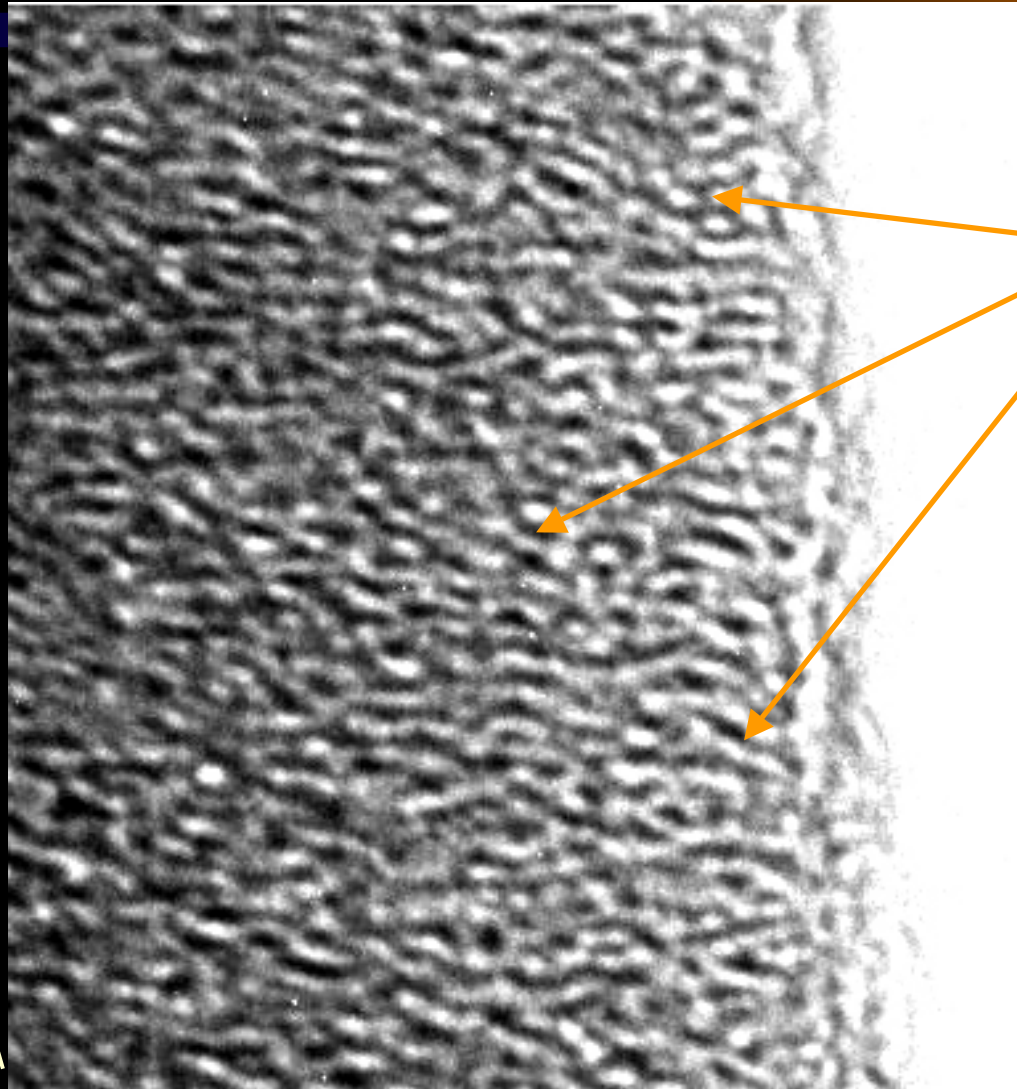
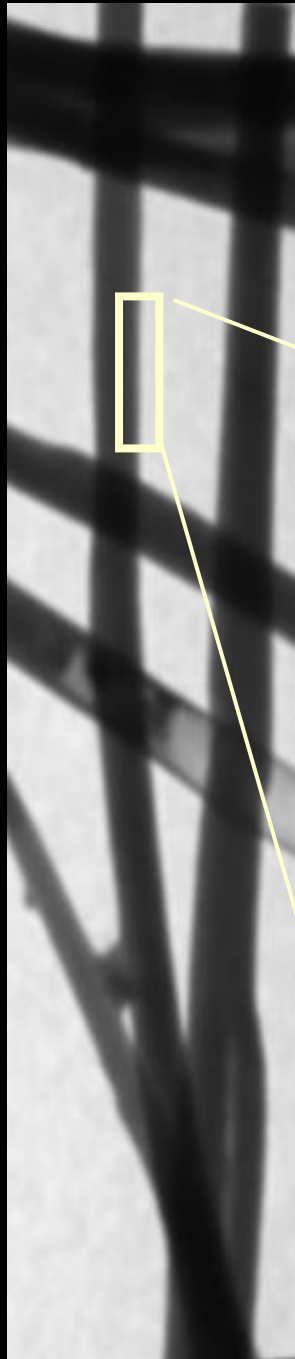
Nanochannel alumina

