Functional Nanostructures by Ionic Self-Assembly

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Challenges in the design of functional nanostructures

Is it really that easy?

Focus of this session

- - expertise and projects
- - mid/long term goals
- - opportunities and/or challenges

Outline

- Background – why?
- Goals – what?
- How?
- Conclusion and Outlook
- Acknowledgements

Background (why?)

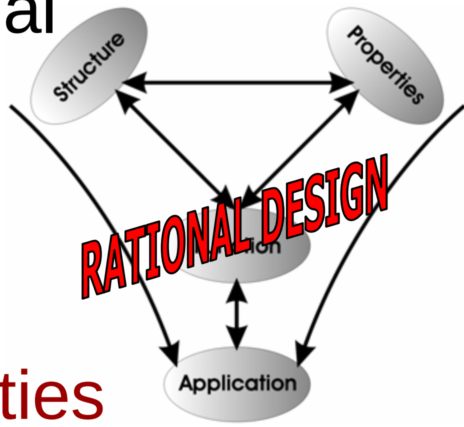
- Construction with noncovalent interactions
- Self-organisation of tectons / codons
    - Beyond pre-organisation
    - Spontaneous but controlled / directed organisation at the molecular and supramolecular level
- Coupling of properties:
    - molecular ⟺ macroscopic
    - stimulus ⟺ response
- Dynamic devices (switching)

Goals (what?)

- Preparation of nanostructured bulk material

  soft (lc)

  functional

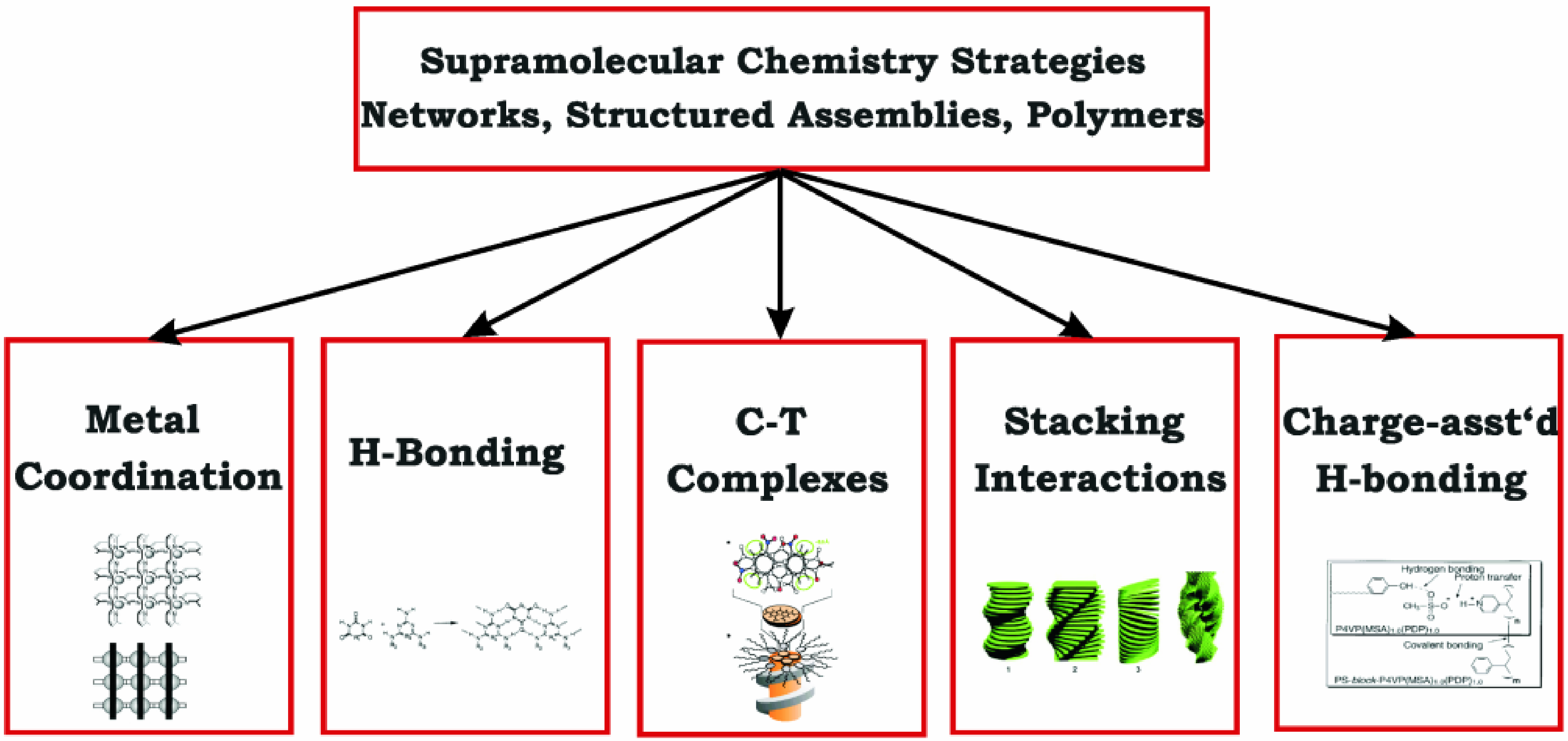


- Control over the structure-function-properties relationship through careful choice of starting materials
- Inclusion of dynamic properties to ensure switchability

  (programmed or directed synthesis, codons)

Syn. Met. ***2004***, *147*, 63

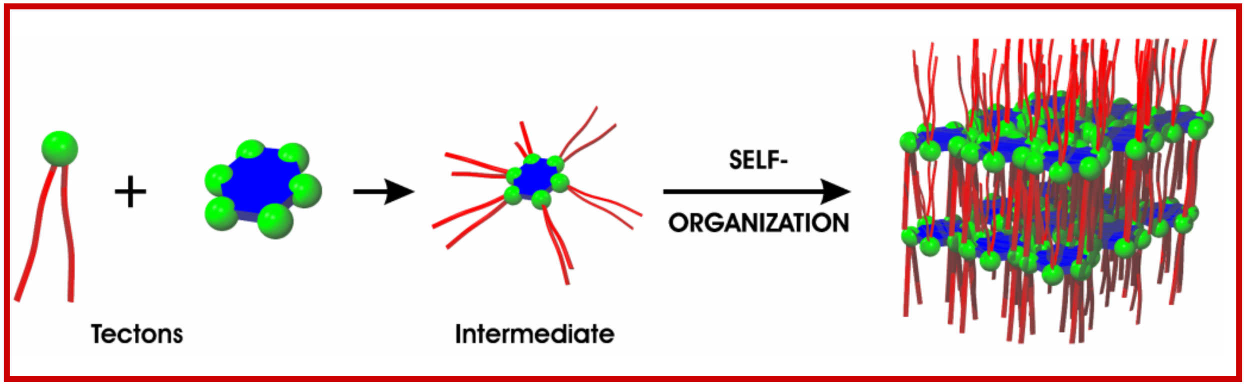
Noncovalent Strategies (How?)



- Simplexes
- Catanionic
- LbL

Ionic Self-Assembly (How? Our expertise)

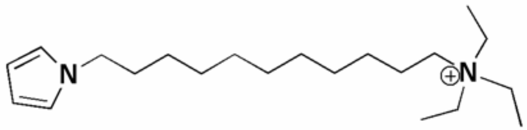
- Oligoelectrolyte-surfactant complexes

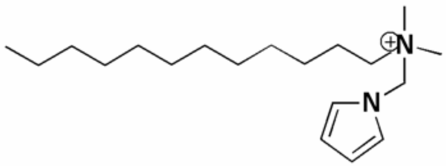


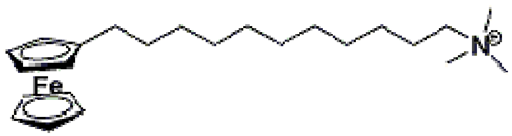
- Electrostatic interactions to drive the organisation of matter + secondary packing motives
- Modular approach: multiple noncovalent interaction strategy, introduce functionalities

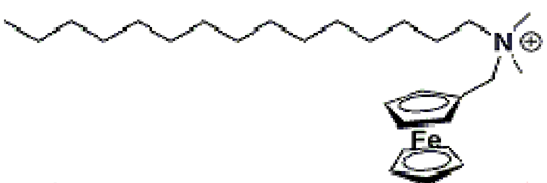
Adv. Mater. **2003**, 15, 673

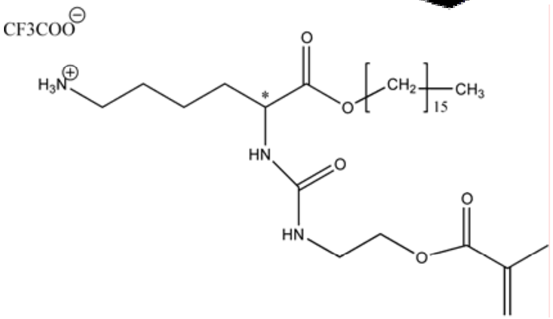
Molecular Toolbox

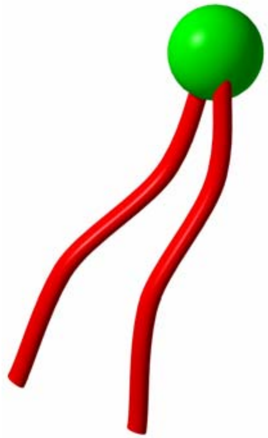


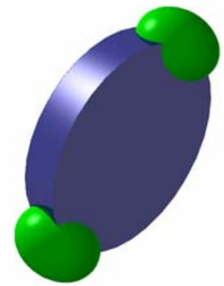


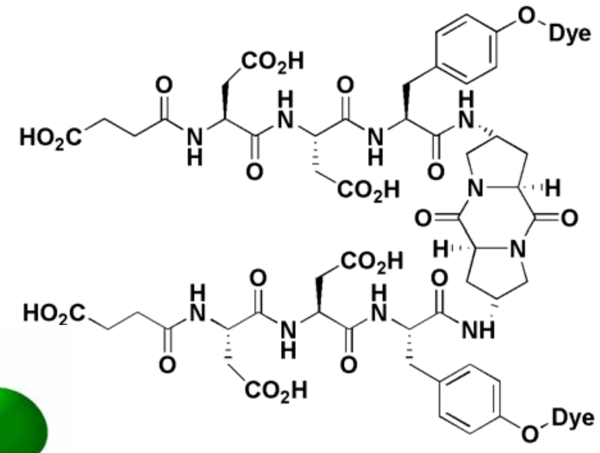


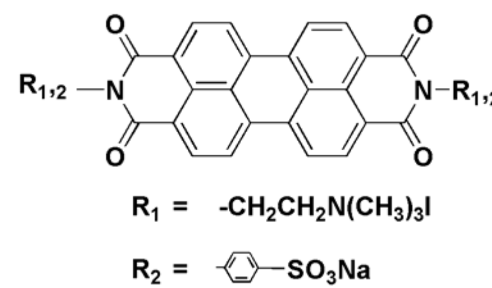


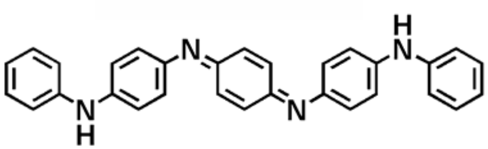


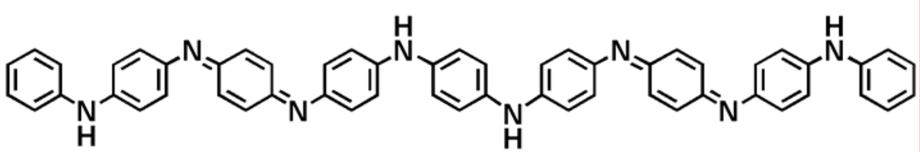












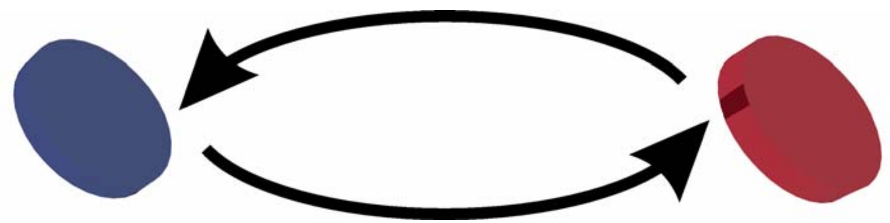
toolbox not black box!

