Introduction to Nanotechnology

- Textbook：

  Nanophysics and Nanotechnology

  by:

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Classroom: A209
Time: Thursday; 13:40-16:30 PM
Office hour: Thur., 10:00-11:30 AM or by appointment

Self-Assembled Nano-Structure in Nature and Industry

Subjects:

1. Self-assembly Systems
2. Carbon atom
3. Nano-tube
4. Nano-wire
5. Quantum Dot
6. Nano-crystal
7. Nano-particles in Bacterial life
8. Smooth Surface

SELF-ASSEMBLY

Other present day techniques are HOPELESSLY slow and/or expensive

So attractive alternative is **SELF-ASSEMBLY**

Setting things up so that Mother Nature does the fine scale work

But to ferret out where Mother Nature may give us a hand, must span:

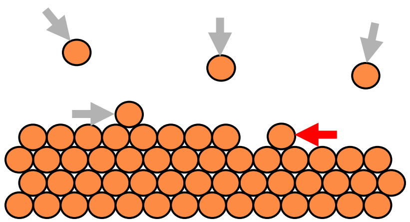
Physics, Chemistry, Biology, Materials Science . . .

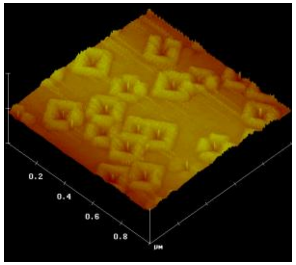
So I will also put major effort into providing insights into those fields

i.e., "**Opening Doors**" into those subjects for you

Nanoscale Self-Assembly

Early forms of self-assembly that man tamed (such as crystal growth)

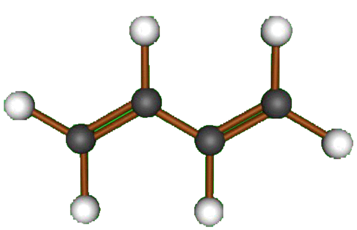


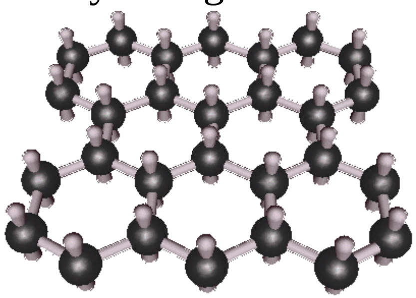


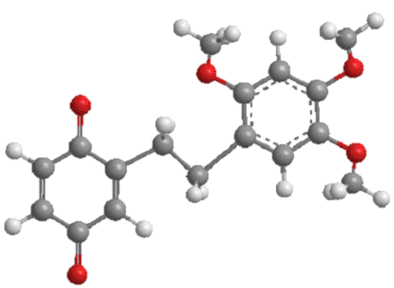
Leading us to the master of self-assembly: Mother Nature

Or what a billion years of random experimentation produced, including:

Self-assembly of organic molecules







1. Self-assembly Systems

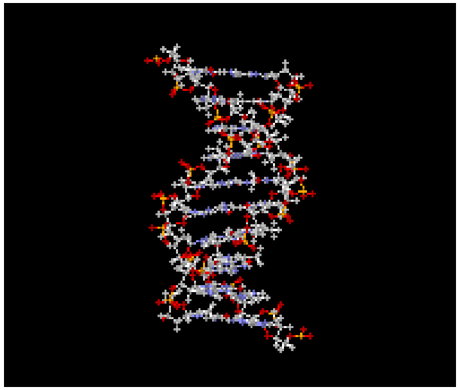
Self-assembly is definitely the preferred route to the formation of atoms.

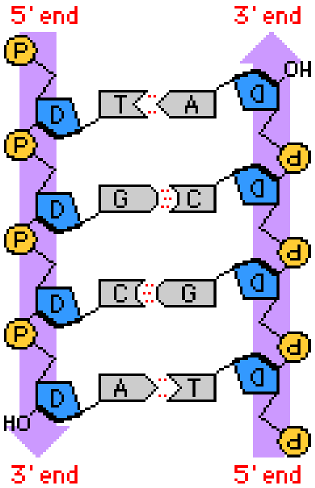
Molecules are mostly self-assembled and available in nature.

Biological Molecules: are self-assembled.

Concept 1 Review: DNA

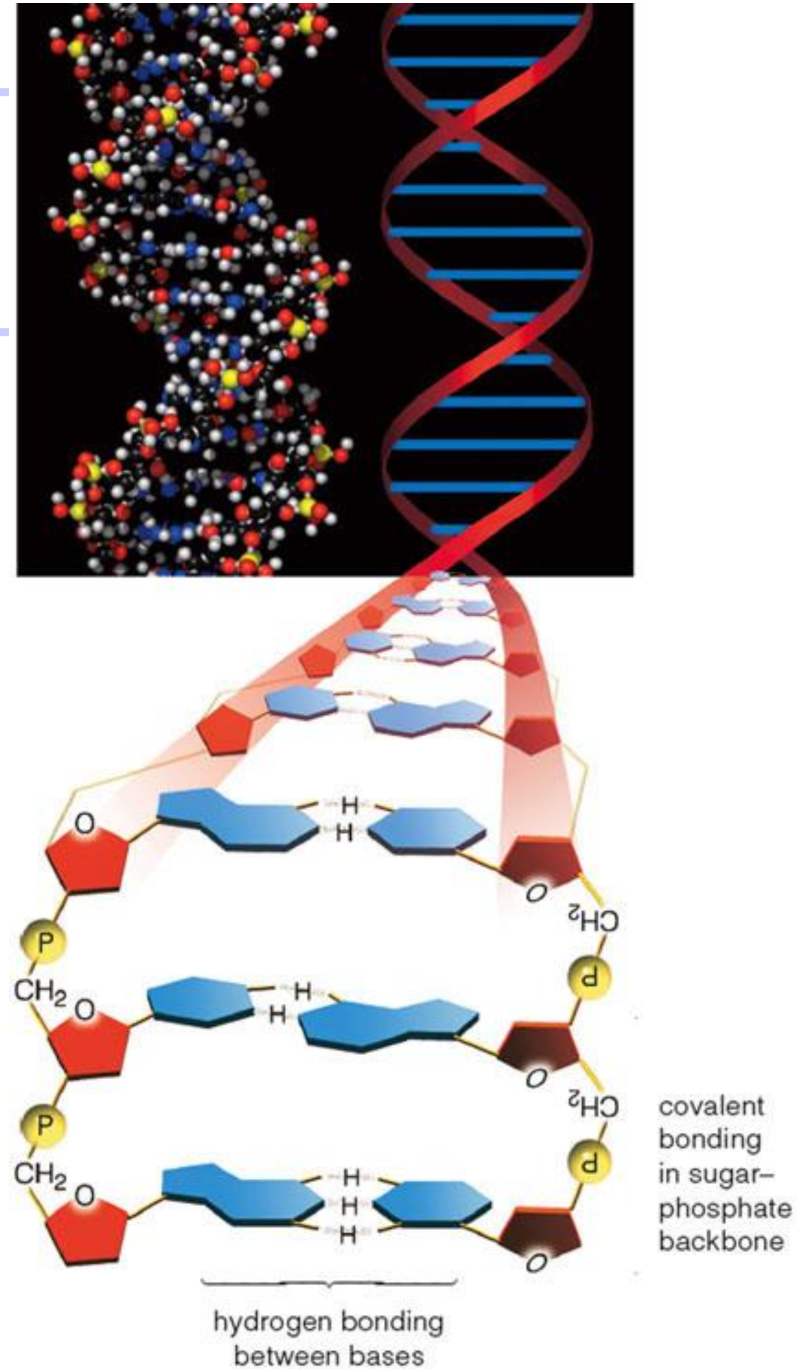
DNA, made by polymerizing deoxyribonucleotides, forms a double-stranded molecule used for information storage.

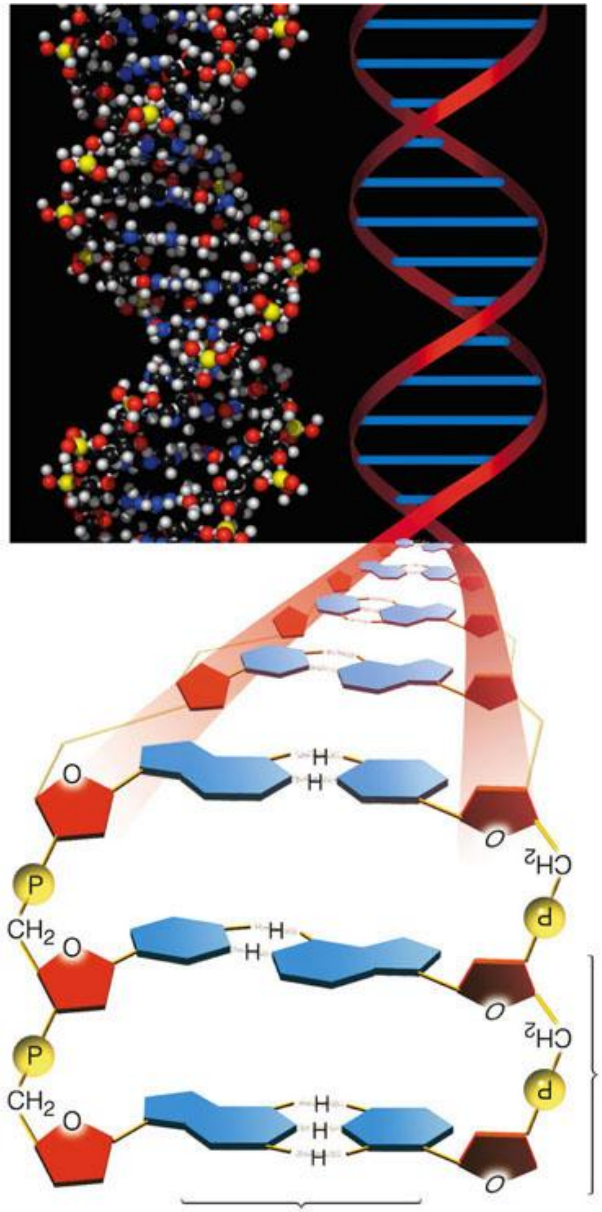




Each strand of DNA consists of a "backbone" of alternating units of phosphate and deoxyribose. Purine or pyrimidine bases are attached to the 5-C deoxyribose sugar, and form base pairs with purine or pyrimidine bases from the opposite strand. The only effective pairs are adenine with thymine (A-T pairs) and guanine with cytosine (G-C pairs).

The DNA Molecule





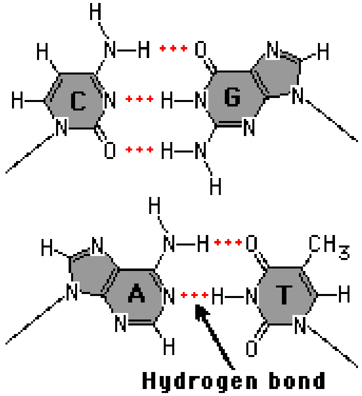
covalent bonding in sugar–phosphate backbone

hydrogen bonding between bases

Concept 1 Review: DNA Base Pairing

A-T and G-C base pairs allow the specific interation of nucleotides on different DNA strands.

The purine and pyrimidine bases in DNA can associate together by forming hydrogen bonds.



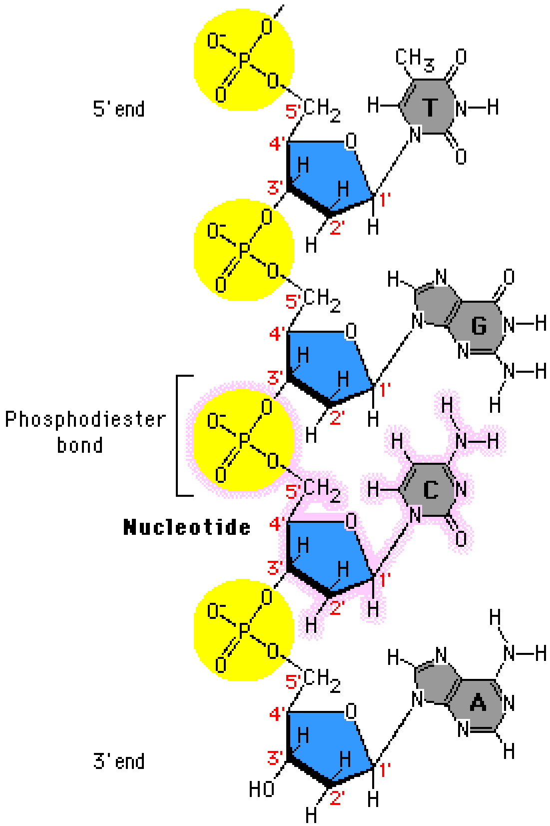
Most pairings produce only a single hydrogen bond at a time, but two types of base pairings allow for multiple hydrogen bonds. When A and T are brought into close contact, two hydrogen bonds can form simultaneously. When G and C are brought into close contact, three simultaneous hydrogen bonds can form.

The overall bond strength of many hydrogen bonds is additive. In zipper-like fashion, the presence of multiple A-T and G-C base pairs bonds the two strands of DNA tightly together.

Concept 1 Review: The Chemistry of DNA

Atoms in each DNA nucleotide can be identified by specific numbers. The ends of a DNA molecule are called 3' and 5' ends, based on the numbering of carbon atoms in deoxyribose sugars.

Chemists identify specific atoms in a molecule by numbering the backbone atoms: C1, C2, etc. In a complex nucleotide, the atoms of the purine or pyrimidine ring are first numbered 1, 2, 3, etc. Carbon atoms in the deoxyribose sugar are then numbered 1', 2', 3', 4', and 5' (shown in red in the figure below).

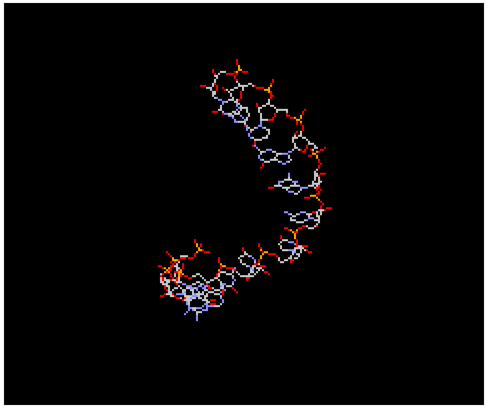


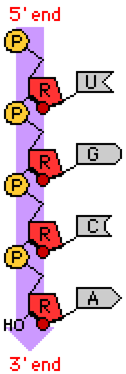
Notice that phosphate groups are attached to the 5'- and 3'-carbon atoms of each sugar to form the backbone chain of DNA. One end of the chain carries a free phosphate group attached to the 5'-carbon atom; this is called the 5' end of the molecule. The other end has a free hydroxyl (-OH) group at the 3'-carbon and is called the 3' end of the molecule.

When two DNA strands assemble in a double helix, the two strands always face in opposite directions; the 5' end of one strand is paired with the 3' end of the other strand.

Concept 2 Review: RNA

RNA, made by polymerizing ribonucleotides, forms single-stranded molecules used in information processing.





An RNA consists of a "backbone" of alternating units of phosphate and ribose. Purine or pyrimidine bases are attached to the 5-C ribose sugar.

Many bases in RNA molecules, such as ribosomal RNA and transfer RNA, are chemically modified after polymerization, a process that makes these molecules more stable.

For further practice, try the exercise on Transcribing an RNA Molecule in the Transcription Lab Simulations activity.

RNA

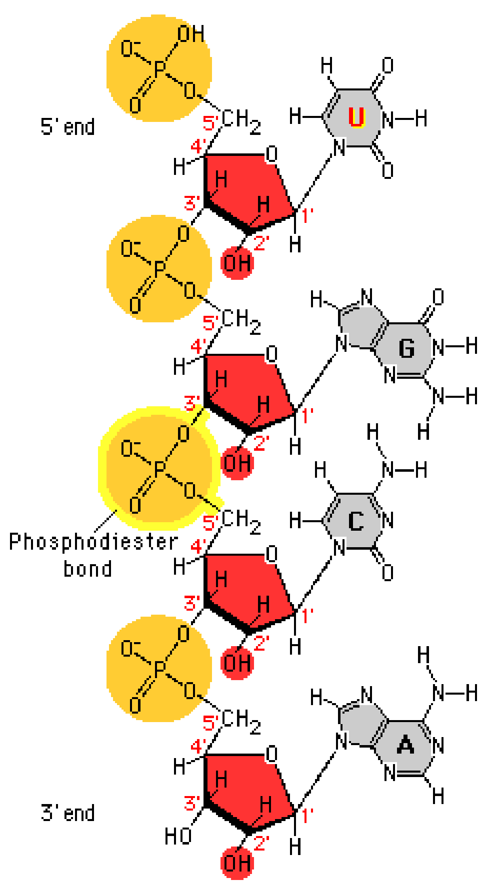
- **RNA (ribonucleic acid)**
  - Contains four kinds of nucleotide monomers, including ATP
  - Important in protein synthesis
  - Is always at direction (and creation of) the DNA
  - Is a single helix (helix simply means curved)

Concept 2 Review: The Chemistry of RNA

Atoms in each RNA nucleotide can be identified by specific numbers. The ends of an RNA molecule are called 3' and 5' ends, based on the numbering of carbon atoms in ribose sugars.

Chemists identify specific atoms in a molecule by numbering the backbone atoms: C1, C2, etc. In a complex nucleotide, the atoms of the purine or pyrimidine ring are first numbered 1, 2, 3, etc. Carbon atoms in the ribose sugar are then numbered 1', 2', 3', 4', and 5' (shown in red in the figure below).