capillary infiltration

Discotic mesophase pitch

"Orthogonal" Carbon Nanofibers

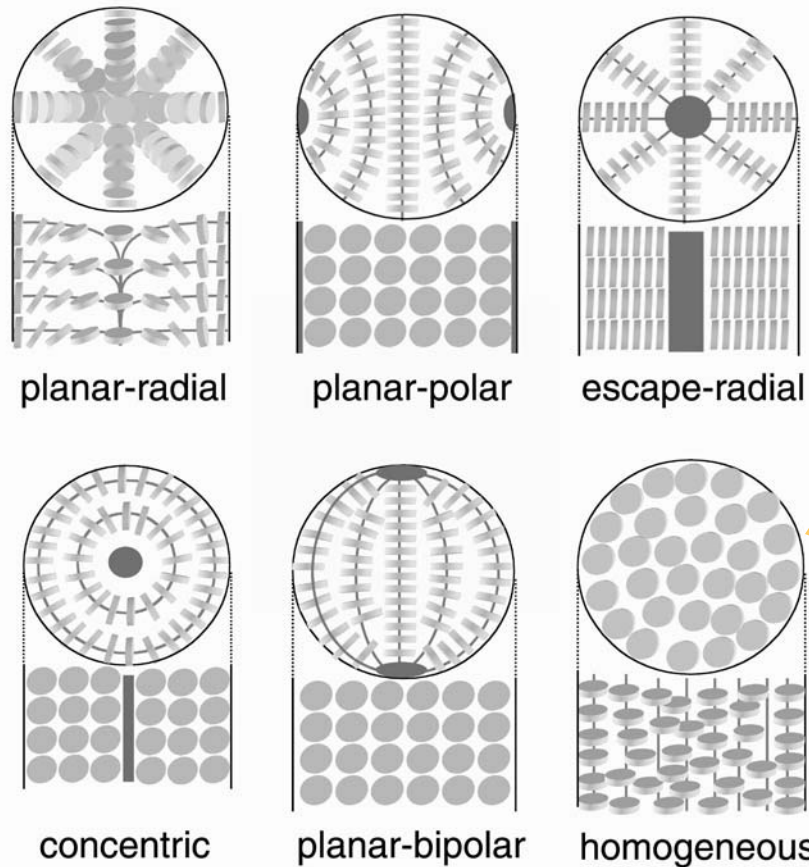
[Jian et al., *Advanced Materials*, 15(2) 164-167 (2003)]