Current Projects

Functionality and Switching

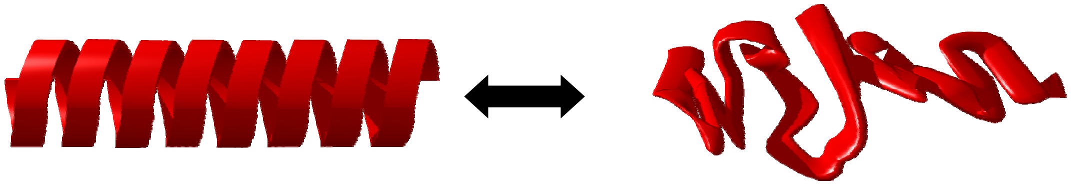
The Questions ...

- What is the use of having a function if you cannot reversibly switch between two states?



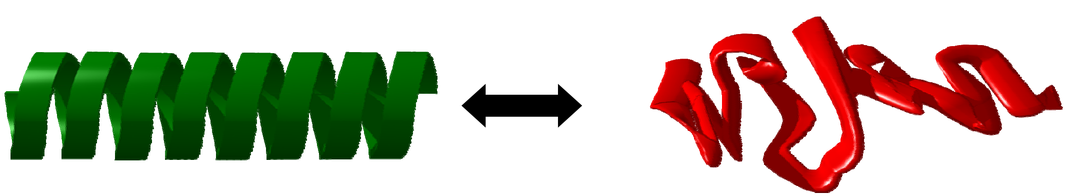
- Routes to reversibly switching function:
  - through direct chemical action / interaction (doping, protonation etc.)
  - through switching structure (phase or chemical)

Switching structure (step-by-step approach)



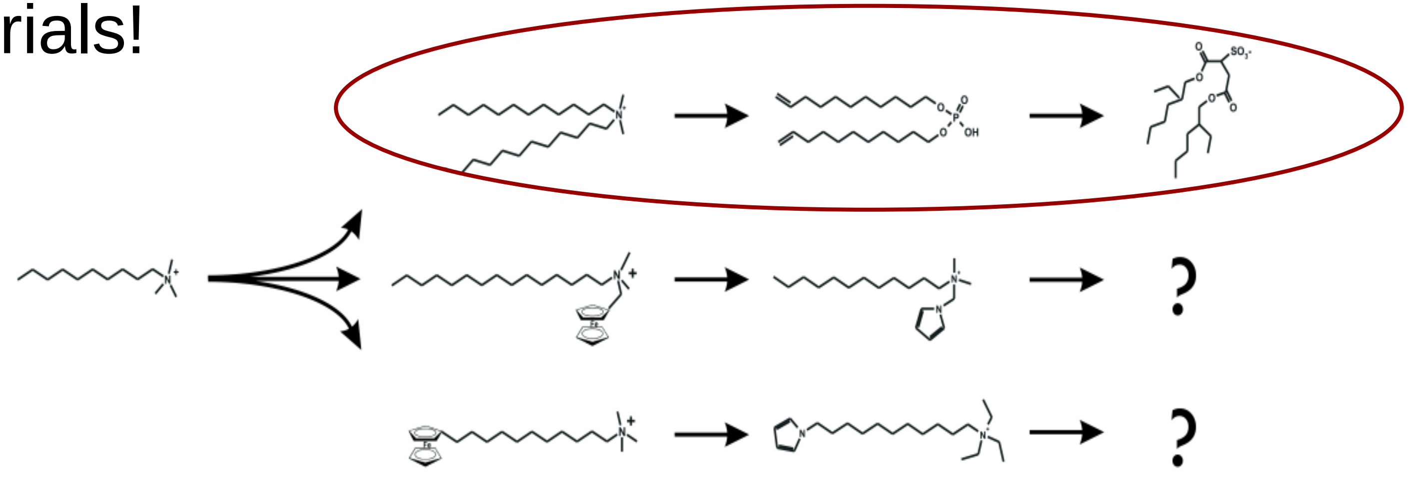
- Is the dynamic nature of noncovalent interactions needed?
- What are the crucial materials property needed to address this question?
- Next level of complexity –

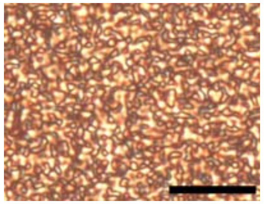
  switching of structure/phase to lead to switching of function

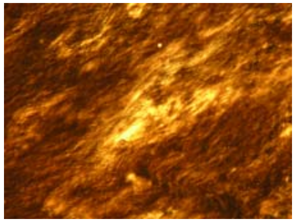


Liquid Crystallinity

- Large alkyl volume for the facile production of LC materials!





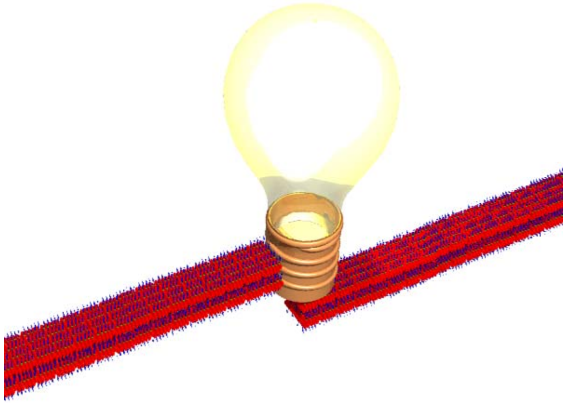


- Control over materials properties through external stimuli
  - temperature, solvent, magnetic fields, electric fields etc.