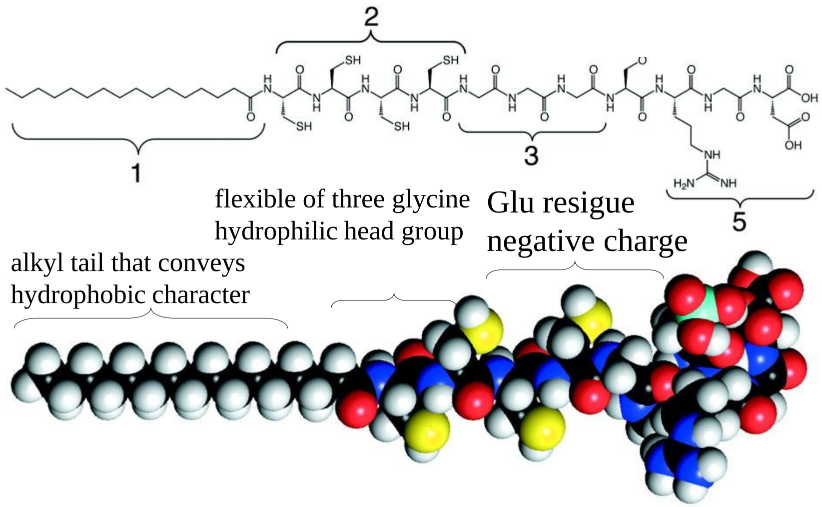
RNA polynucleotide chain



Notice that phosphate groups are attached to the 5'- and 3'-carbon atoms of each sugar to form the backbone chain of RNA. One end of the chain carries a free phosphate group attached to the 5'-carbon atom; this is called the 5'end of the molecule. The other end has a free hydroxyl (-OH) group at the 3'-carbon and is called the 3' end of the molecule.

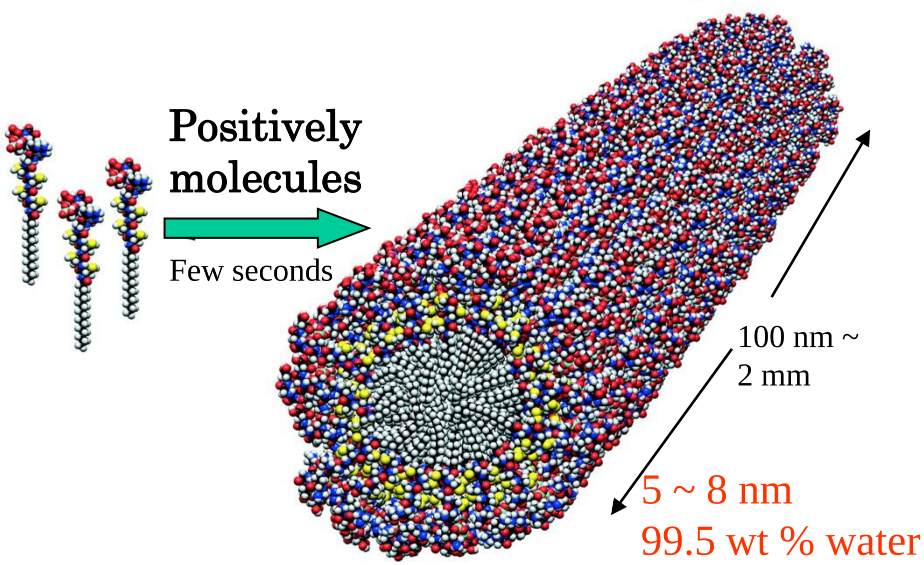
When new RNA molecules are synthesized, they are always made by the sequential addition of nucleotides at the 3' end of the chain. This is sometimes called 5'-to-3' synthesis. When RNA serves as a message to be translated into a polypeptide, the RNA is read starting at the 5' end and moving toward the 3' end.

Notice the presence of a hydroxyl (-OH) group at the 2' carbon of the ribose sugar. This differs from deoxyribose, where the 2' carbon lacks a hydroxyl group.



Samuel I. Stupp of Northwestern University in Chicago has discovered and considered to Peptide Amphiphile (PA) as its great capacity to form nanofibers (**Science, Vol 303, 2004**)

PA can self assemble into sheets, spheres, rods, disks, or channels depending on the shape, charge, and environment

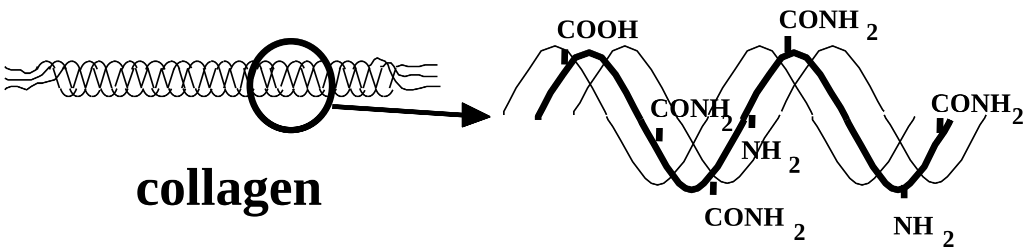


Amphiphiles with a conical shape in which the hydrophilic head group is somewhat bulkier than its narrow hydrophobic tail have been shown to form cylindrical micelles.
PA with mono- or di-alkyl tails were found to associate in conformations such as triple helical structures found in collagen.

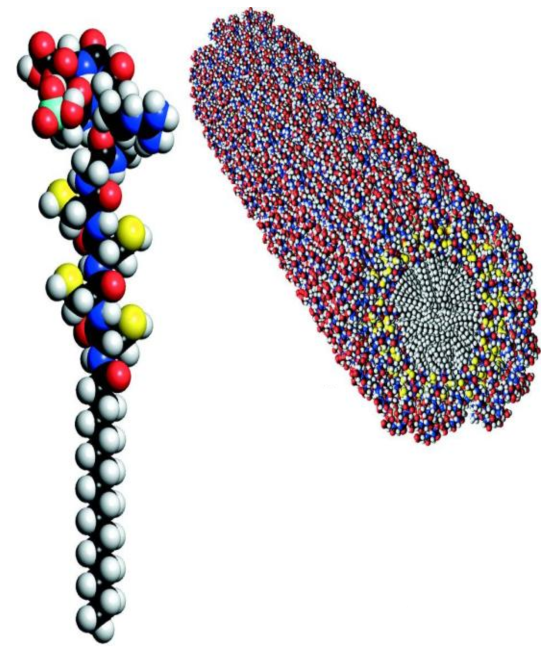
Cations can screen electrostatic repulsion among Peptide, and 3-D nonofiber are driven to assemble by hydrogen bond formation and electrostatic interactions, nonspecific van der Waals interactions, hydrophobic forces, and repulsive steric forces.

High aspect ratio
High surface area

natural Collagen ~ self-assembled peptide amphiphile



collagen



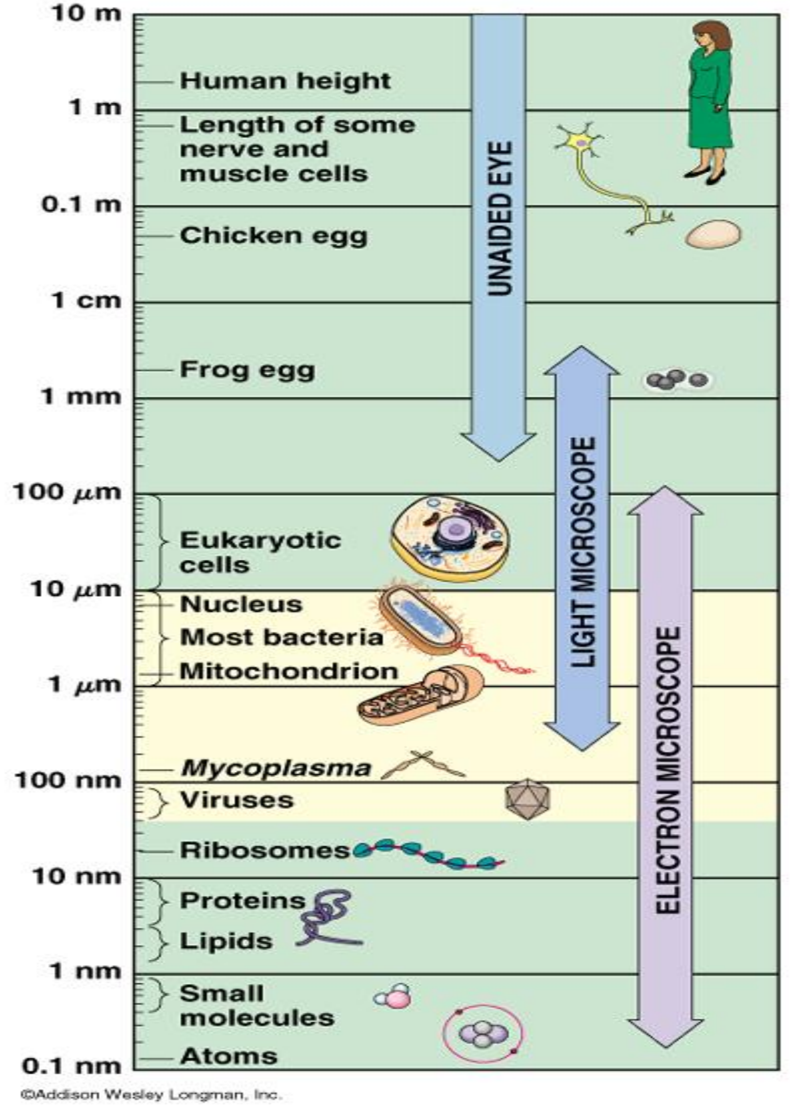
Collagen is main components of Extracellular Matrix, which make up all soft tissues consists proteins such as Collagen,Cadherins, Focal adhesion kinase, fibronectin and laminin form distinct tissue-specific networks that regulate the cell comportment.

Characteristic Atomic Bonds

		Bonding Energy		
Bonding Type	**Substance**	**kJ/mol**	**eV/Atom, Ion, Molecule**	**Melting Temperature (ºC)**
Ionic	NaCl	640	3.3	801
	MgO	1000	5.2	2800
	Si	450	4.7	1410
Covalent	C (dia)	713	7.4	>3550
	Hg	68	0.7	-39
	Al	324	3.4	660
Metallic	Fe	406	4.2	1538
	W	849	8.8	3410
van der Waals	Ar	7.7	0.08	-189
	Cl_2	31	0.32	101
Hydrogen	NH_3	35	0.36	-78
	H_2O	51	0.52	0

Adapted from: Fundamentals of Materials Science and Engineering / An Introduction," William D. Callister, Jr., John Wiley & Sons, NY, NY, 2001 or http://www.scribd.com/doc/8680373/Fundamentals-of-Materials-Science-and-Engineering-Callister

Scale


10 m
Human height
1 m
Length of some nerve and muscle cells
0.1 m
Chicken egg
1 cm
Frog egg
1 mm
100 µm
Eukaryotic cells
10 µm
Nucleus
Most bacteria
Mitochondrion
1 µm
Mycoplasma
100 nm
Viruses
Ribosomes
10 nm
Proteins
Lipids
1 nm
Small molecules
Atoms
0.1 nm
UNAIDED EYE
LIGHT MICROSCOPE
ELECTRON MICROSCOPE
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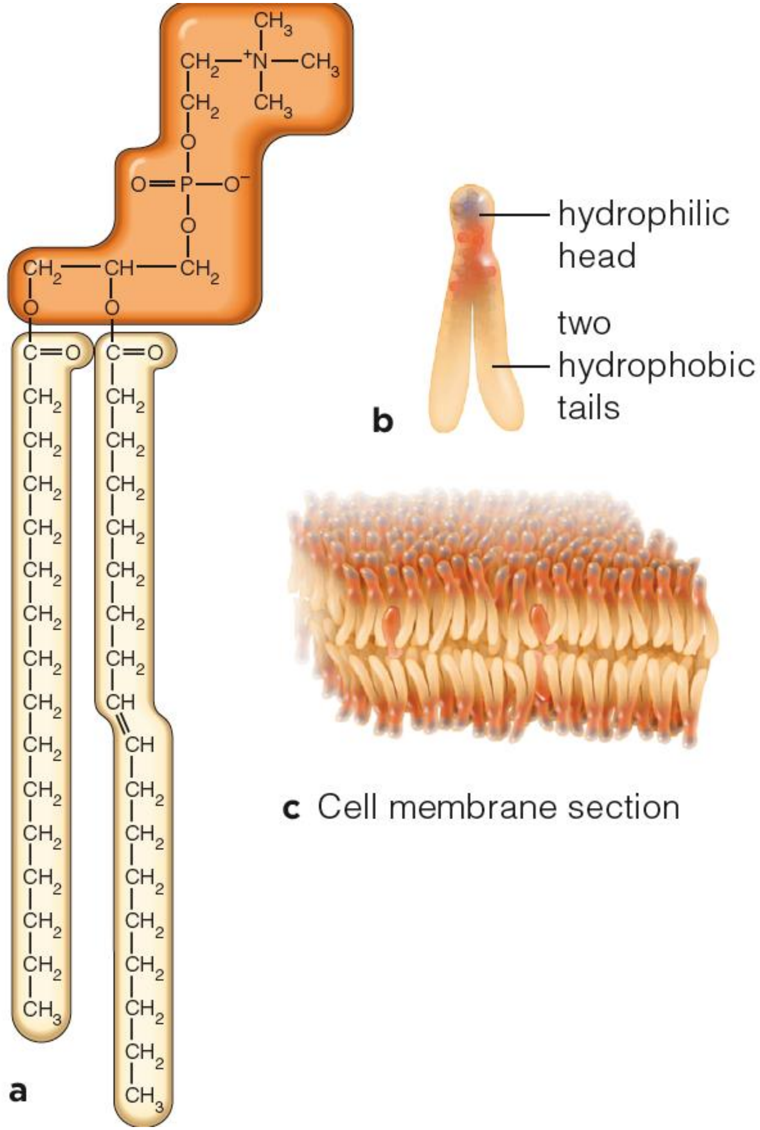
Phospholipids

- **Phospholipids**
  - Molecules with a polar head containing a phosphate and two nonpolar fatty acid tails
  - Heads are hydrophilic, tails are hydrophobic
  - The most abundant lipid in cell membranes
  - Note that it is a double layer with the hydrophilic heads points "out" while hydrophobic tails are "in"

Phospholipid Structure



Concept 3: Lipids

Lipids include various biomolecules whose common property is their insolubility in water.

Lipids include a variety of molecular types, such as neutral fats, oils, steroids, and waxes. Unlike other classes of biomolecules, lipids do not form large polymers. Two or three fatty acids are usually polymerized with glycerol, but other lipids, such as steroids, do not form polymers.

Lipids perform many important functions in biological systems, including:

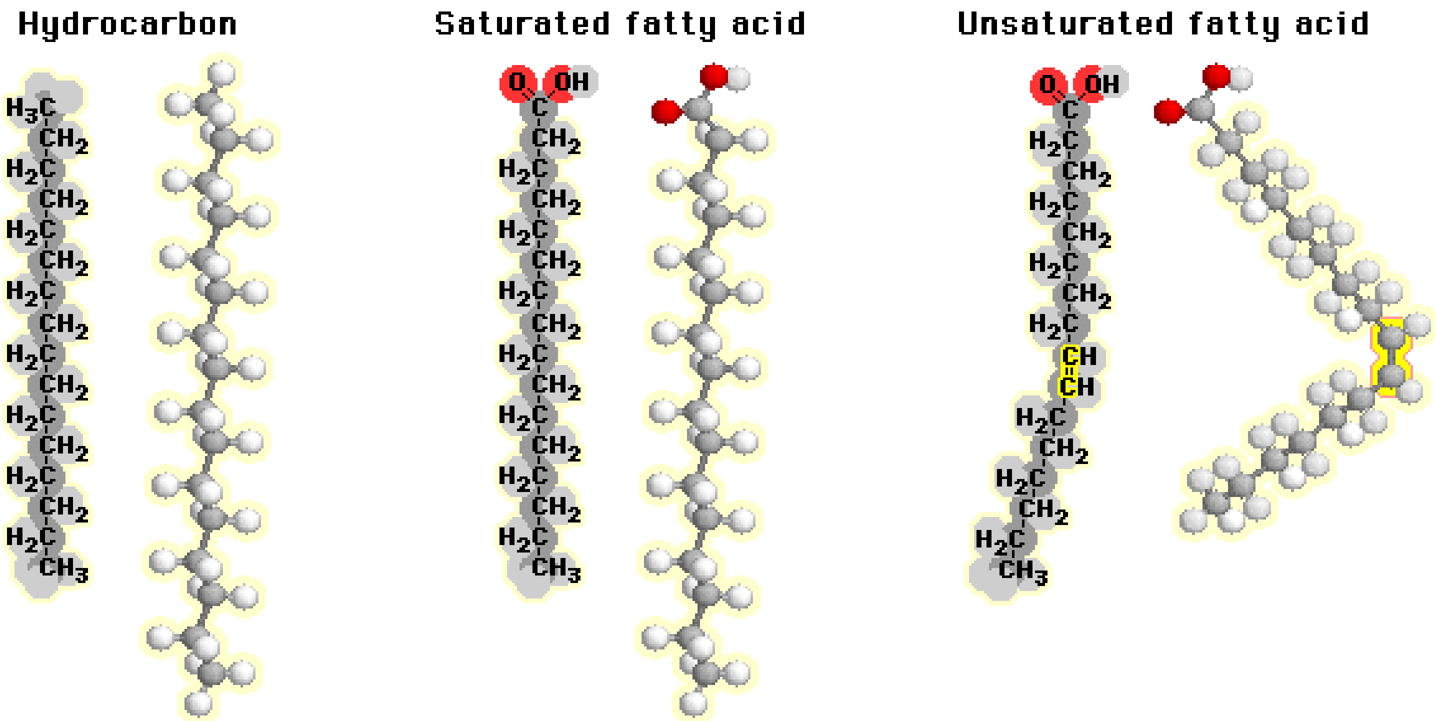
- contributing to the structure of membranes that enclose cells and cell compartments
- protecting against dessication (drying out)
- storing concentrated energy
- insulating against cold
- absorbing shocks
- regulating cell activities by hormone actions

Steroids function both as hormones (such as the sex hormones estrogen and testosterone) and as structural material (such as cholesterol, an integral part of animal cell membranes).

