

### 3 – MATERIALS AND DESIGN

#### 3.1 – Introduction

You will be aware of the many wonders of modern electronic gizmos and gadgets, such as the ‘must have’ Apple i-pod, that is spreading world-wide. These only exist as a result of the work done by scientists. In this chapter you will learn more about the role of chemists in developing new materials and designing new molecules. Taking the i-Pod as an example, among other features, this has an LCD screen and a rechargeable battery, all in a very small plastic case. LCD screens, rechargeable batteries and the plastic casing all originate from the work of chemists.

In this section you will find out about new developments in these technologies, such as the bright new Organic Light Emitting Diodes and the work on fuel cells to replace traditional dry batteries. You will learn about nanotechnology – science on a very small scale. You will also take a look at the ways in which chemists are working to improve medical treatments, both in designing new drugs and in making sure these drugs reach the cells in your body where they need to act. Finally you will take a look at the ways in which chemists are working to combat environmental problems, developing new ways of cleaning up contamination and researching alternative fuels.

#### ***Designing new drugs to cure diseases***

The developments of modern medicine have undoubtedly had a great positive impact worldwide – the development in the last century of antibiotics, transplant surgery and many other life-saving advances have transformed the way we live. But there are ever more challenges for the medicinal chemist. As average life expectancies improve, diseases such as cancer become more common. As bacteria become immune to antibiotics, new ones must be developed. And there is the challenge of new diseases such as HIV/AIDS and bird flu that spread worldwide.

This chapter looks at two of the ways in which chemists are trying to combat disease. Firstly much chemical research is directed at developing and synthesising new drugs to target specific diseases. One way of doing this is to start from natural products – molecules that are synthesised by plants and other organisms - that have been shown to have beneficial effects, for example, the drug Taxol®, found in yew tree leaves. Taxol® has been found to be effective against some cancers. As only small amounts of the Taxol® can be extracted from yew, chemists around the world have established the structure of Taxol® and have sought, and successfully found, synthetic pathways to produce the drug in quantity.

Secondly, chemists are investigating means of getting drugs to the specific part of the body where they need to act. Such methods can reduce side effects and the quantities of drugs needed. Two of these methods will be studied. One involves liposomes, where, in effect, the drug is delivered in a “bag” to the diseased body site.

#### ***Can chemists make artificial silk?***

Not as yet, but they are getting closer! A good deal of interest has been directed at silk because it is incredibly strong. Silk is a natural polymer containing amino acids. It is a condensation polymer. You will revisit both addition and condensation polymerisation and discover how chemists have made use of both types of polymerisation to create new products such as conducting polymers as well as a condensation polymer known as Kevlar. Kevlar resists fires and is five times as strong as steel. An early use of Kevlar was to replace the steel in motor tyres. The tyres were lighter and lasted longer than the steel reinforced tyres.

Chemists have become particularly interested in spider silk because spiders produce the strongest silks known. There is considerable potential for strengthening bullet-proof jackets or fireproof clothing using related materials.

#### ***Nanotechnology***

A modern soccer-ball is a sphere made from pentagons and hexagons; it is the same shape as a “buckyball” molecule, the third allotrope of carbon with the molecular formula C<sub>60</sub>. Yes, a buckyball contains just 60 carbon atoms! Think of the number of atoms in the extended structures of graphite

and diamond. The size of the 60 carbon molecule is just less than a nanometre, and nanotechnology involves the applications of molecules of this sort of size. You will get a better feel for these sizes later in the chapter.

Nanotechnology has been described as the science of the very small with big potential. Already many new molecules have been created from carbon that have a similar structure to buckyballs and other materials have been used to create other molecules of similar sizes that have interesting properties.

If nanotechnology involves such small molecules, how can we be certain about their structures? Two new types of microscope are involved, the Atomic Force Microscope (AFM) and the Scanning Tunnelling Microscope (STM). With such equipment it has become possible to move individual atoms around. Researchers at IBM were the first to demonstrate this, in 1990. They used an STM to move Xenon atoms on a nickel surface to produce the letters IBM.

### ***Green Chemistry and Sustainability***

The media makes much of stories of environmental contamination, whether this is of soil, water or air, and chemists often find themselves under fire from the public for causing this pollution. While the previous parts of this section discuss how chemists are involved in advances in technology and medicine, this section encourages you to think about the problems that can occur as a result of these advances, how chemists seek to solve these problems and how they research alternative technologies that are less polluting and make the most of our resources.

Chemists are very much to the fore when it comes to cleaning up sites that have been chemically contaminated. Sites may be contaminated in different ways. For example oil slicks at sea may kill many sea birds as well as other animals. Chemists have now improved existing methods for removing oil slicks by over 100% using materials known as sorbents.

On land, soils are often contaminated when waste products are dumped or accidentally spilled. The method of clean-up can take advantage of the contaminant's physical properties or chemical properties. For example, organic molecules can be flushed out with solvents in which they are soluble, or they can be degraded by adding other chemicals.

Chemists have also found ways to clean water supplies. For example, water contaminated with arsenic has been cleaned and made fit to drink by using a local plant that absorbs the arsenic. The improvement of soils and water supplies is called remediation.

While there will always be a need to combat pollution, it is clearly preferable if pollutants can be replaced with alternatives. One of biggest pollution stories of recent decades has been the release of CFCs into the atmosphere and the resulting loss of the ozone layer in the stratosphere. This layer of ozone is the Earth's protective sunscreen that shields us from high-energy ultraviolet rays that cause skin cancer. You will see later in this chapter how it is important that chemists understand the mechanism by which these reactions occur, in order to design alternatives.

Concern about the environment has resulted in sustainability becoming a very important part of the work of many chemists. The intention is to reduce the impact on the environment by reducing and recycling materials used. To assist this, the American Chemical Society and the US Environmental Protection Agency have agreed a set of 12 principles to provide a framework for guidance to achieving sustainability.

Possibly the biggest problem facing mankind is the supply of oil. Oil is currently crucial to a developed world, both as a supply of energy and as a raw material. So far we have not come up with alternatives that are sufficient to supply our current or future needs, but there is much research into sustainable alternatives as well as cleaner fuels.

### ***And finally...***

You will probably find that many parts of this chapter raise more questions in your mind than they answer. If you want to find out more, try visiting the website listed at the end of this chapter, do your own websearch, or visit your local library. Many of the examples in this chapter are from Western companies as they actively advertise their technological advances to demonstrate their value to

society, but innovation in science is both an international and a local endeavour and you should look for examples in your own region or local university.

As you are exploring, think about how what you find relates to the chemistry you have learned in the rest of your course. Lastly, take a second to step back and think about the huge variety of activities that chemists are involved in worldwide. Consider what your environment might be like without the work of chemists, and how different your understanding of the world around you would be without the understanding you are gaining through the study of chemistry.

### 3.2 – Medicinal chemistry and drug delivery

By the end of this section you should be able to:

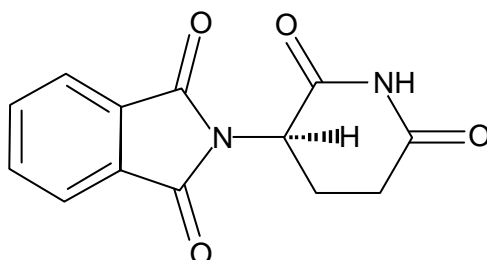
- discuss the challenges of drug design and explain in simple terms how molecules may be identified and developed to overcome these problems;
- discuss the challenges of drug delivery and explain in simple terms how materials may be identified, designed and developed to overcome these problems.

#### Designing drugs

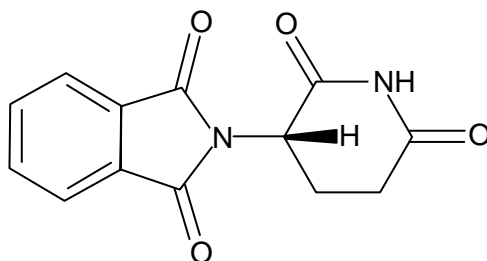
When a molecule is to be used as a drug it is important that it is effective in achieving its desired effect *and* that undesirable side effects are avoided.

Undesirable effects proved to be a particular problem with the drug thalidomide that was prescribed to pregnant women as a sedative in the early 1960s. Thalidomide was, at this time, the preferred sedative during pregnancy as the alternatives, such as Valium, were addictive.

At that time the thalidomide produced was a mixture of two optical isomers. Unfortunately one of the isomers of thalidomide proved to have disastrous side-effects, causing babies to be born with congenital deformities such as shortened limbs (the drug is said to be teratogenic).



(R) – Thalidomide desirable properties: sedative and antinausea drug



(S) – Thalidomide teratogenic: causes birth defects

Figure 3.1 – the two enantiomers of thalidomide

Nowadays, there are many reasons why the same mistake is much less likely to be made. One of these is the methods that are available to chemists to design drugs and gain an understanding of their action. Think back to the section of this booklet on the chemistry of life and the action of enzymes. You will have learned about the lock and key model of enzyme catalysis and about competitive inhibition. Drug molecules act by binding to receptors, and in many cases these receptors are enzymes. Drugs can be competitive inhibitors of enzymes and if a drug has optical isomers, only the isomer that is complementary to the shape of the enzyme active site will fit.

In order to bind to its receptor a drug must not only have the shape to fit, but must also be able to interact with the groups on the receptor molecule by hydrogen bonds, ionic interactions or dipole-dipole interactions. Chemists are able to use computer simulations to model how their drugs will fit into the receptor site. They can also search databases to see if their drug will interact with other enzymes to get an idea of possible side effects. These computational methods have proved very powerful both in designing new medicines and in understanding how drugs act.

