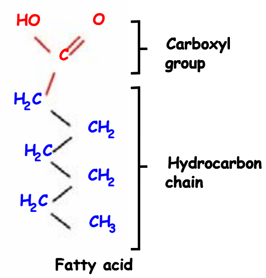
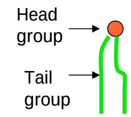
Lipids

- Organic compounds
- Amphipathic
  - Polar head group (hydrophilic)
  - Non-polar tails (hydrophobic)
- Lots of uses
  - Energy storage
  - Membranes
  - Hormones
  - Vitamins

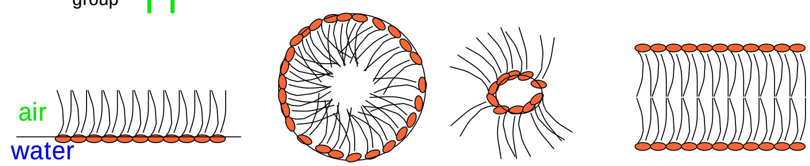


Some lipid structures

- Hydrophobic interactions are important



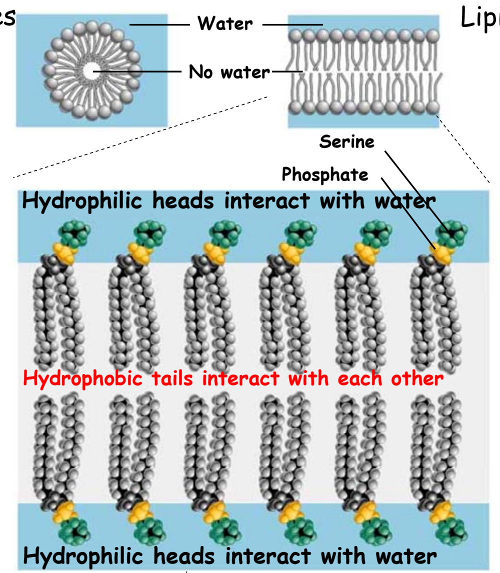
- Lipid is an amphipathic molecule, but rarely exists as a monomer.