Concept 3 Review: Saturated and Unsaturated Fatty Acids

The presence of double bonds (unsaturation) in fatty acids changes the melting point of resulting lipids.

The simplest lipids are pure hydrocarbons, compounds containing only hydrogen and carbon atoms. These molecules are very nonpolar, because electrons are shared almost equally by carbon and hydrogen bonds.



Pure hydrocarbons are not found in living cells. Instead, living cells use modified hydrocarbons called fatty acids. Fatty acids have a carboxyl group at one end of a hydrocarbon molecule. Carboxyl groups are very polar. Even though the rest of the fatty acid is water insoluble, the region around the carboxyl group is soluble. This limited solubility allows cell enzymes, which function in an aqueous environment, to recognize and interact with fatty acids.

The carbon atoms in saturated fatty acids are linked entirely by single C-C bonds; unsaturated fatty acids contain one or more double bonds. Double bonds cause molecules to bend, and they can pack less tightly. As a result, their freezing point (the temperature at which a liquid turns into a solid) changes.

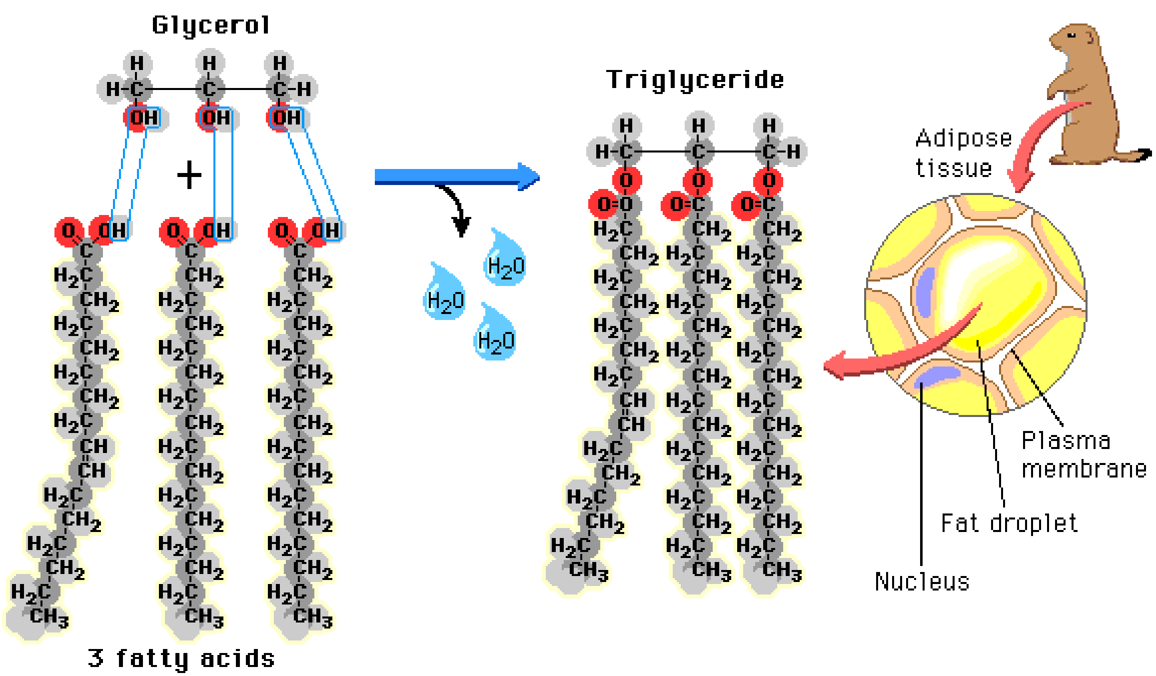
Fatty acids do not accumulate in large amounts inside cells; instead, they serve as monomers for the assembly of triglycerides and phospholipids.

Vegetable oils typically contain higher concentrations of unsaturated fatty acids than do animal fats, which contain mainly saturated fatty acids.

Concept 3 Review: Glycerol and Glycerides

Fatty acids are typically linked to glycerol, forming glycerides with one, two, or three attached fatty acids.

Fatty acids are usually linked to glycerol, a 3-carbon molecule. A diglyceride is a glycerol linked to two fatty acids; a triglyceride is a glycerol linked to three fatty acids.



Triglycerides are among the most common lipids. They are the main ingredient of fatty, or adipose, tissue, and are stored in fat droplets inside adipose cells.

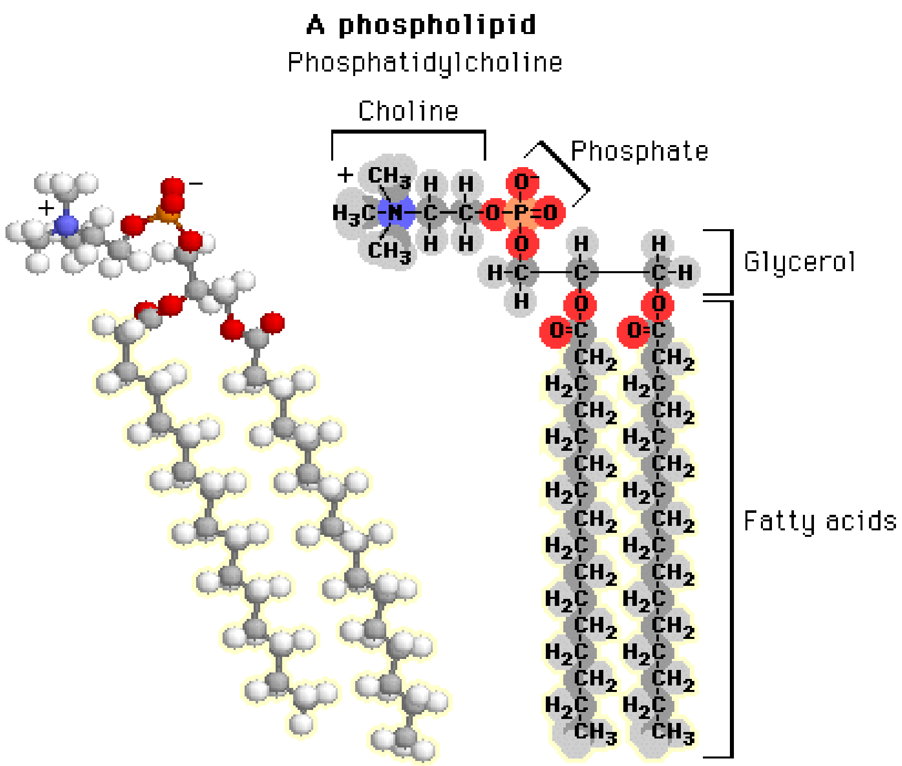
Triglycerides perform several important functions. They store large quantities of energy. However, it takes considerable time for the body to break down this energy because triglycerides are so poorly soluble in water.

Triglycerides can serve as insulation from cold. An extreme example is blubber found in whales and seals. Triglycerides also function in shock absorption by cushioning the organs.

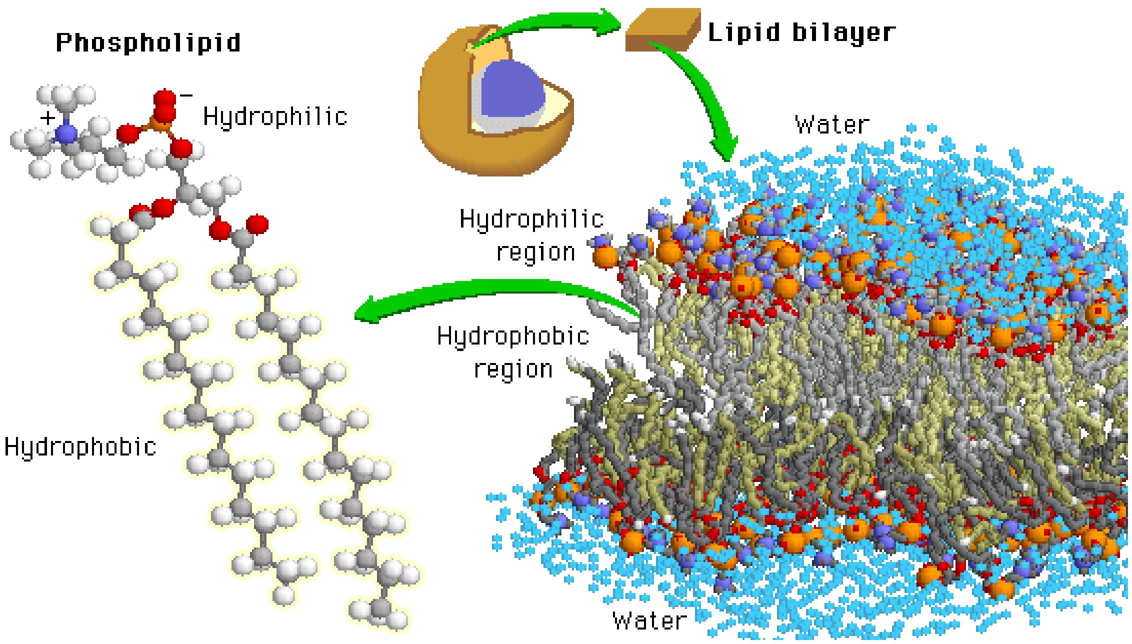
Concept 3 Review: Phospholipids and the Lipid Bilayer

Phospholipids spontaneously form lipid bilayers, which generate biological membranes.

Diglycerides contain two fatty acids linked to glycerol. Many diglycerides contain a phosphate group attached to the third -OH group of glycerol, producing a phospholipid. Phospholipids often contain additional charged groups attached to the phosphate.



In phospholipids, the two fatty acids are hydrophobic, or insoluble in water. But the phosphate group is hydrophilic, or soluble in water. When phospholipids are mixed with water, they spontaneously rearrange themselves to form the lowest free-energy configuration. This means that the hydrophobic regions find ways to remove themselves from water, while the hydrophilic regions interact with water.



The resulting structure is called a lipid bilayer. All biological membranes (except for those found in certain unusual bacteria, members of the Archaea) contain lipid bilayers, as well as proteins, which provide membranes with stability and specialized functions.

The image above is based on original work by H. Heller, M. Schaefer, & K. Schulten, "Molecular dynamics simulation of a bilayer of 200 lipids in the gel and in the liquid-crystal phases", J. Phys. Chem. 97:8343-60, 1993.

Carbon:
Molecules of Life

Organic Molecules

- All molecules of life are built with carbon atoms
- We correctly call carbon the signature atom of life and living forms, past and present
- We can use different models to highlight different aspects of the same molecule

Carbon – The Stuff of Life

- **Organic** molecules are complex molecules of life, built on a framework of carbon atoms – all the biological macromolecules below have a carbon backbone – the first two are rigid; proteins are uniquely flexible, and nucleic acids make up the DNA and RNA of heredity
  - Carbohydrates
  - Lipids
  - Proteins
  - Nucleic acids

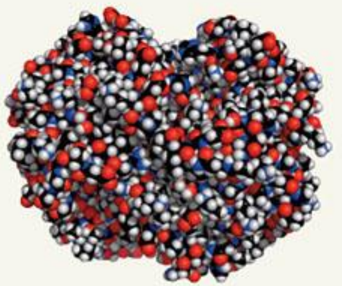
Carbon – The Stuff of Life

- Carbon atoms can be assembled and remodeled into many organic compounds
  - Can bond with one, two, three, or four atoms
    (only four because of electrons in outer V-shell)
  - Can form polar or nonpolar bonds
  - Can form chains or rings

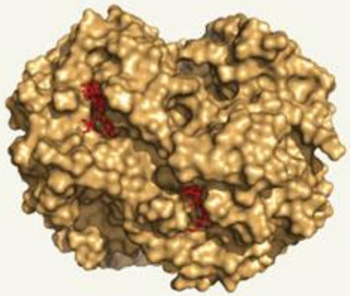
Three Models of a Hemoglobin Molecule

It's a protein and you can see the twists and coils and flex shapes.

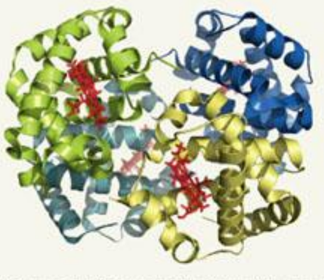
red blood cell



A A space-filling model of hemoglobin shows the complexity of the molecule.



B A surface model of the same molecule reveals crevices and folds that are important for its function. Heme groups, in *red*, are cradled in pockets of the molecule.



C A ribbon model of hemoglobin shows all four heme groups, also in *red*, held in place by the molecule's coils.

From Structure to Function

- The function of organic molecules in biological systems begins with their structure

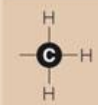
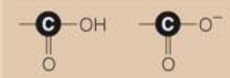
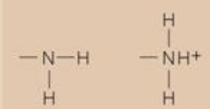
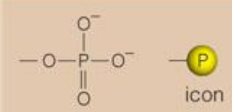
- The building blocks of carbohydrates, lipids, proteins, and nucleic acids bond together in different arrangements to form different kinds of complex molecules

Functional Groups

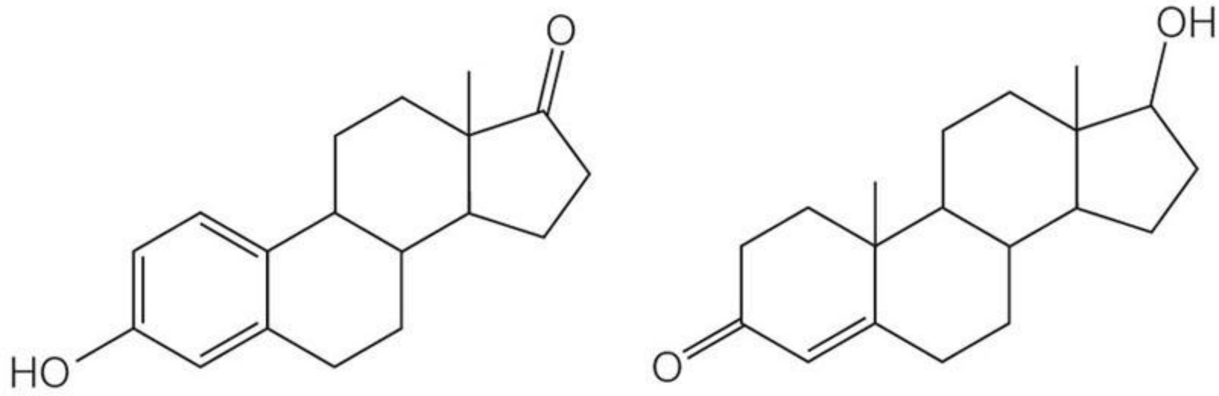
- **Hydrocarbon**
  - An organic molecule that consists only of hydrogen and carbon atoms

- Most biological molecules have at least one **functional group** (A cluster of atoms that imparts specific chemical properties to a molecule ex. polarity, acidity)

Common Functional Groups in Biological Molecules

Group	Character	Location	Structure
hydroxyl	polar	amino acids; sugars and other alcohols	—OH
methyl	nonpolar	fatty acids, some amino acids	
carbonyl	polar, reactive	sugars, amino acids, nucleotides	
carboxyl	acidic	amino acids, fatty acids, carbohydrates	
amine	basic	amino acids, some nucleotide bases	
phosphate	high energy, polar	nucleotides (e.g., ATP); DNA and RNA; many proteins; phospholipids	
sulfhydryl	forms disulfide bridges	cysteine (an amino acid)	—SH —S—S— (disulfide bridge)

Effects of Functional Groups: Sex Hormones



one of the estrogens

testosterone

Key Concepts:

Carbohydrates

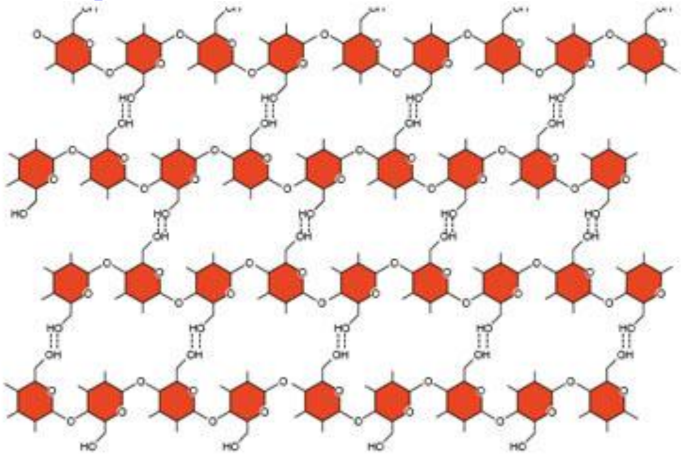
- *Carbohydrates are the most abundant biological molecules*
- *They function as energy reservoirs and structural materials*
- *Different types of complex carbohydrates are built from the same subunits of simple sugars, bonded in different patterns*

