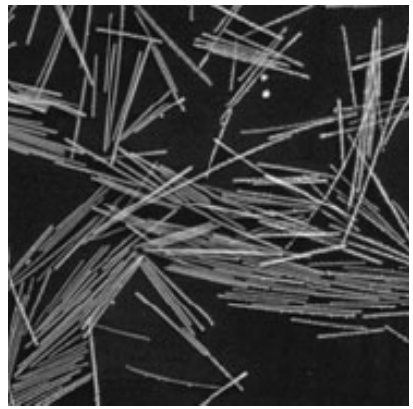
Organic Bottom Up Nanostrucures



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MB-JASS 2006

Introduction

- What is Bottom Up Design
- How it is perfomed in Nature - Proteins
- Micelles – self-assembly with simple methods
- Anisotropic Growth – simple anorganic Structures
- Monomers – what can be done
- DNA Templates
- Conclusion: What may be possible

Introduction

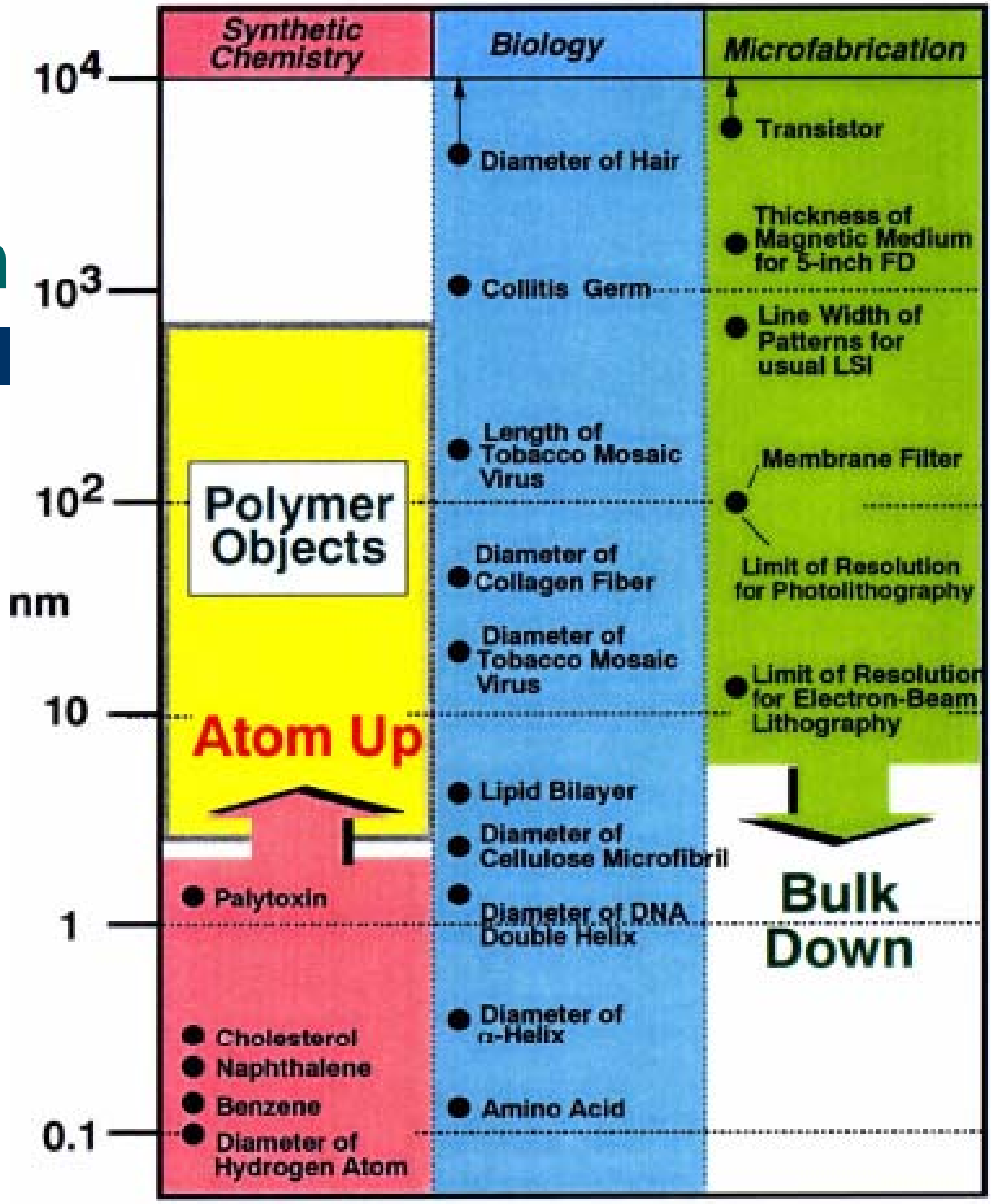
Four major production methods

1. Chemical Synthesis
2. Photolitography
3. Mechanical Manufacturing
4. Construction

5. Growth

Introduction

Why grow things at all ?



Introduction

Why growing makes sense:

- a gap in current production methods could be closed
- new technologies offer new possibilities (see also first example)
- to get the foundation of further nanostructure growth

Introduction

Is bottom up design suitable for mass production

- it competes with litography and synthesis
- in some applications it has the potential to be the most inexpensive method
- it uses little energy
- it is very accurate

Introduction

new phenomena associated with nanometer sized structures

- size dependent excitation or emission
- quantitized (or ballistic) conductance
- Coulomb blockade (or single electron tunneling, SET)
- metal insulator transition

Introduction

What can be achieved by nanostructures

- integrated circuits become smaller(=better)
- information storage
- electro-optical applications
- biology in future investigations

Introduction

How is self-assembly supposed to look like (for one-dim structures)?

like in chrystal growth atoms/molecules put themselves into the energetically most favourable order

the problems are in the control of the dimensions, the morphology and the monodispersity (or instead of mondis the phase purity and chemical composition)

Introduction

Forces used for the self-assembly

- coordination bonds
- hydrophobic interactions
- hydrogen bonds
- mechanical linkages

Proteins-An Example from Nature

Proteins are the perfect example for bottom-up nanostructures

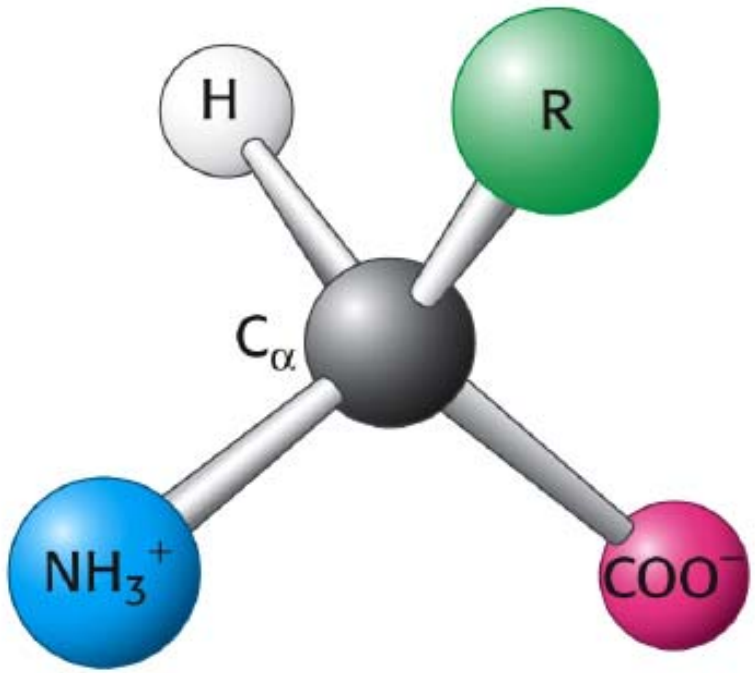
- perform numerous different tasks (walking, ecymatic activity, ion-punping, ect.)
- are made from a one-dimensional chain of twenty different amino acids
- build three-dimensional structures

Proteins-Primary Structure

Amino Acids (20+n)

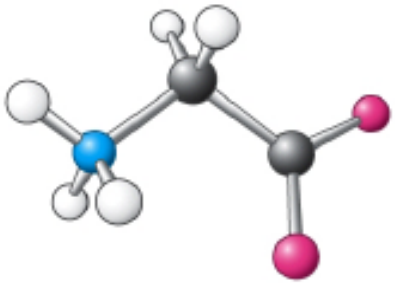
structure is the same for all Amino Acids

20 different amino acids have been observed being used in nature so far, but there could be more

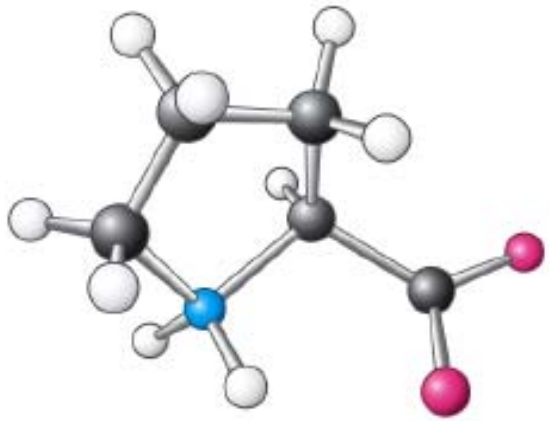


Proteins-Primary Structure

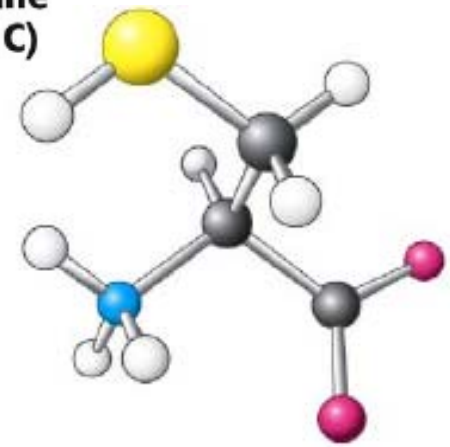
Glycine
(Gly, G)



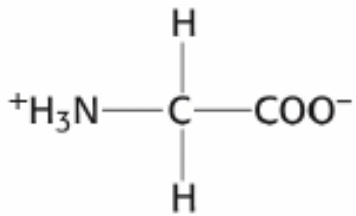
Proline
(Pro, P)



Cysteine
(Cys, C)



Proteins-Primary Structure



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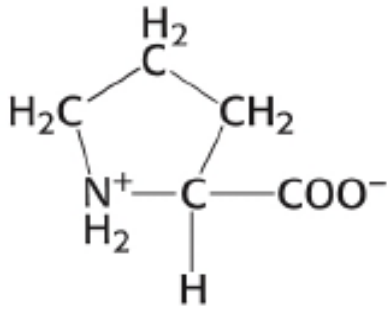

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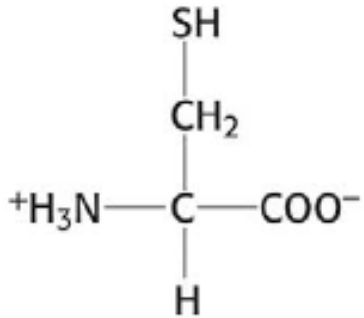
(Pro, P)



Cysteine
(Cys, C)