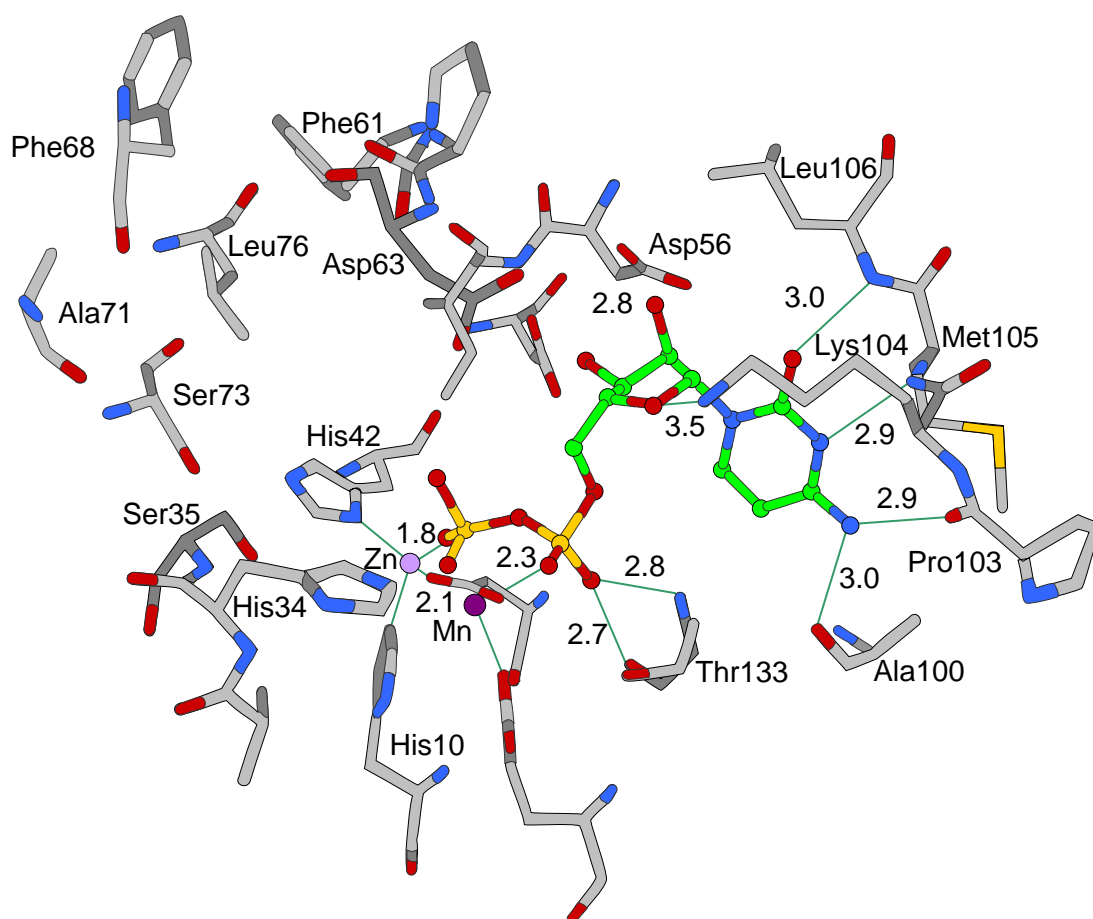


Figure 3.2 – Computer-generated model of a drug in the active site of an enzyme, showing hydrogen bonds

Another reason for only using one optical isomer is economics. Where a synthetic route to a pharmaceutical produces two chiral molecules, chemists seek a route that produces only the active molecule that is desired. This process is called **asymmetric synthesis**. A key reason for this change is that when two chiral molecules are produced, they are produced in equal quantities, so half of the reactants are wasted. Asymmetric synthesis therefore saves on resources and costs.

Actually, these changes alone would not have had an effect on the thalidomide story, as the molecule can switch between enantiomers at the pH of the blood. So even if the desirable enantiomer is administered, it would turn into a mixture in the bloodstream within hours. A successful example of asymmetric synthesis is in the treatment of Parkinson's disease. This disease causes much suffering and is characterised by tremors in the hands and loss of balance but a molecule called L-dopa (the L enantiomer of dopa) can alleviate the symptoms. The L-dopa must be free of D-dopa, as the latter has many unpleasant side effects. Chemists now make pure L-dopa for use by patients.

When chemists are seeking a new pharmaceutical they may start from a natural product molecule (a molecule synthesised by a plant or other organism) that is known to have a positive effect. You will probably be familiar with the story of aspirin, a derivative of the salicylic acid present in willow bark and willow leaves. A more recent example of a natural product being used medicinally is the anticancer drug Taxol®. Taxol® is found in yew trees. It acts by binding to protein molecules in the cell and preventing the cell from dividing. However, only small amounts of Taxol® can be isolated from yew trees, so it became important to find ways of synthesising Taxol®. As you can see it is an incredibly complex molecule with many different functional groups.

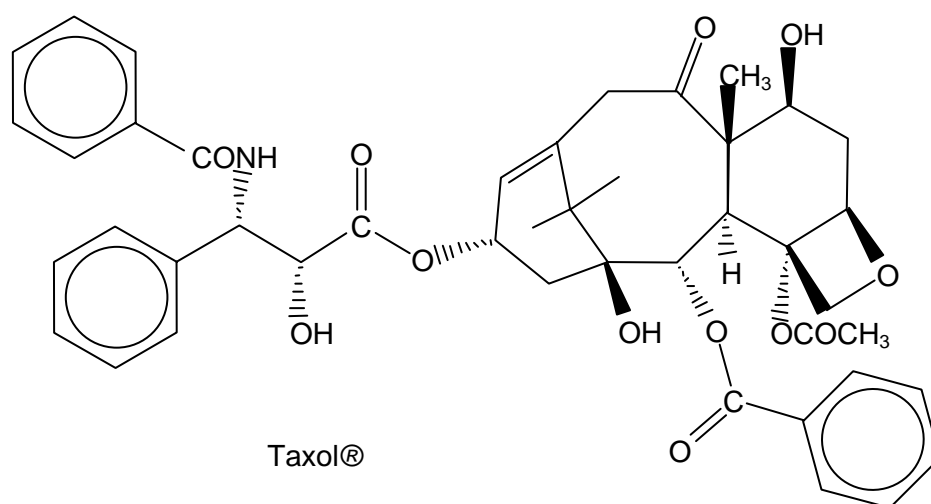


Figure 3.3 – structure of Taxol®

**SAQ 1.** See how many different functional groups you can identify in the molecule of Taxol®.

Synthesising a molecule as large and complex as Taxol® is a major challenge and requires a sound knowledge of many different kinds of reactions, many of which you will have encountered in the organic chemistry part of your course. The race to synthesise Taxol® from basic starting materials was taken on by many groups of chemists worldwide. To do this requires chemists to firstly, know the structure of the Taxol®, and then work out ways of making the drug. The structures of such molecules can be worked out by the NMR and X-ray techniques you will have met in the previous chapter. Chemists may also use techniques such as computer modelling in the process to plan the best route to take.

The first groups achieved their goal in 1994, but research continues as chemists are keen to minimise the number of reactions needed to make the synthesis more efficient in terms of cost and resources. They are also keen to make similar molecules with slightly different shapes and functional groups in order to try and find a molecule that is even more effective with fewer side effects.

### Delivering drugs

As you have seen, it is a major challenge to make drug molecules that interact with specific targets in the cell, but there is a second part of the challenge of finding effective therapies, and that is to get the drug molecule to that target site. This process is termed “drug delivery”.

You have already looked at the different functional groups of Taxol®. Now think about the different environments and barriers that a drug might encounter on its journey to the target cell. If it is in the form of a pill that you swallow, it will encounter the acid pH of your stomach and the enzymes that are there to break down your food. It will then have to pass from your stomach into your bloodstream, which has a different pH and more enzymes. When it reaches the right cell it will have to get through the cell membrane. And how does it know which cells to target? As you can see there are many problems with delivering drugs, one of which is how to get the drug to its target in one piece and avoid it being broken down by enzymes or degrading in extremes of pH.

One successful method of delivery involves the use of liposomes. These are artificial microscopic vesicles consisting of an aqueous core enclosed in one or more phospholipid layers. A phospholipid is a molecule that is hydrophilic (water-loving) at one end and hydrophobic (water-hating) at the other end. Hence, in water-based solutions such as blood, lipids group together to form double layers with their hydrophilic groups on the outside, forming polar interactions with the water, and their hydrophobic groups on the inside, away from the water. These bilayers can wrap into spherical vesicles.



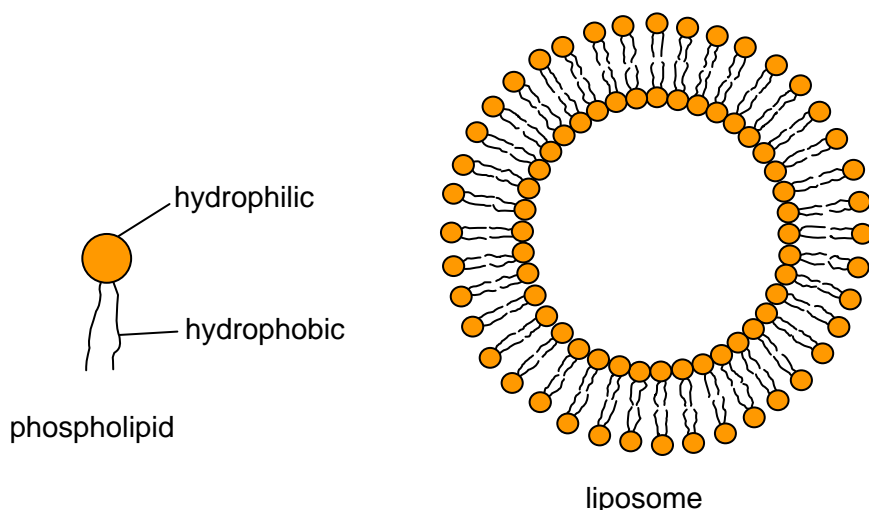


Figure 3.4 – a phospholipid and a cross-section of a liposome

Liposomes are biodegradable and non-toxic and can be used to carry vaccines, drugs, enzymes, or other substances to target cells or organs. They can carry both *hydrophilic* molecules (polar molecules that form hydrogen bonds with water and hence dissolve) and *hydrophobic* molecules (non-polar molecules that do not dissolve in water).