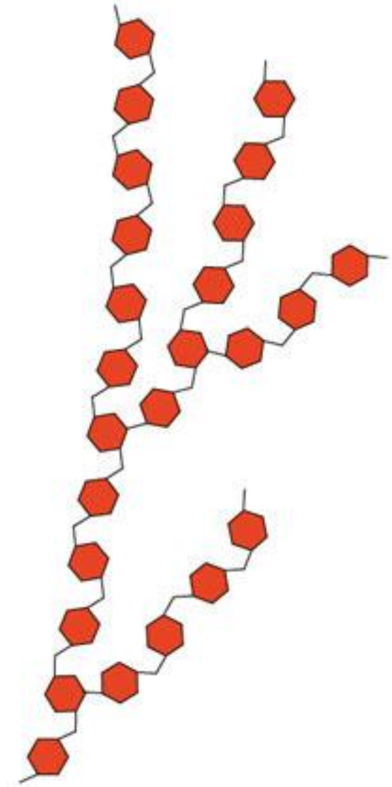
Complex Carbohydrates

- Polysaccharides
  - Straight or branched chains of many sugar monomers

- The most common polysaccharides are cellulose, starch, and glycogen
  - All consist of glucose monomers
  - Each has a different pattern of covalent bonding, and different chemical properties

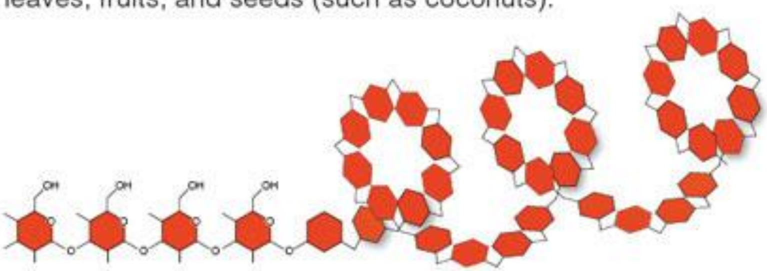
Cellulose, Starch, and Glycogen





a Cellulose, a structural component of plants. Chains of glucose units stretch side by side and hydrogen bond at many —OH groups. The hydrogen bonds stabilize the chains in tight bundles that form long fibers. Very few types of organisms can digest this tough, insoluble material.

b In amylose, one type of starch, a series of glucose units form a chain that coils. Starch is the main energy reserve in plants, which store it in their roots, stems, leaves, fruits, and seeds (such as coconuts).

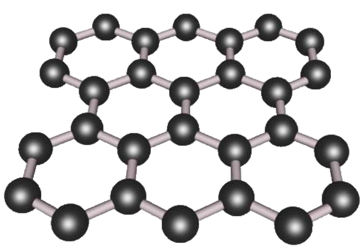


c Glycogen. In animals, this polysaccharide functions as an energy reservoir. It is especially abundant in the liver and muscles of active animals, including people.

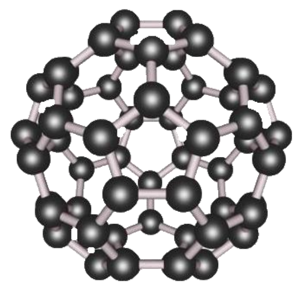
*When people talk about Nanoscience, many start by describing **things***

Physicists and Material Scientists point to ***things*** like new nanocarbon materials:

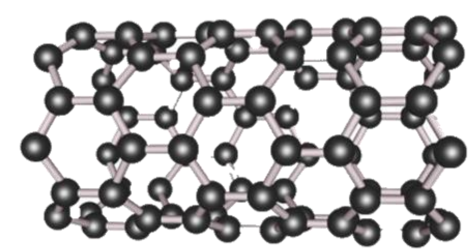
They effuse about nanocarbon's strength and electrical properties



Graphene



C60 Buckminster Fullerene

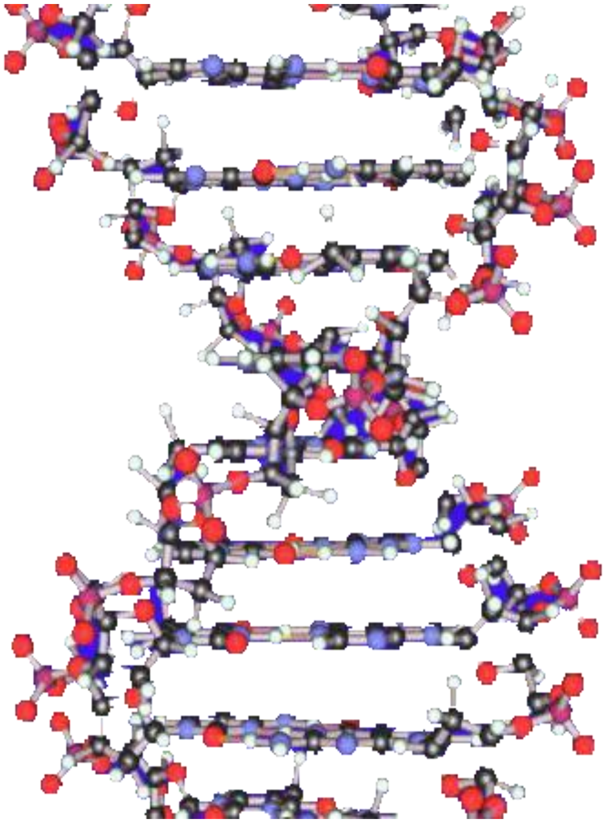


Carbon Nanotube

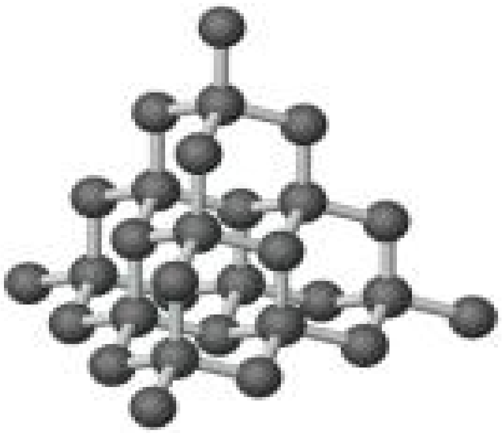
Biologists counter that nanocarbon is a recent discovery

THEY’VE been studying DNA and RNA for *much* longer

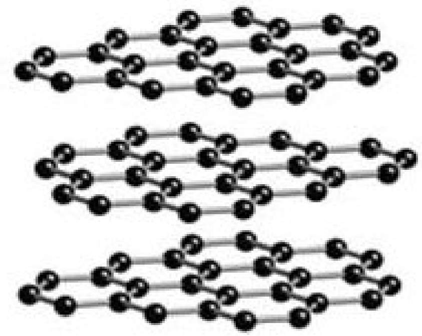
(And are *already* using it to transform our world)



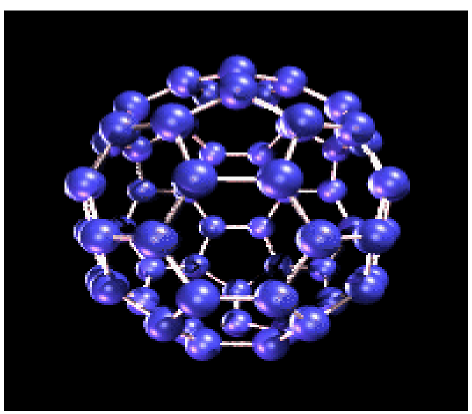
Different forms of elemental carbon: from diamond to graphite to ***buckyballs***!



Diamond

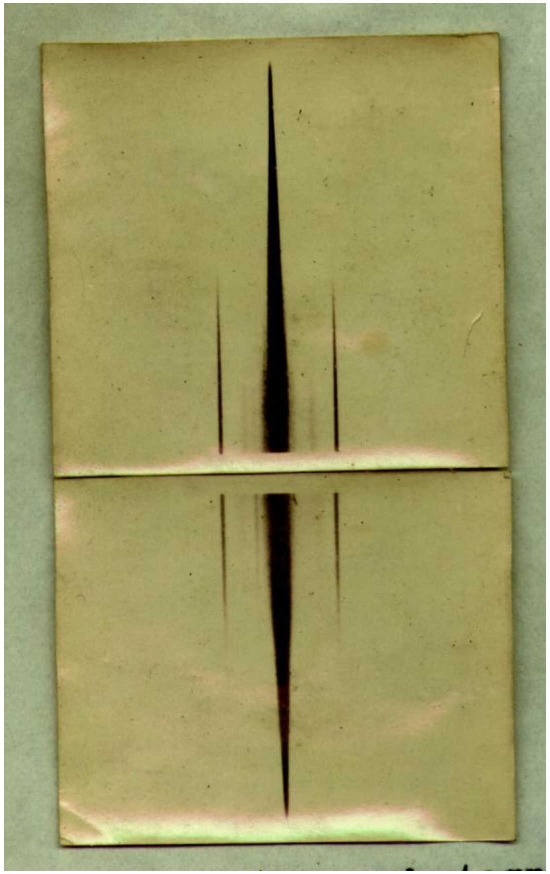


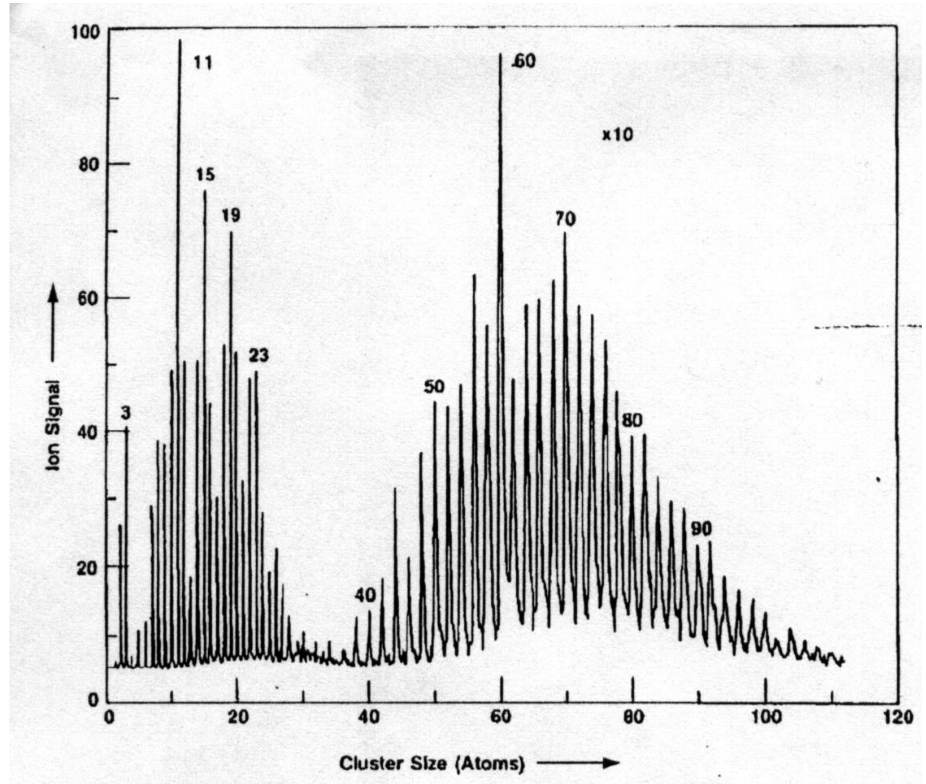
Graphite



C_{60}

H_2@C60





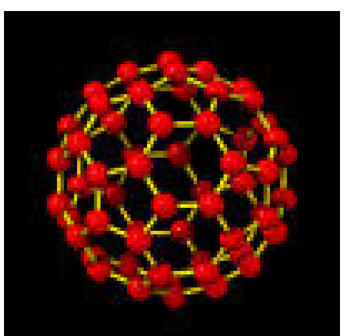
Discovery of Deuterium
Nobel Prize: 1934

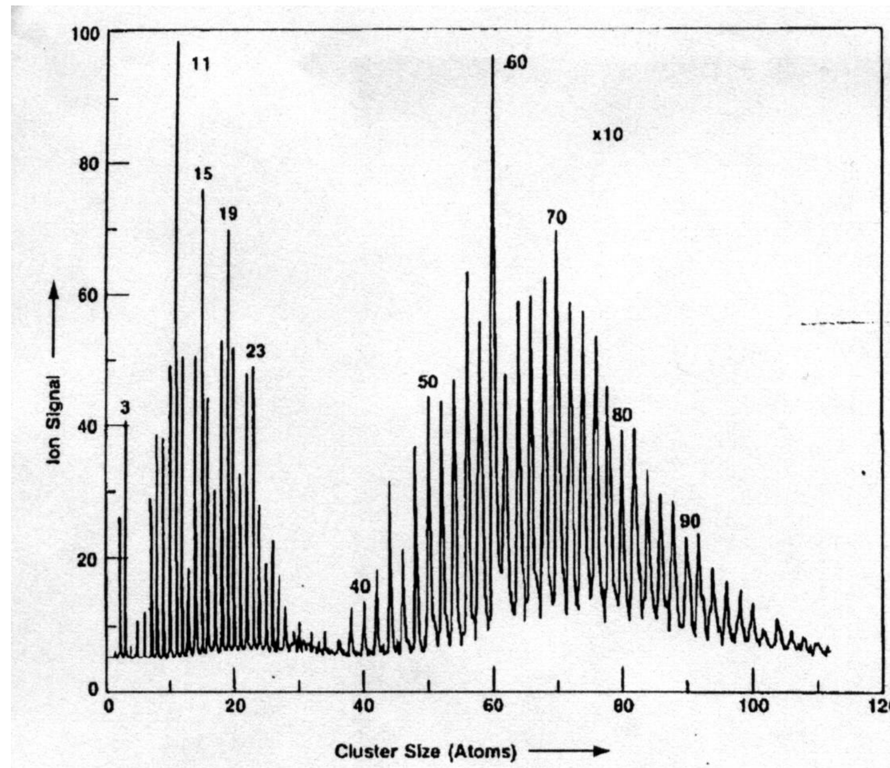
Discovery of C_{60}
Nobel Prize: 1996

An Extraordinary Claim: Carbon can exist in an elemental form that has a structure reminiscent to a soccer ball.

The first "evidence" for the special stability of C_{60}

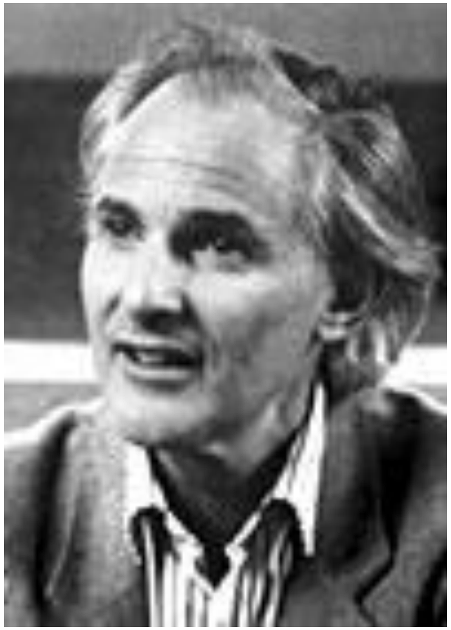
Discovery of C_{60}
"Buckyballs"
Pathological Science or Revolutionary Science?





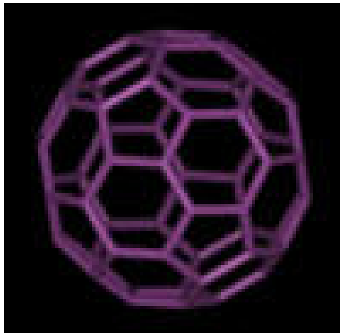
Would you have predicted a Nobel Prize?