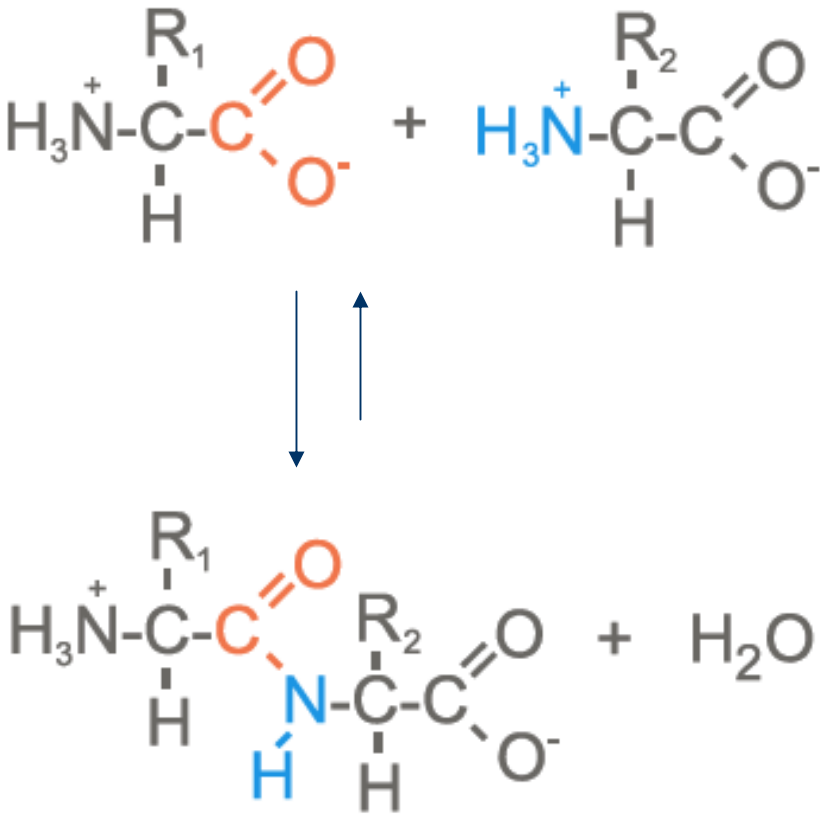
Proteins-Primary Structure

The Amino Acids are linked with peptide bonds

Peptide bonds: bonds that are formed between the carboxyl group and the amino group, releasing a molecule of water

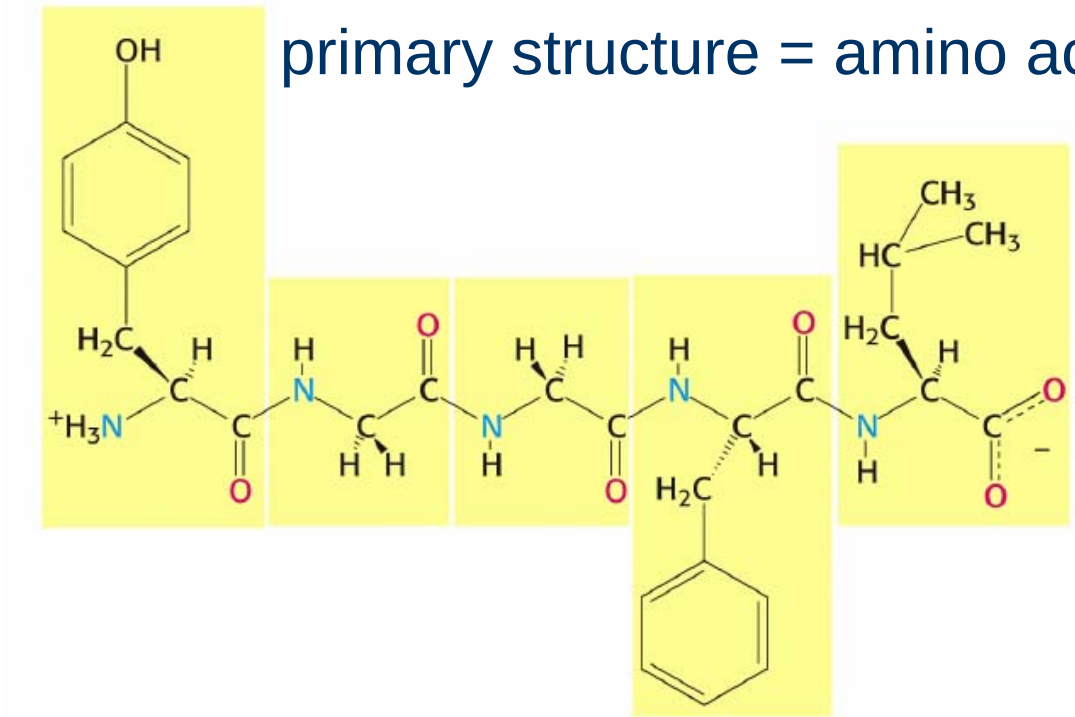
the reactive groups have to be activated first

Proteins-Primary Structure



Proteins-Primary Structure

primary structure = amino acid sequence



Proteins-Secondary Structure

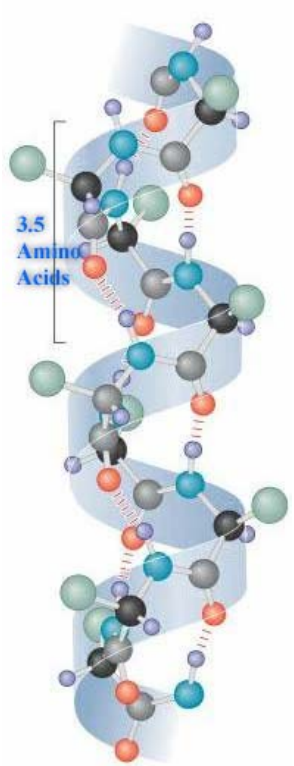
Primary Structure: gives information about the one diminsional order of the acids,

Secondary Structure: tells about the general three-dimensional form of local regions or overall shape of biopolymers. It may include regions of alpha helices, beta sheets, turns, and random coil, or a few less common structures.

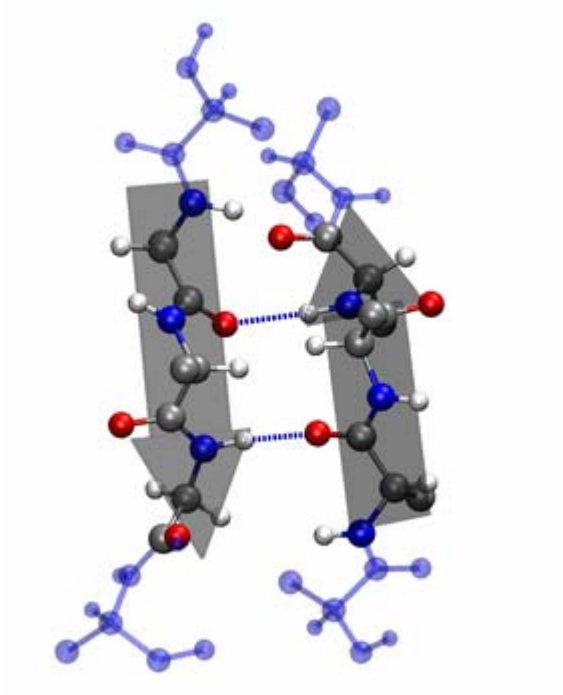
It does not, however, refer to specific positions in three-dimensional space, which are considered to be tertiary structure.