Orthogonal
graphene
layers

Fiber
axis

Possible molecular configurations in confined discotic liquid crystals

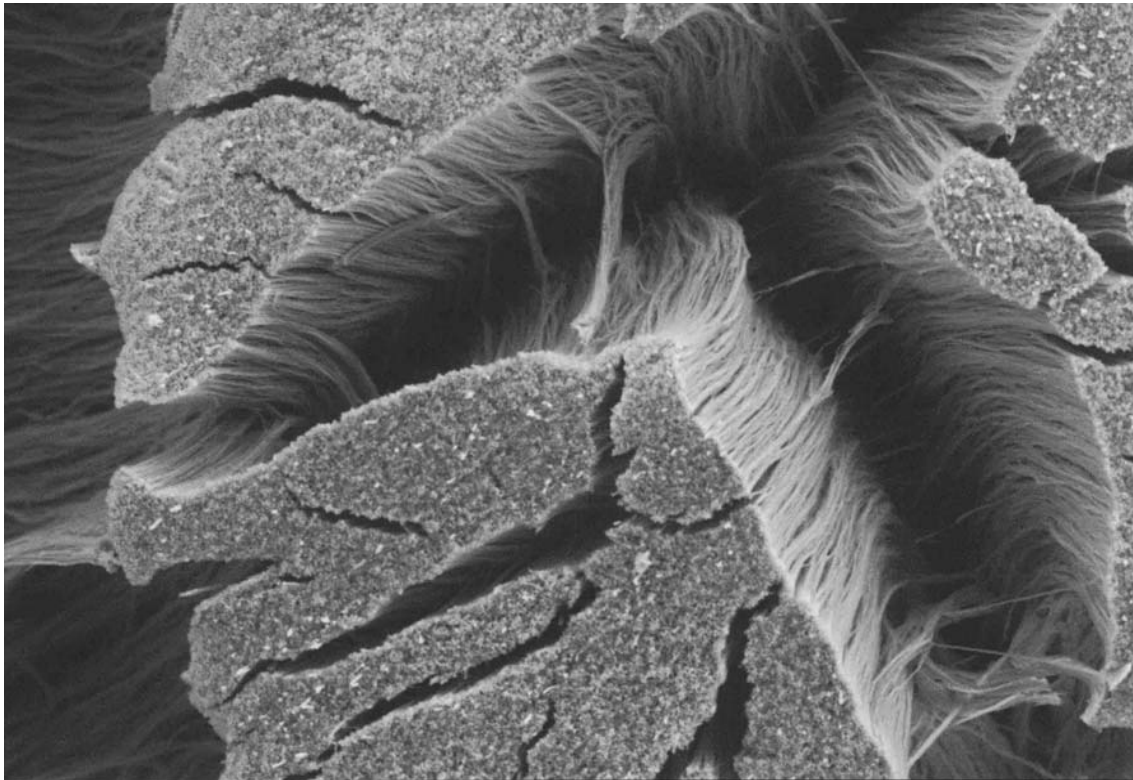


Face-on anchoring states
(disallowed)

Only the homogeneous
(orthogonal) configuration
achieves edge-on anchoring
with no elastic strain

[Jian et al.,
Advanced Materials, 2003]

*Nanofiber forms:
mats, nanocomposites, and free-standing arrays*



10 μ m

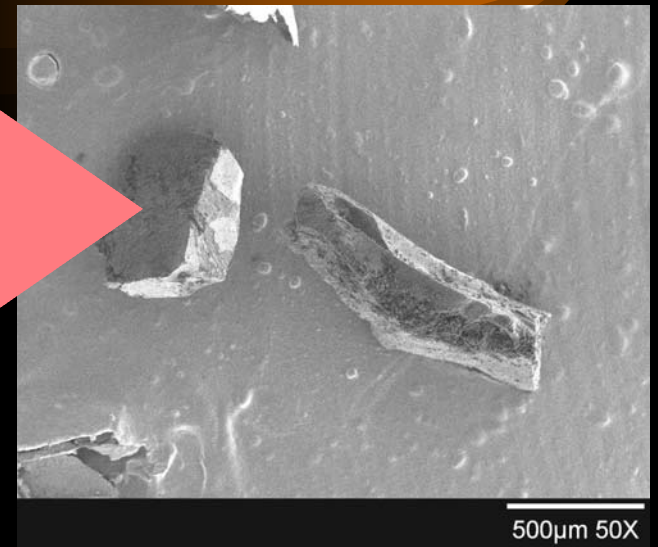
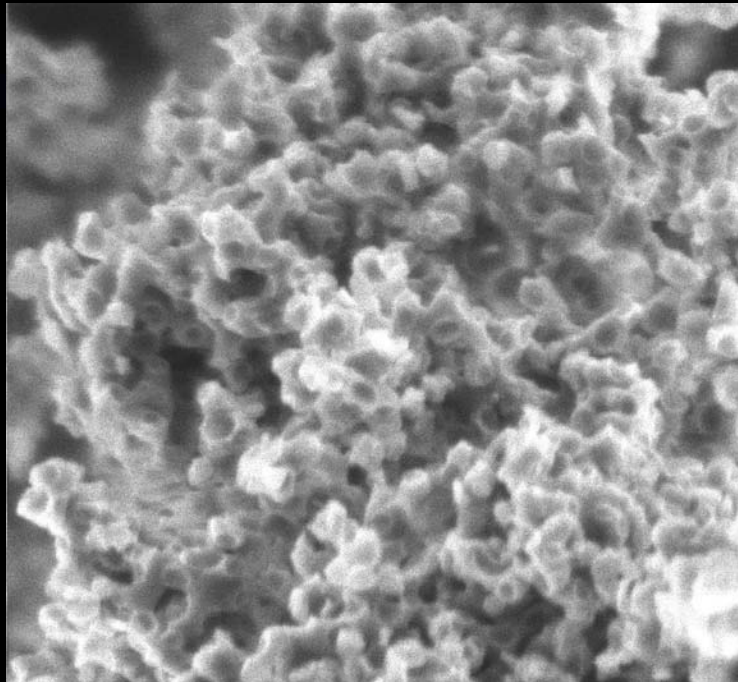
EHT = 5.00 kV
WD = 6 mm