monolayer *Micelle* *Inside-out (in nonpolar solvent)* *Lipid bilayer*

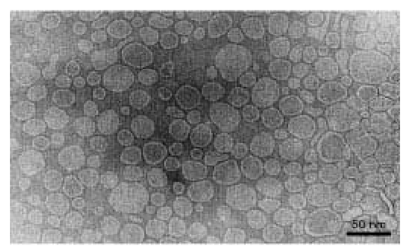
Micelles/Bilayers

Lipid micelles

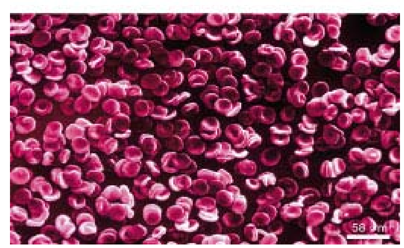


Lipid bilayers

Examples



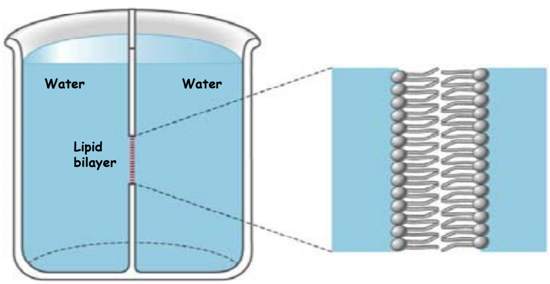
Lipids and water form tiny compartments



Red blood cells

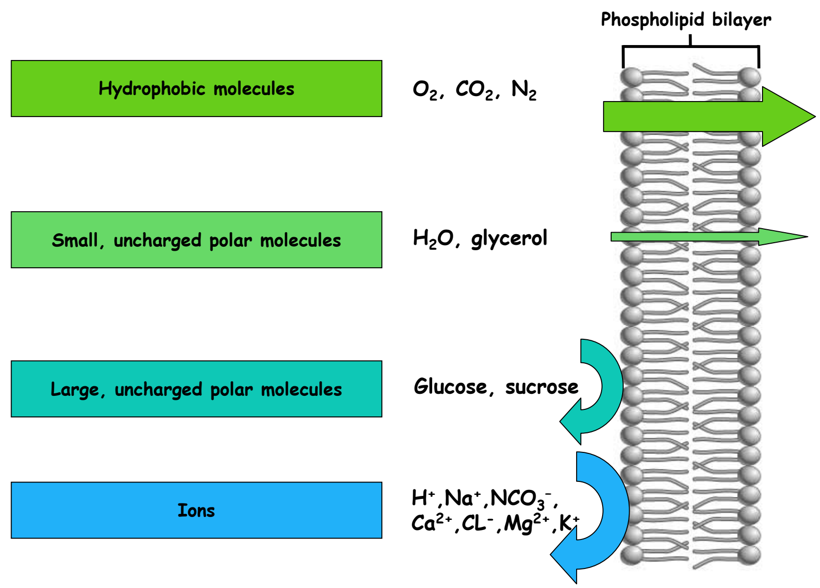
Using Lipids as Membranes

Planar bilayers: Artificial membranes



Membrane is selectively permeable

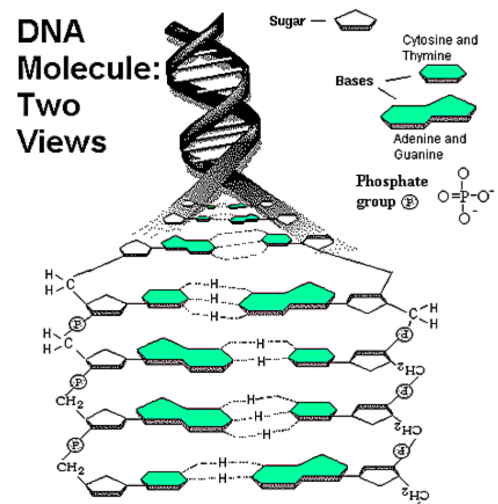
Relative Permeabilities



DNA/RNA/Proteins

- Why study?
- Here are just the basic basics
- DNA
  - made up of double strands of **adenine (A), guanine (G), cytosine (C)** and **thymine (T)**
  - Pair up: C-G, A-T
- RNA
  - Single stranded
  - U for T
- Proteins do the work
- DNA -> RNA -> Proteins

DNA

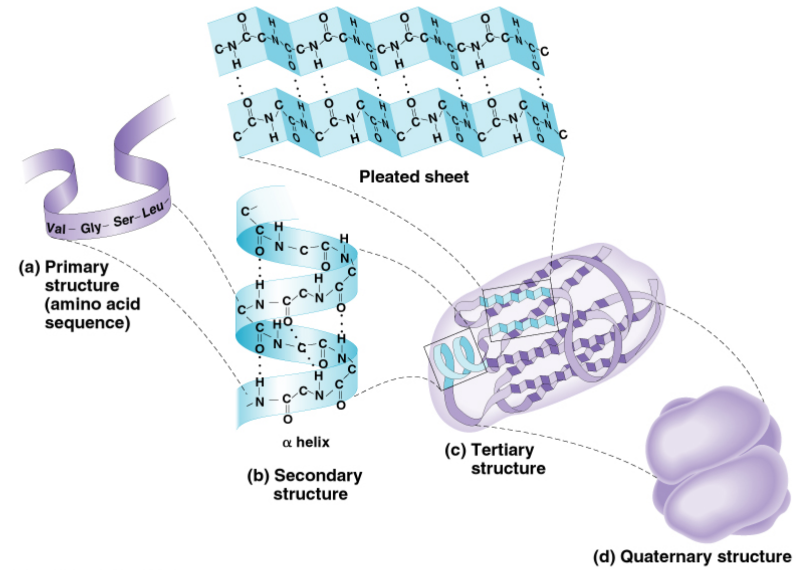


H-bonds

Protein

- Linear polymer of amino acids linked by peptide bonds
- Average 200 amino acids, can be >1K
- Complex structure
  - Primary structure – sequence of AAs
  - Secondary structure – local arrangements
  - Tertiary structure – how the local structures pack in 3D
  - Quaternary structure – how chains fold

Levels of Structure



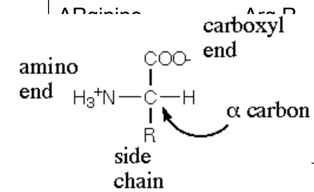
Forces determining structure

- Van der Waals .4 – 4 KJ/mol
- Hydrogen bonds 12-30 KJ/mol
- Ionic bonds 20 KJ/mol
- Hydrophoic interactions <40KJ/mol