Proteins-Secondary Structure

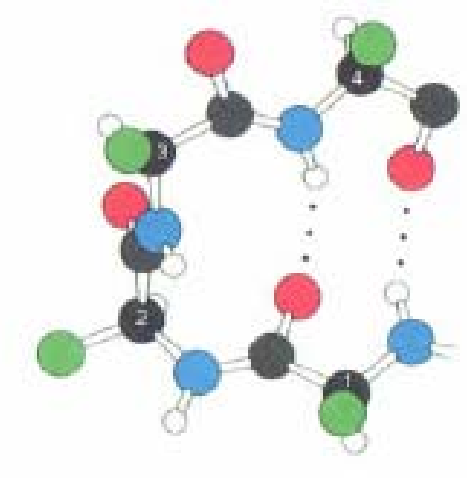
alpha helix



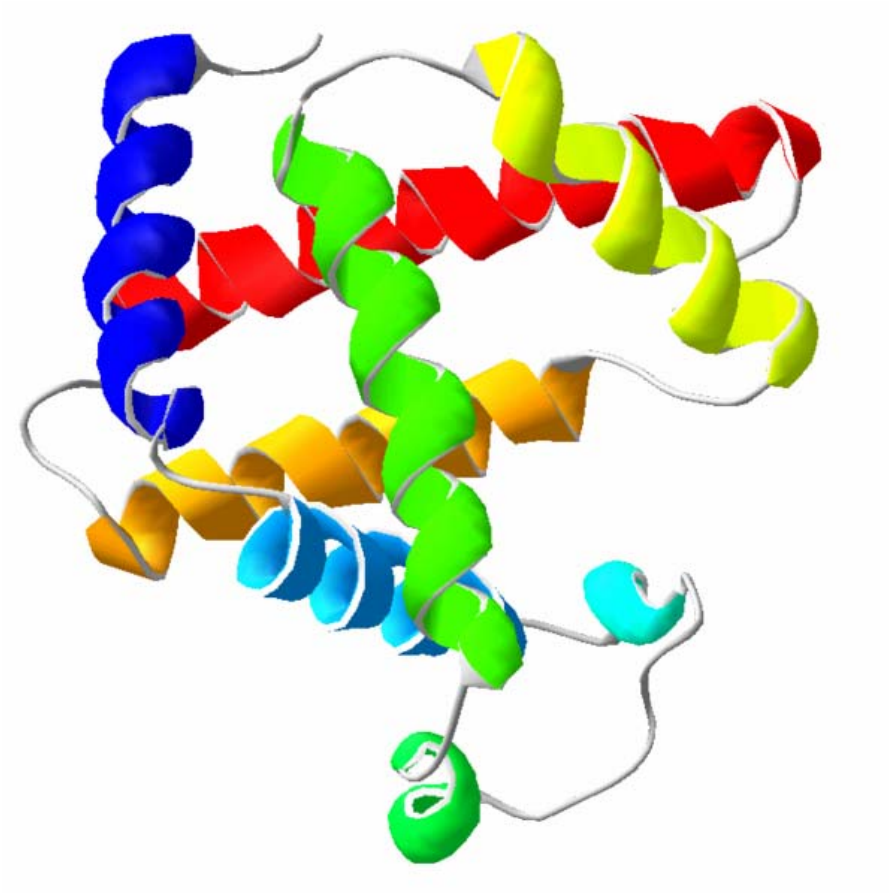
beta-sheet



random-coil



Proteins-Secondary Structure



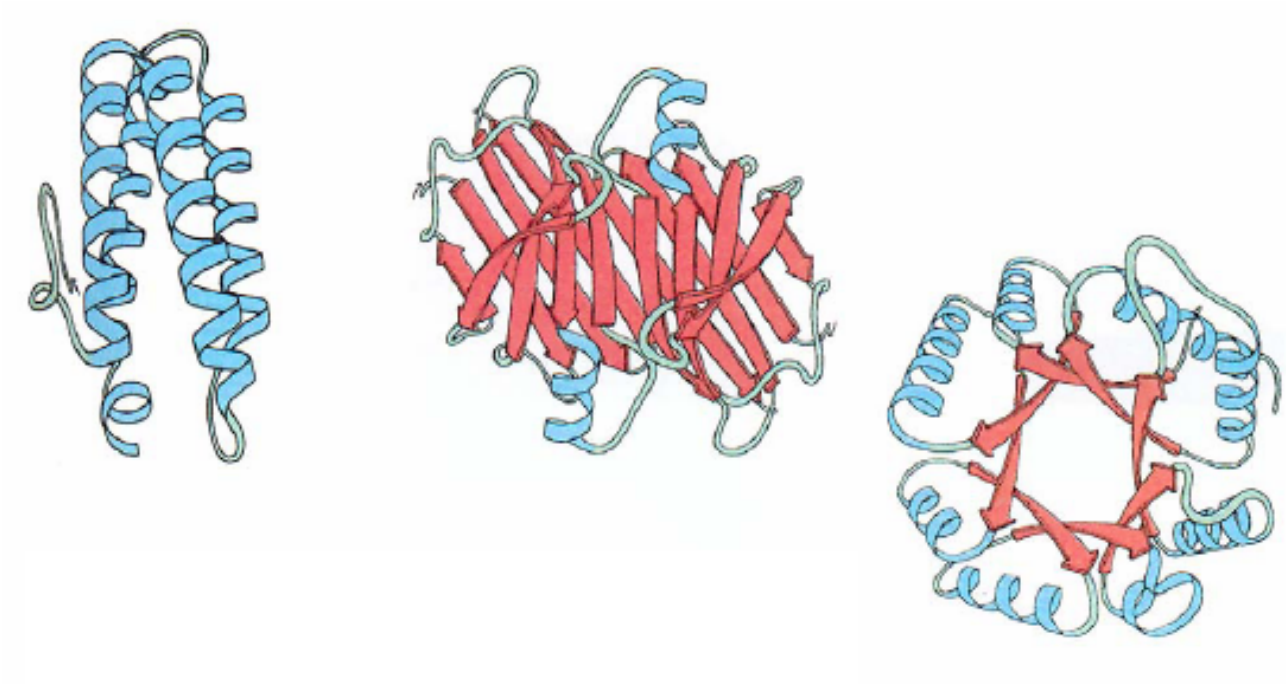
Proteins-Tertiary Structure

Usually the final structure of a Protein because quarternary structures do not exist for all proteins

while mainly hydrogen bonds are needed to form the secondary structure, the tertiary structure uses disulfur bonds

this stage is reached by folding, a technique little understood

Proteins-Tertiary structure



α β α/β

Proteins-Quarternary Structure

This structure does not exist for all proteins

It is made of different tertiary structures and sometimes involves strange atoms

It is stabilized with hydrogen bonds, ionic bonds and van-der-waals bridges

Proteins-Folding

Little is known about the exact way proteins fold

there are several competing unproven theories

The acids have different properties such as being sour, basic, hydrophob or hydrophil, which influences the folding process

It is very certain that hydrophobic interactions are the major reason for proteins to fold

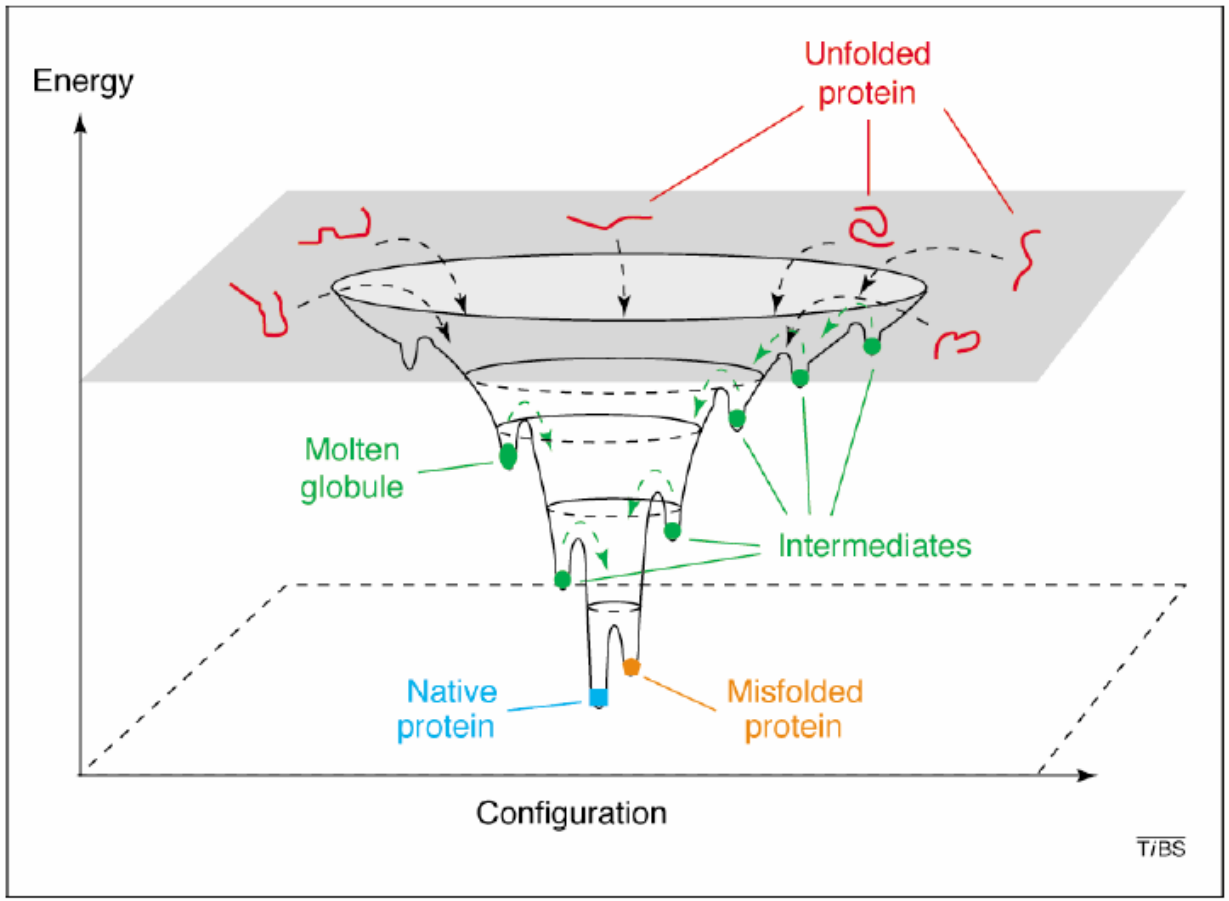
Proteins-Folding

The folding can be destroyed by changing any of the following parameter

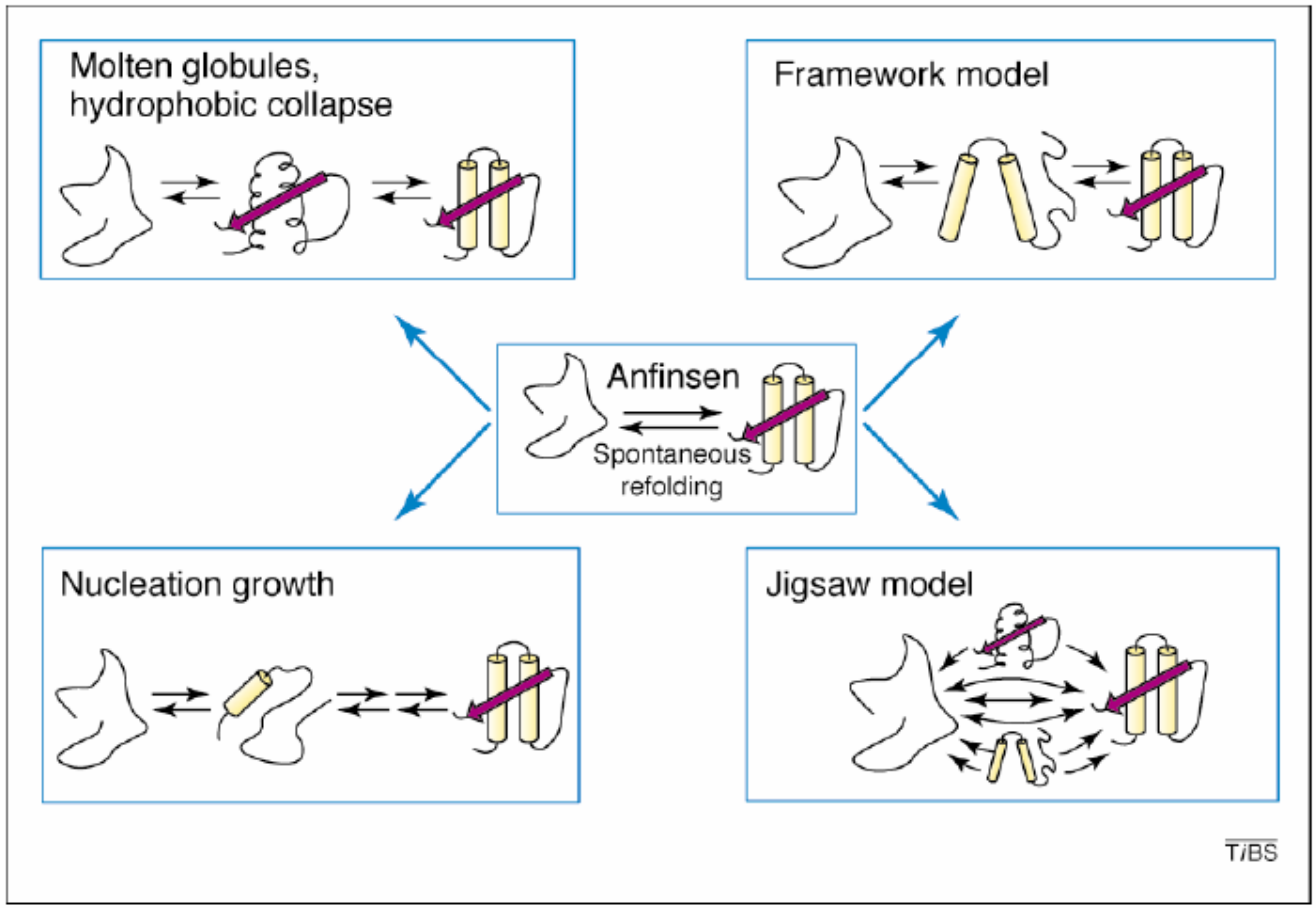
- Temperature
- Solvent
- pH

The Sequence of a protein completely determines its folded strucre, which is the minimun of its free energy

Proteins-Folding



Proteins-Folding



Proteins-Folding with Hydrophobicity

Protein folding carries a large entropic penalty

additional entropy loss through immobilization of each amino acid‘s side chain

Hydrogen Bonds give the drving force

Each amino acid has a different value of hydrophobicity

Polypetidechains would bury their hydrophobic residues in the interior

Proteins-Folding with Hydrophobicity

Experimentally confirmed:

- Most hydrophobic residues of proteins tend to be in the interior
- Analogous Proteins from different species can differ in their sequence, but the hydrophobicities of the core remain the same
- Artificial Proteins vary most when the exchanged sequences was most different in hydrophobicity

Proteins-Folding with Hydrophobicity

Experimentally confirmed:

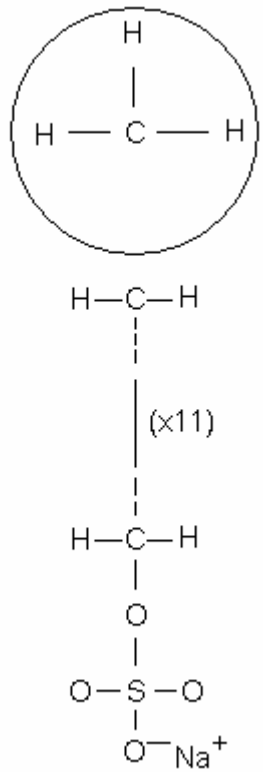
- Proteins unfold at high (55°C) and at low (20°C) temperatures
- Proteins denature in nonpolar solvents
- an extremely small amount of surfactants can unfold proteins (they shield hydrophobic regions of the chain, hindering them to interact)

Proteins-Conclusion

- Proteins show how complex self-assembeled nano devices could be designed
- should not limit the ideas (i.e. magnetic interactions are not used)
- understanding the folding process can give new insights into how to grow other structures

Usage of Hydrophobicity

- Amphiphiles are easy to create and self-assemlbe in polare solvents
- The hydrophobic effect evens out the loss in entropy
- If in the right concentration, they form micelles
- Two tailed amphiphiles form bilayers



Self-Assembly using Micelles

An example from state of the art technololgy:

Ordered deposition of gold nanoparticles from micellar block copolymer films

Au was ordered with poly(styrene)-*block*-poly(2-vinylpyridine) in toluene

Self-Assembly using Micelles

- Diblock-copolymers were dissolved in toluene
- they associated to micelles at a rather low concentration
- the amount of molecularly dissolved block-copolymers was vanishing small

Self-Assembly using Micelles

- The micelle solution was treated with $HAuCl_4$
- $HAuCl_4$+ were bound as counter-ions in the polar core of the micelles by protonating the pyridine untis
- The micelles were formed in equilibrium and the amount of Gold per micelle varied only in narrow limits

Self-Assembly using Micelles

- Typically one $HAuCl_4$/2VP can be taken by such a micellar solution
- The Au3+ ions were reduced by mixing the solution with anhydrous hydrazine in dry toluene to form one gold particle in each micelle

Self-Assembly using Micelles

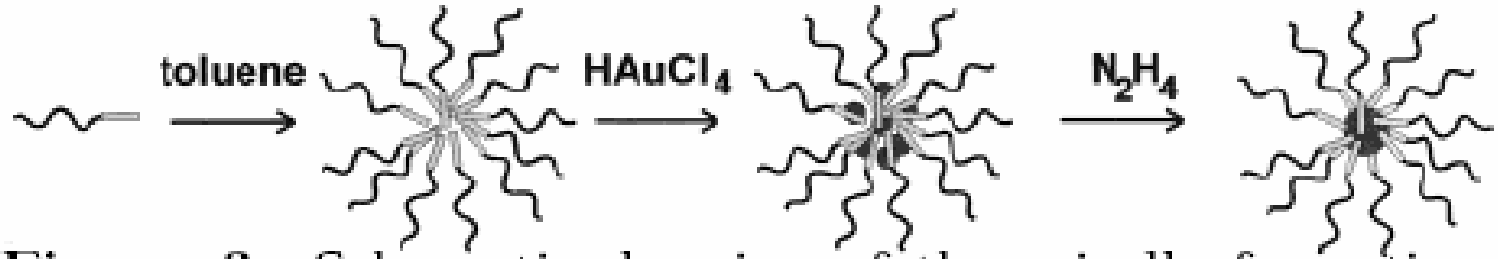


Figure 2. Schematic drawing of the micelle formation of poly(styrene)-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) block copolymers in toluene. After complexation of $HAuCl_4$ to the pyridine units in the micellar core, the metal compound can be reduced to the zero-valent state by chemical conversion, leading to exactly one gold particle in each block copolymer micelle.

Self-Assembly using Micelles

- To prepare a thin film, a suitable flat substrate (i.e. a glas plate) was dipped into the solution and pulled out at a constant velocity (~10mm/min)
- The fast evaporation of the solvent in combination with the vitrification of the polymere did not allow any major structural changes during the formation of the dry film

Self-Assembly using Micelles

The formation of a closed monofilm is effected by

- long range van-der-Waals interactions
- capillary forces between micelles acting during evaporation
- gold particles stabilizing the micelles as a ionic core block

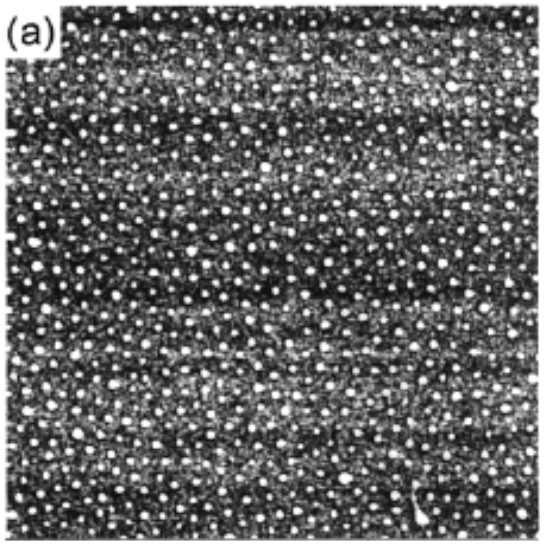
Self-Assembly using Micelles

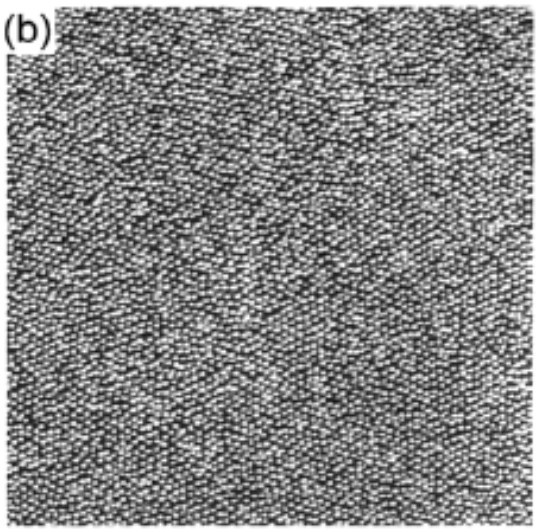
The result was a relatively thick, stable monomicellar film

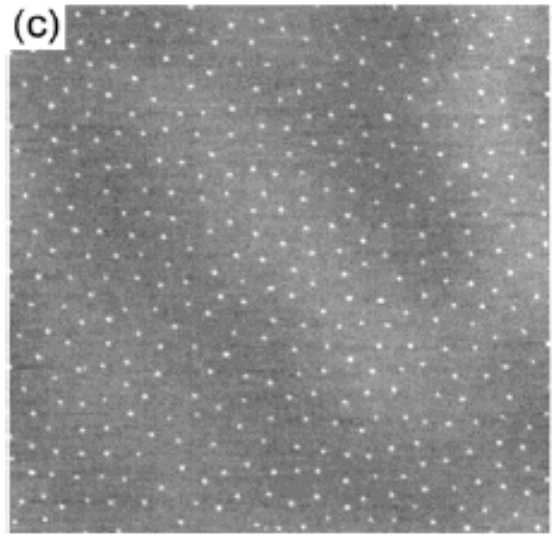
The coverage of the substrate with the film can be varyied by

- concentration
- velocity

Self-Assembly using Micelles





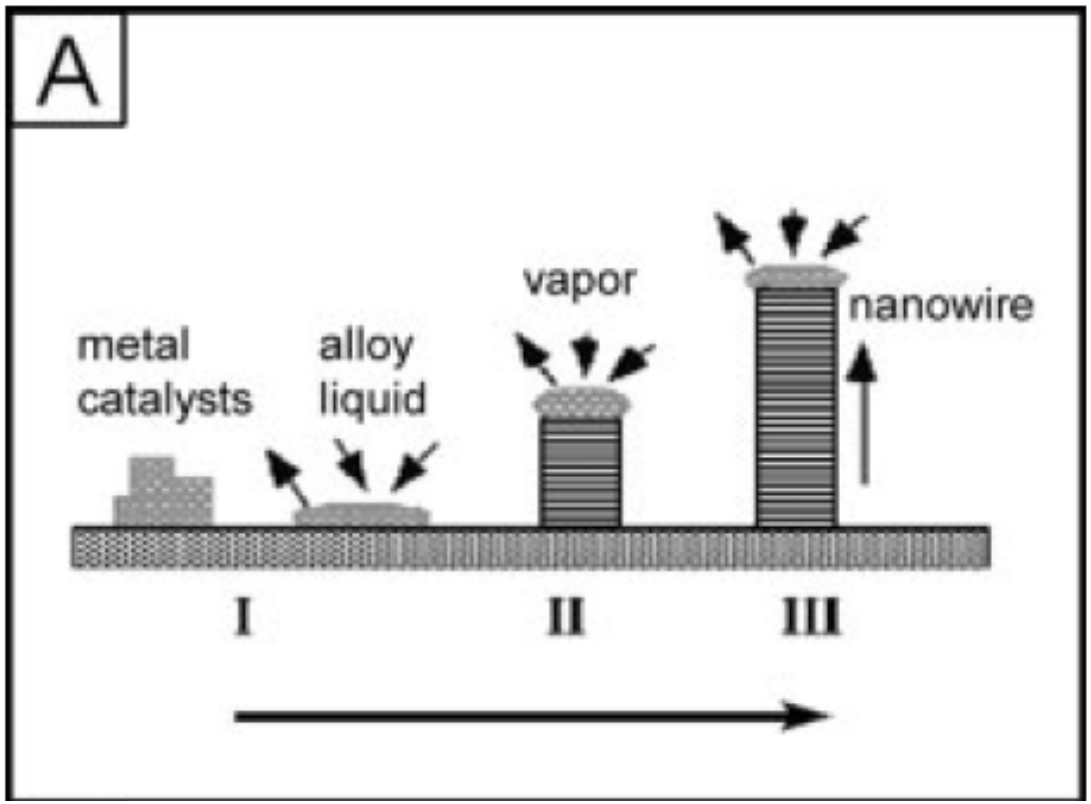


Self-Assembly using Micelles

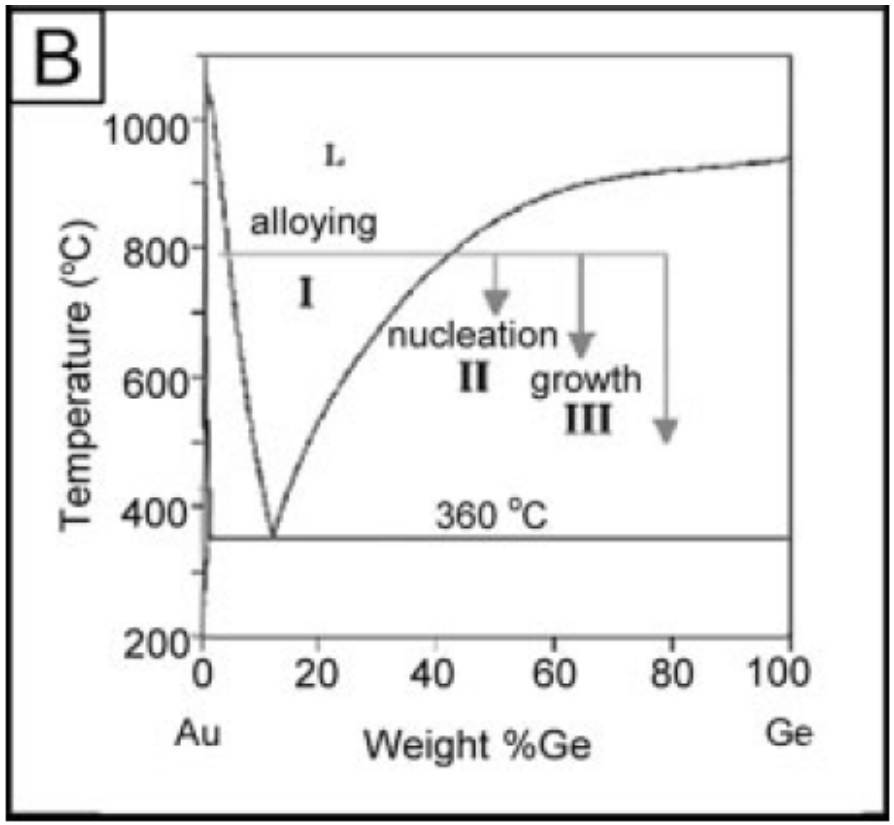
Applications:

- wetting experiments
- studies on cell immobilization
- as a substrate for crystall growth

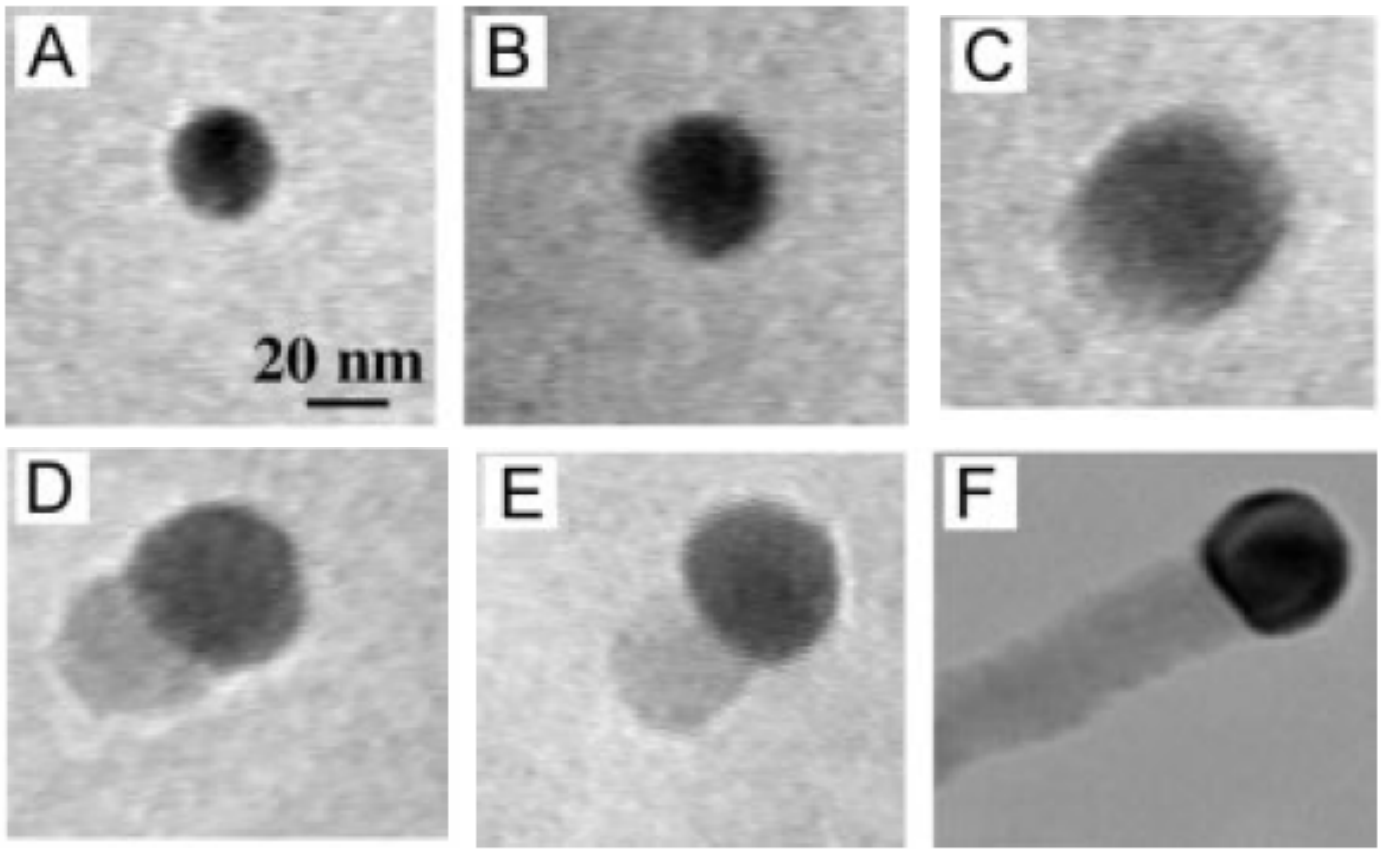
Applications of Gold Arrays



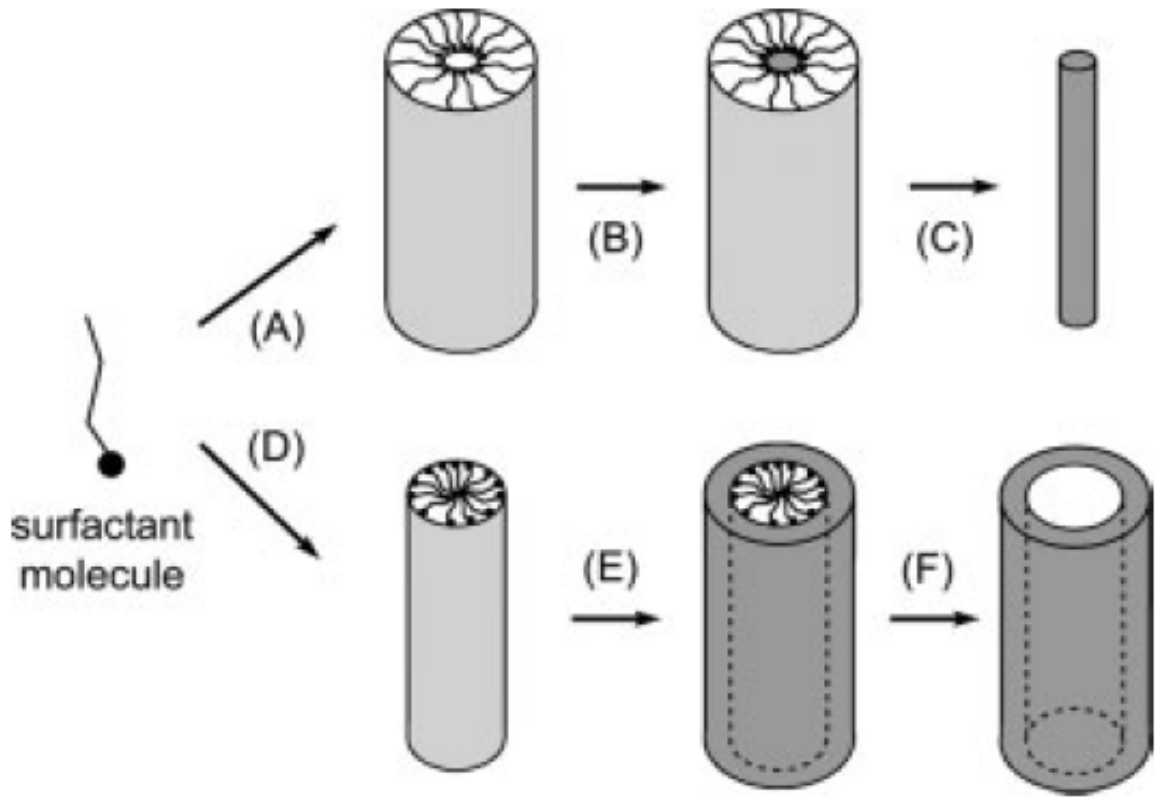
Applications of Gold Arrays



Applications for Gold Arrays



Templating on Micelles



Templating on Micelles

The principle remains the same:

- Surfactants form micelles
- coupling with appropriate chemical or elektrochemical reactions will promote the formation of nanorods

This method is commonly used

The main problem remains the removal of the template

Anisotropic Structur Growth

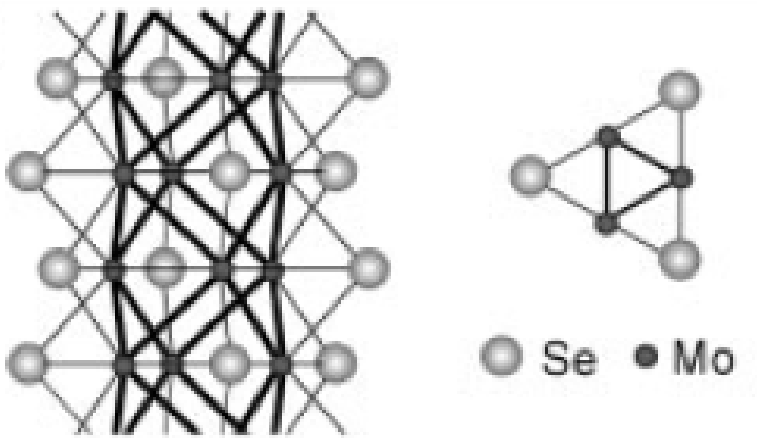
- Many solid materials naturally grow in 1D nanostrucutres
- such as poly(sulphur nitride) $(SN)_x$, asbestos and chrysolite
- many polymeric and biological systems like cellulose and collagen exist in fibrous form

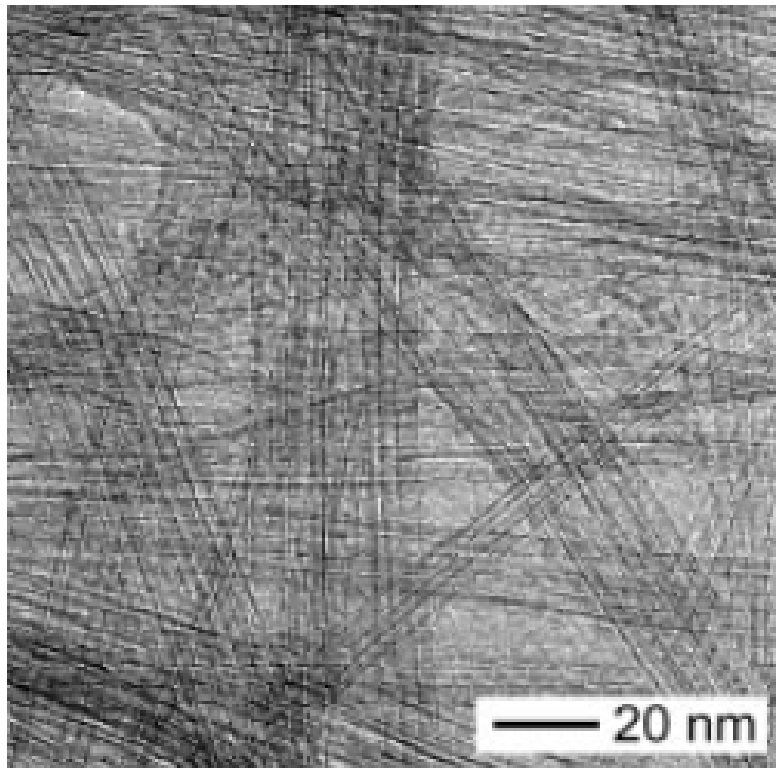
Anisotropic Structur Growth

Molybdenum chalcogenides ($M_2Mo_6X_6$; X=Li, Na ; X=Se, Te) contain hexagonal close-packed linear chains of M_2Mo_6