Robert Curl



Harold Kroto

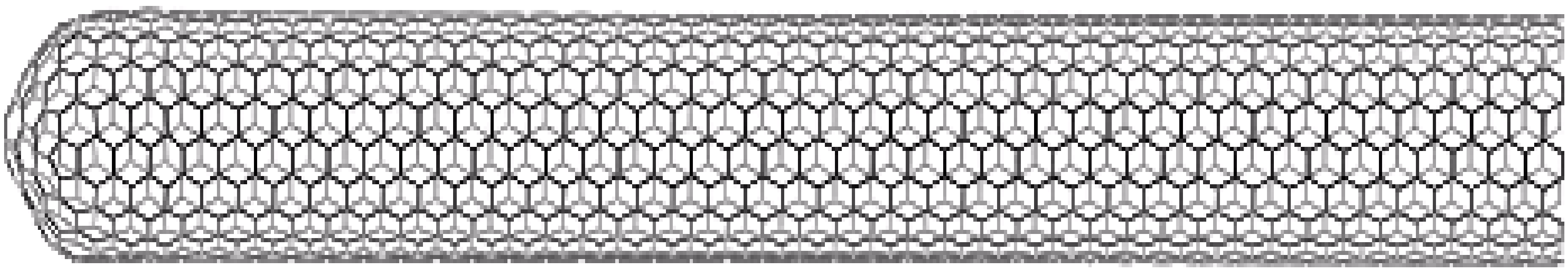
Richard Smalley

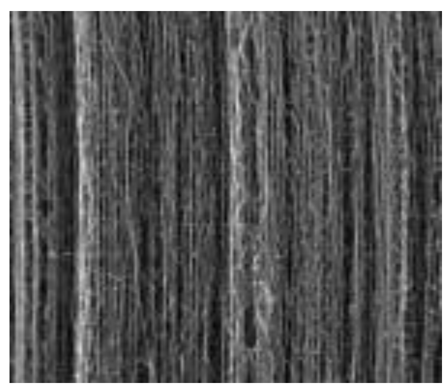


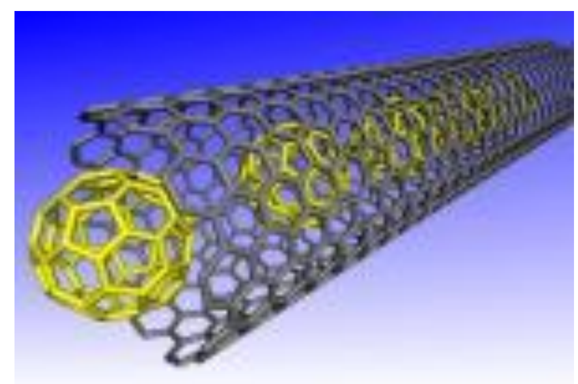
The Nobel Prize in Chemistry 1996
"for the discovery of fullerene"

The proposal of Buckeyballs turned out to be *revolutionary* science

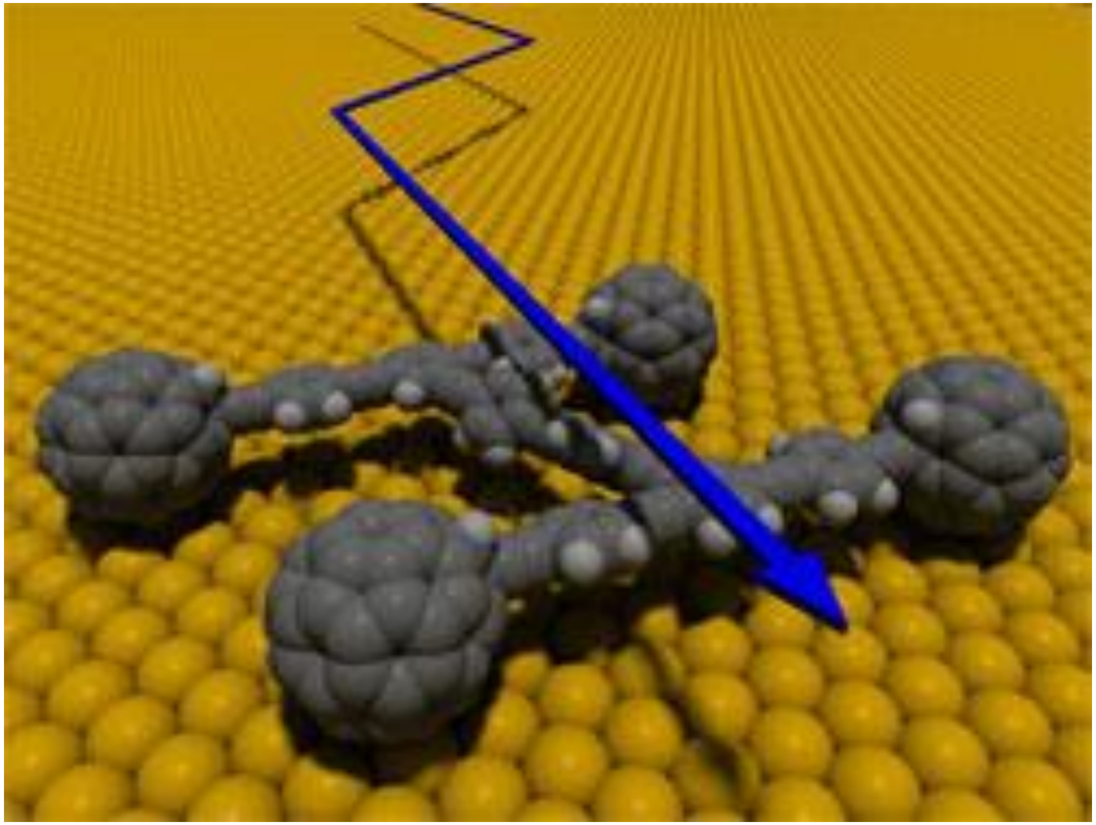
Buckyballs pulled into nanowires: Carbon nanotubes!





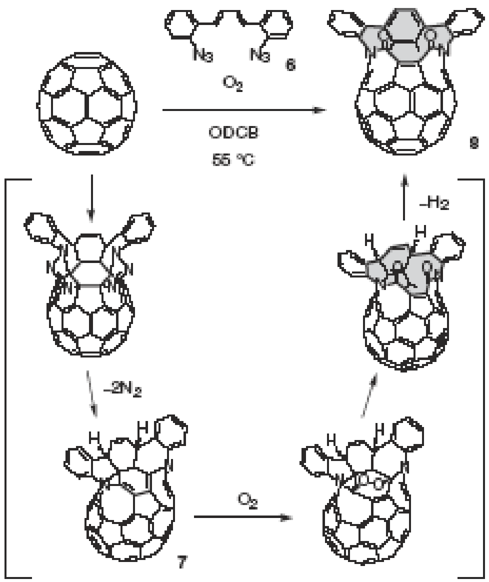


Nanodevices: A carbon nanocar rolling on a gold surface

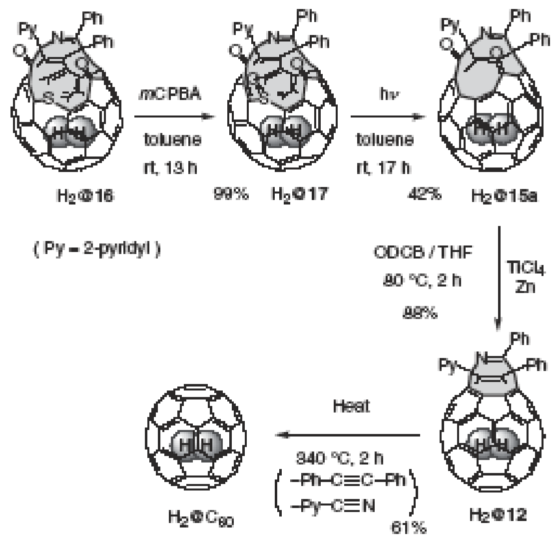


Thanks to Whitney Zoller

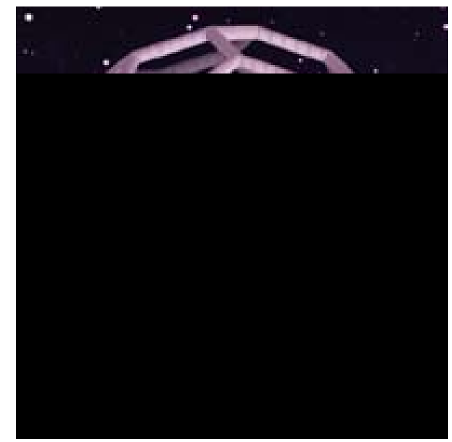
Putting H_2 inside a buckyball!



Open the buckyball



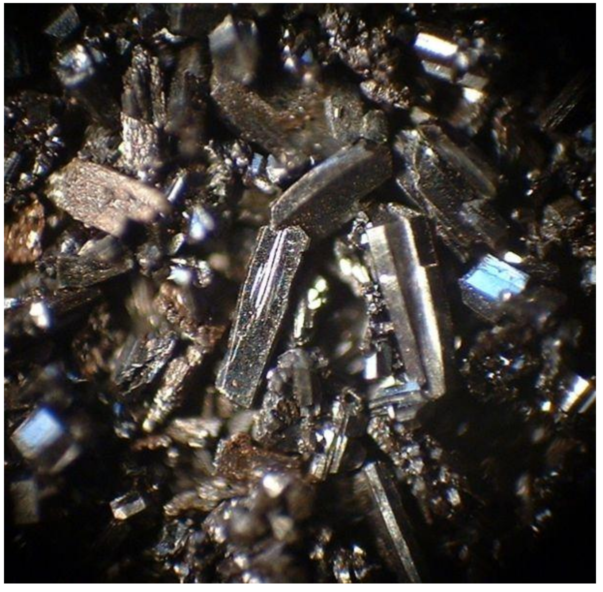
Put in H2, then close buckyball



H_2@C60

Collaborator: Professor Koichi Komatsu (Kyoto University)

Bit More About Buckyballs

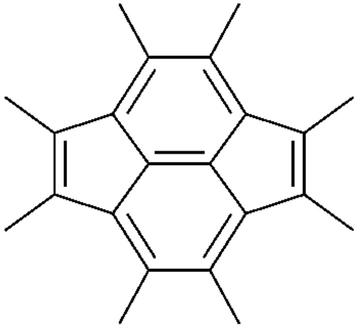


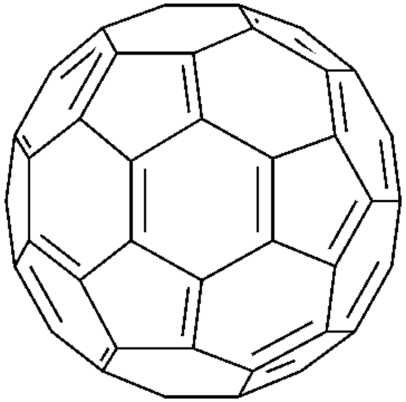
Buckyballs in crystalline form

- Buckyballs are also called fullerenes (after architect Richard Buckminster Fuller)
- Buckyballs were discovered in 1985 by Robert Curl, Harold Kroto and Richard Smalley
  - these scientists won the 1996 Nobel Prize in Chemistry for discovering this new allotrope of carbon.

The Structure of C_{60}

- 12 pentagons surrounded by 20 hexagons (corannulene substructure)
  - Two types of ring junctions (6,6 and 5,6)
  - Isolated pentagon rule (pyracylene subunits)





Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157-161.

Important Properties of C_{60}

- Structural
  - Unique geometry
    - High symmetry
    - Closed, spherical structure
  - 7 Å diameter—can encapsulate other atoms

- Electronic
  - Small HOMO-LUMO bandgap (3 degenerate orbitals form LUMO)
    - Easily reduced by up to 6 electrons
  - Strongly electronegative
  - Highly conjugated, but not "superaromatic"
    - Bent π bonds reduce conjugation

- Photosensitizer

Low Solubility of C_{60}

- Highly hydrophobic molecule
  - Limited solubility in many organic solvents
  - Completely insoluble in water

Solvent	Solubility (μg/mL)
Water	**--**
hexane	40
Dioxane	41
cyclohexane	51
carbon tetrachloride	447
Benzene	1,440
toluene	2,150
carbon disulfide	5,160

Sivaraman, N. et al. *J. Org. Chem.* **1992**, *57*, 6077-6079.

Outline

- Approaches to water-soluble C_{60}
  - Non-covalent
  - Covalent
- Biological applications of C_{60} derivatives
  - HIV-1 protease (HIVP) inhibition
  - Neuroprotective properties
  - Antibacterial properties
  - Gene transfection and related properties
- Toxicity of C_{60} and derivatives
  - Pristine C_{60} (unmodified)
  - Functionalized C_{60}
- Conclusions and Outlook

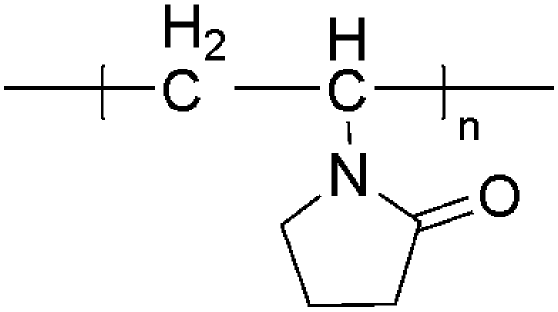
Water-Soluble C_{60}

- Pristine C_{60} can be suspended in water
- Biological uses of fullerenes require genuine water solubility and little or no aggregation
- Complexation with water-soluble supramolecules is one effective approach
  - Surfactants
  - Polyvinylpyrrolidone (PVP)
  - Cyclodextrins

Non-Covalent Methods: C_{60}-PVP Solutions

- PVP is a dispersant used in cosmetics and medicines.

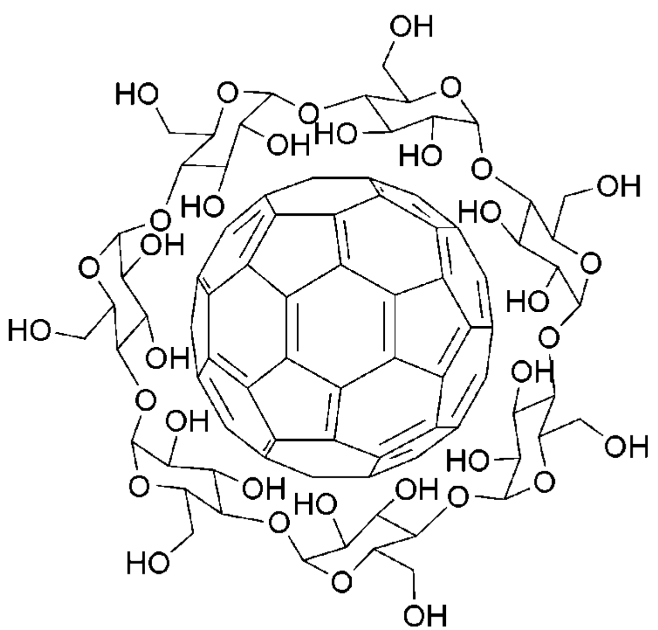
- C_{60}-toluene mixed with PVP-chloroform, solvents evaporated, and residue dissolved in water
  - Highest [C_{60}] obtained was 400 μg/mL, using 100:0.8 PVP:C_{60} w/w



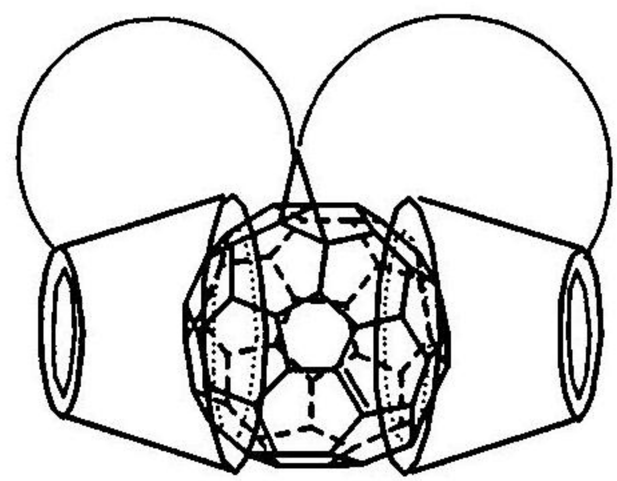
Yamakoshi, Y.N. et al. *Chem. Comm.* **1994**, 517-518; Sera, N. et al. *Carcinogenesis* **1996**, *17*, 2163-2169; Ungurenasu, C.; Airinei, A. *J. Med. Chem.* **2000**, *43*, 3186-3188.

C_{60}-Cyclodextrin Complexes

- Non-covalent or covalent complexes enhance water solubility
  - Aggregation phenomena encountered with 1:1 complexes



γ-cyclodextrin



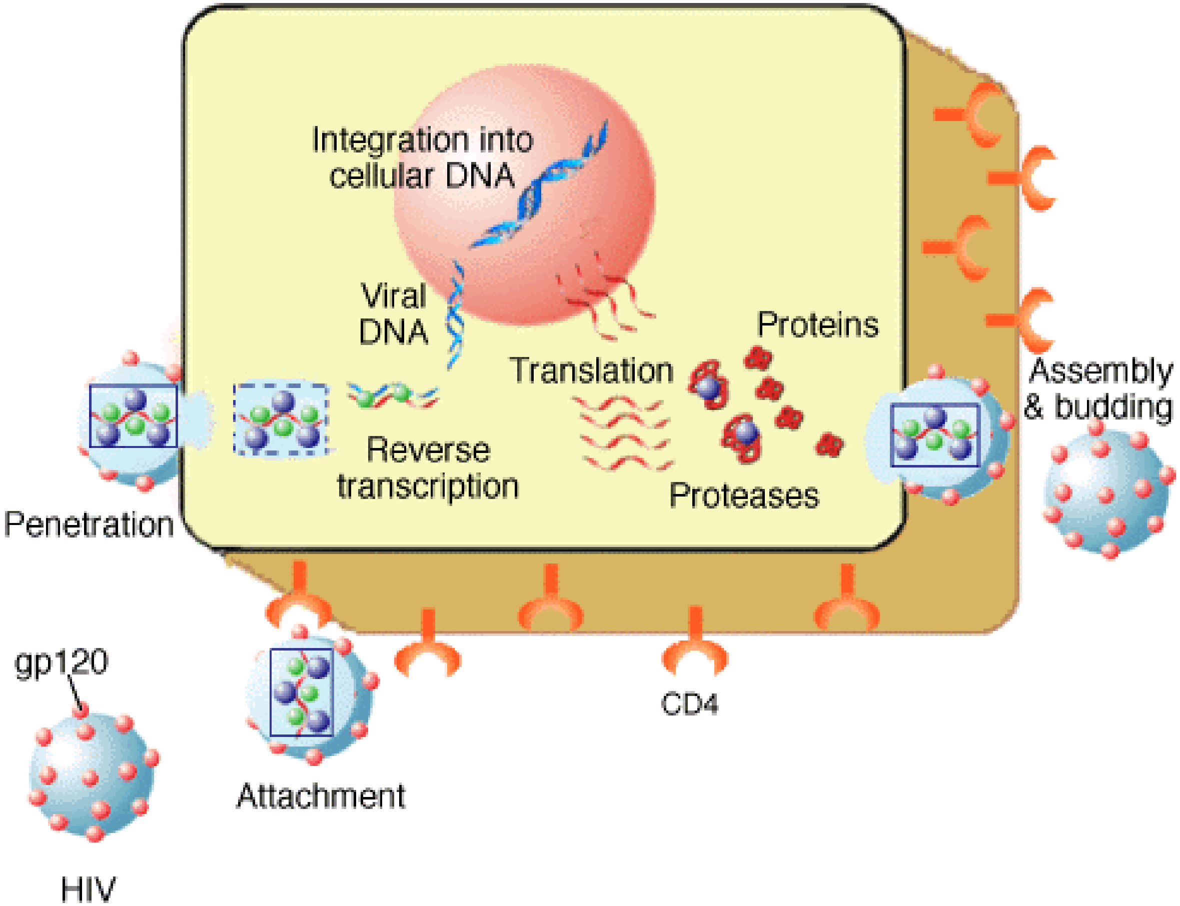
β-cyclodextrin

Andersson, T. et al. *Chem. Comm.* **1992**, 604-606; Filippone, S. et al. *Chem Comm.* **2002**, 1508-1509; Liu, Y. et al. *Tetrahedron Lett.* **2005**, *46*, 2507-2511; Chen, Y. et al. *Tetrahedron* **2006**, *62*, 2045-2049.