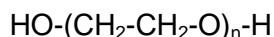
**SAQ 2.** Indicate on the diagram where you think the liposome will carry hydrophobic molecules, and where it will carry hydrophilic molecules.

As liposomes are made from biological molecules they are easily degraded by the body. By modifying surface of liposomes biochemists have developed long-circulating liposomes, which do not degrade quickly and have a better chance of reaching their target. Once the liposome reaches its target, the drug will be transferred to the target.

#### Interested?

If you found liposomes interesting, try searching for on the web for virosomes that have diameters of around 150nm. They are a biological application of nanotechnology (see section 3.3).

A second method of protecting drugs while they are circulating in the bloodstream is to attach them to polymers. A popular polymer to use is polyethylene glycol, or PEG.



When the polymer chain is quite short i.e.  $n$  is a relatively small number, PEG is soluble in water. The disadvantage of PEG compared with a liposome is that it can only carry two drug molecules.

**SAQ 3.** Draw a PEG molecule with three repeats. Indicate the two places on the molecule where the drug can be attached. Suggest a reaction and conditions by which you could attach a drug molecule with a carboxylic acid group.

To improve the number of drug molecules that a polymer can deliver, different polymers can be made where some of the monomers have side chains that can link to the drug molecules.

**SAQ 4.** Look back at the organic chemistry part of your course and suggest a pair of functional groups that could be coupled together when one is the side chain of the polymer and the other is in the drug molecule.

### **Summary**

- The aim of drug design is to produce drugs that achieve their desired effect with minimal undesirable side-effects.
- Many drug molecules are chiral and it is important that only the enantiomer with the desired effect is used.
- Asymmetric synthesis – synthesis of just one enantiomer – saves resources.
- Drug molecules act by binding to receptors such as enzymes and must have the correct shape and functional group to interact with the receptor.
- Natural products are often a good starting point for drug design.
- For maximum effect it is important to deliver a drug safely to the point at which it acts.
- Liposomes and polymers can be used to protect drugs from degradation and deliver them to their target.



### 3.3 – Properties of polymers

By the end of this section you should be able to:

- discuss the properties and structures of polymers based on their methods of formation (addition or condensation);
- discuss how the presence of side-chains and intermolecular forces affect the properties of polymeric materials (for example spider silk).

You have already encountered an application of a polymer in the previous section on drug delivery. In this section you will refresh your knowledge of polymerisation and explore further properties and applications of polymers.

#### Addition polymerisation

Check your understanding of addition polymerisation with the following SAQ.

**SAQ 5. (a)** Draw the structure of poly(phenylethene).

**(b)** Write an equation to show the addition polymerisation of three poly(phenylethene) molecules.

**(c)** Circle a repeating unit in your diagram of poly(phenylethene).

**(d)** Explain why this polymerisation is called addition polymerisation.

Polymers made from alkenes only contain carbon and hydrogen atoms. The physical properties of polymers are determined by the van der Waals' forces present in the polymer. The electronegativity difference between carbon and hydrogen is small. Intermolecular forces will consist of temporary dipoles only.

The properties of addition polymers can be modified in a number of ways. Addition polymers tend to deform easily and once deformed do not return to their original shape. Try stretching a piece of plastic cut from a "soft" plastic bag (not the sort that rustles) placed in contact with your lips, you will find it becomes warm as you stretch the plastic film. You will also find that the material does not return to its original shape. Generally, the longer the polymer chains, the stronger the van der Waals' forces.

Aside from the length of the polymer chain, another factor is the number of side chains. Generally, unbranched chains can pack together better than polymers with lots of side chains. This is the difference between plastic bags that rustle and those that are "soft". The "soft" bags are made from low density poly(ethene) (LDPE), which has lots of side chains and is relatively weak and easy to deform. The type of bag that rustles is made from high density poly(ethene) which has fewer side chains.

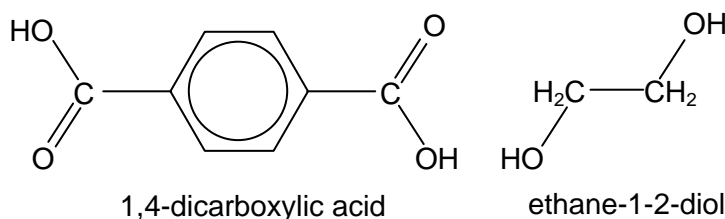
The properties of a polymer are also affected by different kinds of bonding, for example the presence of chlorine atoms in poly(chloroethene) results in permanent dipole interactions between carbon and chlorine because of the polarity of the carbon-chlorine bond.

#### Condensation polymerisation

Unlike addition polymerisation, where an alkene molecule joins to itself, condensation polymerisation usually requires two different molecules that can react together to form a bond such as an ester or amide bond with the elimination of a small molecule such as water. Examples include synthetic polymers such as polyesters and polyamides as well as peptides and proteins.

Polyester is widely used to make a variety of items from drink bottles to clothing and carpeting. It is made by polymerising ethane-1,2-diol with 1,4-benzenedicarboxylic acid (terephthalic acid) with the elimination of water. The product is widely known as *Terylene*. The 1,4 links in this polymer produce a linear polymer that is suitable for spinning into fibres.

The formulae of the two monomers are shown below. Check your understanding of condensation polymerisation by answering the SAQ.



1,4-dicarboxylic acid

ethane-1,2-diol

**SAQ 6. (a)** Write an equation to show the formation of **one** repeating unit of the polyester chain.

**(b)** The amino acid alanine has the following structure –  $\text{H}_2\text{NCH}(\text{CH}_3)\text{CO}_2\text{H}$ .

Draw the structure of the tripeptide formed by three molecules of alanine

**(d)** How many water molecules are lost in this condensation reaction to form the tripeptide?

**SAQ 7.** Cellulose is the polymer responsible for the strength of fibres such as cotton. Cellulose is a linear polymer of sugars with many –OH groups. Suggest, in terms of bonding, why cellulose is so strong.

### Spider Silk

Based on weight, spider silk is five times stronger than steel of the same diameter. There are records where bullets have not broken through a silk handkerchief. George Emery Goodfellow (a doctor at Tombstone, Arizona, US) wrote in the spring of 1881, “I was a few feet from two men quarrelling, they began shooting, two bullets pierced the breast of one man, who staggered, fired his pistol and crumpled onto his back. Despite fatal injuries, not a drop of blood had come from either of the two wounds.”

Further investigation located a bullet wrapped within a silk handkerchief. It appears that the bullet had passed through clothes, flesh and bones but not his silk handkerchief. More recently, it has been suggested that a strand of spider silk as thick as a pencil would stop a jumbo jet in flight!

Spider silk is a protein that is in the same protein group as hair, nails and ligaments. The Golden Orb-Weaving spider produces a dragline silk (a dragline connects a spider to its web) that is the strongest form of spider silk. The protein in dragline silk is called fibroin. There are actually seven different kinds of spider silk, each being produced by different glands. Each type has a different function. See what you can find out on the web or in the library about the other kinds of silk.

Fibroin has a molecular mass of 200 000 – 300 000 and consists of 42% glycine and 25% alanine, with the remainder coming from just seven other amino acids. The alanine molecules occur in polyalanine regions, where between 4 and 9 alanine molecules are linked in a block. The elasticity of spider silk comes from regions that are rich in glycine. In these regions a sequence of five amino acids is repeated. After each sequence a  $180^\circ$  turn occurs producing a spiral. Ordinary silk, produced by silk moths has a  $\beta$ -pleated sheet structure, held together by hydrogen bonds, see below.

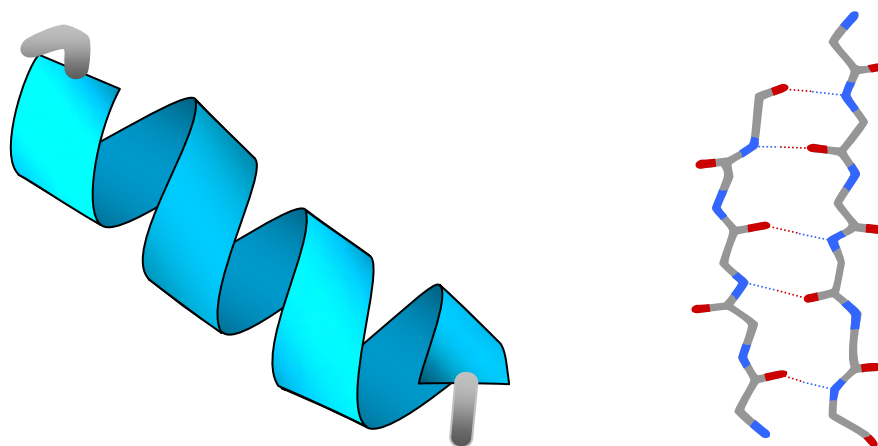


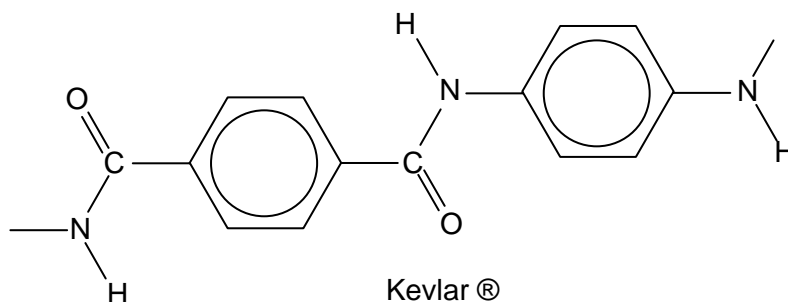
Figure 3.5 – the spiral structure of spider silk and the  $\beta$ -pleated sheet structure of ordinary silk

The most elastic spider silk is 'capture silk' that has about 43 repeats and can extend to 200% of its length. Dragline silk with only about 9 repeats can only extend by about 30% of its length.