It can be considered a prismatic column formed by staggered stacking the M_2Mo_6 triangular units with a repeating distance of 0,45 nm

Anisotropic Structur Growth





Anisotropic Structur Growth

When dissolved in highly polar solvent (i.e. dimethylsulfoxide) they mainly exist as chains ~ 2 nm in diameter

It is possible to fabricate a polymeric matrix containing mostly (Mo_3Se_3-) mono- and biwires by polymerizing in situ a dilute solution of $LiMo_3Se_3$ in vinylene carbonate

Anisotropic Structur Growth

The result were molecular wires 0,6-2 nm in diameter and 5-10 nm in length

This method falls between chemical synthesis and growth (depending on definition)

This is also true for its dimensions

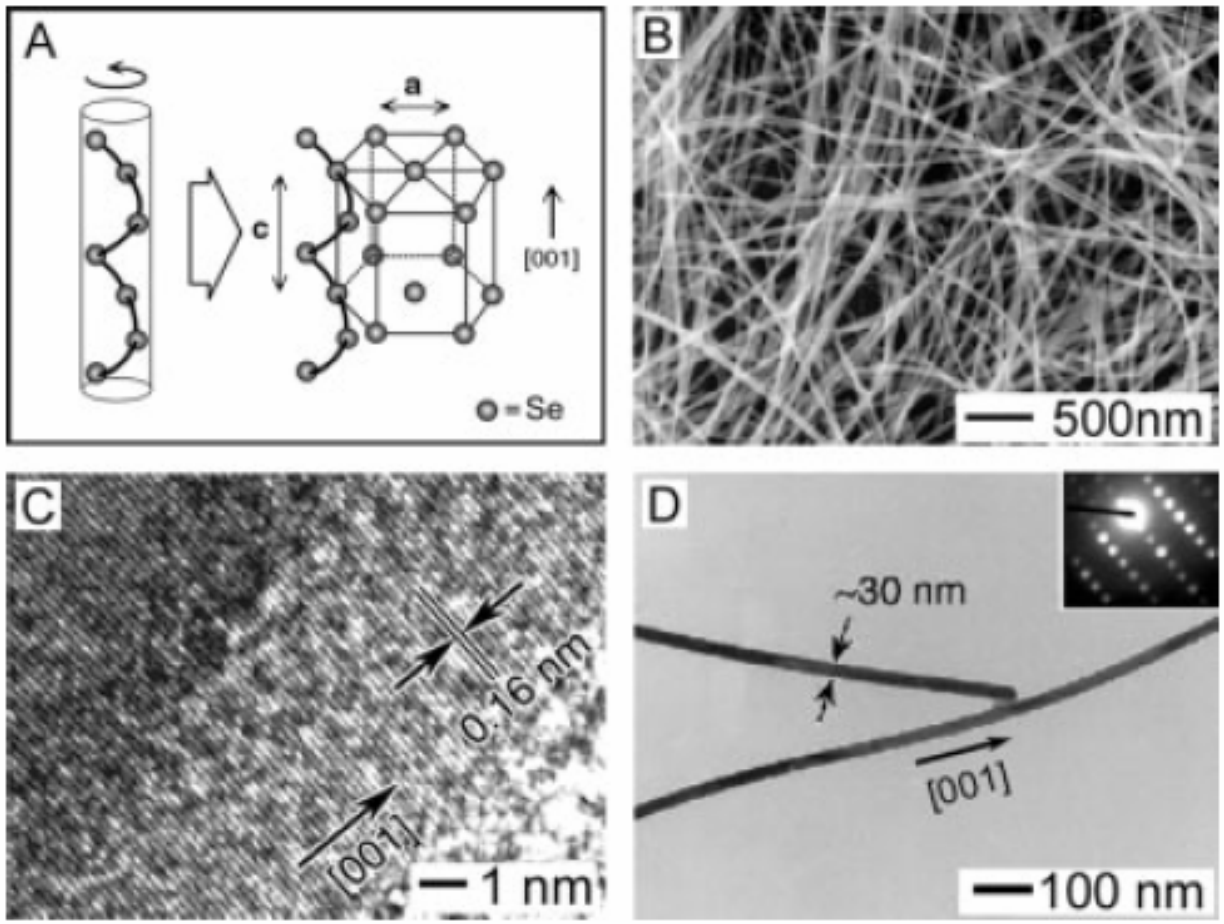
Anisotropic Structur Growth

A second exemple: The chalcogene Selenium (Se)

It has a unique crystall structure as it tends to form polymeric, helical chains through covalent bonding

They can be packed into a hexagonal lattice by van-der-Waals interactions

Anisotropic Structur Growth



Anisotropic Structur Growth

Production method for a Se-Chain

formation of Se in aqueous solution through the reduction of selenious acid with excess hydrazine by refluxing this reaction mixture at an elevated temperature

$$H_2SeO_3 + N_2H_4 \longrightarrow Se\,(\downarrow) + N_2\,(\uparrow) + 3H_2O$$

Anisotropic Structur Growth

Production method for a Se-Chain

first product amorphus Se colloids

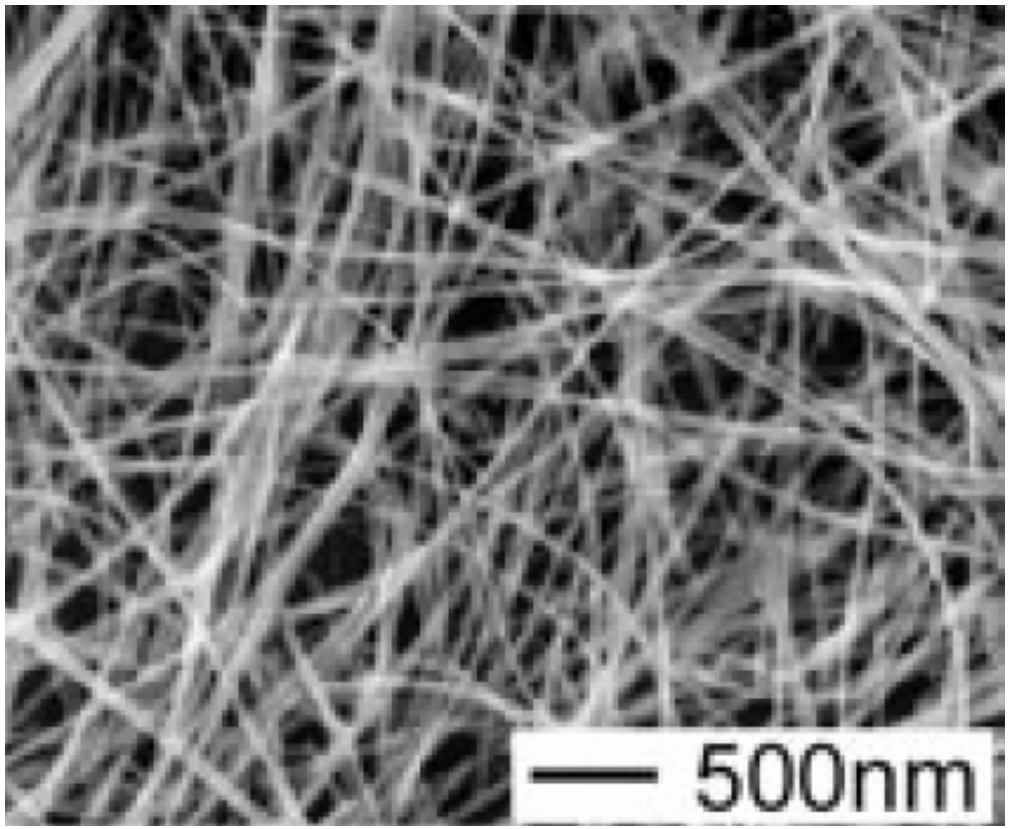
at lower temperature nanocrystallites of t-Se came from the dissolved Se

the a-Se slowly dissolved

the dissolved Se grew as crystalline nanowires of t-Se

Result:

Anisotropic Structur Growth



Anisotropic Structur Growth

- the linear morphology was determined by the intrinsic anisotropy of the building blocks (the extended, helical chains of Se atoms in the trigonal phase)
- each nanowire was essentially a single crystall characterized by a uniform diameter alongs its longitudinal axis
- the diameter varied with the temperature of the reaction

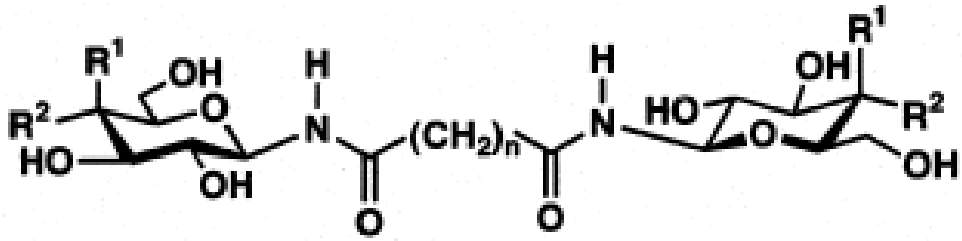
Structure Design with Monomers

- To achieve structural growth, many times the hydrogen bond is used
- The enthalpy gain upon hydrogen-bonding compensates well for the entropy loss of bound water molecules
- Hydrogen-bond networks are stabilized with increasing the hydrogen bond energy and the number involved

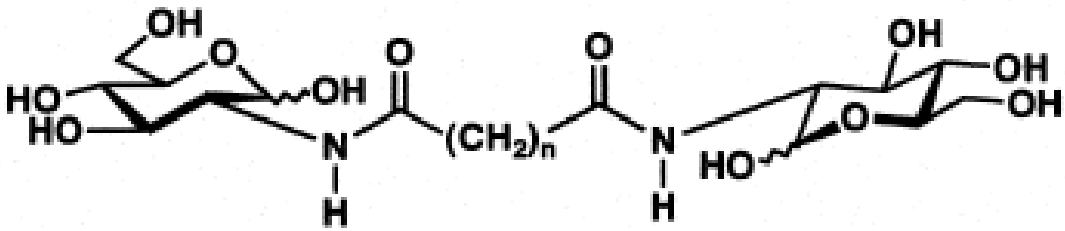
Structure Design with Monomers

- Sugar based bolaamphiphiles were effectively synthesized in high yields
- When saturated, hot aqueous solutions containing SBB‘s were allowed to gradually cool, a variety of supramolecular nanometer-sized fibers spontaneously and reproducibly appeared
- Self-assembled morphologies were obtained in water

Structure Design with Monomers



1(n): R^1 = H, R^2 = OH (n = 6,9,10,11,12,13,14, and 18)
2(n): R^1 = OH, R^2 = H (n = 10, 11, and 12)



3(n): (n = 9,10,11,12,13,14,16, and 18)

Structure Design with Monomers

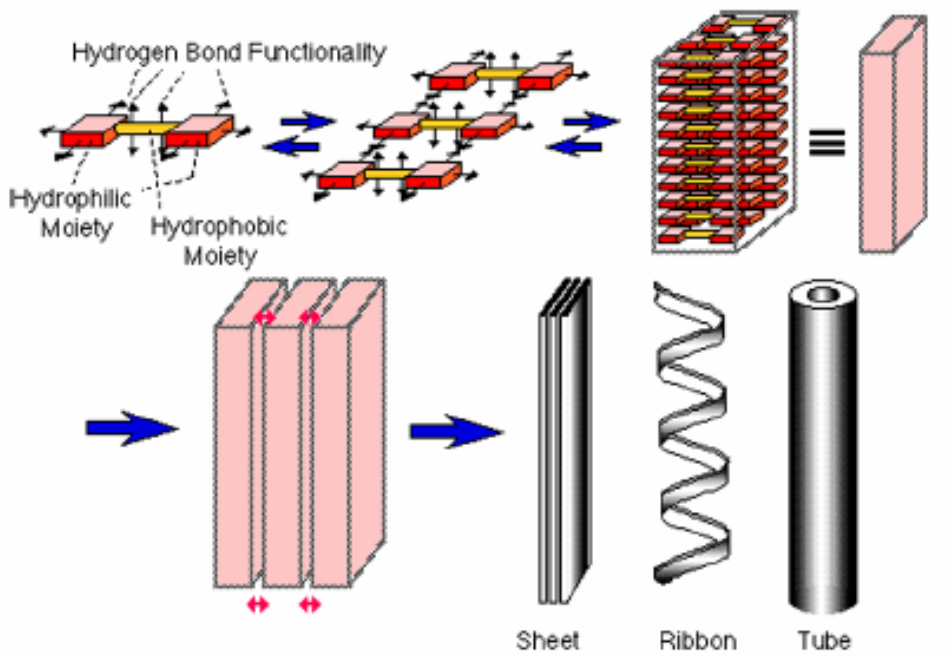


Figure 3. Schematic illustration of the self-assembly process into high-axial-ratio nanostructures (HARNs) using bolaamphiphilic monomers. The arrows indicate hydrogen bond functionalities.