Overview of Biological Activities of C_{60} Derivatives

- Antioxidant
- DNA cleavage
- Membrane disruption
- Photodynamic therapy
- Drug delivery (e.g. paclitaxel)
- X-ray contrast agents
- Inhibition of β-amyloid aggregation
- **Free radical sponge**
  - **Neuroprotection**
- **Antibacterial**
- **Gene transfection**
- **Enzyme inhibition (HIVP, etc.)**
- **And more…**

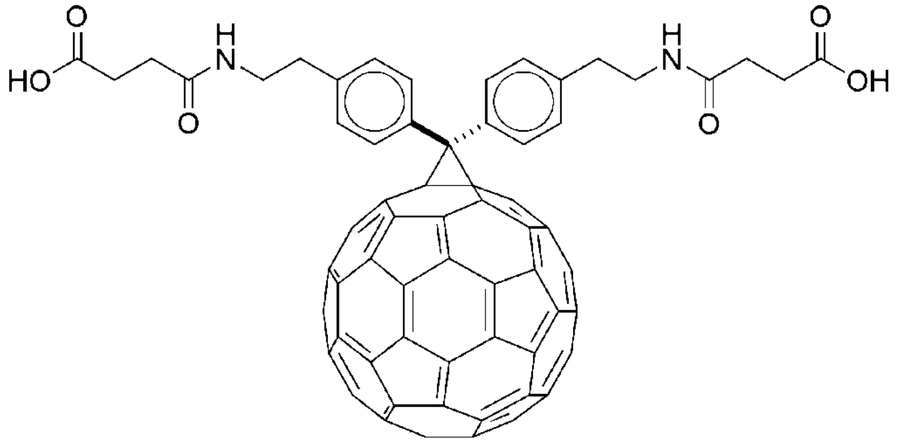
Life Cycle of the HIV Retrovirus



http://www.ovc.uoguelph.ca/BioMed/Courses/Public/Pharmacology/pharmsite/98-409/HIV/AIDS_images/HIV_life_cycle.gif

First Discovery of Biological Activity of a Fullerene

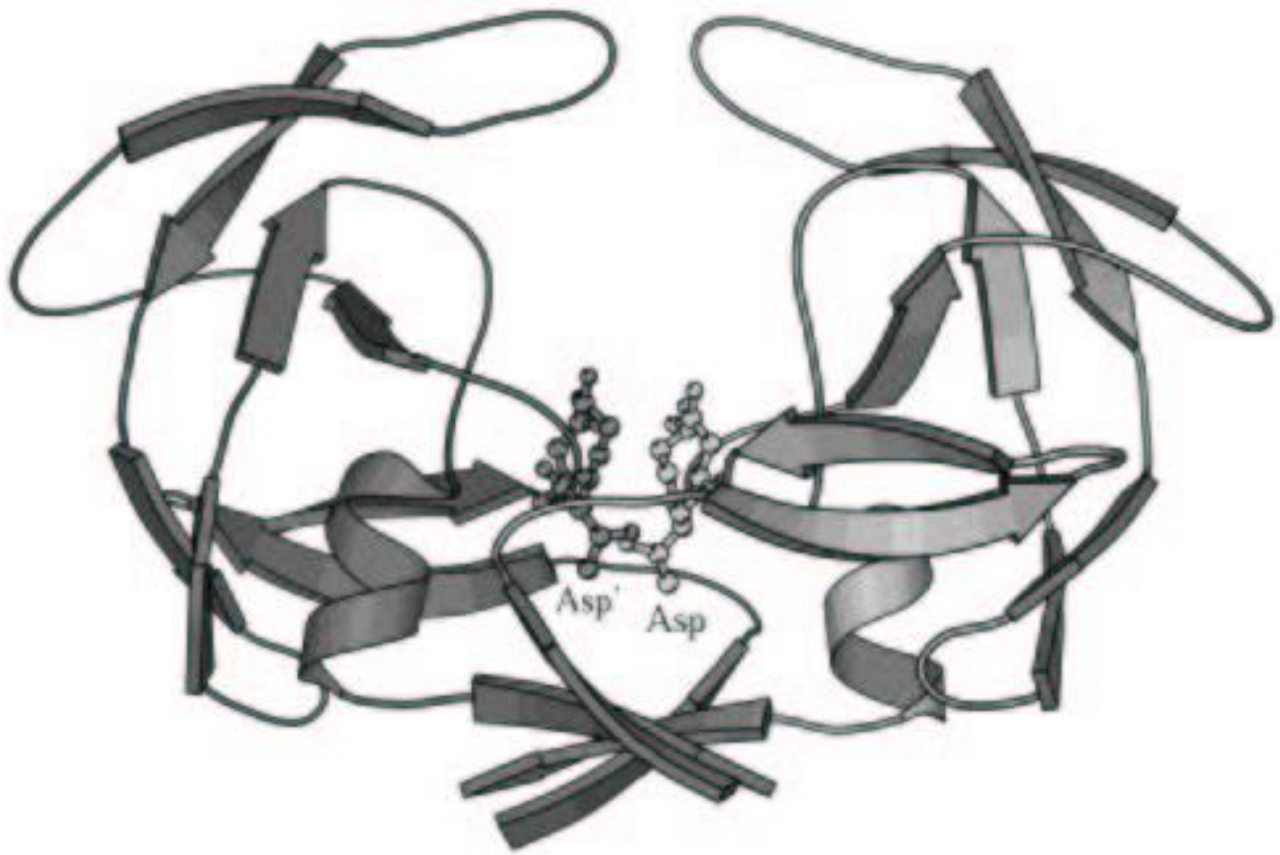
- Hydrophobic, 7-8 Å binding pocket of HIV-1 protease (HIVP) is an attractive target for fullerene inhibition
  - Computational analysis suggested C_{60} fits snugly in the active site of HIVP
- Properties
  - K_i = 5.3 µM (Best inhibitors are nanomolar or lower)
  - Toxic even against drug-resistant HIV-variants



The first fullerene-based inhibitor of an enzyme

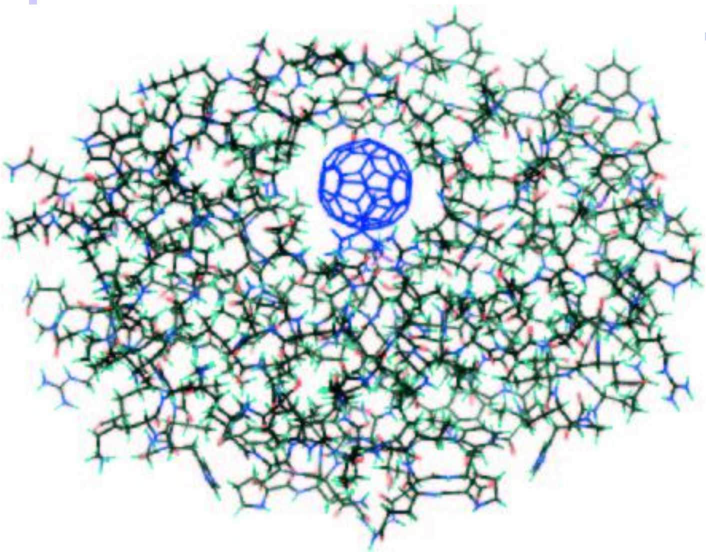
Kenyon G.L. and co-workers. *J. Am. Chem. Soc.* **1993**, *115*, 6506-6509 and 6510-6512.

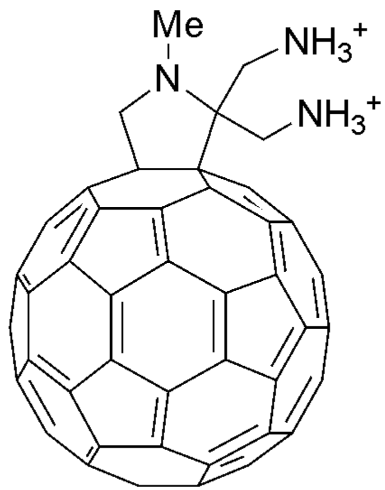
Improving HIVP Inhibitors

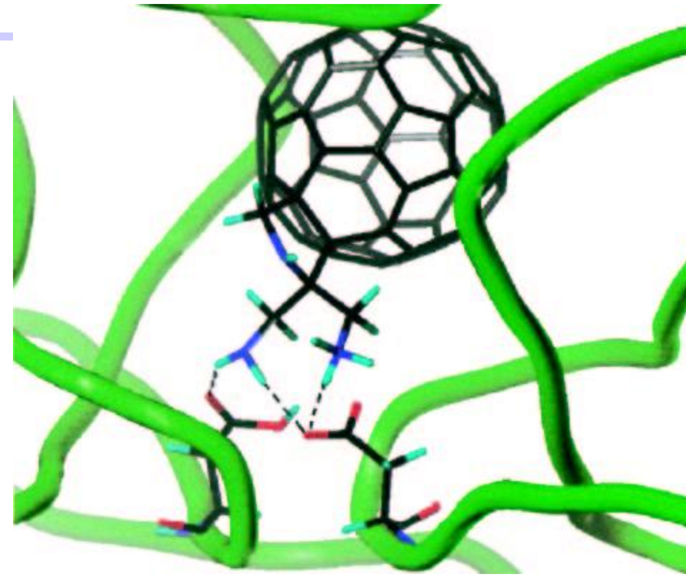


Zhu, Z. et al. *Biochemistry* **2003**, *42*, 1326-1333.

Improving HIVP Inhibitors



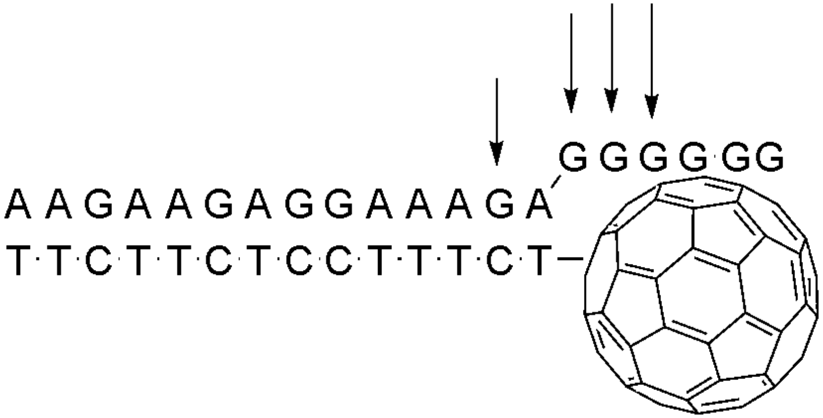




Marcorin, G.L. et al.*Org. Lett*. **2000**, *2*, 3955-3958.

C_{60} and DNA

- Water-soluble fullerenes oxidatively cleave DNA when photo-excited
  - C_{60}-oligonucleotide complexes enable site-selective cleavage (at G sites) and water solubility
  - Potentially applicable to photodynamic therapy (PEG derivatives)



- Can water-soluble fullerene derivatives be synthesized that will bind DNA and transport it through cell membranes, without damaging it?

Tokuyama, H. et al. *J. Am. Chem. Soc.* **1993**, *115*, 7918-7919; Boutorine, A.S. et al. *Angew. Chem Int. Ed. Engl* **1994**, *33*, 2462-2465; Tabata, Y. et al. *Jpn. J. Cancer Res.* **1997**, *88*, 1108-1116.

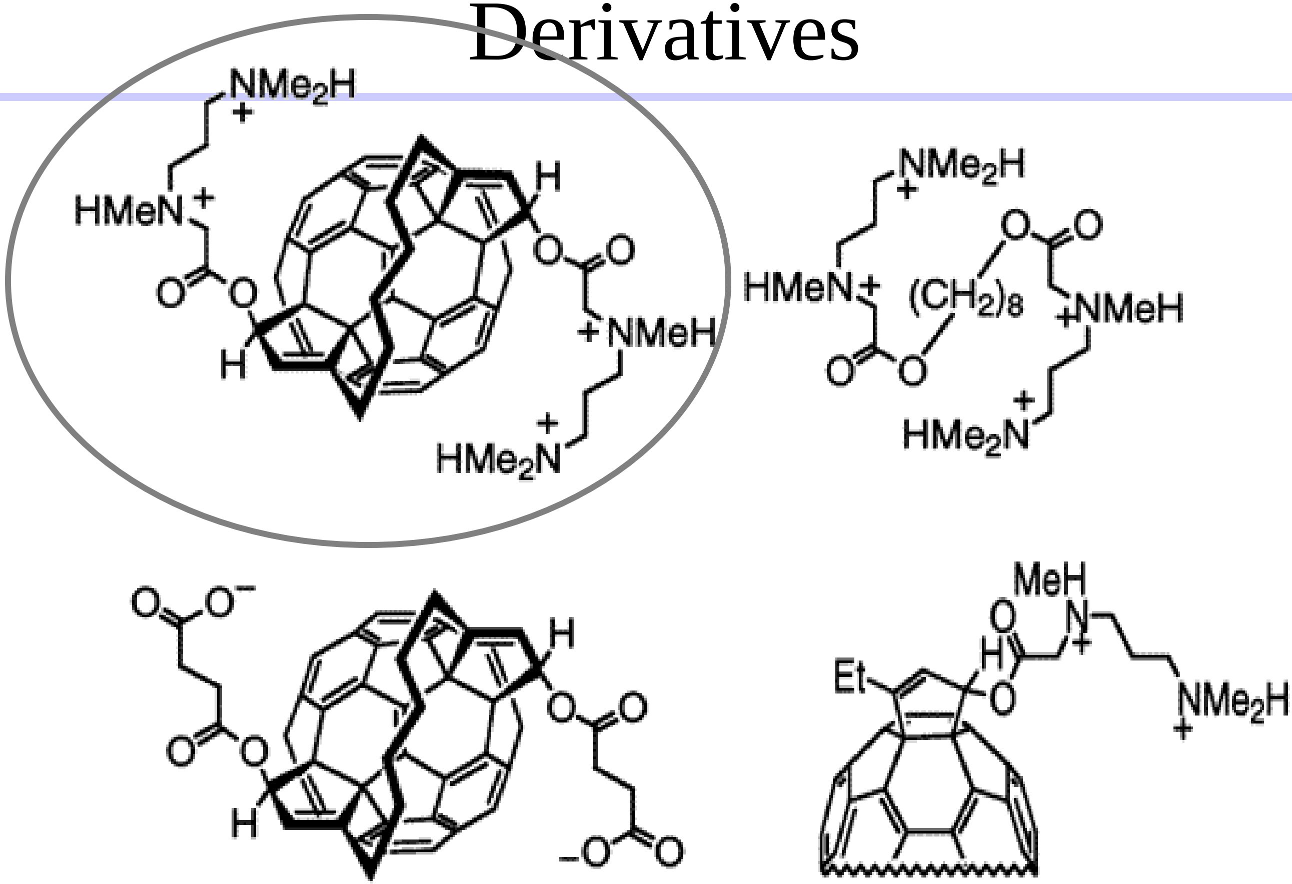
Gene Transfection

- Common methods
  - Microinjection
  - Viral vectors (short DNA)
  - Chemical methods
    - Cationic lipids and polymers
    - Commercial reagents for transfection are available

- Discovery of other methods could reduce cytotoxicity and enhance efficiency and reliability of transfection methods

Isobe, H. et al. *Mol. Pharm.* **2006**, *3*, 124-134.

Non-Viral Gene Delivery with C_{60} Derivatives



Nakamura, E. et al. *Angew. Chem. Int. Ed. Engl.* **2000**, 39, 4254-4257.
Isobe, H. et al. *Chem. Lett.* **2001**, 1214-1215.