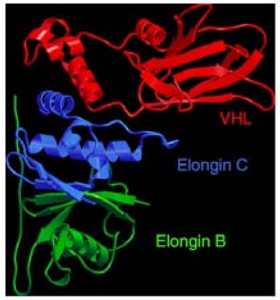
Amino Acids

- 20 natural ones
- Formed from
  - Central carbon
  - Amino group
  - Carboxyl group
  - H
  - Side-chain
- Only difference is side-chain
- Polar/non-polar

Alanine	Ala A
Cysteine	Cys C
Aspartic AciD	Asp D
Glutamic Acid	Glu E
Phenylalanine	Phe F
Glycine	Gly G
Histidine	His H
Isoleucine	Ile I
Lysine	Lys K
Leucine	Leu L
Methionine	Met M
AsparagiNe	Asn N
Proline	Pro P
Glutamine	Gln Q



Secondary structures



- Alpha helix
- Beta Sheet
- Loop regions
  - Often binding sites
  - Often hydrophilic
  - Come between alpha's and beta's
- Represented as ribbon diagrams
  - Coiled – alpha
  - Arrow – beta
  - Thin - loops

VHL protein

Stebbins et al, *Science*, 284:455.

Using all this info

- Protein-based memory
- DNA as wires
- DNA-based assembly
  - Templates
  - Smart-glue
  - tiles

DNA as wires

- DNA is conducting, 1986 and on
  - π-bonding
  - D-A, holes, Hopping
- DNA is insulator, 1999 and on
  - λ-bridge between oligos on gold
  - Insulator
  - Lower T -> more insulating
- DNA is semiconductor, 2000 and on
  - Consider series of quantum dots
  - Maybe difference in fermi-level with contacts
- Conclusion?

DNA-templates for wires

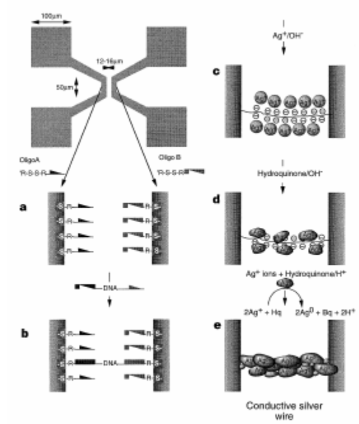


Figure 1 Construction of a silver wire connecting two gold electrodes. The top left image shows the electrode pattern (0.5 × 0.5mm) used in the experiments. The two 50 μm long, parallel electrodes are connected to four (100 × 100 μm) bonding pads. **a**, Oligonucleotides with two different sequences attached to the electrodes. **b**, λ-DNA bridge connecting the two electrodes. **c**, Silver-ion-loaded DNA bridge. **d**, Metallic silver aggregates bound to the DNA skeleton. **e**, Fully developed silver wire. A full description of the preparation steps can be found in the Methods section.

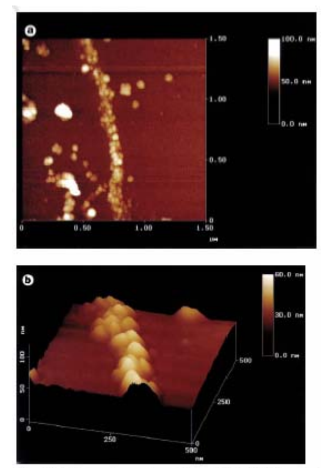


Figure 3 Atomic force microscopy images (Dimension 3000, Digital Instruments) of a silver wire connecting two gold electrodes 12 μm apart. **a**, 1.5 μm; **b**, 0.5 μm field sizes. Note the granular morphology of the conductive wire.