Mol. Cryst. Liq. Cryst. **2006**, *450*, 55

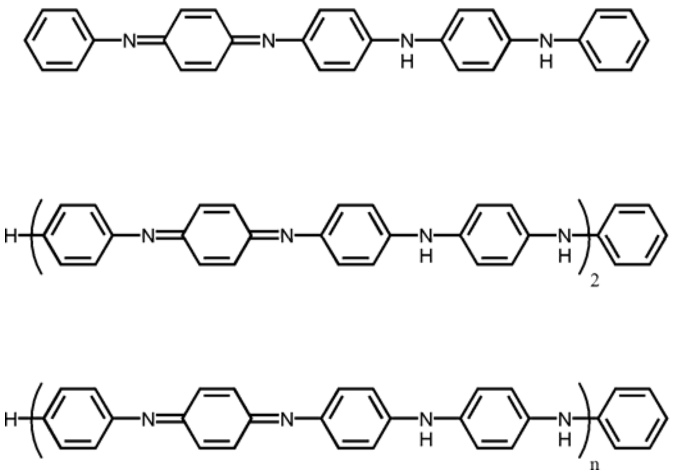
Current Theme 1

Switching structure and function



Conductivity

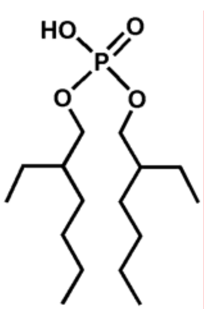
Aniline-based nanostructures…



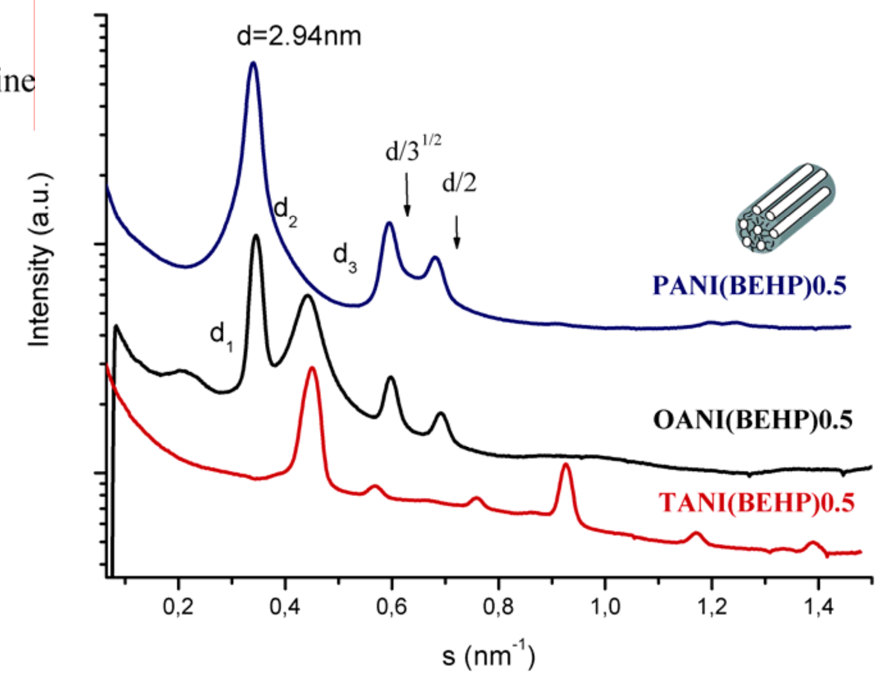
Tetraniline

Octaaniline

Polyaniline

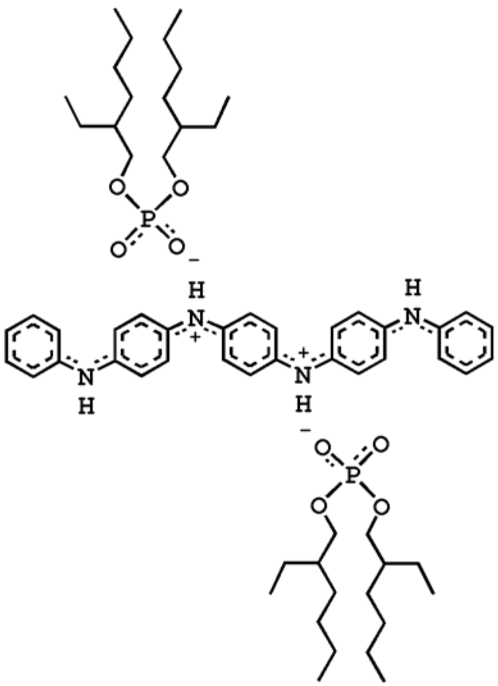


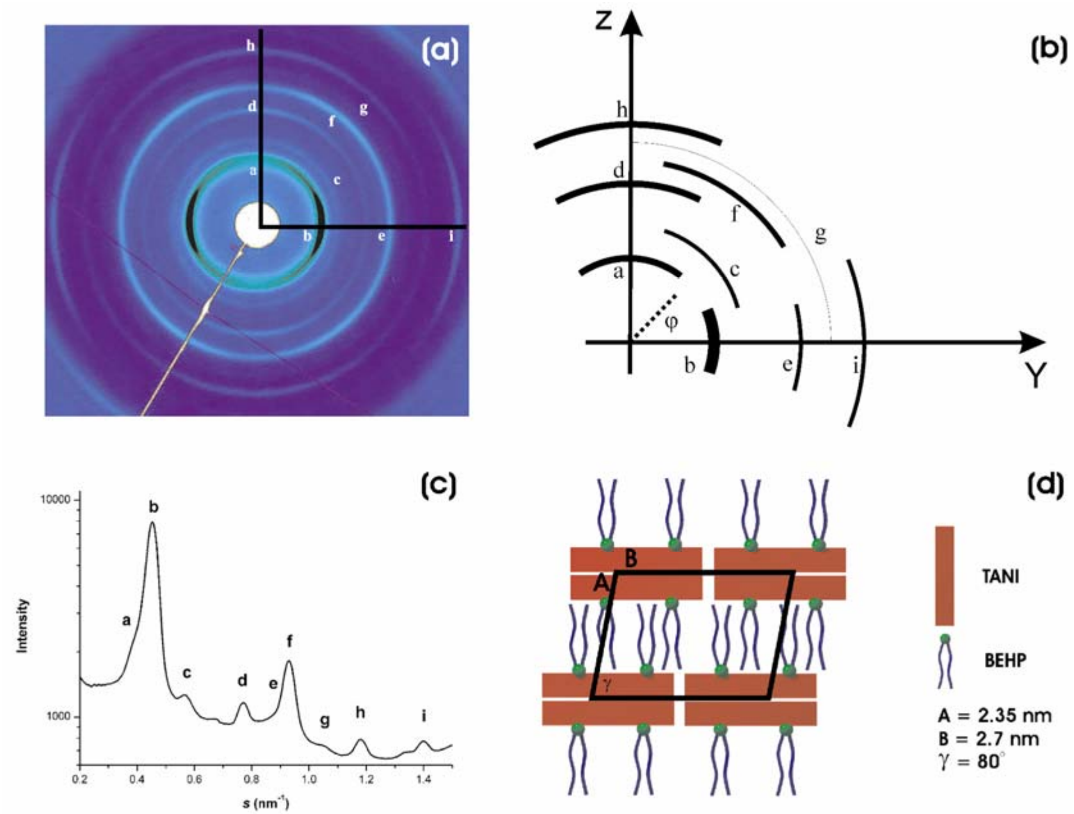
- PANI(BEHP)$_x$
  - Hexagonal phases
- OANI(BEHP)$_x$
  - Mixture of phases



Oligoanilines

- TANI-surfactant

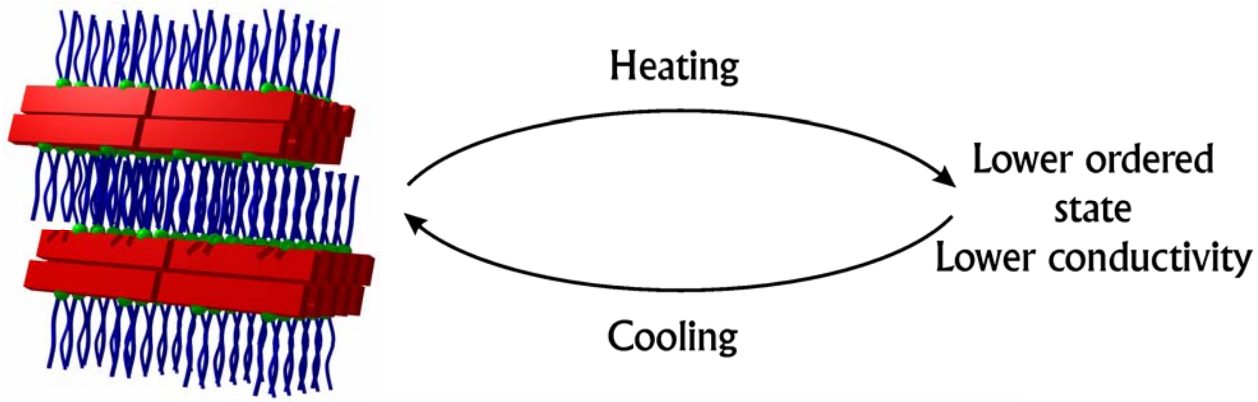


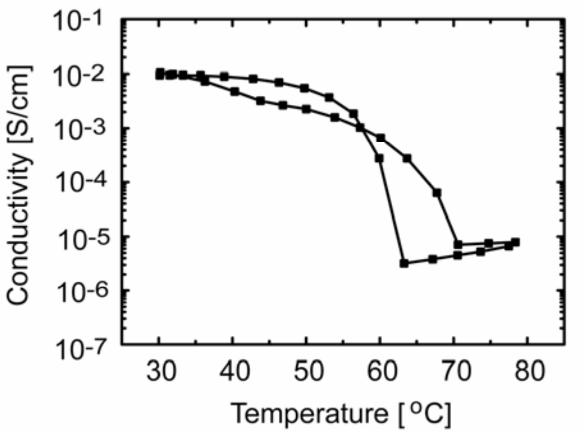


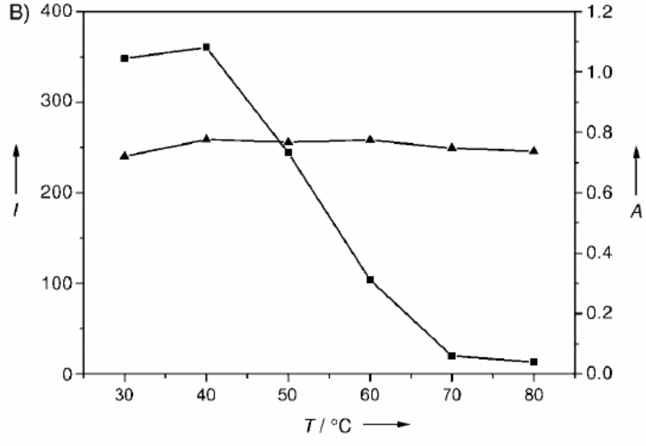
- 15-20 nm stacks of TANI units

Oligoanilines (cont'd)

- Conductivity?







(X-ray vs. UV)

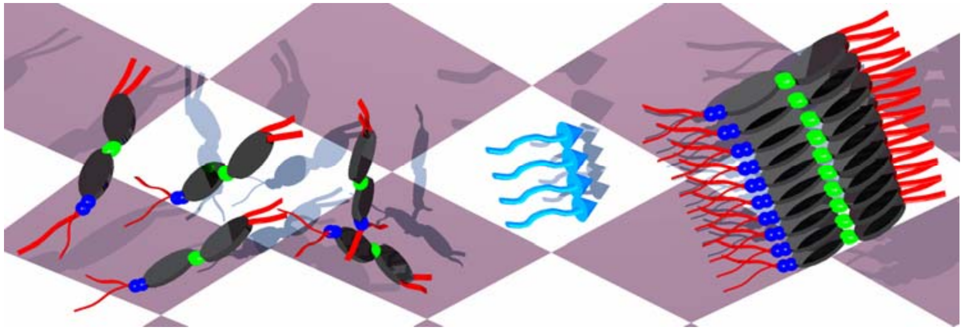
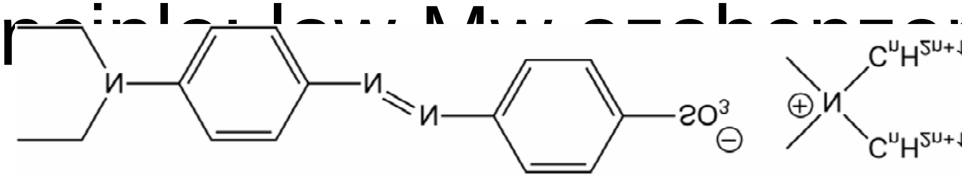
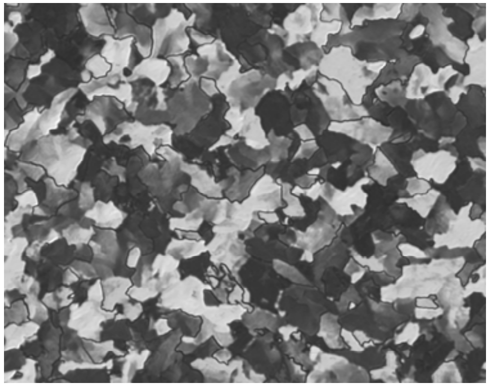


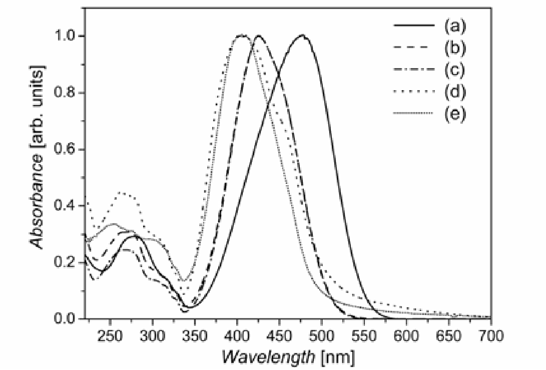
Photo-orientation & Anisotropic properties

Photo-orientation

- Non-mechanical approach to alignment
- Relevant & Important for display technologies
- Proof-of-prin[illegible]ne materials







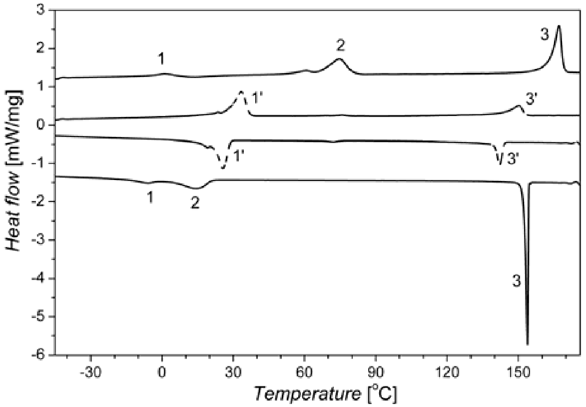
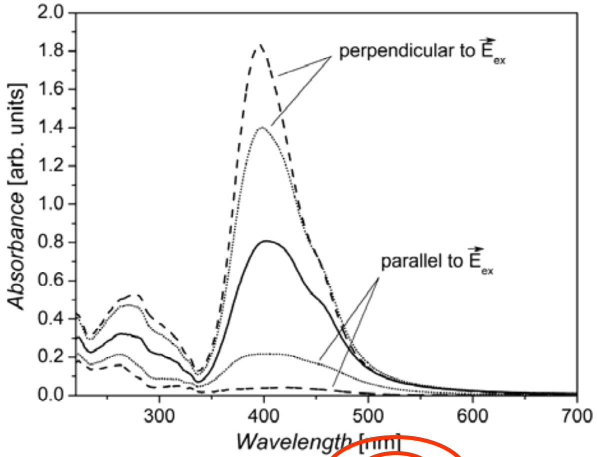
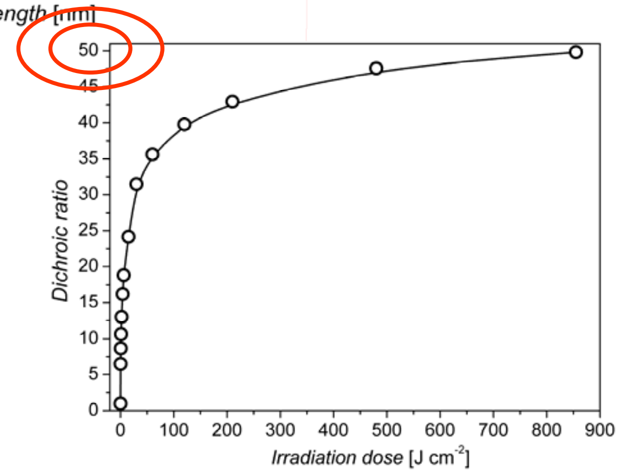
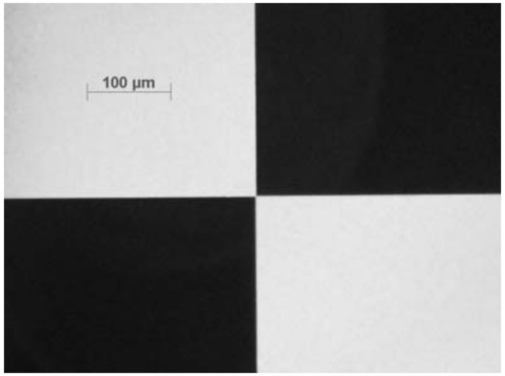