Signal A = MPSE
Photo No. = 15

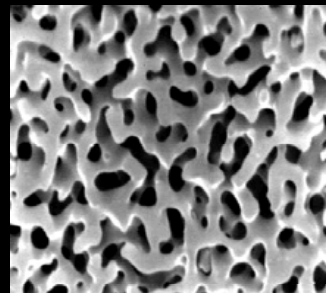
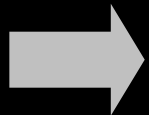
Date :5 Sep 2003
Time :18:53:24

free-standing array
of "orthogonal"
carbon nanofibers
(top view)

"Nanophase Mesocarbon"



Mesophase pitch



Nanoporous glass

Carbonization



Glass / carbon nanocomposite

NaOH etching

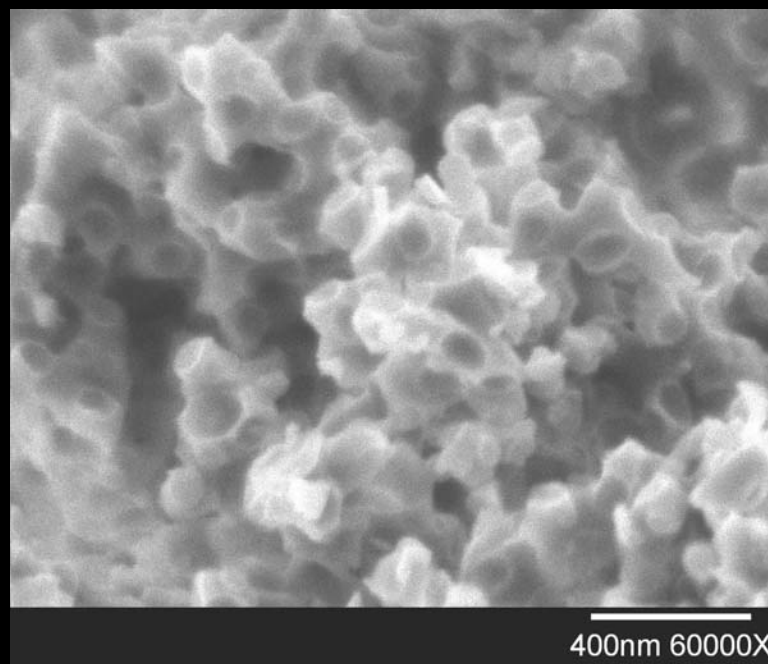
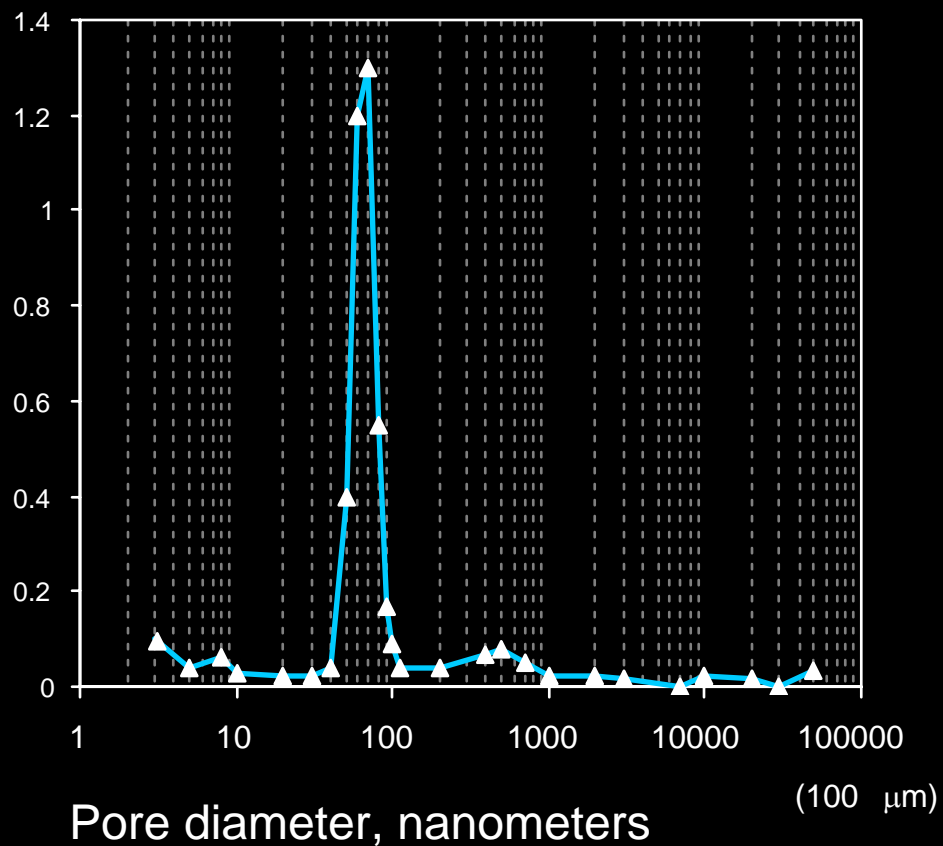