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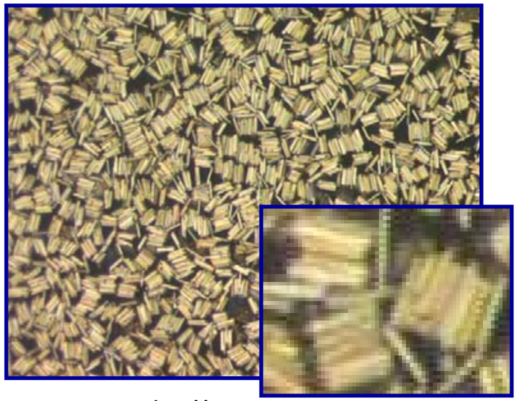
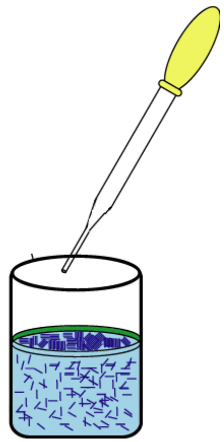
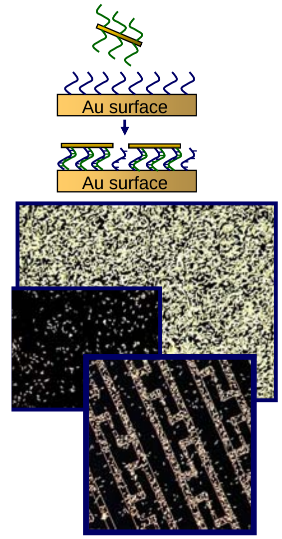
Interfacial Nanowire Assembly





- Challenges:
  - *Gravity*
  - *High interfacial tension*
  - *Incompatible with DNA, high salt*

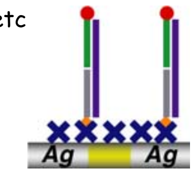
DNA as "glue"

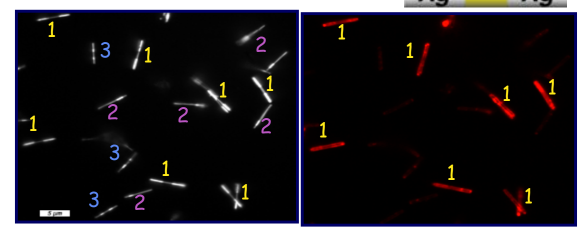


Selectivity
- 4^n unique sequences for oligo of length n
- base pairing determines thermodynamic stability

Versatility
- sequence
- 5′ or 3′ terminal -SH, -NH_2, biotin, etc

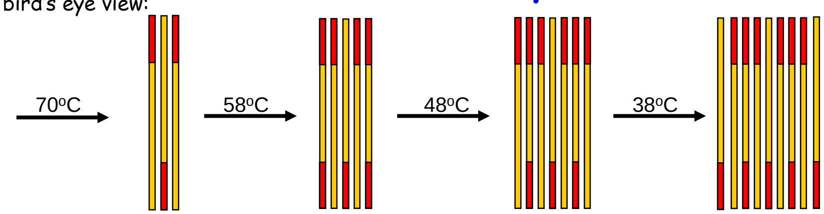
Reversibility
- temperature, base



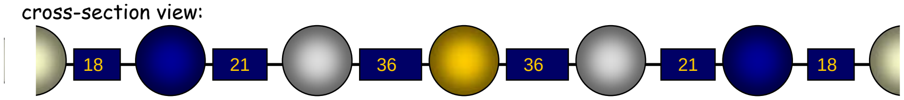


Temperature-programmed Raft Assembly

bird's eye view:



cross-section view:



5′ HS-$C_{12}H_{24}$-TTG AGA CCG TTA AGA CGA GGC AAT CAT GCA ATC CTG 3′

Length	T_m
36-mer	75°C
21-mer	61°C
18-mer	51°C
15-mer	41°C
9-mer	28°C

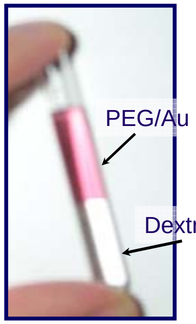
Deterministic rafts will be assembled at the aq/aq interface via sequential assembly of nanowires harboring decreasing lengths of oligonucleotides A and A′ as the sample is cooled.

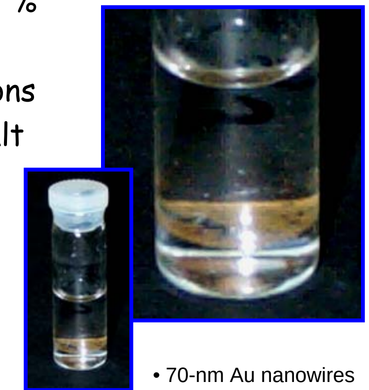
Necessary components of raft assembly:

- Hybridization-compatible interface
- DNA-coated nanowires at the interface
- Hybridization-driven nanowire assembly
- Thermal control over assembly process