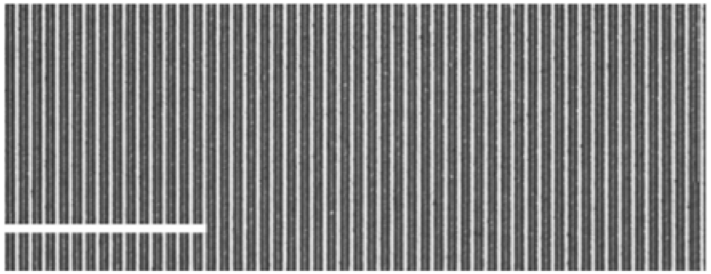
Photo-orientation

- Irradiation with polarized Ar laser, 488 nm









After irradiation with two circularly polarized interfering beams

Properties ...

- Dichroic Ratios in the range of 20 – 50
- Satisfactory diffraction efficiency
- Efficient LC alignment layer
- Long-term and thermal stability
  - >12 months, up to 200°C
- Ease of synthesis, processability
  - (spin-coating, benign solvents)

Adv. Mater. **2006**, *18*, 2133

Possible opportunity

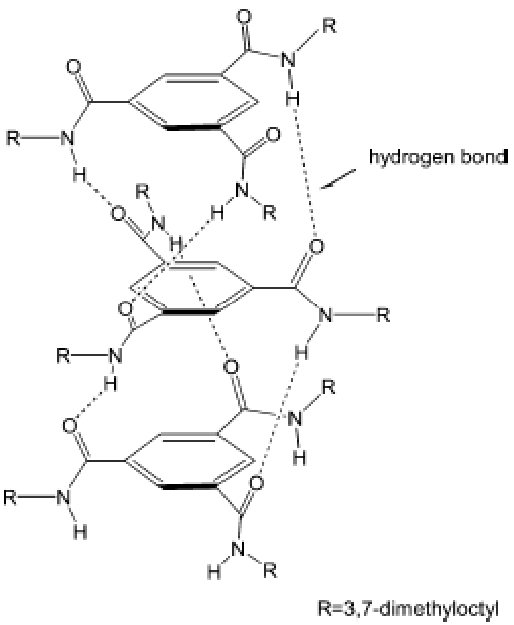
- Combination of biological tectons with conducting TANI tectons?
- Defined biological function now switchable through phase changes?

Current Theme 2

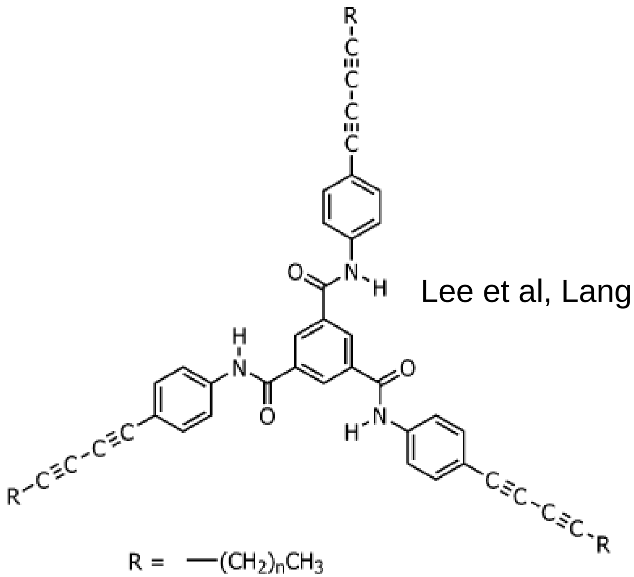
Switching structure

New system – one step back

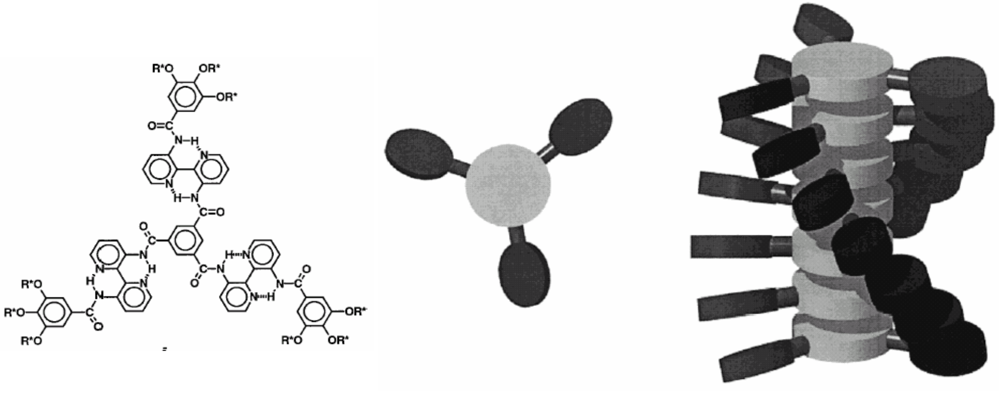
Covalent and H-bonding ...



Shikata et al, JPC B, 2004, 108, 508



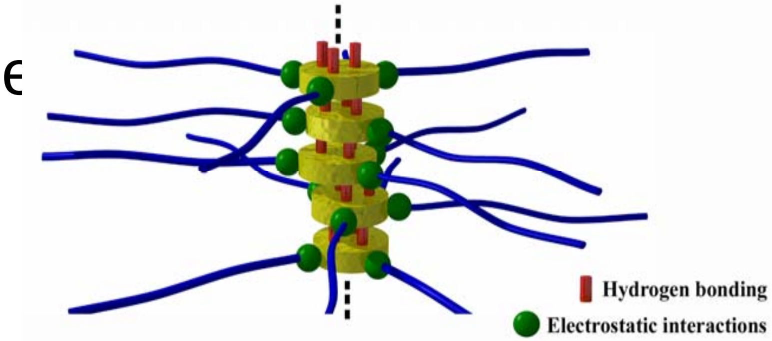
Lee et al, Langmuir 2004, 20, 9513

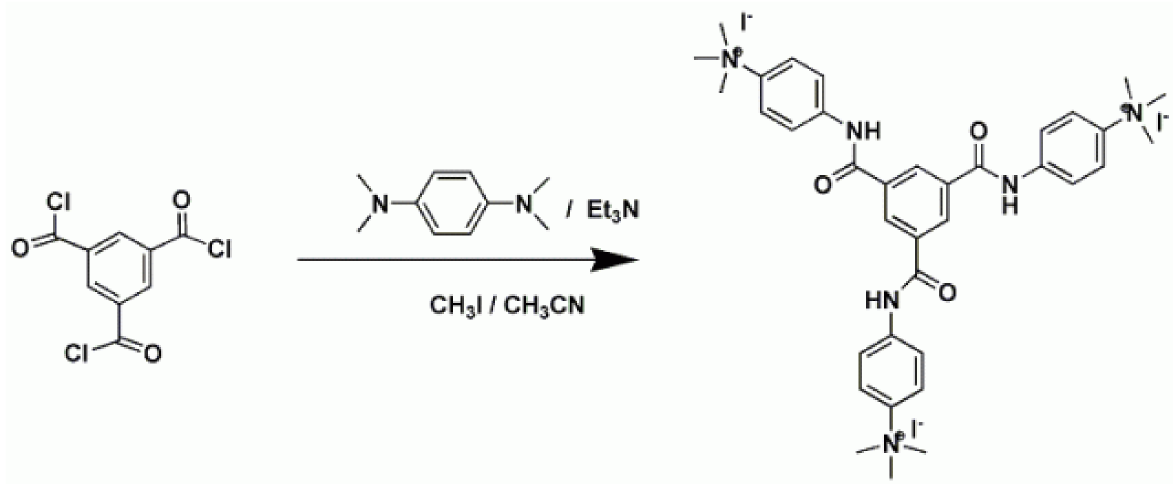


Van der Schoot et al., Langmuir 2000, 16, 10076

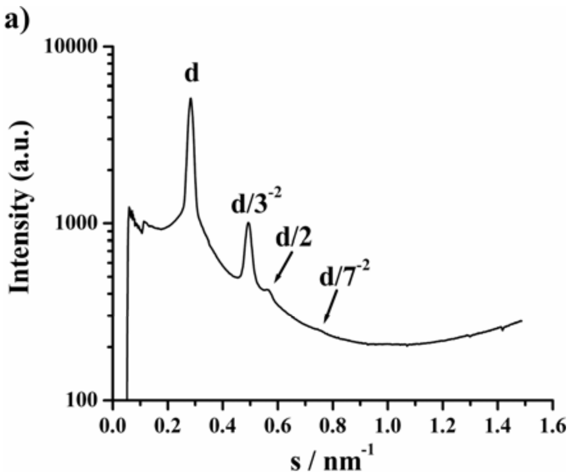
Electrostatic & H-bonding

- Combination of noncovalent interactions?
  - Directionality from the H-bonds (covalent analogue)
  - Organised mesophase
  - Organogelator?
  - Switchability?