Pore structure of nanophase mesocarbon

Differential
pore
Volume
(ml/gm-decade)

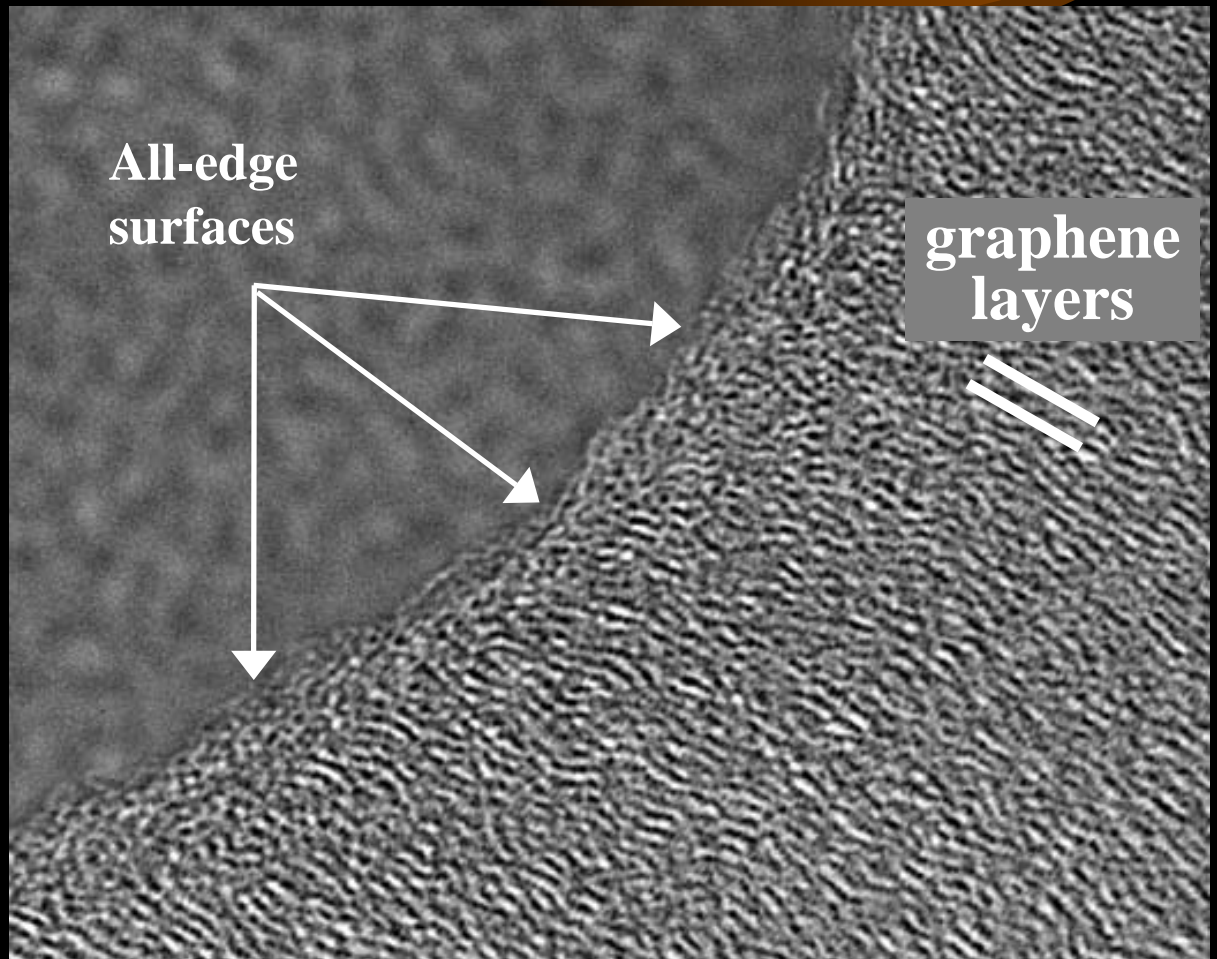


Total area: 32 m²/g

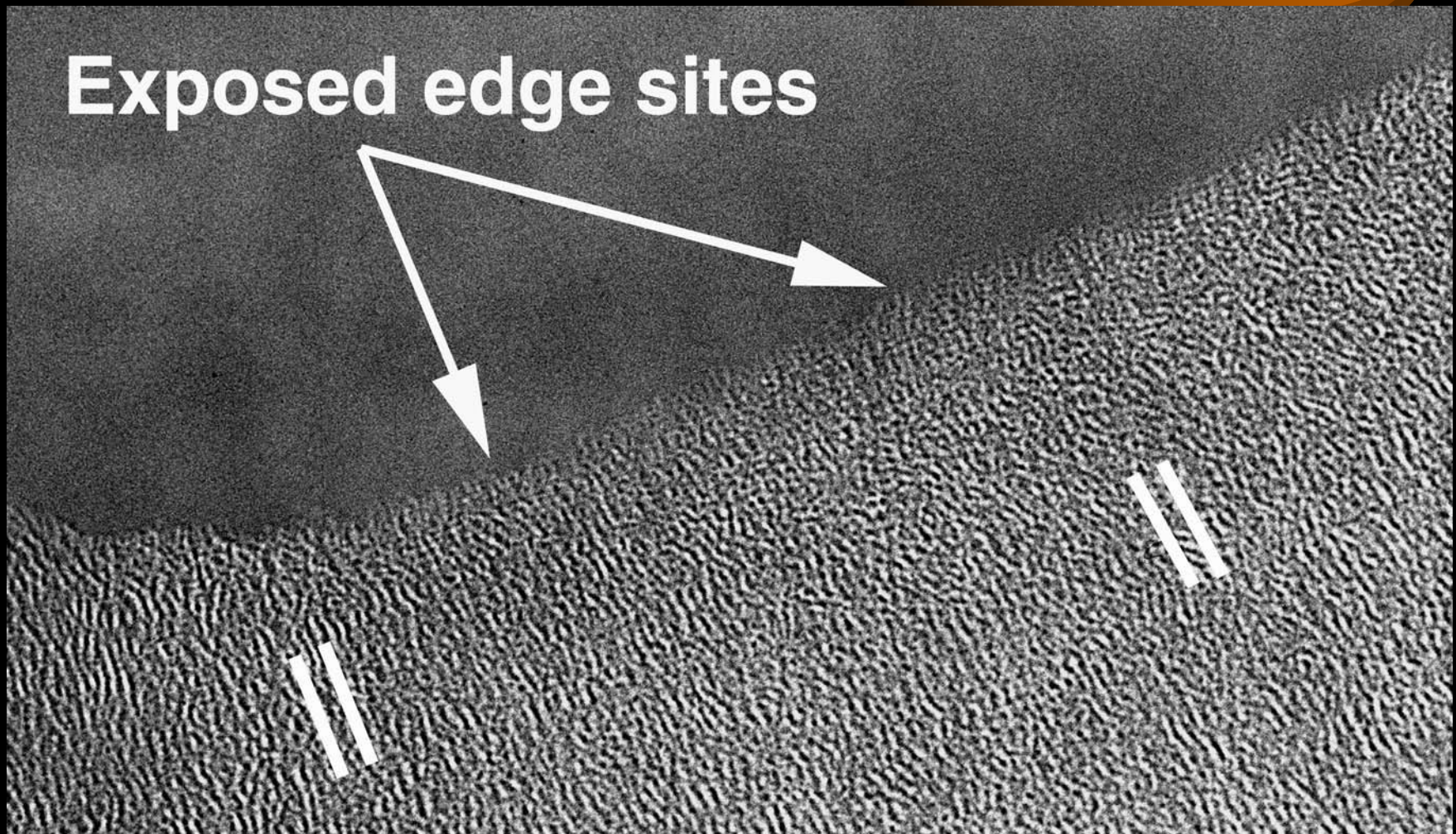


All-Edge Surfaces in Nanophase Mesocarbon

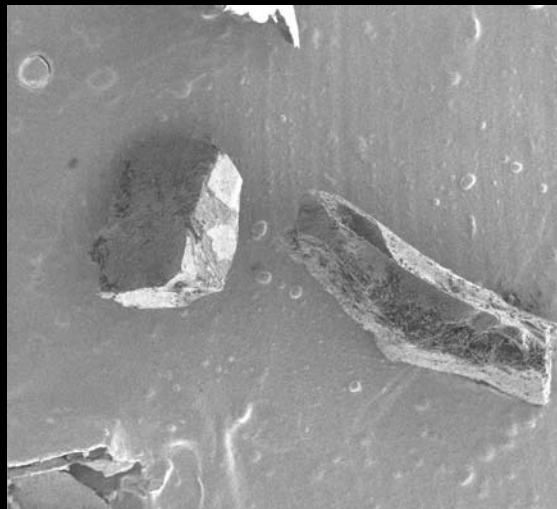
Concave surfaces are
pristine (non-fractured)
material from former
pitch/glass interface



*Example of Clean, All-Edge Surface
in Nanophase Mesocarbon*