To find out more about the different types and uses of spider silk visit websites given at the end of the chapter.

Clearly the properties of spider silk are very valuable and chemists are researching man-made polymers that have similar properties. Kevlar® is a very tough polymer produced by DuPont™ that is similar in strength to spider silk. Kevlar® is used for bulletproof vests; re-enforcing Kevlar® with spider silk would make these vests even stronger. Kevlar® has replaced steel in rubber tyres, with the weight reduction leading to a small reduction in fuel consumption.

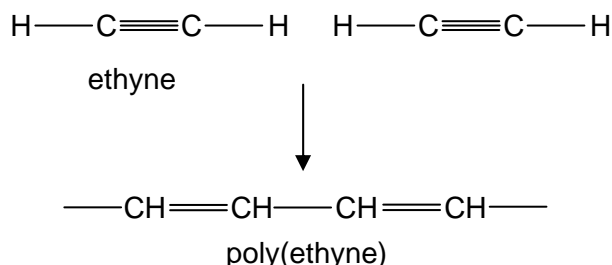
To find out about Kevlar® production visit the websites given at the end of the chapter or see what you can find in your library.



- SAQ 8.** (a) When you have carried out this research, write an account of the uses of Kevlar®, together with the reasons for each use.
- (b) Copy the above structure and then draw another copy alongside your first structure so that N-H aligns with C=O.
- (c) What type of bonding do you think will occur between these two groups?
- (d) Explain how this bonding arises.
- (e) Name another type of polymer that forms spirals with the same type of bonding.
- SAQ 9.** Which type of polymerisation, addition or condensation, would you expect to produce polymers that are biodegradable? Explain your answer.

### Plastics that conduct electricity or emit light

Conducting polymers were discovered by accident by a Japanese student. Polymerisation of ethyne (acetylene) produces poly(ethyne) by addition polymerisation. This material has alternating single and double bonds. Poly(ethyne) has two forms, cis and trans.

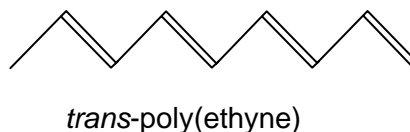
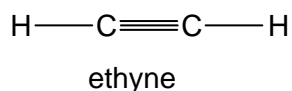


- SAQ 10.** Draw sections of poly(ethyne) containing three ethyne units to show the cis and the trans isomers.

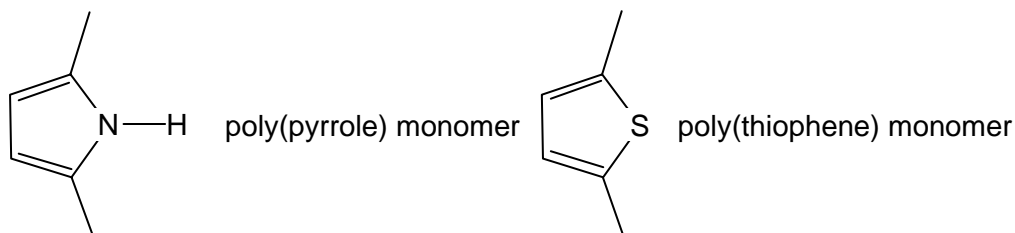
The two isomers have different colours, **trans-poly(ethyne)** is blue or silver coloured; **cis-poly(ethyne)** is red or copper coloured. Molecules that have alternating single and double bonds have "conjugated systems". Benzene is another molecule with a conjugated system of  $\pi$  bonds. The realisation that **trans-poly(ethyne)** had conjugated  $\pi$  bonds led to the discovery that this polymer could conduct electricity! Until this discovery, our expectations of polymers were that they do **not**

conduct electricity. Three scientists, Alan Heeger, Alan MacDiarmid and Hideki Shirakawa were awarded the Nobel Prize for Chemistry in 2000 in recognition of their work on conducting polymers.

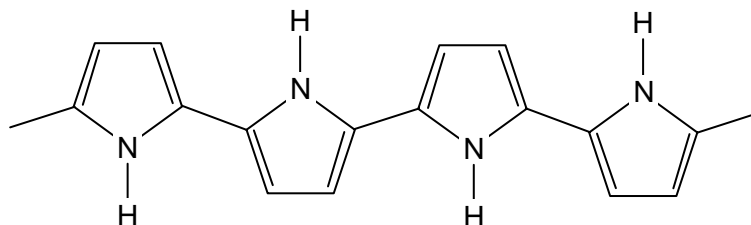
The conjugated system in **trans-poly(ethyne)** is shown below.



Other conducting polymers include compounds such as poly(pyrrole) and poly(thiophene). Technically, these conducting polymers are semi-conductors, unlike the nanotubes in the section on Nanotechnology.



Polypyrrole has the structure below.



**SAQ 11.(a)** Circle the repeating section of polypyrrole.

**(b)** Draw a section of poly(thiophene).

Uses for conducting polymers are surprisingly few, despite the interest raised by their discovery. For these polymers to conduct, they need to be 'doped', meaning that some electrons are removed (by oxidation) or introduced (by reduction) leaving 'holes' allowing the electrons (or the 'holes') to flow.

Most of the interest in conducting polymers lies in electronics. These polymers are of interest to both physicists and chemists. In the 1980s AGFA engineers had a major problem with their photofilm production. Static discharges were ruining the film, which was very costly to produce. The problem was found to be due to the inorganic salts AGFA traditionally used as an antistatic coating. This coating failed when the humidity dropped below 50%. The parent company Bayer AG used its research team to develop a new antistatic coating. Surprisingly, a conducting polymer poly(thiophene), was found to overcome the problem.

Another use is 'Smart' windows that have been developed to reduce glare from sunlight. The windows are coated with a conductive polymer in contact with a layer of black particles. When current is passed through the polymer, these molecules particles align and let light through. When the current is stopped, they become disordered and block light.

### **The traffic lights are changing**

Particular interest lies in semi-conducting polymers that have been developed into light-emitting diodes, solar cells, displays for mobile phones and wristwatch size television screens.

Traditionally, traffic lights have been lit with a single bulb that shines through coloured glass. However, we all know that ordinary light bulbs are likely to fail sooner or later, causing confusion at the lights. These new lights, outside the English Houses of Parliament, contain an array of OLEDs, organic light emitting diodes. If you look carefully, there is no sign of the light bulb that has been replaced by this array. If one of the OLEDs fail, there are still plenty left, so you will be able to cross on the green.



*Figure 3.6 – OLED (organic light emitting diode) traffic lights in London, UK*

Light emitting polymers were first discovered in the Chemistry Department at Cambridge University and have now become a major area of research bridging both chemistry and physics. One of the biggest challenges was finding a blue OLED and this has now been achieved.

OLED displays are appearing in a number of applications. For example Kodak have designed a camera with an OLED screen instead of a liquid crystal display screen. The OLED screen has two advantages as it can be viewed even in sunlight as light is being emitted. In addition it has a wider viewing angle. However, current OLEDs, particularly the blue ones, have a shorter lifetime than liquid crystal displays.

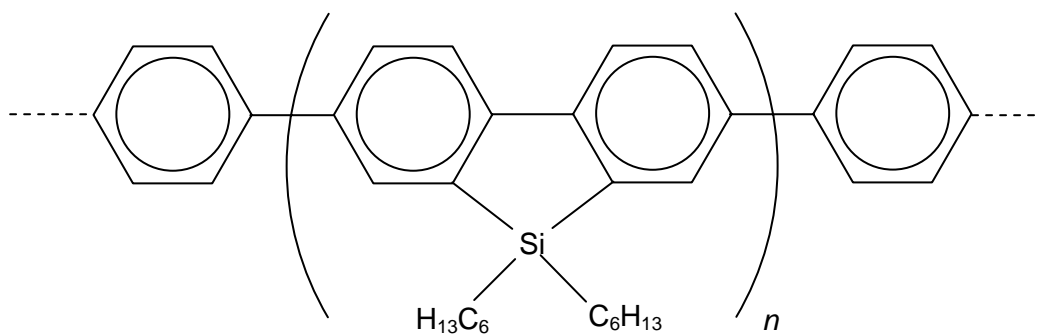


*Figure 3.7 – photo of screen on Kodak camera, courtesy of Jessops.*

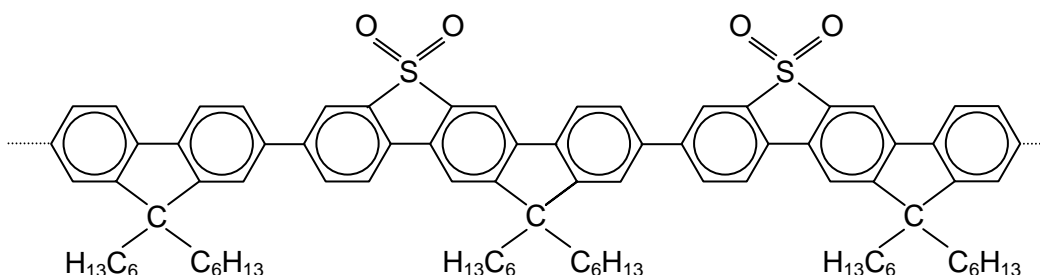
Research published in 2005 has found blue-emitting materials that may overcome the problem of the shorter lifespan of blue pixels in OLEDs compared to the red and green-emitting pixels in OLED displays.