Non-Viral Gene Delivery with C_{60} Derivatives

- Fullerene transfection agents proved as good or better than traditional lipofection agents
  - Lower cytotoxicity
  - Higher transfection efficiency
  - Both transient and stable transfection possible
  - Fullerene does not appear to interfere with gene expression (esters cleaved in the cell?)
  - No problems with photo-induced DNA cleavage
- Fullerene transfection agents could be an improvement over viral vectors
  - Not introducing a potentially harmful virus
  - Enable addition of larger nucleotide sequences
- Methodology for large-scale synthesis of related amino-fullerene derivatives could enable commercialization

Isobe H. et al. *J. Org. Chem.* **2005**, *70* 4826-4832; Isobe, H. et al. *Mol. Pharm.* **2006**, *3*, 124-134.

Summary

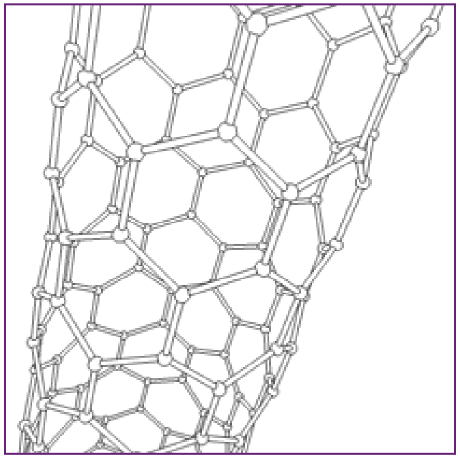
- Unusual properties of the buckyball have generated interest in broadly ranging fields

- Biological applications of fullerenes are broad and rapidly evolving

  - Water-solubility issues have been addressed synthetically
  - Enzyme inhibition, gene transfection, neuroprotection, and other biological applications may become commercially viable

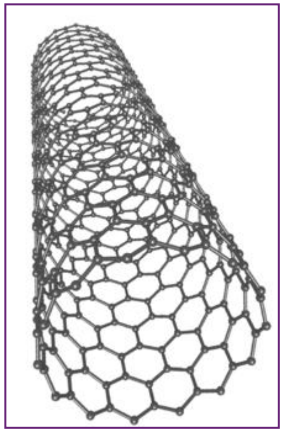
Nanotubes

- Carbon nanotubes, composed of interlocking carbon atoms, are 1000x thinner than an average human hair – but can be 200x stronger than steel.



Which Of These Object Are Made From Carbon?




Water	Diamond	Graphite	Nanotube	Coal

Activity 1

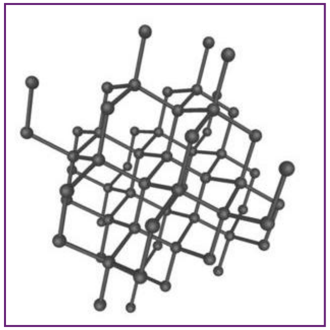
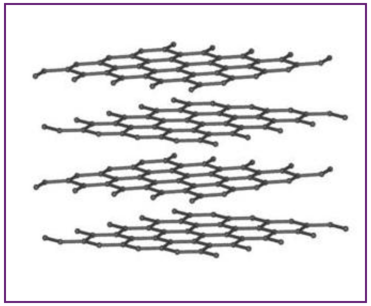
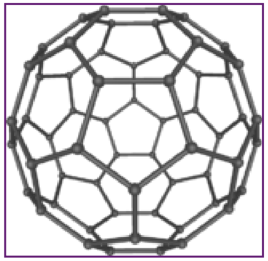
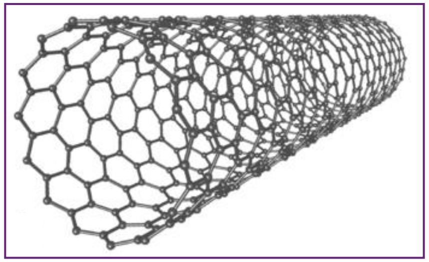
Perform the *Researching Carbon Activity* to learn more about the following allotropes (different forms) of carbon:

coal, graphite, diamond, buckyballs, carbon nanotubes.

Activity 1 Researching Carbon

Allotrope	Structure	Properties	Uses/ Applications
Coal			
Graphite			
Diamond			
Buckyballs			
Carbon Nanotubes			

Allotropes of carbon have different covalent bonding arrangements.

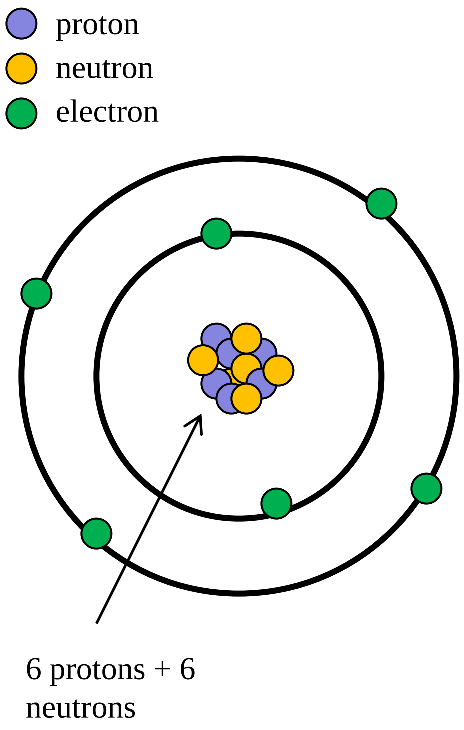





diamond **graphite** **buckyball** **nanotube**

- Carbon atoms form covalent bonds by sharing outer shell electrons with each other
- Diamond, graphite, buckyballs and carbon nanotubes all have different covalent arrangements of carbon atoms
- The differing covalent arrangements of carbon atoms lead to the different properties of carbon allotropes.

Covalent Bonding

Sharing Electrons

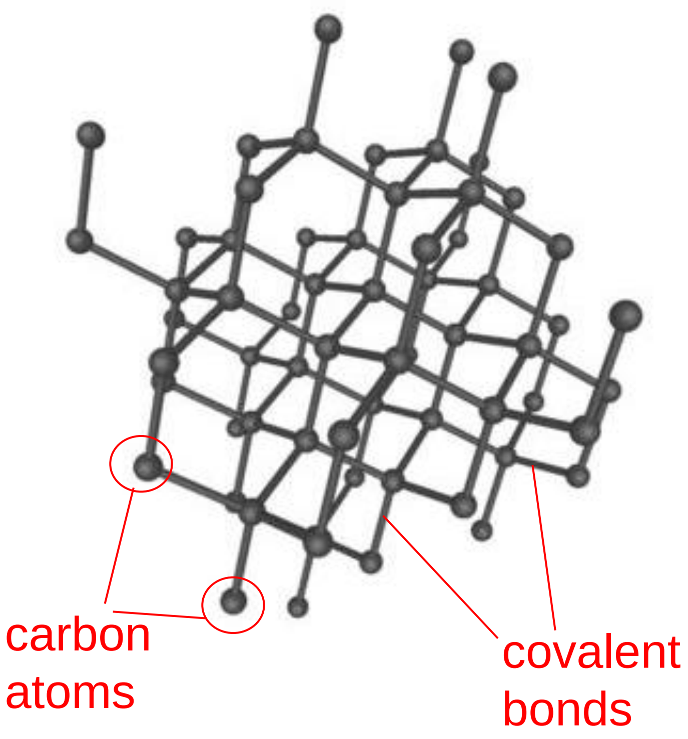


A **covalent bond** is a form of chemical bonding that is characterised by the sharing of pairs of electrons between atoms

Valence electrons are the electrons in the outer shell or energy level of an atom that form covalent bonds

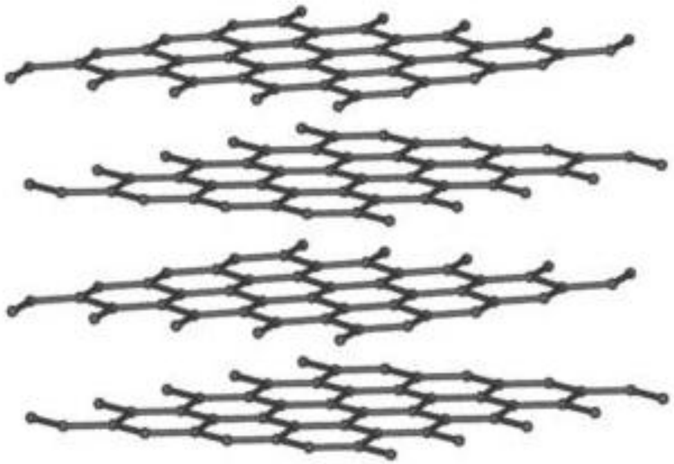
A carbon atom has 6 electrons, 4 of which are Valence electrons
Therefore, carbon atoms can form up to 4 Covalent Bonds

Covalent Bonds In Diamond



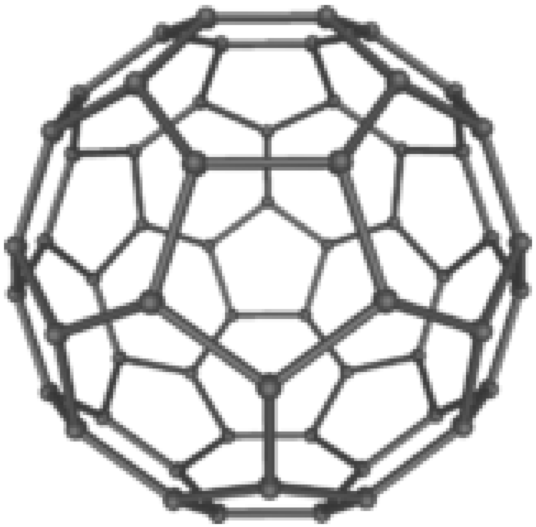
- Diamond is formed by a 3D box-like network of carbon atoms
- The continuous nature of the covalent arrangements forms a giant molecule
- Electrons are fixed.

Covalent Bonds In Graphite



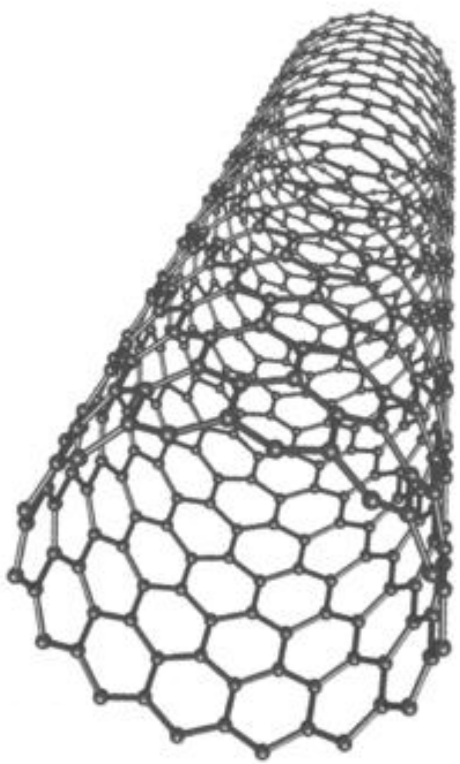
- Graphite is formed by hexagonally-arranged carbon molecules forming 2D layers of sheets
- Electrons are free to move between each carbon sheet.

Covalent Bonds In Buckyballs



- Carbon atoms in buckyballs are arranged in a soccer ball shape
- C60 Buckyballs have 20 regular hexagon faces and 12 regular pentagon faces
  - these faces come together at 60 carbon atom vertices
- Electrons are localised internally due to the curvature of the structure.

Covalent Bonds In Carbon Nanotubes



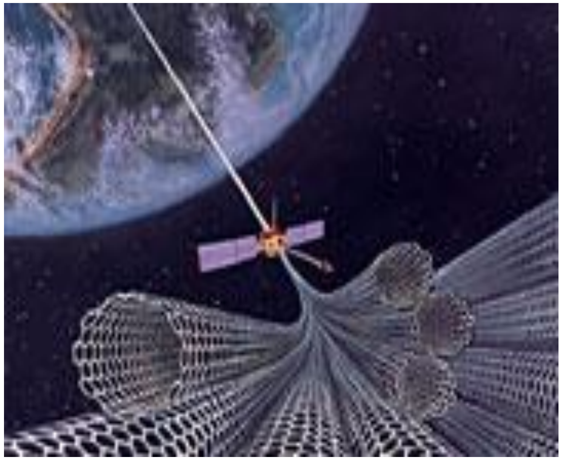
- Carbon nanotubes are formed by a layer of hexagonally-arranged carbon atoms rolled into a cylinder
  - usually have half buckyballs on one or both ends
- Electrons are localised internally, and some can move along the length of the tube by ballistic transport
- Carbon nanotube diameter ~ 1nm
- Carbon nanotube length can be a million times greater than its width
- Nanotubes can be
  - single-walled (d = 1-2 nm), or
  - multi-walled (d = 5-80 nm).

Properties of Carbon Allotropes

Allotrope	Hardness	Tensile strength	Conducts heat	Conducts electricity
Coal	+	+	+	no
Graphite	++	++	+++++	+++++
Diamond	+++++	Not known	+++	no
Buckyballs	+++++	++++	+	+
Carbon Nanotubes	++++++	+++++	+++++	++++++

Unique Properties Of Carbon Nanotubes

- 200x stronger than steel of the same diameter
- The first synthetic material to have greater strength than spider silk
- Excellent conductors of electricity and heat
- Have huge potential for product development.



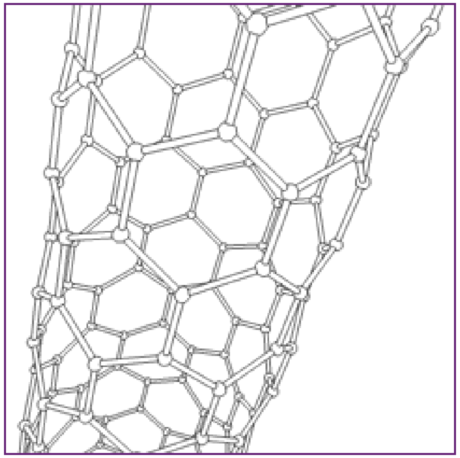
Space elevator?

Activity 2

Perform the *Allotropes of Carbon Activity* to further explore the molecular structure and properties of carbon allotropes.

Carbon Nanotubes

Given their unique properties, what can carbon nanotubes be used for?



Nanotubes In Efficient Solar Cells

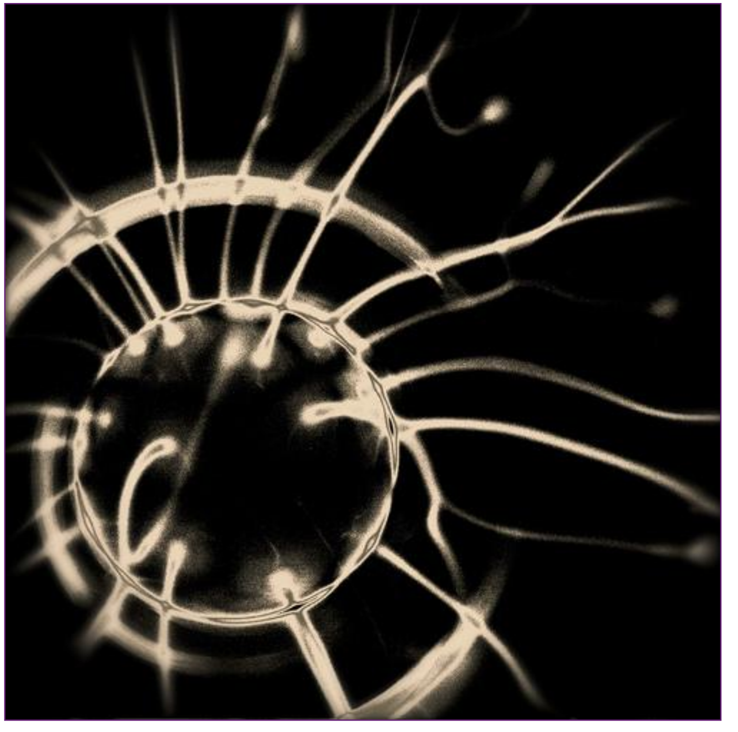
- Scientists have developed the ‘blackest black’ colour using carbon nanotubes
- The carbon nanotubes are arranged like blades of grass in a lawn
  - they absorb nearly all light
- Use of carbon nanotubes in solar cells could vastly improve their efficiency.

Nanotubes In Sporting Equipment

- Badminton racquet manufacturer Yonex incorporates carbon nanotubes into their cup stack carbon nanotubes racquets (www.yonex.com)
- American baseball bat manufacturer Easton Sports has formed an alliance with a nanotechnology company Zyvex to develop baseball bats incorporating carbon nanotubes
- Tennis racquets also incorporate carbon nanotubes (www.babolat.com).

Nanotubes In Miniaturised Electronics

- Branching and switching of signals at electronic junctions is similar to what happens in nerves
- A carbon nanotube ‘neural tree’ can be trained to perform complex switching and computing functions
- Could be used to detect/respond to electronic, acoustic, chemical or thermal signals.

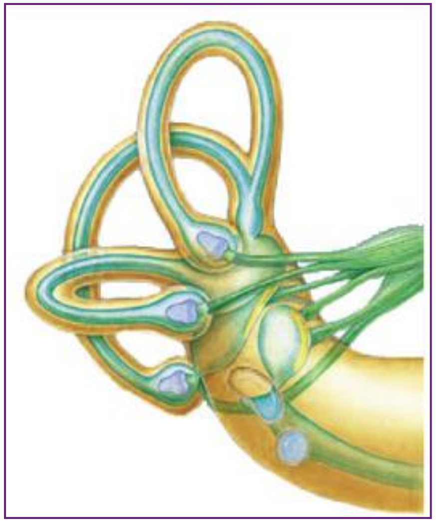


Nanotubes In AV Technology

- Carbon nanotubes are being used to develop flat screen televisions with higher resolution than the human eye can detect
- Your next TV screen could be thin, ultra-light and foldable…

Graphene Sheets

A new form of carbon with many potential uses.