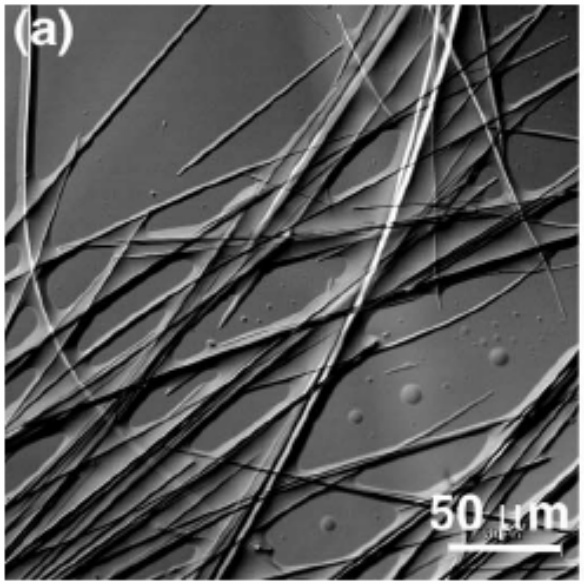
Structure Design with Monomers

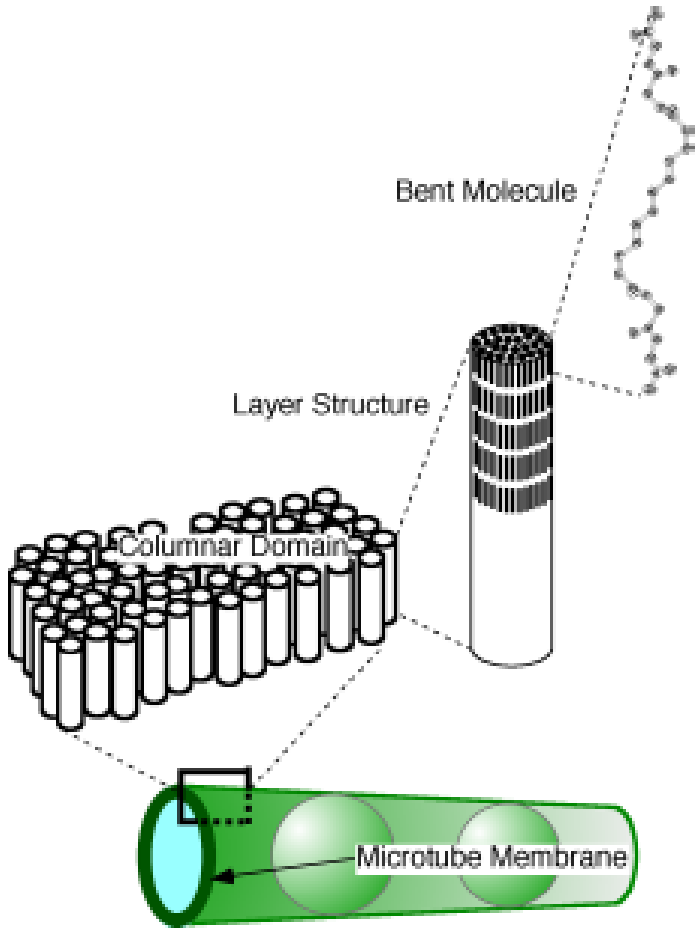
Table 1. Representative morphologies of self-assembled structures derived from synthetic amphiphilic monomers.

Hydrophilic moiety	Amphiphile	Self-assembled morphology	Solvent	Width / nm	Length / μm	Reference
sugar	**1(8)**, **1(10)**, **1(12)**	helical fiber	water	30–3000	ca. 1000	[59]
sugar	**1(9)**, **1(13)**	amorphous solid	water	n. d.[a)]	n. d.[a)]	[59]
sugar	**1(11)**	platelet	water	3×10^5	ca. 800	[59, 64]
sugar	**2(10)**, **2(12)**	needle crystal	water	ca. 5×10^4	ca. 90	[72]
sugar	**3(10)**, **3(12)**, **3(14)**	helical fiber	water/ethanol (1 : 1)	8–25	ca. 20	[56]
sugar	**3(11)**, **3(13)**	thin ribbon, sheet	water/ethanol (1 : 1)	10–150	ca. 20	[56]
sugar	**6(9)**, **6(10)**, **6(11)**	helical fiber	water	30–100	ca. 1000	–
sugar	**8**	nanofiber	ethyl acetate/hexane (3 : 7)	6–30	n.d[a)]	[85]
sugar	**10**	nanofiber and ribbon	water/THF (1 : 9)	50–300	n. d.[a)]	[86]
sugar	**25** + **26** + **27** + **28**[b)]	nanocoil, nanotube	water	50–100	ca. 1000	[153]
sugar	**28**	twisted nanofiber	water	50–100	ca. 1000	[153]
peptide	**11(6)**, **11(8)**, **11(10)**	microtube	water (pH 7–10)	1000–3000	ca. 1000	[104]
peptide	**11(6)**, **11(8)**, **11(10)**	vesicle	water (pH 7–10)	100–3000	0.1–3	[103]
peptide	**11(10)**	rod-like micelle	water (pH 7–10)	10	0.05–0.3	[103]
peptide	**11(10)**	needle	water (pH 7–10)	20–50	2–10	[104, 112]
peptide	**12(6)**, **12(10)**	microtube	water (pH 7–10)	ca. 1000	ca. 1000	[103]
peptide	**13**, **14**, **15**, **16**	solution	water (pH 7–10)	n. d.[a)]	n. d.[a)]	[103]
peptide	**17(*n*)** ($n \geq 7$)	nanofiber	water (pH 7–10)	10–15	ca. 10	[123]
peptide	**18(8)**	ribbon	water (pH 5–6)	10^3–10^5	ca. 1000	[124]
peptide	**19(8)**, **19(10)**, **19(12)**	nanofiber	water (pH 5–6)	10–15	ca. 10	[124]
nucleobase	**20(10)**	double-helical rope	water/ethanol (9 : 1)	200–1000	ca. 1000	[137]
nucleobase	**21(*n*)** ($n = 10, 11, 12$)	microcrystal	water/ethanol (9 : 1)	10^3–10^4	1–10	[137]
nucleobase	**22(12)**	nanofiber	water/ethanol (1 : 1)	15–150	15–100	[137]

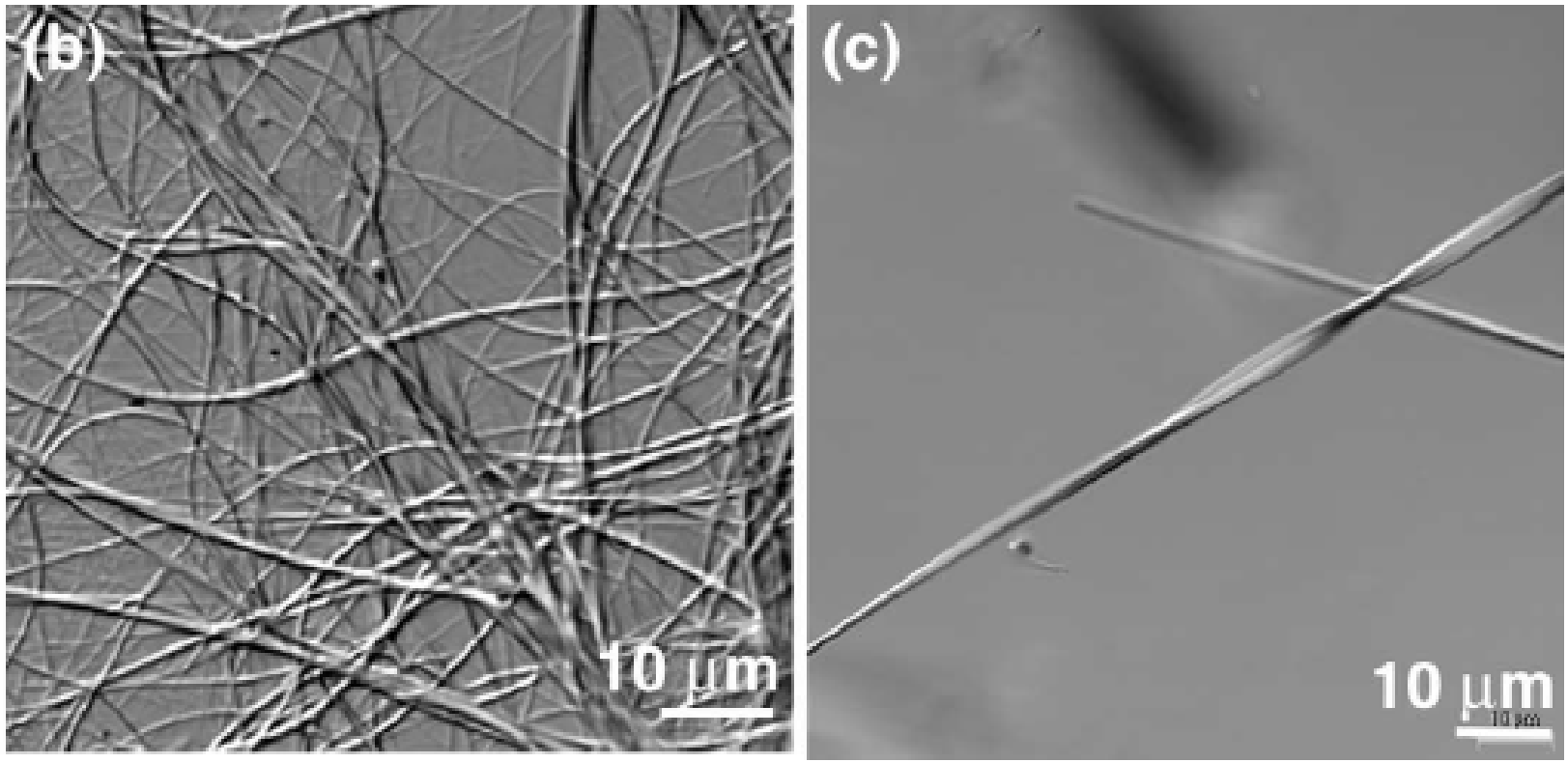
[a)] n.d.: not determined.
[b)] Mixture of cardanyl glucosides **25/26/27/28** of 29 : 16 : 50 : 5 wt.-%.