A team from Cambridge in the UK created the blue-emitting polymer, shown below.





A second independent team, working between the Donetsk University in the Ukraine and the University of Durham, UK has discovered a similar blue-emitting material. The structure of their polymer is shown below.



**SAQ 12.** Identify the repeat unit in this polymer by drawing brackets and adding a label 'n' as in the first polymer above.

### Summary

- Addition polymers are formed from monomers with carbon-carbon double bonds and incorporate all of the atoms of the monomer into the polymer.
- Addition polymerisation is used to form simple hydrocarbon polymers.
- Hydrocarbon polymers tend to deform easily. Their properties are primarily dependent on chain length and van der Waals forces between chains and can be modified by the number and nature of side chains.
- Conjugated hydrocarbon polymers can conduct electricity or emit light
- Condensation polymers are formed when two different monomers combine with the loss of a water molecule.
- Condensation polymerisation can result in polymers with a variety of properties, for example elasticity, that depend on their functional groups and side chains.
- Many natural polymers are condensation polymers.

### 3.4 – Nanotechnology

By the end of this section you should be able to:

- show awareness of nanotechnology and, given information and data, be able to discuss the chemistry involved with reference to the core syllabus.

#### What is nanotechnology?

Nanotechnology has been described as “the science of the very small with big potential”. “Very small” in this context means of an order of nanometres – you will see below just how small a nanometre is. The technology covers chemistry, physics, biology and related sciences such as materials science. As with other new science developments, the word nanotechnology is slowly becoming familiar to the general public. Much of the news coverage has been very positive, placing the emphasis on the excitement and promise of the science. However, there have also been scare stories predicting overwhelming numbers of nanorobots and grey goo!

So what is nanotechnology and why are scientists so excited about it? Do the public really have cause to be worried, or are we worrying because it is new and we don't understand it? The following section aims to give you some background information so you can start to form your own opinion on this complex issue.

#### Getting down to nanometres

One nanometre is 0.000000001 m. It can be written as 1 nm or  $1 \times 10^{-9}$  m. Table 3.1 shows the scale of length showing where nanometres fit in.

Table 3.1 – the scale of length

Small	attometre	am	0.0000000000000000001 m	$1 \times 10^{-18}$ m
	femtometre	fm	0.0000000000000001 m	$1 \times 10^{-15}$ m
	picometre	pm	0.000000000001 m	$1 \times 10^{-12}$ m
	<b>nanometre</b>	<b>nm</b>	<b>0.000000001 m</b>	<b><math>1 \times 10^{-9}</math> m</b>
	micrometre	$\mu\text{m}$	0.000001 m	$1 \times 10^{-6}$ m
	millimetre	mm	0.001 m	$1 \times 10^{-3}$ m
	centimetre	cm	0.01 m	$1 \times 10^{-2}$ m
	metre	m	1 m	$1 \times 10^0$ m
	decametre	dm	10 m	$1 \times 10^1$ m
	hectometre	hm	100 m	$1 \times 10^2$ m
	kilometre	km	1000 m	$1 \times 10^3$ m
	megametre	Mm	1000000 m	$1 \times 10^6$ m
	gigametre	Gm	1000000000 m	$1 \times 10^9$ m
Large	terametre	Tm	1000000000000 m	$1 \times 10^{12}$ m

The metre is the standard SI unit of length. Every other unit is stated as a number bigger or smaller than this. The short word put before metre is called a prefix. Many of these are from Greek. The same prefixes are used to change the unit of mass, the kilogram, into smaller and larger units. Atoms and molecules are nano- and picometre sized. Science involving nano-sized particles is called nanoscience.



### Buckyballs – a new allotrope of carbon

A bucky ball, or to give it its full name, buckminsterfullerene, is composed entirely of carbon atoms. It is a third allotrope of carbon. A total of 60 carbon atoms are present forming a sphere consisting of five-carbon and six-carbon atom rings arranged in the same pattern as a modern soccer ball. It is just less than a nanometer in size.

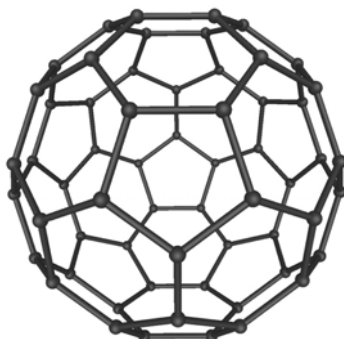


Figure 3.8 – a buckyball, or buckminsterfullerene

**SAQ 13.(a)** Explain what is meant by an allotrope.

**(b)** Name the other two allotropes of carbon.

Buckminsterfullerenes were initially discovered in 1985 during experiments with carbon clusters in supersonic beams. Three scientists shared the Nobel Prize for Chemistry in 1996 for their work on the discovery of fullerenes - Sir Harold Kroto, Robert F Curl Jr and Richard E Smalley. As well as  $C_{60}$ , other sized balls have been created. Unlike other forms of carbon, fullerenes may be soluble, as shown in the photograph below.  $C_{60}$  is pink and  $C_{70}$  is red in solution.

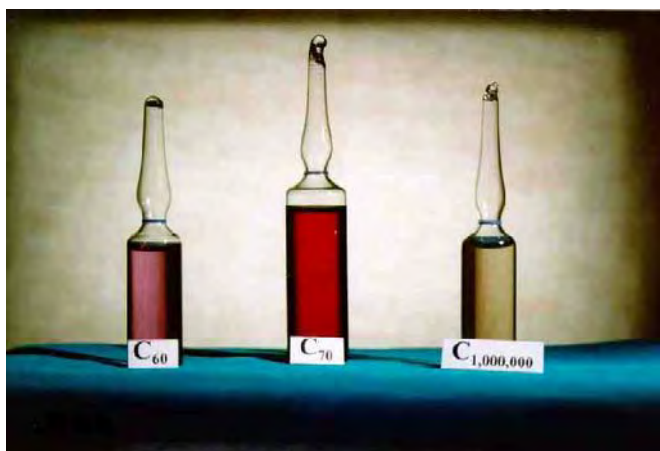


Figure 3.9 – bucky balls in solution

Buckyballs have unusual properties which led to a lot of excitement about their potential. They

- may be harder than diamond
- may be more slippery than Teflon
- may be insulators or conductors

A buckyball can enclose an atom of another element inside itself. This can be a reactive element or molecule such as a lanthanum atom. The highly reactive atom becomes trapped like a 'tiger in a cage' – while it is protected by the carbon cage it cannot react, but as soon as the cage is removed it can react again. The structure below shows a lanthanum atom in the centre of a buckyball.

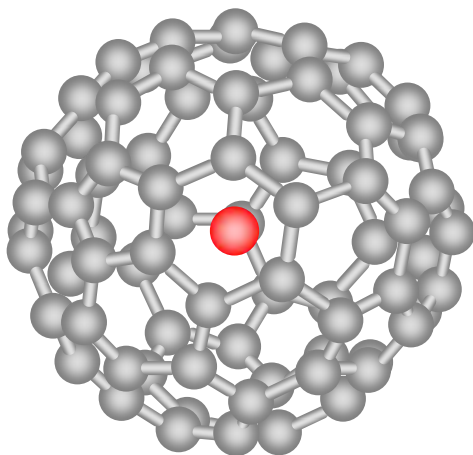


Figure 3.10 – lanthanum atom caged in a bucky ball

### Carbon nanotubes

The discovery of buckyballs led to the discovery of other forms of carbon that are structurally related, for example, carbon nanotubes. These are cylindrical in structure and also resemble a rolled-up sheet of graphite, with the carbon molecules arranged in repeating hexagons. They have a diameter of a few nanometers and can be open at both ends, sealed at one end or sealed at both ends.

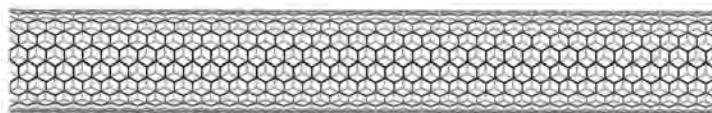


Figure 3.11 – a carbon nanotube open at both ends

Carbon nanotubes have proved to have very useful properties. ‘Mini but Mighty’, they are many times stronger than steel. The mechanical (stiffness, strength, toughness), thermal and electrical properties of pure buckytube materials enable a multitude of applications, from batteries and fuel cells to fibres and cables to pharmaceuticals and biomedical materials. They are found in the batteries of most laptop computers.

The world’s smallest test tube has been made from a carbon nanotube and has been accepted for the Guinness Book of World Records. One end of the tube is closed by a fullerene cap that contains both pentagons and hexagons. The tube has a volume of  $10^{-24}$  dm<sup>3</sup>. The tube has enabled Oxford scientists to use the tube’s one-dimensional cavity to provide a template for the synthesis of unbranched polymer chains of C<sub>60</sub>O, fullerene oxide.



Figure 3.12 – a carbon nanotube closed at one end – a nano “test-tube”

This process normally requires expensive catalysts that are sensitive to air and water. Without the one-dimensional cavity the polymer would branch in all directions.

The potential of nanoscale test-tubes for carrying out reactions is being explored. The nanoscale test tube below has various derivatives attached. These could, for example, be immobilised enzymes enabling fast reactions in the synthesis of new drugs. There are distinct advantages of carrying out these reactions on the nanoscale. In a normal test tube, the particles have to collide to react and these collisions rely on random movement. In many reactions not all the particles react, or unwanted side-products are produced, as you will have found in the organic chemistry section of your course. These problems result in reduced yield. By contrast, a nanoscale reaction, where individual molecules are brought together, can have an exceedingly high yield.