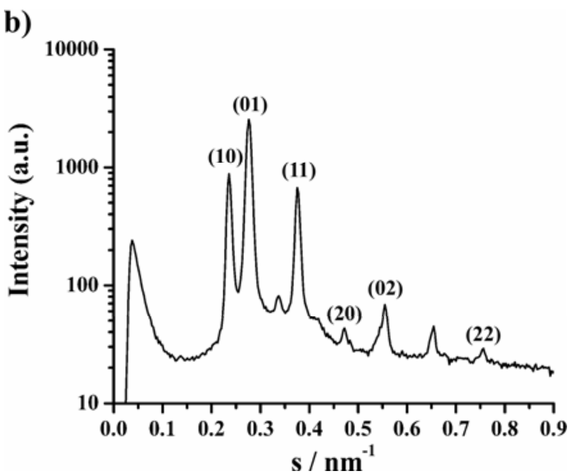


Multiple Interactions (cont'd)



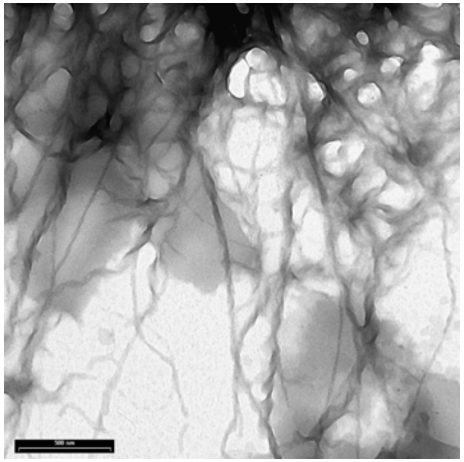
$C_{16}SO_4^-$

No gel formation



$DiC_{16}PO_4^-$

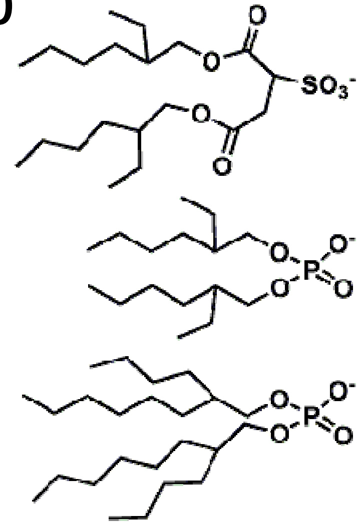
DMSO



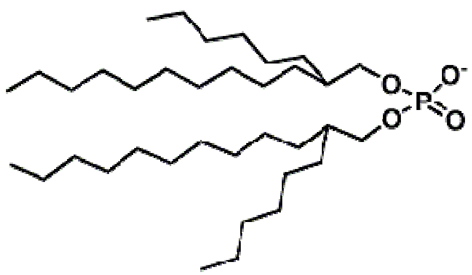
Chem. Commun., **2003**, 1958

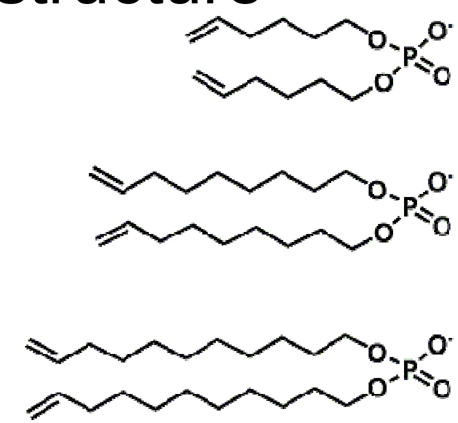
Towards addressable structures…

- Investigate structure-properties relationship
  - synthesize new phosphodiester surfactants
  - changes in alkyl volumes, functionality



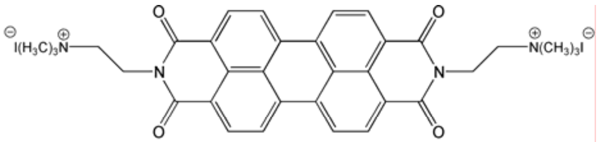
- Simple external stimuli
  - temperature, solvent for gelation
- Investigate changes in structure
  - synchrotron
  - solid-state NMR
  - IR etc.



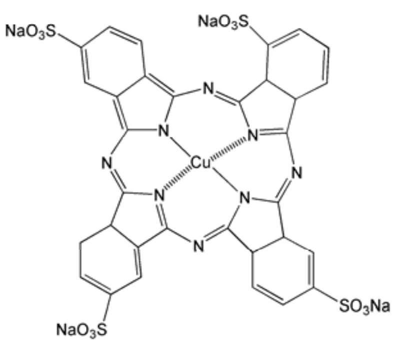


Electrostatic & Stacking

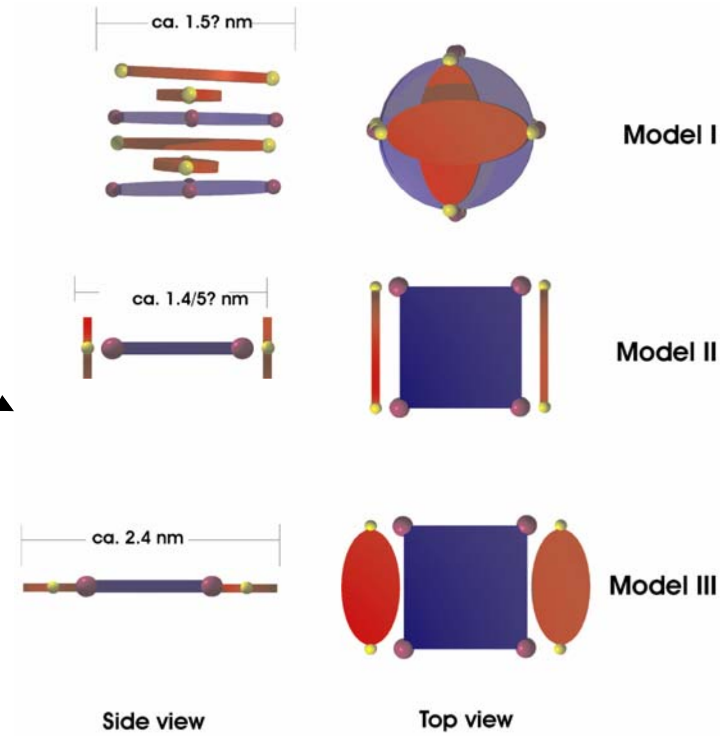
3D Network



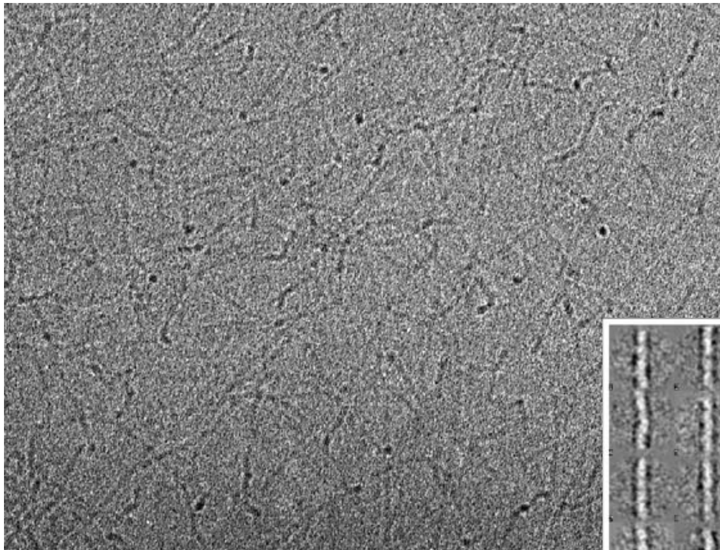
PTDI-1

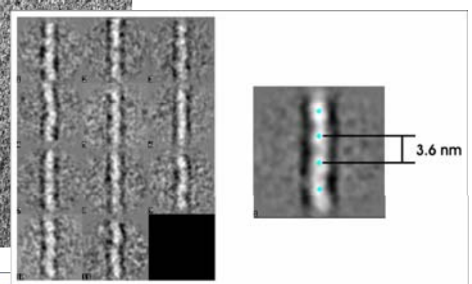


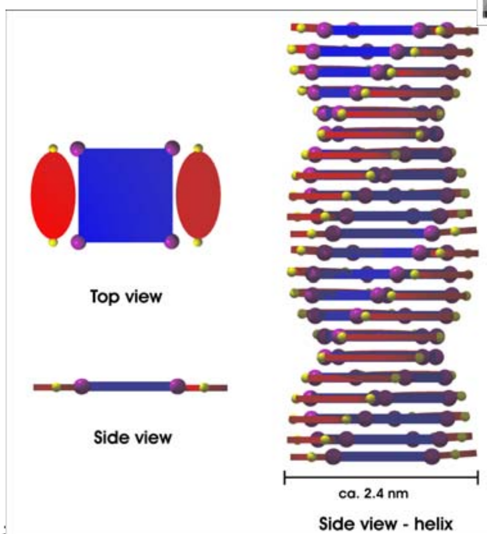
CuPcTS

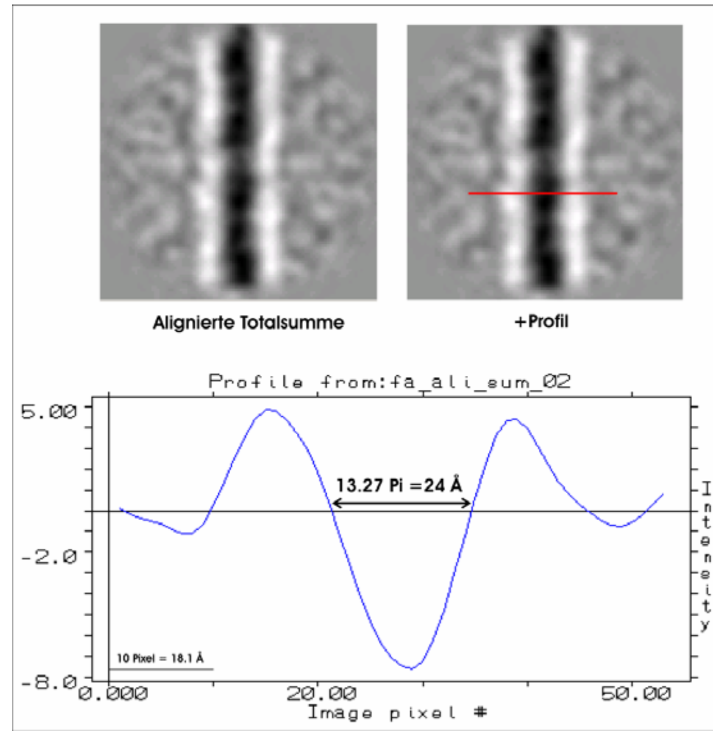


Hydrogelator







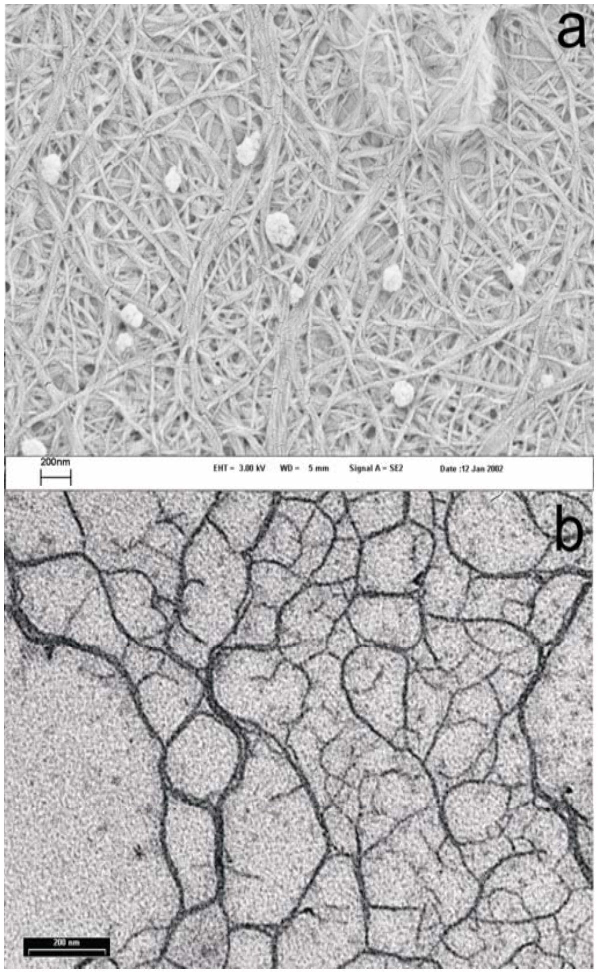


- *X-ray, UV, fluorescence*

University of BRISTOL

Cryo-TEM (C. Böttcher, FU Berlin)