Structure Design with Monomers





Structure Design with Monomers



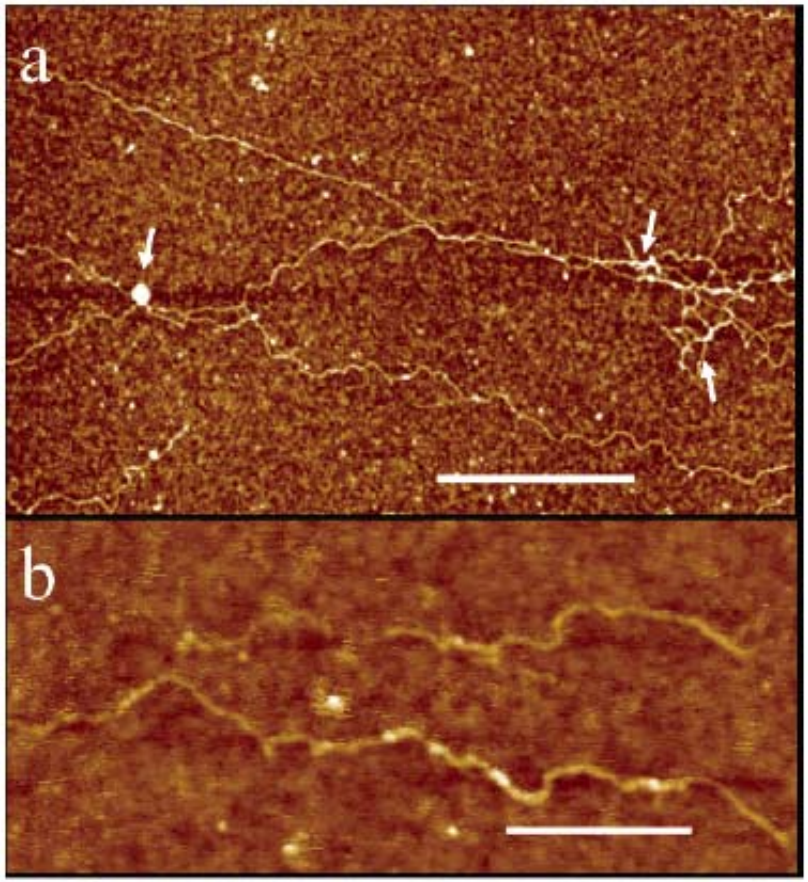
DNA Templates

- Goal: Use of DNA to arrange and bind circuit components to a surface, taking advantage of the specificity with which DNA pairs interact
- Surface adsorbed DNA has low intrinsic conductivity
- Techniques must be developed to provide conductive electrical connections

DNA Templates

- double stranded DNA solution was pipetted onto a polished Si-wafer
- held in place by surface tension between microscope slide cover slip and the substrate, then lineary moved across the surface using a three axis translation stage

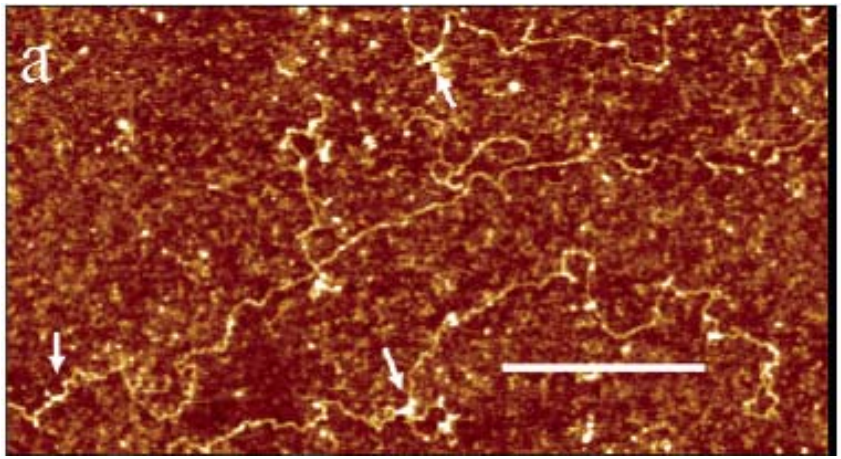
DNA Templates

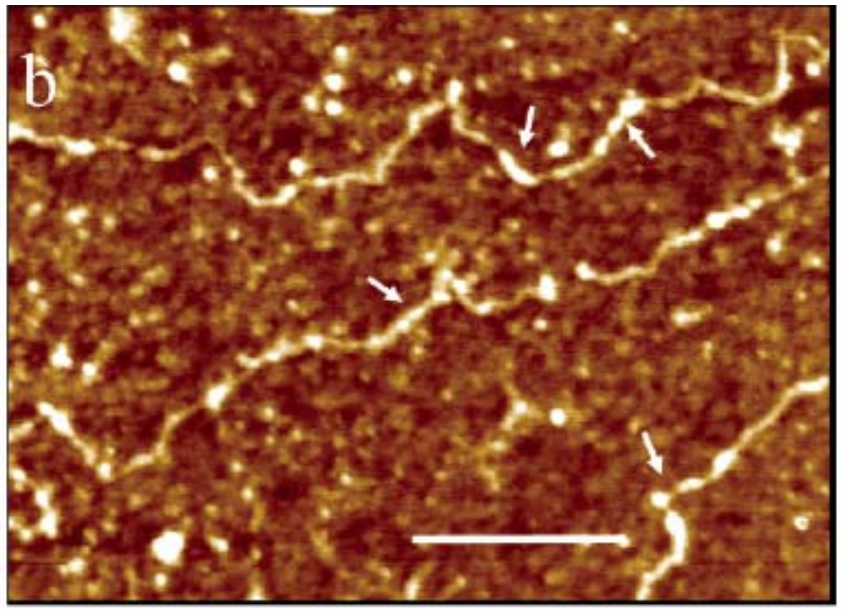


DNA Templates

- The surface of the DNA was treated with a Cu solution Cu(NO3)2
- The positive charged copper ions associated with the negatively charged DNA phosphate groups
- After eight minutes, the solution was rinsed off again

DNA Templates

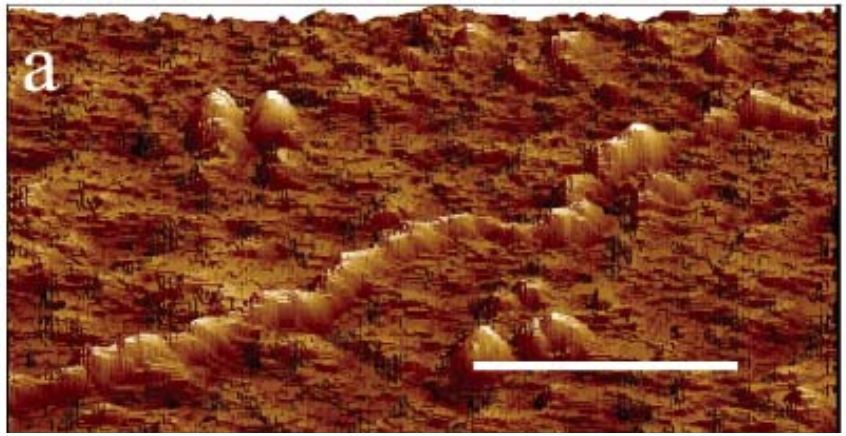


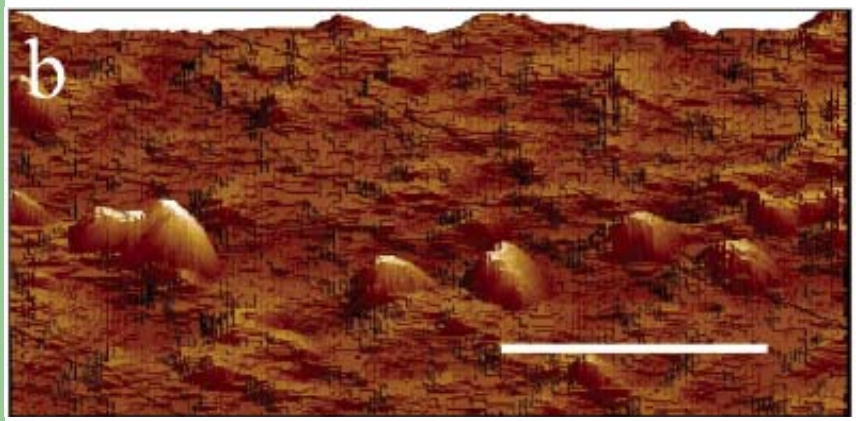


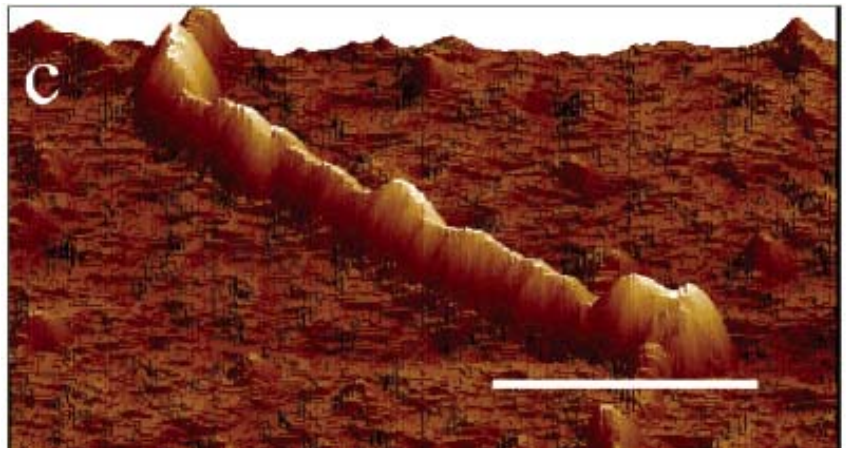
DNA Templates

- The surface of the DNA had numerous sections with raised height, due to Cu deposition
- Nonspecific Cu depositions also occured, because of Cu being reduced by ascorbic acid
- Repeated treatments still left uncovered DNA, which was also cleaved

DNA Templates







DNA Templates

Future research will optimize the treatment process such that conductivity experiments can be performed

Table 1. Height of DNA after Various Treatments

		one Cu(II) treatment		two Cu(II) treatments	
	untreated DNA	metallized[a]	unaffected[b]	metallized[a]	unaffected[b]
average height (nm)	1.22	3.03	1.18	3.15[c]	1.36
std dev (nm)	0.43	0.69	0.24	0.73	0.28
% of DNA	100	10–25	75–90	30–50	50–70
surface roughness (nm)[d]	0.20	0.22		0.25	

Conclusion

- Proteins demonstrate that bottom up design can perform huge things
- On a low level bottom up design can give good results
- They are not necessary competitive
- None of them can be used in mass production this instant

Conclusion

- Maybe i.e. the understanding of protein folding will give new approaches
- Bottom up design might find its place between the established methods
- Its strength is to do something completely new with it
- Applications are in the way from micro- to nanoelectronis, new materials and biology

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