Aqueous-aqueous interfaces

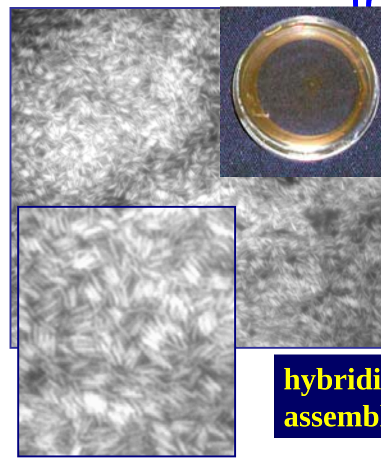
- polymeric solutes, few weight %
- particles collect at interface
- low, tunable interfacial tensions
- compatible with DNA, high salt
- stable up to 95°C



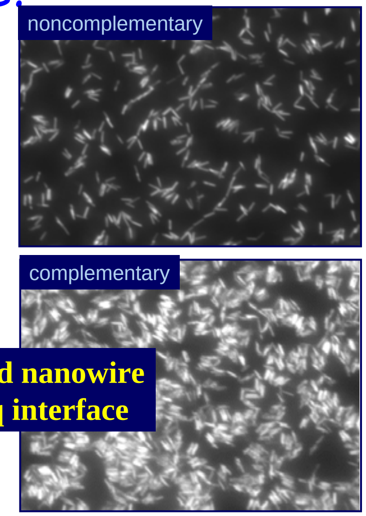


- 70-nm Au nanowires
- MESA-derivatized
- PEG/dextran ATPS
- hybridization buffer

DNA-directed assembly at the interface?



Minutes after removal from shaker



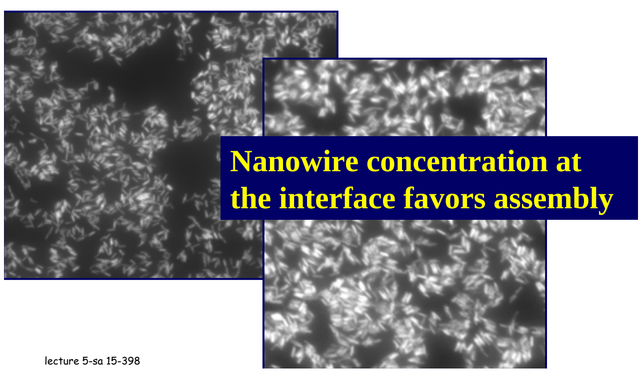
hybridization-induced nanowire assembly at the aq/aq interface

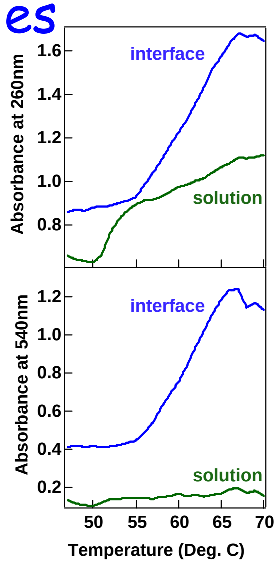
- DNA-coated nanowires at aq/aq interface – form reflective interface after gentle agitation

Melt curves for interface and solution assemblies

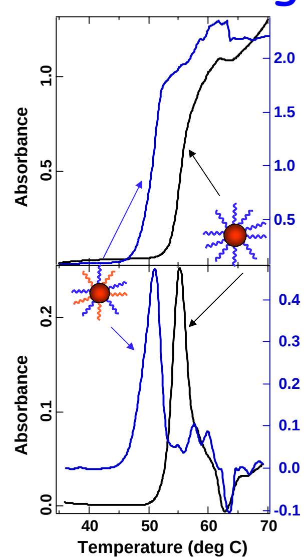
Nanowire rafts removed from interface

- Higher T_m than solution-prepared counterparts
- Large aggregates lead to high scattering
- Observe greater change upon melting
  - *more DNA was hybridized*
  - *interface concentrates nanowires for assembly*