Template / Scaffold



$CaCO_3$

CdS

Nanoparticle synthesis

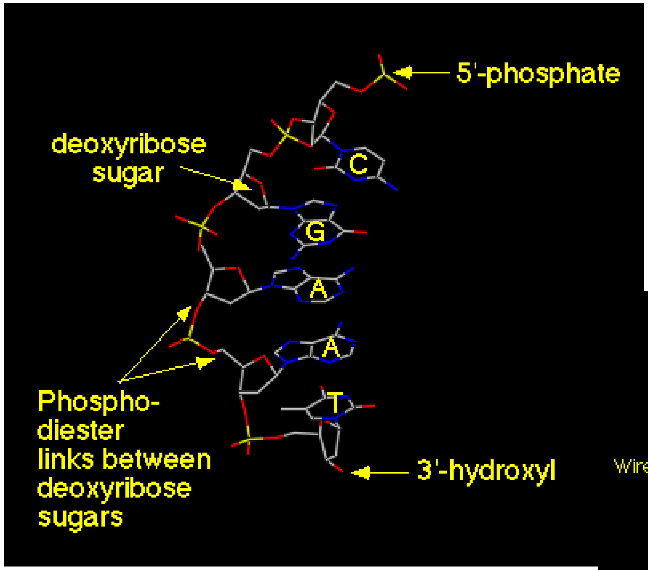
Possible opportunity

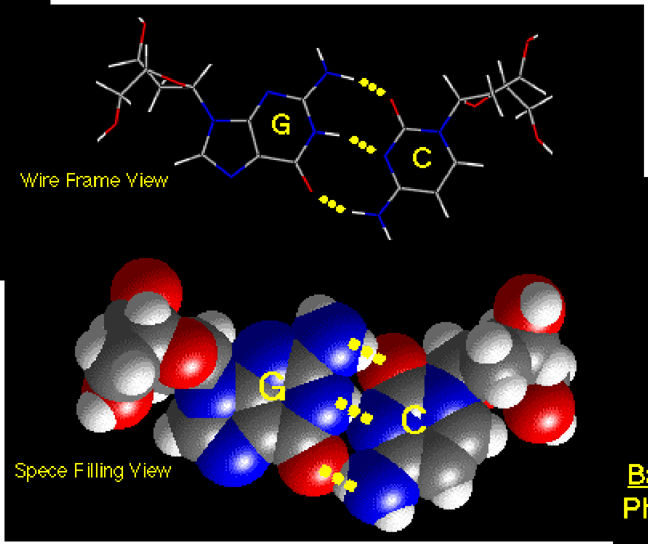
- Combination of biologically relevant tectons to form gels?
- Presentation of defined biological function in gel?

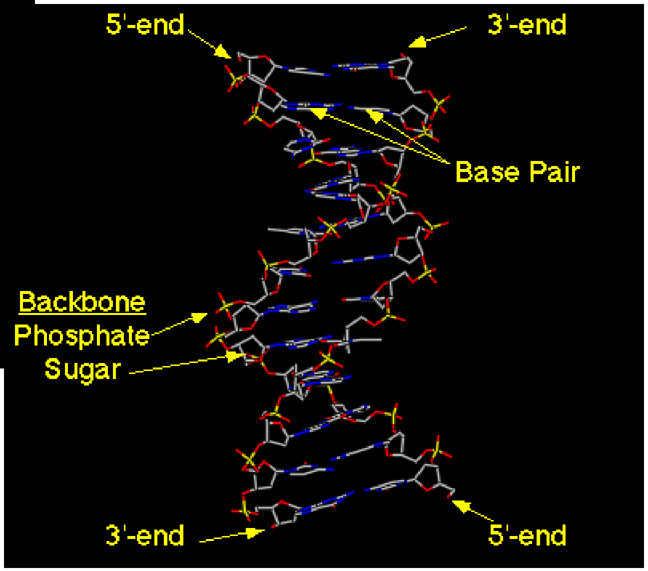
Current Theme 3

Investigating binding & structure

Biological design?

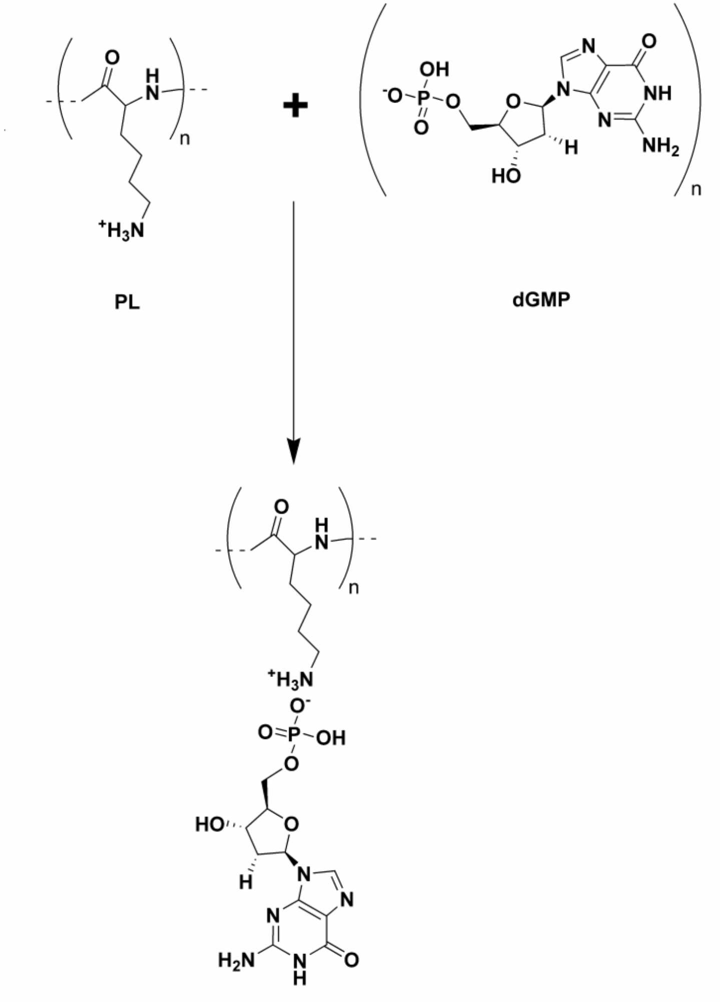




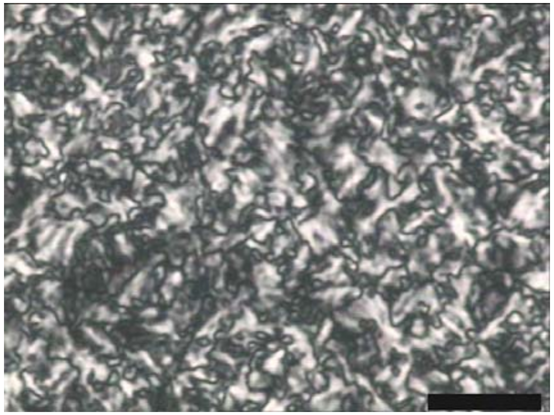


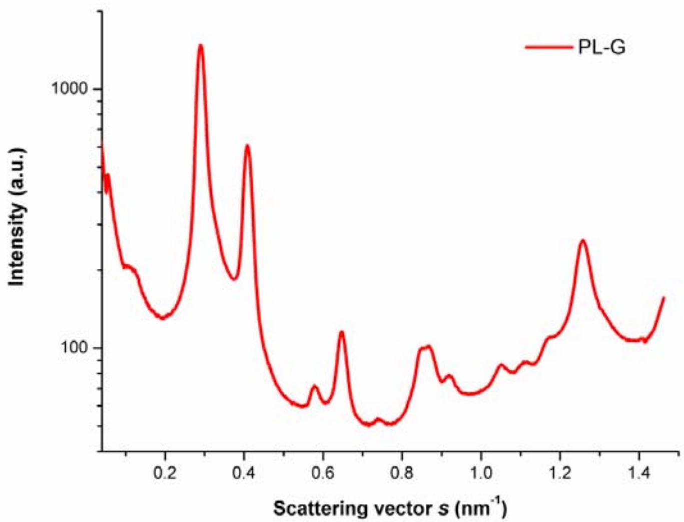
http://www.blc.arizona.edu/Molecular_Graphics/DNA_Structure/DNA_Tutorial.HTML

more Bio than DNA?