- this new form of carbon just one atom thick

  “The very unusual electronic properties of graphene sheets means they could be used in solar cells or new battery technology,” he says

  “Because of the biological affinity of carbon, they might also be useful as electrodes for a range of medical bionic devices such as cochlear implants”

- Graphene sheets could also be used to create transparent electrodes and coatings that prevent the build up of static electricity.

How Are Nanosized Carbon Structures Made?

Manufacturing Carbon Nanotubes

Molecular Engineering

- Carbon nanotubes can be made using molecular engineering
- Molecular templates are created
  - under the right chemical conditions carbon atoms arrange themselves into nanotubes on the template
- This process is also known as **chemical synthesis** or **self-assembly**, and is an example of the **‘bottom-up’** approach to molecular engineering.

Molecular Engineering

2 Approaches

- ‘**Bottom-up**’ approach: structures are built atom by atom
  - can use self-assembly or sophisticated tools (eg scanning tunnelling microscope, atomic force microscope) which can pick up, slide or drag atoms or molecules around to build simple nanostructures
- ‘**Top-down’** approach: traditional engineering techniques such as machining and etching are used at very small scales
  - products tend to be refinements of existing products, such as electronic chips with more and more components crammed onto them.

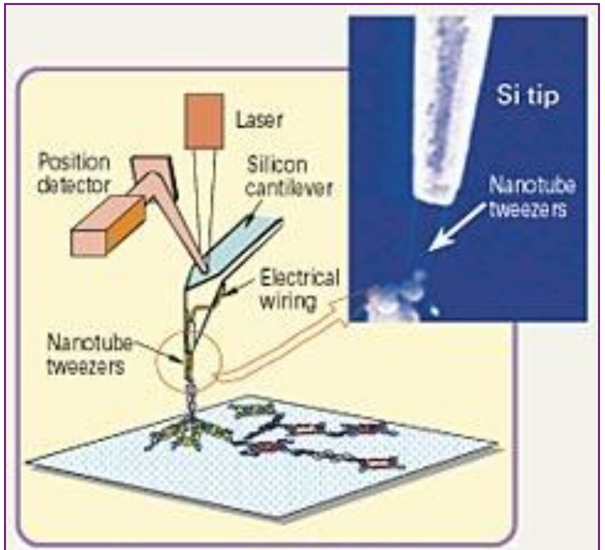
Down Vs Bottom Up Nanotechnology

Watch the video found at the following website to improve your understanding of the difference between top-down and bottom-up approaches to manufacturing:

www.nanohub.org/resources/96/

Bottom Up Approach:

Using Nanotube Tweezers



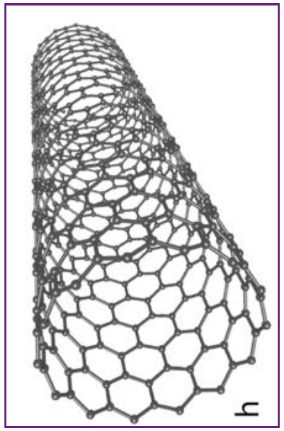
Construction of a molecular device

- Molecular devices can be constructed using nanotube tweezers
- The tips of the nanotube tweezers can be opened and closed by switching on and off a voltage between the two Carbon Nanotube probes
- Nanotube tweezers are tools for use in the bottom-up approach.

Activity 3 – Research Questions

Are there any safety issues associated with the use of carbon nanotubes?




Peform the Safety Issues of Carbon Nanotubes activity

General classification and diameter range

- **Single-walled carbon nanotubes (SWNTs)**

  0.4-3nm, usually 1-2 nm

- **Double-walled carbon nanotubes (DWNTs)**

  ~3nm

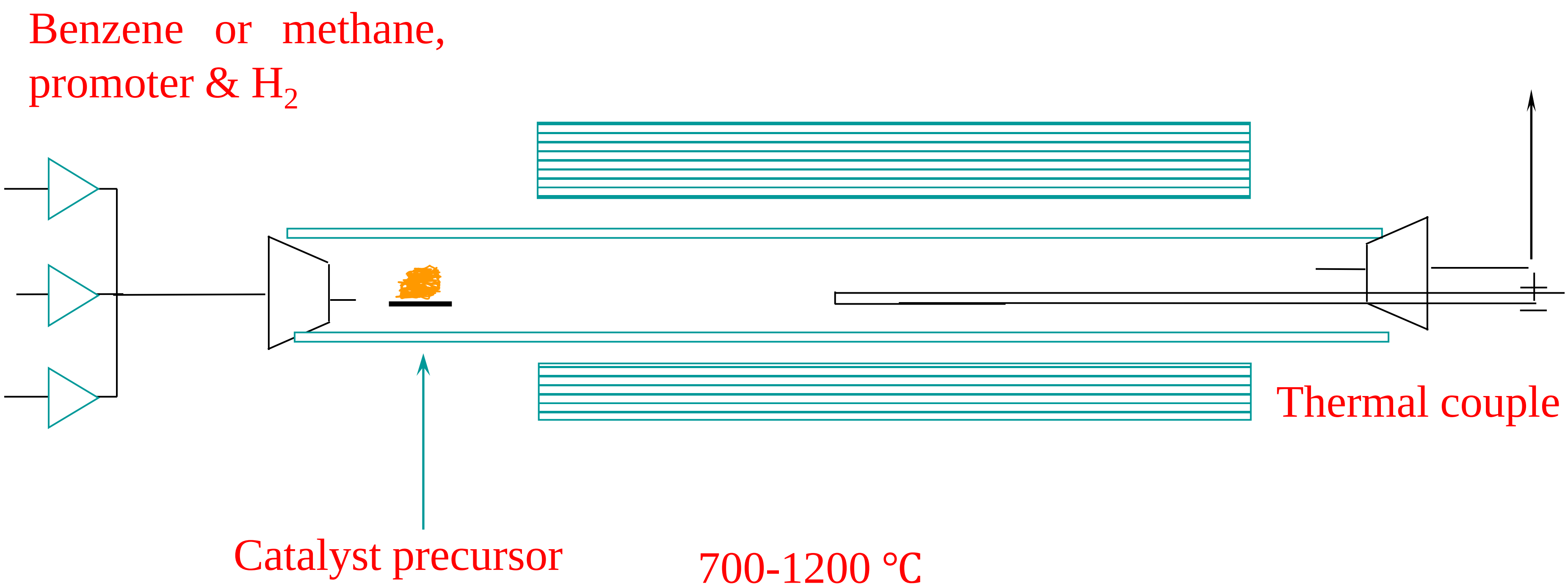
- **Multi-walled carbon nanotubes (MWNTs)**

  <100 nm

Methods for the synthesis of CNTs

- Hydrogen arc discharge
- Floating catalyst technique
- **Laser ablation**

Apparatus for the floating catalyst method



Factors tunable for controlling the diameter and morphology of CNTs

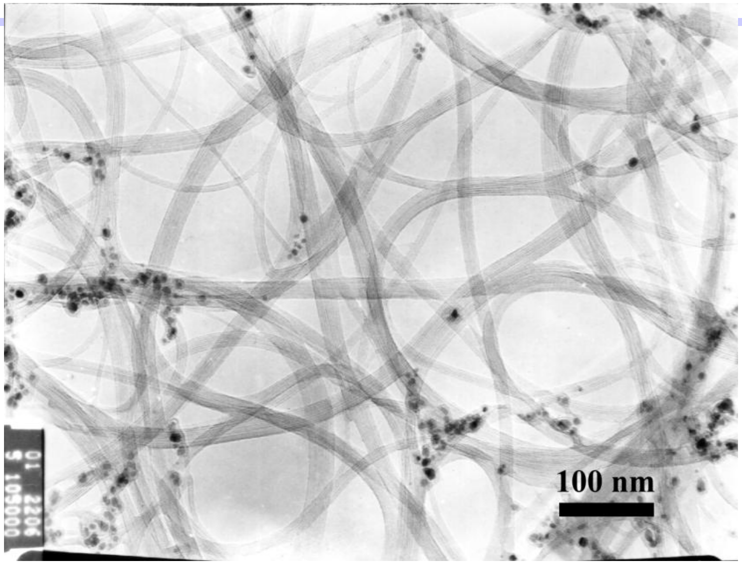
- **C/H ratio**

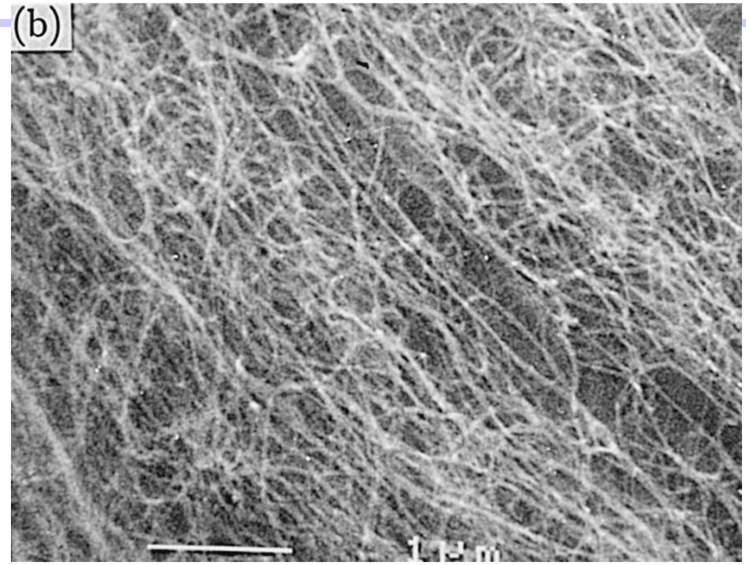
  Flux ratio of H2 and hydrocarbons

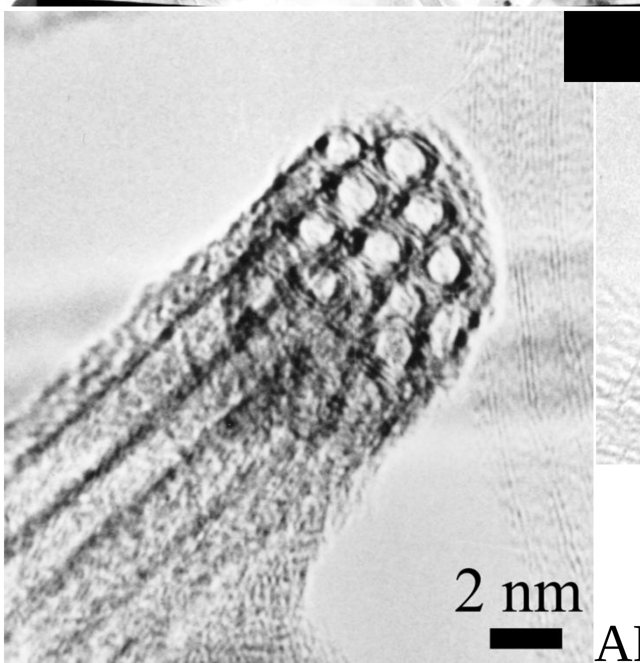
  Selection of carbon sources

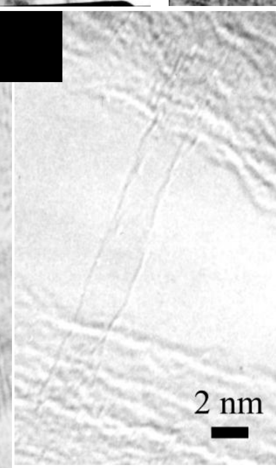
- **Temperature**
- **Carrier gas flux**
- **Amount of sulfur growth promoter**
- **Gas flow direction**

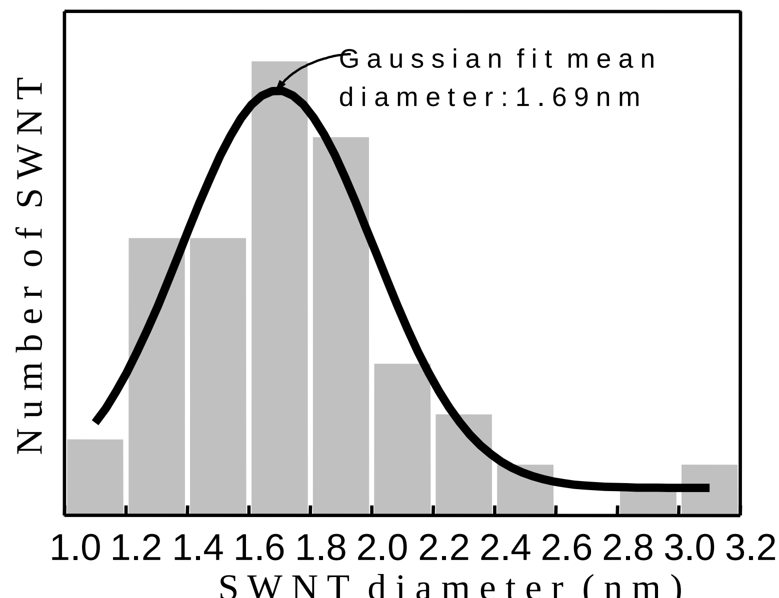
SWNTs









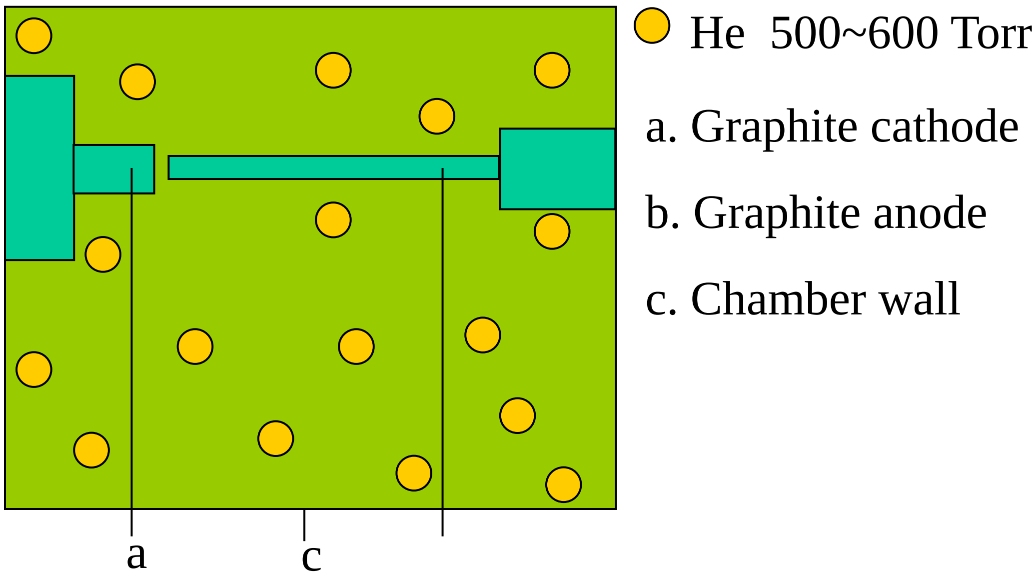


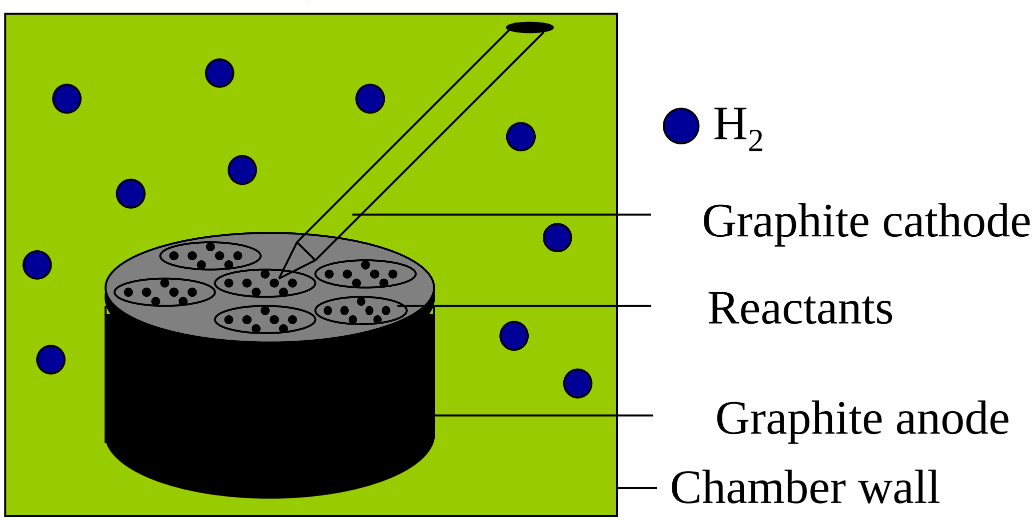
APL & CPL 1998

Photographs of the as prepared SWNTs

Carbon & Science 1999

Synthesis of CNTs by hydrogen arc discharge method





Summary

- Covalent bonds form when atoms share electrons
- Carbon exists in many forms due to its ability to stably form different covalent bonding arrangements
- The bulk properties of materials are determined by the covalent bonding arrangement of atoms
- Carbon nanotubes have very different properties compared to the other carbon allotropes
  - these unique properties offer huge potential in product development.

Revision

1. What are carbon nanotubes and why are scientists so interested in them?
2. How are carbon nanotubes made?