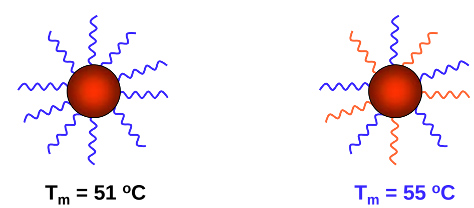


Controlling T_m by surface dilution

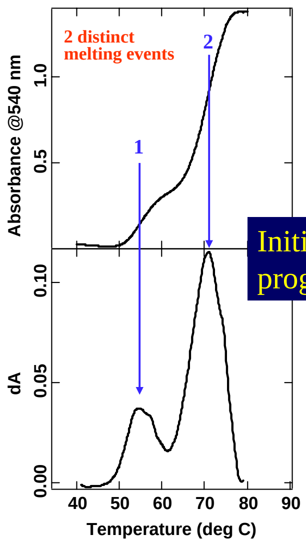


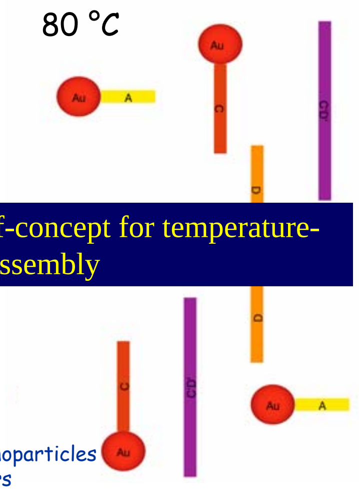
- Surface dilution of proper DNA sequence decreases T_m
- We can control coverage from 1-5 x 10^{13} strands/cm^2 (40-150/particle)
- This approach can be used to tailor T_m's for temperature-programmed assembly

surface diluted w/ polyA



Temperature-controlled Dissociation

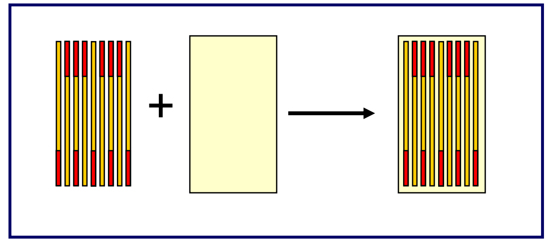


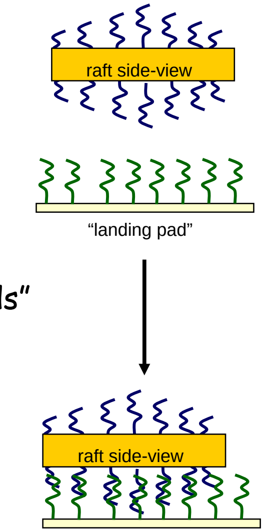


Initial proof-of-concept for temperature-programmed assembly

12-nm Au nanoparticles
A, B = 12 mers
C, D = 18 mers

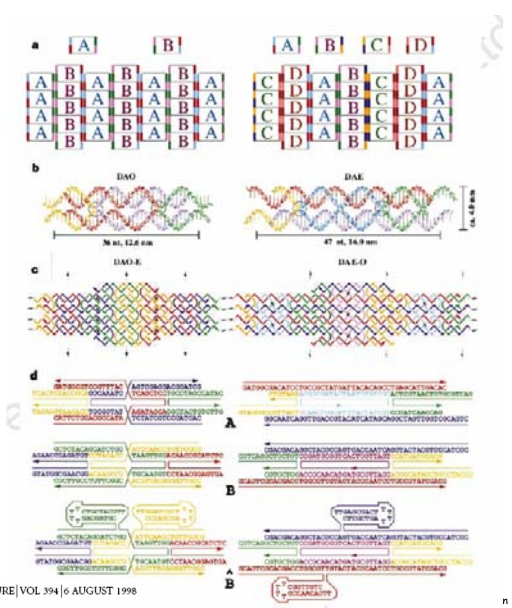
Potential-Assisted Raft Positioning





- lithographically-defined "landing pads"
- derivatize with complementary DNA
- hold at positive potential
- allow rafts to hybridize to pads
- reverse potential for stringency

DNA Tiles



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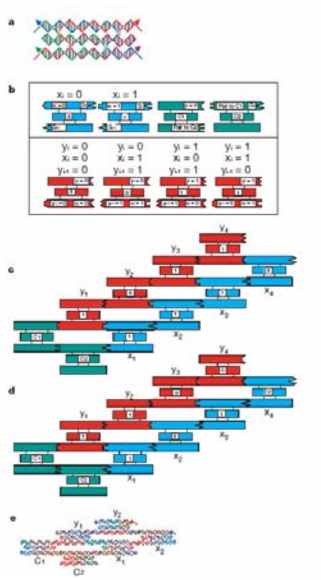

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