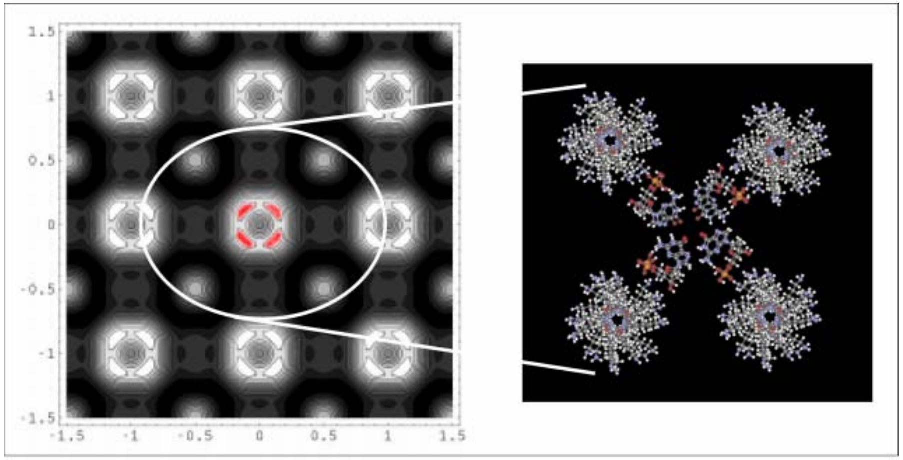


Polylysine-dGMP (PL-G) ISA Complex

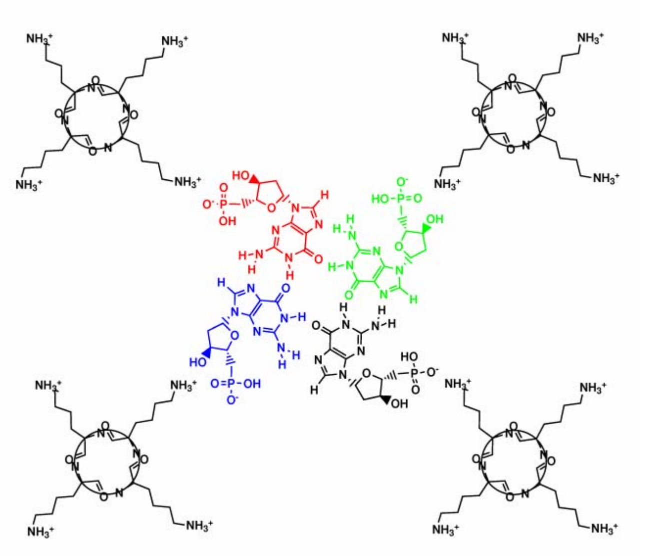




G-quartet structure

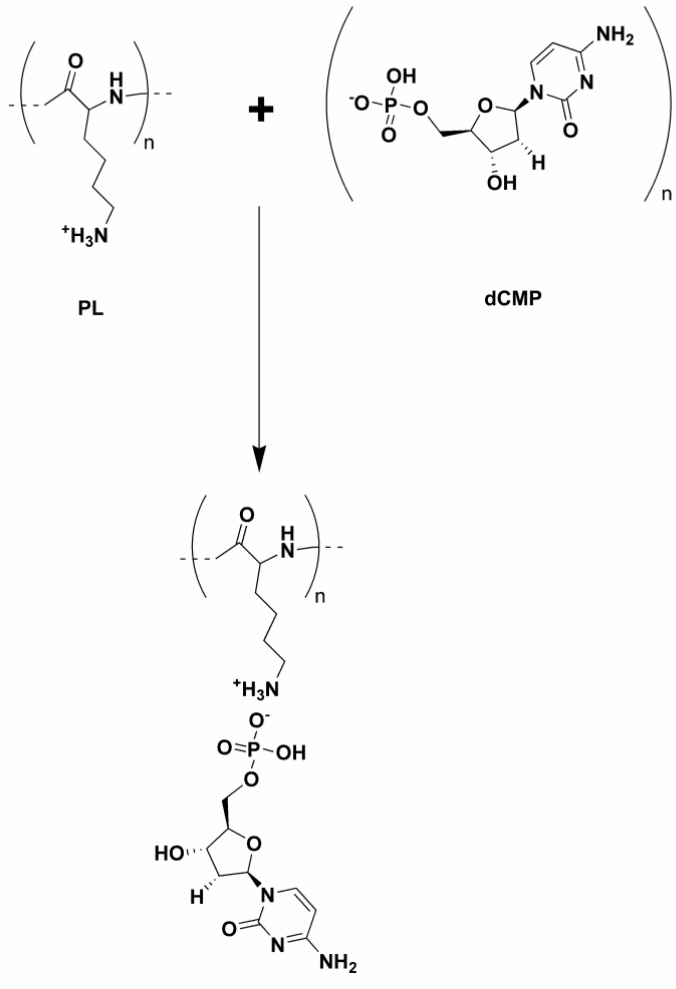


G-quartet



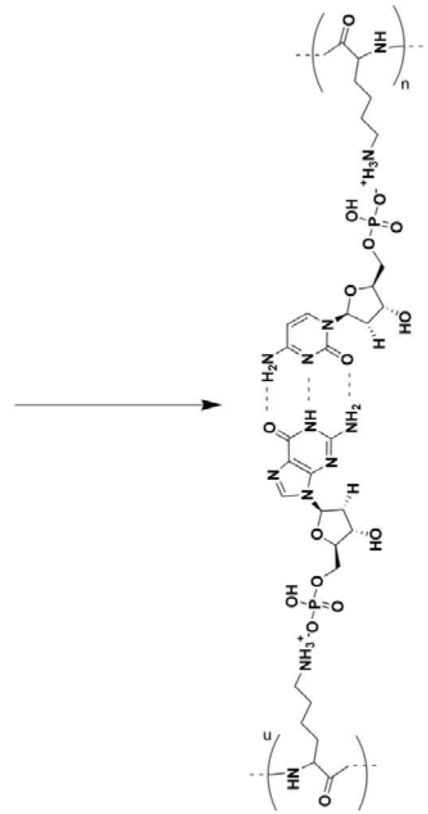
- Use IR for sugar conformation
- pLys?
- Geometrical considerations

DNA analogue…



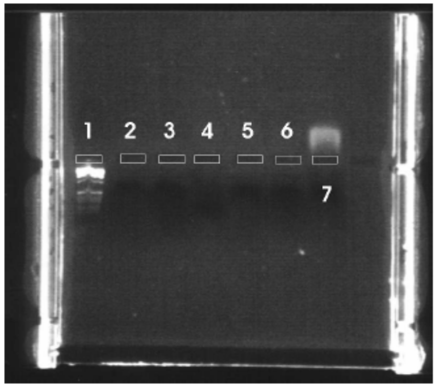
Polylysine-dCMP (PL-C) ISA Complex

PL-C



PL-G

-



+

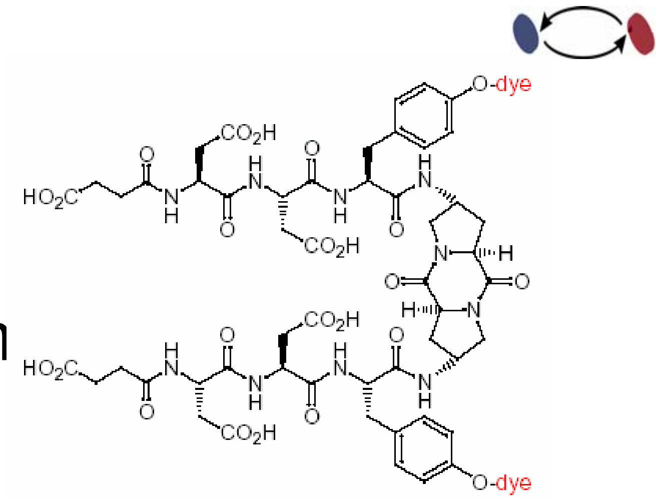
Some open questions ...

- What exactly is the degree of binding?
  - dGMP vs dCMP
- What is the conformation of the pLys chain?
  - vs pDADMAC
  - oligopeptides
- What is the structure of the DNA analogue?
- Structure refinement / improvement?

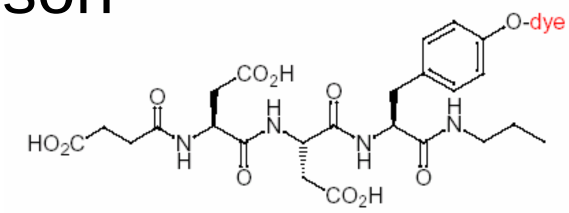
Recognition?

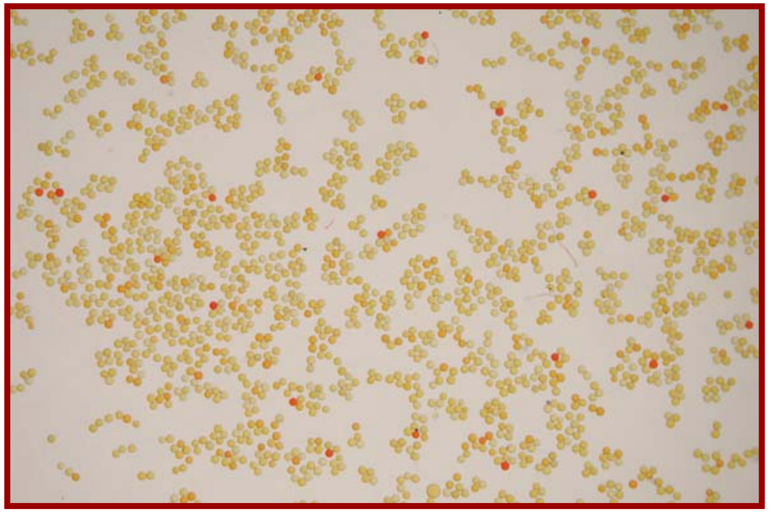
Bio-Recognition

- Diketopiperazine receptor
- Rigid scaffold for recognition
- Two variable arms (tripeptides)
- Dye-marked for comb. approach
  - split-and-mix approach on resin
  - 31^3 possibilities



- Synthesized arm only
- Comparison



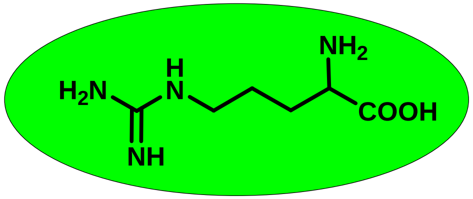


Switching of recognition?

- Binding to Arg-Arg-X (where X = either Arg, Ser, Thr or Cys)
- Binding constants (1:2 binding, ITC experiments)
  - K_1=2.5x10^4 M^{-1} and K_2=150 M^{-1}
- Addition of surfactant – immediate desorption

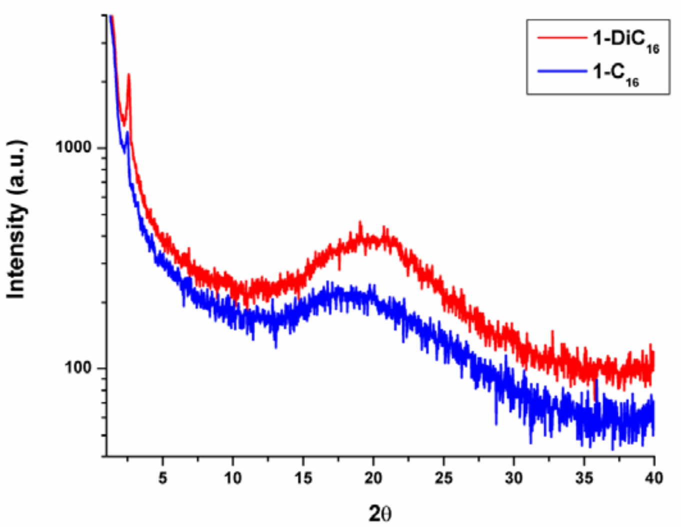
?

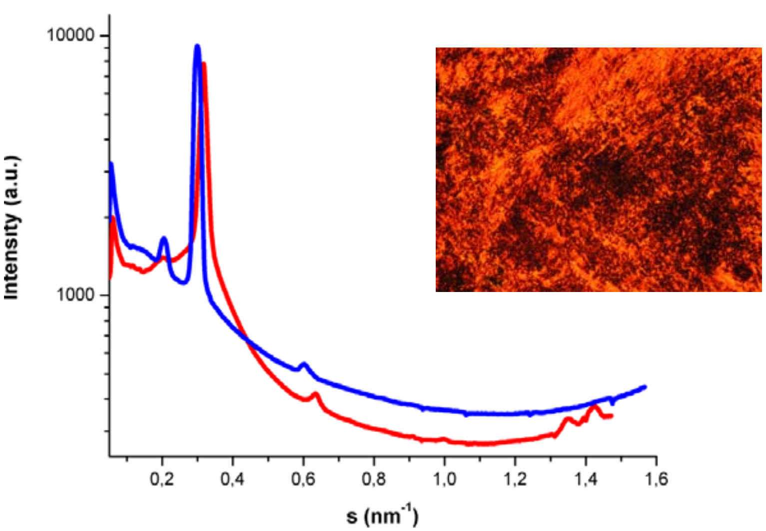
- ON/OFF switch only, or change in recognition?
- Would you be able to make a solid-state sensor?



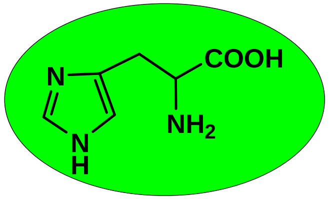
Peptide-Surf Complex

- Made solid state materials – thermotropic LCs





- Checked recognition capability (in solution, on beads)
- Now changed to His-His-X tripeptide sequences!



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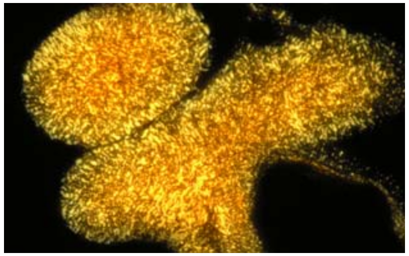
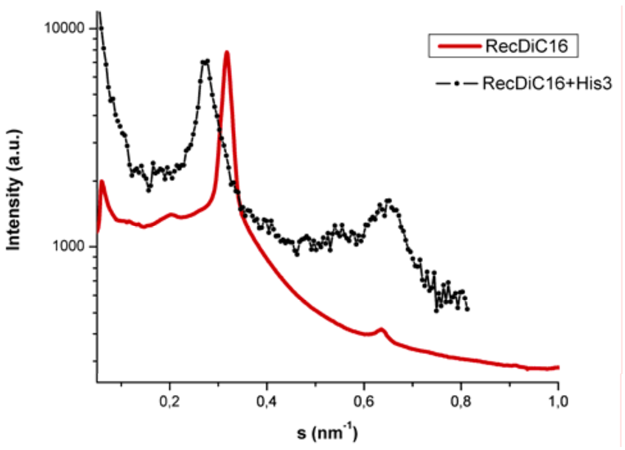
After binding ...