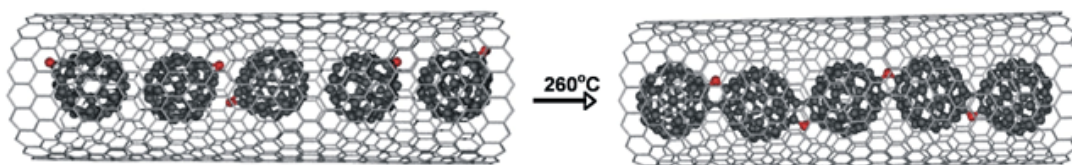


Figure 3.13 – a chemical reaction in a nanotube – polymerisation of  $C_{60}O$  to form  $(C_{60}O)_n$

Another kind of structure being developed involves buckyball cages containing trapped atoms. These buckyball cages are then entrapped inside a nanotube, rather like peas in a pod. The purpose of this work by scientists in Oxford is to investigate the structure as an information storage display.

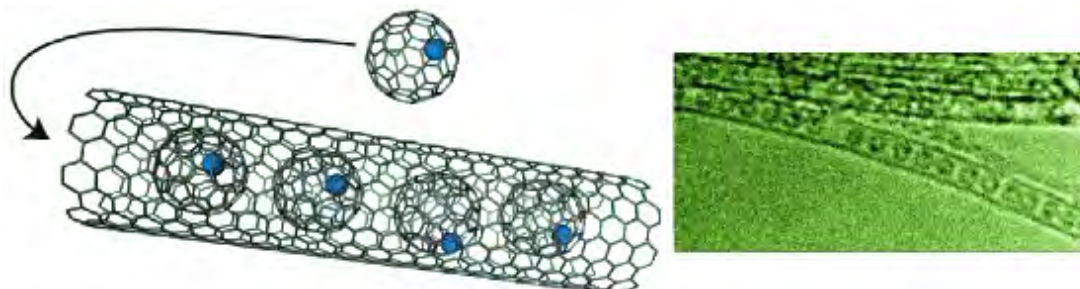


Figure 3.14 – “Peas in a pod” – bucky balls containing trapped atoms, themselves inside a carbon nanotube

### Supramolecular chemistry – making super-molecules

In the section on medicinal chemistry we looked at some of the very large drug molecules that chemists make. We also looked at assemblies of phospholipids to form vesicles held together by hydrophobic and hydrophilic effects. Supramolecular literally means “beyond the molecule”. The phrase was first coined by the French chemist Jean-Marie Lehn. Together with Americans Donald Cram and Charles Pedersen, Lehn won the Nobel prize in 1987 for his work on molecules that recognise each other. In the same way that biological molecules such as enzymes recognise and bind other molecules, Lehn, Cram and Pedersen created synthetic molecules called crown ethers that recognise and bind (form a complex with) metal ions.

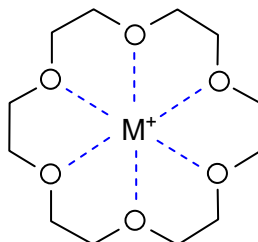


Figure 3.15 – a metal ion bound by a crown ether molecule

**SAQ 14.** Suggest the type of bonding holding the metal ion in the centre of the crown ether.

The field has developed in many directions with chemists synthesising ever more complex and finely-tuned super-molecules from molecules that recognise each other and bind to each other by non-covalent effects, including hydrogen bonding and van der Waals forces. These super-molecules are being designed to be catalysts, to transport drugs, to transmit electricity and to harvest light, among many other things.

In 1999 a research group in the Netherlands made the first molecular motor. The motor is powered by light and the molecule rotates about a carbon-carbon double bond. The groups either side of the double bond are identical and uv light causes these to undergo cis-trans isomerisation. Because of the large size of the groups, which are chiral, the motor can only rotate in one direction.

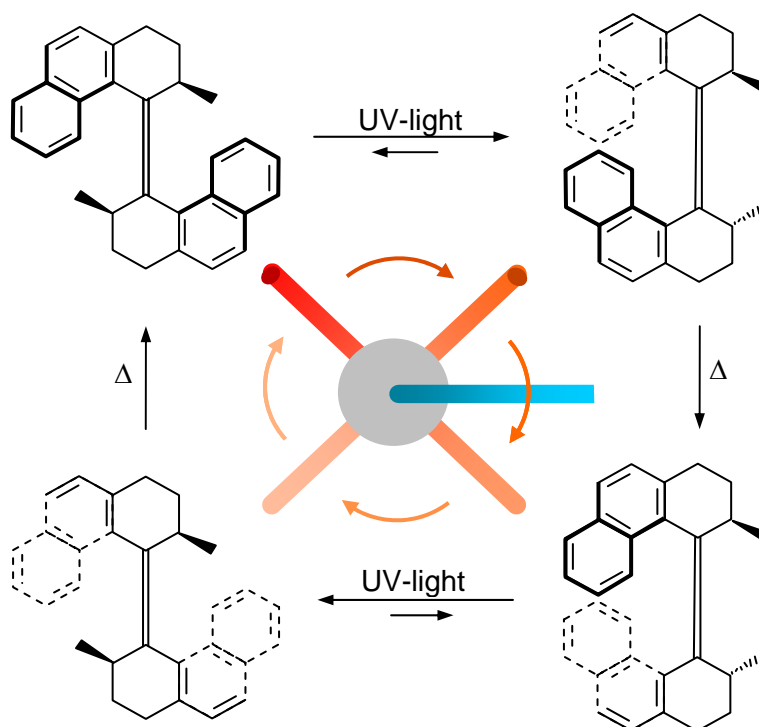


Figure 3.16 – the first light-driven molecular motor

### Quantum dots

Developments in quantum communications and computing could be about to get much easier thanks to the development by Toshiba of a device capable of emitting photons one at a time.



Figure 3.17 – a quantum dot

The device is based on quantum dot technology. Quantum dots are devices that contain trapped electrons. They are made from semiconductor materials such as silicon and have dimensions that are typically between a few nanometres and a few microns. The size and shape of these structures, and therefore the number of electrons they contain, can be precisely controlled; a quantum dot can have anything from a single electron to a collection of several thousands.

The remarkable thing about quantum dots is that although they are macromolecules, they behave more like atoms than like the bulk material. When excited, they emit light, and the dots can be tuned to emit light of a specific wavelength, and even to emit single photons. Prior to this development, single photon sources were extremely difficult to make and relied on either using a laser or exciting single atoms and it was hard to prevent multiple photons being emitted. In contrast, Toshiba's quantum-dot emitter reliably generates single photons on demand when excited by short optical pulses.

It is hoped that the quantum devices will be used in optical computers capable of calculations so vast that today's computer could not even finish them.

This is just one example of how differently nano-scale materials can behave from the bulk material. For further examples of the unusual properties of nanoparticles, try searching the web for some of the following examples and for some more.

- Kodak Ultima inkjet paper has a layer of ceramic nanoparticles. A unique blend of additives is used to "fix" the dyes in the bottom two layers. The top layer contains ceramic nanoparticles to further stabilize the image. Kodak scientists have achieved a significant leap in longevity and colour reproduction with prints predicted to last for up to 100 years.
- Most modern full spectrum sunscreens contain a variety of compounds that absorb UVA and UVB. Some sunscreens contain particles of titanium dioxide. This compound does not absorb UV but reflects the harmful ultraviolet light away from the individual being protected. You will often find titanium dioxide in products described as 'sunblock'. In the sunscreens the particle size is close to nano-size. At this size it still reflects UV light but doesn't give such a white appearance as larger particles. However, there are some concerns about such small particles being able to penetrate the skin.
- Nanocomposites are materials that have a combination of hardness and toughness that is far greater than the component materials. They are made by grinding down clays or ceramics to a nano-sized powder. The powder is mixed with a polymer to form the material.

By now, you may well be wondering how we can obtain images of some of the devices that we have been discussing. The answer is the Atomic Force Microscope (AFM) together with the Scanning Tunnelling Microscope (STM). These instruments allow us to see individual atoms on surfaces. We can also move atoms around on a surface.

There are worksheets at the end of this chapter on manipulating atoms and pictures that show what can be done.

### **Promise and possible problems of nanotechnology**

At the beginning of the chapter we mentioned that while scientists are very excited about the potential of nanotechnology, many people have concerns about problems that the new technologies might cause.

The examples in this chapter have demonstrated that nanoparticles can have very different properties from their related bulk materials and this means that they need to be handled differently. Many applications only require very small amounts of nanoparticles, so this reduces risks considerably. However some uses involve large quantities, for example sun screens. Large scale manufacture can carry the same risk of explosion as production of other materials which have a small particle size and hence large surface area, for example, milling flour. Like any new chemical products, a full risk assessment is required, both for the production of new materials and their subsequent uses.

Scientists predict that the uses of nanotechnology will go far beyond the current applications, and will be used, for example, in environmental remediation, power transmission and disease diagnosis and treatment. Clearly humans and the environment will be increasingly exposed to nanoparticles, and trials must be carried out to ensure their safety. It is the responsibility of scientists to carry out these trials and assess the risks. New technologies always carry new risks and worries and it is also the responsibility of the scientists to engage in debate with the public to ensure their concerns are addressed and the scientific facts of the technology are communicated.



**Summary**

- Nanotechnology involves particles whose size can be measured in nanometers.
- A nanometer is 0.000000001 m or  $1 \times 10^{-9}$  m.
- Nano-sized particles have many useful properties that can be different from bulk materials, due to for example, different surface area to size ratios.
- Super-molecules have the potential to act as catalysts, to transport drugs, to transmit electricity, to harvest light, and many other applications.
- As with all new technologies that have the potential for widespread application, any risk must be adequately assessed.