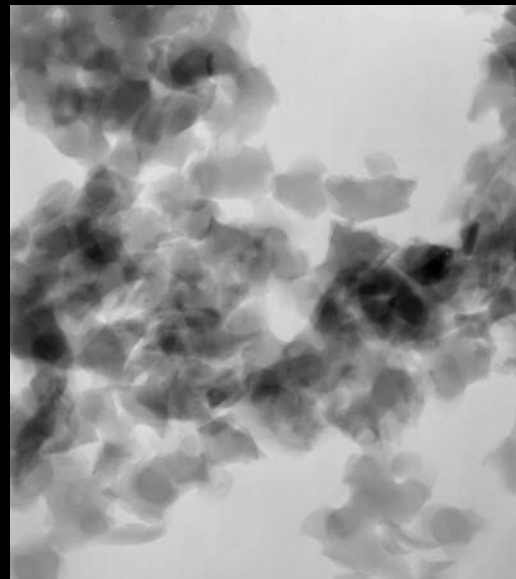
Nanophase mesocarbon: Forms



1 mm

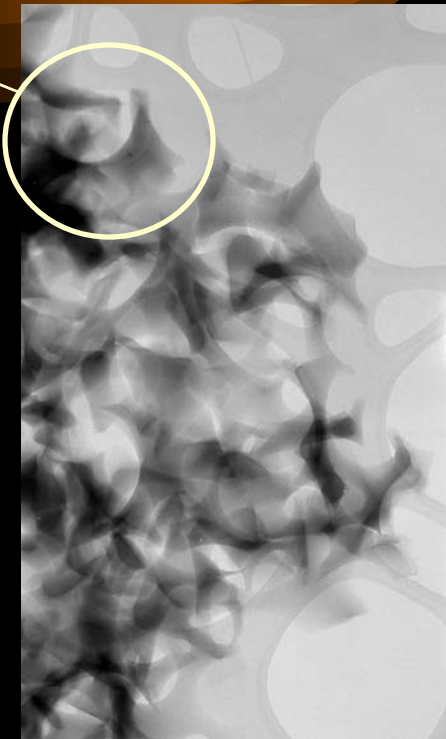
Porous monolith

Inverse sphere structure



500 nm

Nanoparticulate



500 nm

Quenched pitch

Potential features / advantages of the new nanocarbon forms

- simultaneous control of pore structure / form and molecular surface structure
- electrical conductivity (continuous solid phase)
- nanometric grain sizes (high mesoporous surface area and rapid solid state diffusion)
- one-step synthesis from low-cost precursor (no stabilization)

Features specific to "open forms"

- high-activity, all-edge surfaces (catalysis, covalent coupling, chemical sensing, selective adsorption)
- easy access to interlayer spaces (Li battery electrodes)

Surface anchoring and nanoscale confinement provide a new, highly flexible approach for molecular control in carbon nanomaterials