- Contact complex with His tripeptide?
- Marked shift to smaller scattering vector – i.e. larger structure (3.15 nm to 3.68 nm)
- Change in phase:





- from lamellar (layered)
  to (?) hexagonal (columnar)

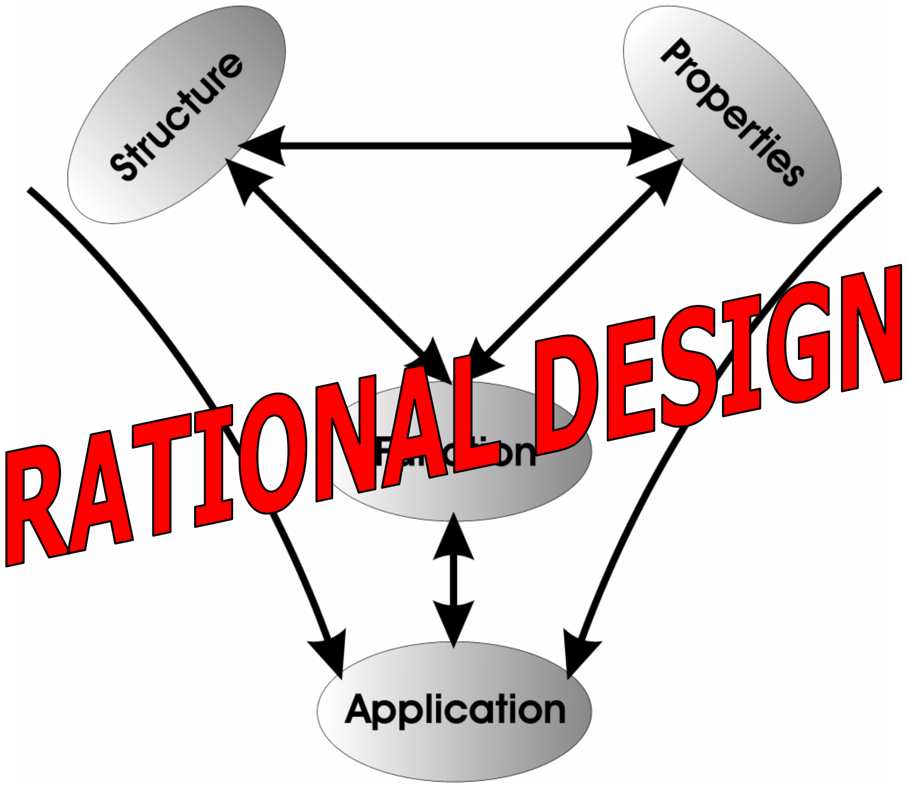
- Change in structure & function!
- Reversibility still an issue ...

Conclusion

- Facile ISA route to organise matter
- Toolbox for the production of functional LC materials
- Use of combinations of noncovalent interactions to tune phase behaviour, structure and function
- Switchability is on the horizon for a wide range of systems
- Still many basic questions to be answered

Towards Applications?

Structure $\leftrightarrow$ (Materials)Properties $\leftrightarrow$ Function



Designer Materials

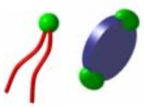
Syn. Met. **2004**, *147*, 63

Future Outlook

ESF SONS Programme: SISAM

– Structure Elucidation of Shear-Oriented ISA Materials

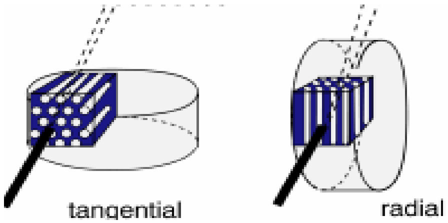
– Prof. Olli Ikalla & Prof. Gerrit ten Brinke

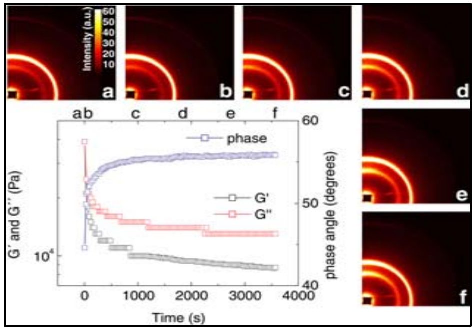


Synthesis of functional tectons, materials

- Surfactants (reactive), substituted perylenes, etc.

- Collaboration with HP
  - Towards devices?





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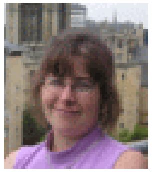


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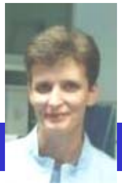
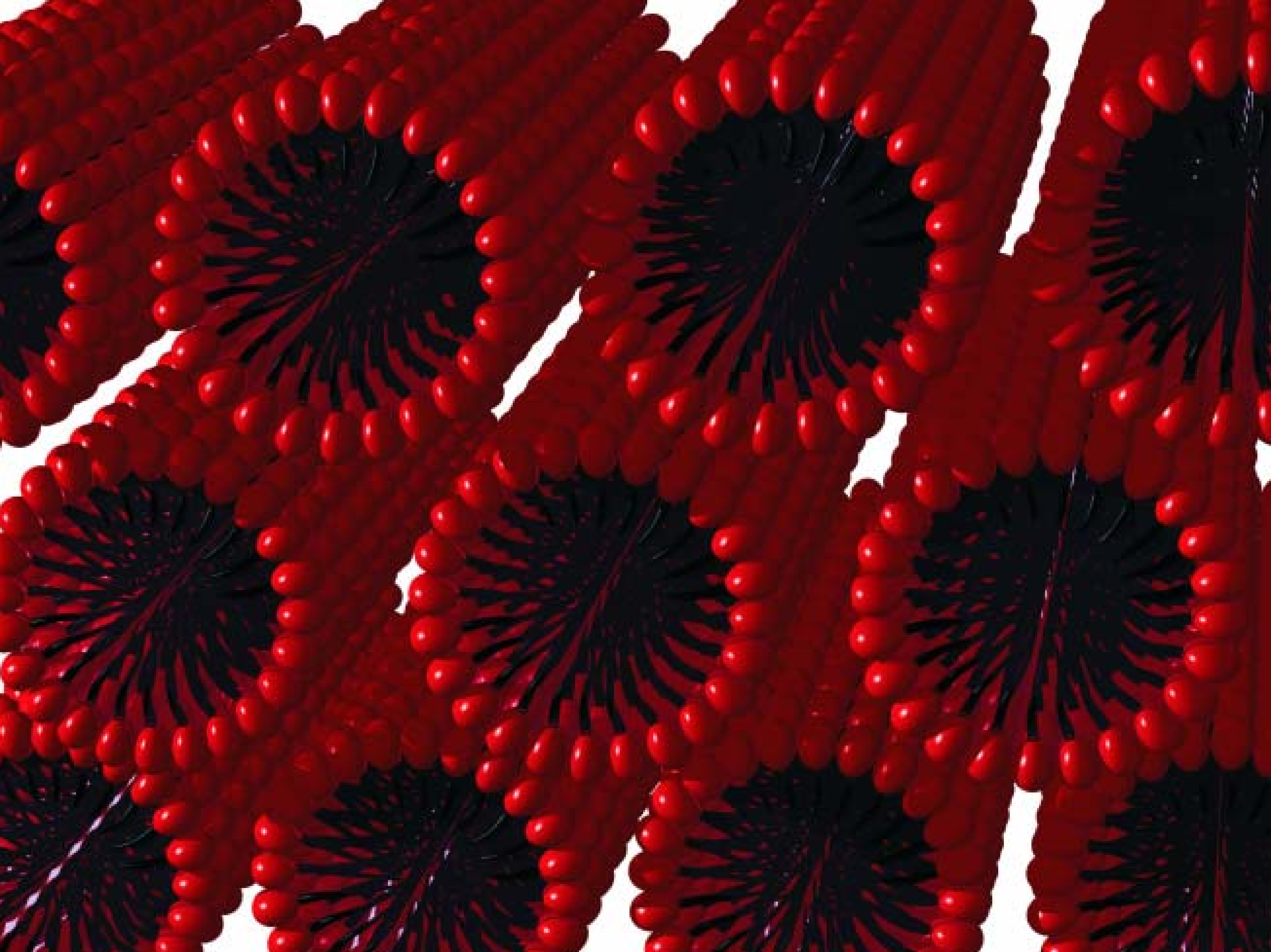
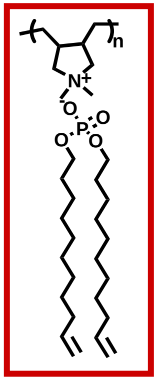


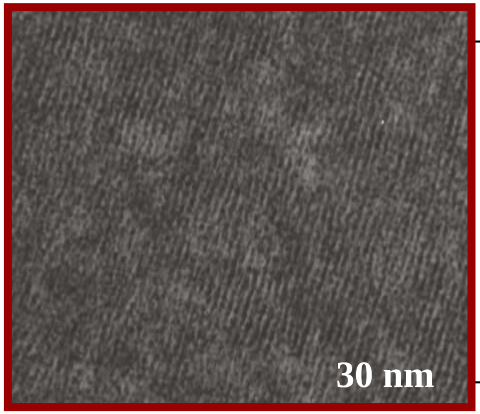



Thank you for your attention!



Polymerisation in Organised Media

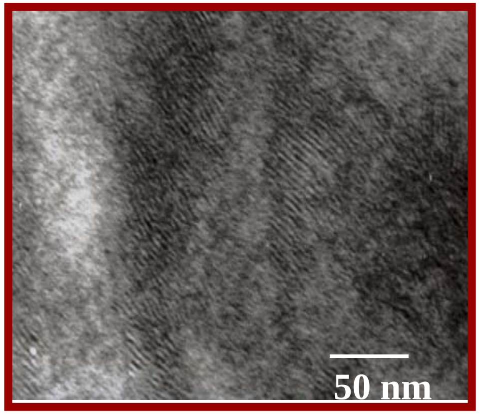




Complex

$HS-(CH_2)_6-SH$

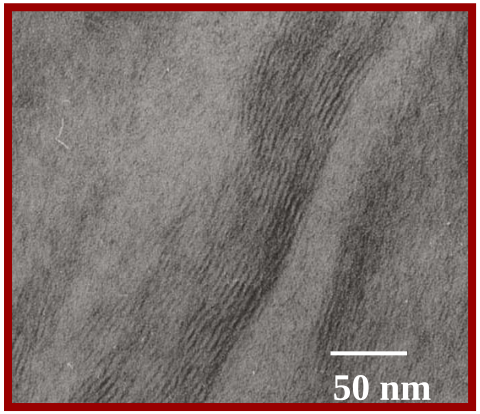
swelling 1:1 ratio
reaction @ 60°C



Complex + 6SH

$HS-(CH_2)_9-SH$

swelling 1:1 ratio
reaction @ 60°C



Complex + 9SH

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Macromolecules **2003**, *36*, 2862