### 3.5 – Environment and energy

By the end of this section you should be able to:

- discuss how a knowledge of chemistry can be used to overcome environmental problems (for example, ground water contamination, oil spillage, CFCs),
- discuss how a knowledge of chemistry can be used to extend the life of existing resources and to improve the efficiency of energy production and use.

#### Chemistry to overcome environmental problems

##### **Oil slicks**

A major environmental problem is the formation of oil slicks when oil is spilled from oil tankers whilst at sea. There have been many instances where tankers have been sunk, either by collision with other ships or in rough seas. The oil spilled floats on the surface of the water and washes ashore with both immediate and long term effects on bird and fish populations. It is crucial to the survival of these species, and to local tourist or fishing industries, that such slicks are prevented from spreading and cleaned up as quickly as possible.

A new method for preventing slicks from spreading is to make booms that can be used to soak up oil spills. Porous materials called *sorbents* exist that will soak up oil. However, these materials also soak up water. This makes them much less effective as they soon sink.

In an effort to overcome this problem, chemists at Lawrence Livermore National Laboratory in California have recently increased, by a factor of over 100%, the ability of these sorbents to absorb oil. This discovery promises the development of much more effective sorbent booms.

This major improvement has been achieved by making a porous fibreglass sorbent boom that repels water and allows oil to be absorbed. The secret is to trap fluorinated molecules in the structure of the fibreglass sorbent. The fluorine has hydrophobic properties and so repels water but allows oil in.

To make the new sorbent the researchers dipped fibreglass into a slurry of silica and then into a chemical containing fluorine. The resulting material is dried and then cut into discs. When tested by shaking with a mixture of crude oil and salt water, as present following a tanker spillage, the discs absorbed over 200 times their weight in oil, and they did not sink. The untreated fibreglass absorbed both water and oil and sank. Scientists now need to develop sorbent booms from this new approach to cleaning up oil slicks.

##### **Remediation of contaminated soils**

Soil remediation involves the improvement of contaminated land to achieve soil that is the same as it was before the contamination. There are two main approaches to cleaning soil. One is to “wash” the contaminants out of the soil, the other is to chemically degrade the pollutants. The first relies on knowledge of the physical properties of the pollutant, and the second on knowledge of the chemical properties.

##### **Soil remediation using physical properties**

Pollutants can move through the soil by diffusion or convection. Diffusion occurs where there are concentration differences in molecules, spreading out the contamination. Convection occurs when molecules are driven by a fluid such as rain or wind. Water picks up particles as it moves through the soil, carrying them further from the initial spill. These mechanisms that spread the spillage can help the process of cleaning up the contaminated soil. In order to wash pollutants from the ground, a suitable solvent must be chosen that will solvate the contaminant. To wash out oil-based contaminants such as diesel fuels, a trick can be borrowed from the oil industry. Before an oil well is completely dry the oil needs to be forced out and a viscose polymer solution is used. To flush contaminants from the ground, a similar viscous fluid or foam can be pumped through the soil from a hole on one side of the region and pumped out of a hole on the other side, with the contaminants dissolved in the foam.



Similarly, gases can be used instead of liquid to transport the pollutant through the soil. Some contaminant chemicals are fairly volatile (they form a gas easily) and can be flushed out of soil simply by pumping air through. Other contaminants can be made to vapourise by heating the soil with warm air and heating coils.

Another property of contaminants that can be exploited is charge. By inserting electrodes into soil, any charged or polar contaminants can be made to move towards one electrode, depending on whether they are positively or negatively charged. This is the same principle as the electrophoresis experiments discussed in chapter 2. A disadvantage is that other molecules in the soil will also be charged and will also move towards the electrodes. When this method is used, the soil near the electrode is removed and treated further before being returned.

### **Soil remediation using chemical properties**

Some soil remediation will happen of its own accord as bacteria in the soil break down complex chemicals into  $\text{CO}_2$ . This process is fairly slow and while it can be sped up by adding oxygen or nutrients for the bacteria, it can still take one or two years. Another way of breaking down the contaminants is to add chemicals to the soil.

Polyaromatic hydrocarbons (PAHs) are a major pollutant of contaminated soils. They result from incomplete burning of carbon-containing materials and have structures based on benzene rings. PAHs are frequently *carcinogenic* (that is they may cause cancer). Ozone has been shown to break down PAHs and can be pumped into the ground to degrade the pollutants as it passes through the soil.

**SAQ 15.** Using your knowledge of oxidation processes, charge and solubility of transition metals, suggest how heavy metal contamination could be dealt with.

### **Remediation of contaminated ground water – plants to the rescue**

There are a number of plants that are capable of cleaning up contaminated ground water. *Ground water* is the water that is present below ground. It may be present in the soil or it may be held in porous rock such as chalk. Chalk is particularly good at filtering and purifying water supplies in the UK, France and Namibia. Much mineral water comes from chalk aquifers.

Often, ground water is of vital importance to residents living above it. In Bangladesh, many new wells were sunk to provide an adequate water supply. However, the ground water was not properly tested before being made available to residents. People became ill from drinking this water and they were found to have arsenic in their bodies. The arsenic had come from the rocks surrounding the ground water. Long term consequences of arsenic poisoning include skin cancer, damage to the nervous system and miscarriages. This arsenic contamination is a very serious threat to millions of people.

Chemists at the De Montfort University in the UK decided to try the effect of a notorious water plant known as water hyacinth. This plant causes a problem by clogging waterways in tropical and subtropical areas, including Bangladesh. Previous research at Bangabandhu Sheikh Mujib Medical University in Bangladesh had shown that the whole plant was able to remove arsenic from water and the recent research exploits the affinity of the plant for arsenic. They chemists used powdered dried roots of the water hyacinth to treat arsenic-contaminated water and found that the powder removed arsenic from the water, reducing the level to below the World Health Organisation's guideline value of  $0.01\text{mg dm}^{-3}$ . They believe that powdered root will be easier to use than the whole plant and is more effective than other methods of removal.

### **Trouble in the stratosphere – replacing CFCs**

CFCs were introduced as a refrigerator compressor liquid by the engineer Thomas Midgley in the 1920s. When they were introduced it was in order to replace existing liquids that were toxic, such as ammonia or sulphur dioxide, with something safer.

Unfortunately CFCs were found to cause a huge environmental problem. CFCs are particularly stable and do not break down until they get to the stratosphere. In the stratosphere CFCs absorb ultraviolet light that causes a photo-dissociation of carbon-chlorine bonds as shown below for  $\text{CF}_2\text{Cl}_2$ .



These radicals catalyse the breakdown of ozone to oxygen. In recent years the ozone layer has been thinned significantly over Antarctica, and to a lesser extent over Northern Europe. Each year that passes produces a thinner layer of ozone.

Why should this trouble us? Primarily because the ozone layer provides us with an important sunscreen that prevents the harmful ultraviolet light from damaging our skin and causing skin cancers. The incidence of skin cancers has increased since the use of CFCs.

**SAQ 16.(a)** Explain what is meant by the term CFC and suggest an example that is different to the one above.

**(b)** CFCs are not the only compounds that can damage the ozone layer. Search the web for another compound that contributes to ozone loss.

The first step in addressing this problem was for chemists to understand how CFCs catalyse the breakdown of ozone. You will have previously learned about the relative strengths of carbon-halogen bonds. As the carbon-chlorine bond is very reactive, it photodissociates in uv light, as shown above.

**SAQ 17.** Explain why the carbon-chlorine bond photodissociates and the carbon-fluorine bond does not.

Chemists have now provided some alternatives to CFCs. In general these are hydrofluorocarbons, for example  $\text{CH}_2\text{FCF}_3$ . Alkanes may also be used. The presence of the C—H bonds is important because this enables the compound to break down before it reaches the stratosphere. And if it does reach the stratosphere, it can't produce the damaging chlorine free-radicals.

CFCs have a second adverse effect on the environment – they contribute to global warming. The new replacements for CFCs may be better in terms of the ozone layer but they are still greenhouse gases. However, they are present in the atmosphere in much smaller quantities than other greenhouse gases such as carbon dioxide.

There are ongoing programmes to monitor ozone levels and there is some evidence that the hole has started to reduce in size. Scientists hope that the 21<sup>st</sup> century will see the recovery of the layer.

### Green Chemistry and Sustainability

Increasing awareness of environmental issues has led to much innovation in chemical research. The challenge for chemists is to develop products and processes that are sustainable i.e. they do not impact on the environment in terms of pollution or depletion of resources. To help chemists work towards this aim, twelve principles of green chemistry have been drawn up.

The twelve principles of green chemistry

1. Prevention of waste is cheaper than cleaning it up once it is formed.
2. The synthesis of a new chemical product is designed to ensure that maximum use of materials takes place.
3. New chemicals are produced with no significant toxicity to humans or to the natural environment.
4. New chemicals are designed to achieve their use, whilst keeping toxicity low,
5. Use of solvents should be avoided.
6. Energy efficiency should be maximised, ideally reactions should be carried out at room temperature and pressure.
7. Feedstocks should be sustainable.
8. Chemists often need to use temporary modifications to a compound in a synthetic route to a target compound. Such modifications should be minimised.
9. It is better for a reaction to use a catalyst than a reaction that is not catalysed.
10. Chemical products should be designed to break down naturally.
11. Analytical monitoring of reaction processes enables prevention of production of hazardous materials.
12. Safer chemistry reduces the risk of accidents.

**SAQ 18.(a)** Using L-dopa as an example, explain principle 2.

**(b)** Using your knowledge of catalysis, explain principle 9. How might use of a catalyst also be good economically? Suggest an instance where use of a catalyst might also be viewed as non-environmentally friendly.

The following are examples where chemists have employed these principals to design a green process or technology.

### Use of supercritical CO<sub>2</sub> as a solvent

A supercritical fluid is a gas that is compressed and heated so that it shows properties of a liquid and a gas at the same time. Carbon dioxide becomes a supercritical fluid at a pressure 7290 kPa and a temperature of 31°C. Other supercritical liquids include xenon and ethane. The diagram below shows the supercritical region for a gas.

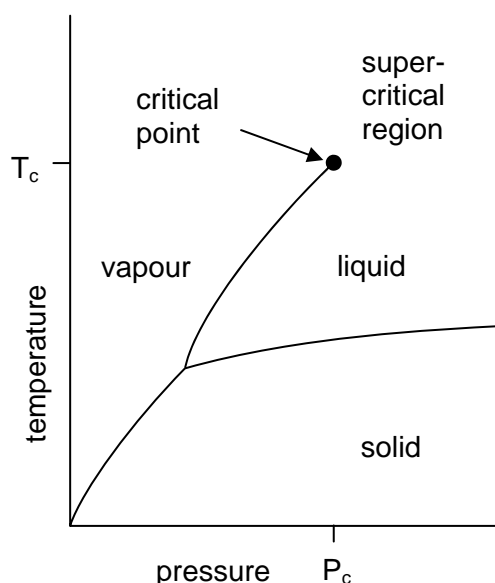
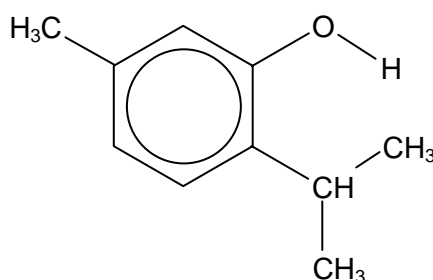


Figure 3.18 – diagram showing the supercritical region

Thymol has the structure shown below. It is used as a perfume, disinfectant and also has medicinal properties. Thymol is also used to make menthol.

**SAQ 19.(a)** Search the web for the structure of menthol.

**(b)** Suggest reagents that could be used to convert thymol to menthol.



thymol

A collaboration between researchers at Nottingham University and two companies, Thomas Swan & Co in England and Schenectady Pratteln in Switzerland, resulted in a process for synthesising thymol using supercritical CO<sub>2</sub> as a solvent and a more environmentally friendly catalyst, anhydrous aluminium oxide.

The use of supercritical CO<sub>2</sub> as a solvent avoids the need for organic solvents, many of which are volatile, flammable and may pose a risk to health and the environment. At the end of the reaction it is

easy to separate the product from the solvent – the conditions can be changed so the  $\text{CO}_2$  turns to gas. The  $\text{CO}_2$  used is a by-product of fermentation, so a waste product is used, and it can be re-used again and again. What's more, by controlling the temperature and pressure, its properties can be fine-tuned to minimise the production of by-products in the reaction and to increase the yield. The process makes chemical reactions possible that were previously too polluting or inefficient.

**SAQ 20.(a)** Which principles does this process fulfil?

(b) Search the web for other chemicals produced using supercritical  $\text{CO}_2$ .

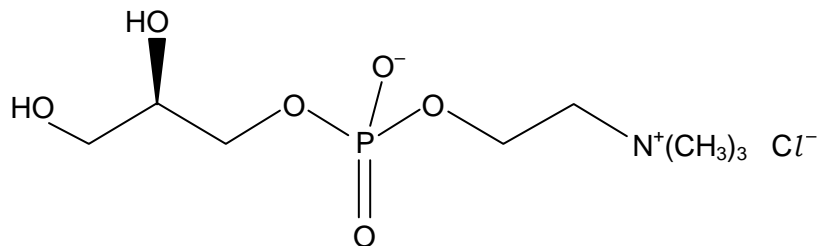
(c) Suggest two hazards of using supercritical  $\text{CO}_2$ .

### Ionic Liquids

Ionic liquids are organic salts that have melting points below  $100^\circ\text{C}$  – they are liquid at R.T.P. Ionic liquids have attracted much interest as solvents for chemical reactions as they can dissolve a wide variety of inorganic and organic compounds. There is however much debate as to how green they are. Ionic liquids, unlike organic solvents, have no vapour pressure and can be re-used. However, little is known about their toxicity or their effects on the environment.

Chromium plating is a highly hazardous process that makes use of chromic acid, a highly toxic and cancer forming compound. A company called Scionix have produced an ionic liquid from chromium(III) chloride and choline chloride (vitamin B4). This liquid has been shown to reduce the risks to chromium plating personnel as well as increasing the overall current efficiency of the process from 15% with chromic acid to 90% with the ionic liquid.

The structure of choline chloride is shown below.



choline chloride (vitamin B4)

In this example significant improvements have been made, even though the ionic liquid cannot be classed as green. The only thing green about chromium(III) chloride is its colour.

This process fulfils around eight of the twelve green chemistry principles.

**SAQ 21.** For this new chromium plating method, suggest at least four of the twelve green chemistry principles that fulfil these principles.

Another use of ionic liquids is in electropolishing of metals such as iron or aluminium, where ionic liquids have replaced sulphuric and phosphoric acids.

### Rock-munching bacteria

When the Romans invaded Britain, they were interested in obtaining metals such as copper, tin and lead. In Wales, records from that time tell of copper being made in pits. It is believed that these pits contained bacteria that, literally 'eat rock', dissolving copper in the process. The copper was displaced from solution by throwing in worn out iron articles such as swords.

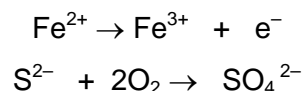
The bacteria involved, *Thiobacillus ferro-oxidans* and *Thiobacillus thio-oxidans*, are now routinely used in copper mining in the US such as at the huge Bingham Canyon mine.



Figure 3.19 – copper mine

Copper mining produces huge piles of waste that still contain copper. However, it is only recently that bacteria began to be used to extract this remaining copper. The process is termed “bacterial leaching”. The bacteria create an acidic solution, dissolving the copper from what was waste ore. The copper is displaced by adding scrap iron, just as the Romans did! 10% of US copper now comes from bacterial leaching.

As their names suggest, the bacteria actually use  $\text{Fe}^{2+}$  and  $\text{S}^{2-}$  ions in their metabolic processes, not the copper. They gain their energy to live from oxidation reactions such as the following.



The bacteria do not actually feed off the copper ore as the ions do not enter their cells. Overall the bacteria produce a solution of iron(III) sulphate and copper(II) sulphate. The process of bacterial leaching is cheaper, more energy efficient, quieter and less polluting than other methods of extraction.

In Australia, a different problem exists. Gold is traditionally extracted from ore mixed with oxide or sulphide ores of other metals using cyanide. However, the cyanide only extracts 10% of the gold and is very toxic to all life. Using bacterial leaching can raise the percentage of gold extracted to 85-100%. However, *Thiobacillus thio-oxidans* prefers a temperature of about 30 °C for optimum performance, much lower than the region where the gold mining takes place.

*Thiobacillus thio-oxidans* uses its unusual metabolism to turn pyrites (iron sulphide) and arsenopyrites ores into iron oxides. Any gold in the material can then be removed.

**SAQ 22.** Discuss the benefits of using bacterial leaching over the use of cyanide.

## Chemistry for energy

### **Biofuels: diesel and ethanol fuels**

The use of ethanol as a fuel has received much attention in recent years as a potential alternative to oil-based fuels that makes use of local resources and is less polluting. For many years Brazil and Columbia have powered their cars from ethanol made from sugar cane. Many countries are overproducing grain crops and are researching ways of using such crops for the production of fuels. In South Africa, plants are being constructed to produce ethanol from maize, to be blended with petrol in proportions ranging from 10% to 85%. In the US, the sugar in maize is also being used to produce ethanol and in Europe, sugar beet is being used to produce ethanol and oilseed rape is being used to provide a fuel suitable for diesel-powered engines. As well as being used to produce ethanol, biomass can be used as fuel in other ways, for example, in Mauritius, “bagasse”, the solid waste from sugar production, has been used to power electricity stations, allowing far more efficient use of biomass.

**SAQ 23.(a)** Find three other materials, other than sugar cane, sugar beet and maize, that can be used to produce bioethanol.



- (b)** *Bioethanol is widely thought to be less polluting than burning fossil fuels, but some people disagree. Carry out some research to find arguments for and against the use of bioethanol as a clean-burning fuel.*

But is bioethanol really green? Perhaps the biggest surprise has happened in the US, where the incentive to use bioethanol is to help mid-west farmers make use of the grain overproduction. Approximately 40 million tonnes of maize are being converted to bioethanol and the market is growing. The fuel is being sold as E85, where 85% is ethanol, the remainder petrol. However, the energy available from this fuel only just exceeds the energy used in the farming to produce the crop. The crop results in 1.2 units of energy so there is a small net gain of 0.2 units of energy. The process is not as efficient as it could be.

Another question that arises is whether we can make better use of the bioethanol, rather than using it all for transport, for example, by using it to generate electricity.

There are other alternatives to oil-based fuels that are being researched and used. Biodiesel is one of these. The term *biodiesel* refers to fuels that can be used in place of diesel and that are usually made from vegetable oils or animal fats.

**SAQ 24.** *Find out whether your country has an initiative to produce bioethanol or biodiesel.*

### **Batteries and fuel cells**

A fuel cell is an electrochemical device similar to a battery but unlike a battery, which runs down over time as the reactants it contains are used up, a fuel cell is designed to use a continuous external supply of reactants. A typical fuel cell is a hydrogen cell and the reactants are hydrogen and oxygen. The attraction of fuel cells is that, with the reactants being hydrogen and oxygen, the only product is water. They are therefore emission-free.

**SAQ 25.** *View the video on the following website, or do your own web or library search for information on hydrogen fuel cells. Discuss the electrochemistry taking place in a hydrogen fuel cell. Include equations for reactions that take place.*

[http://www.utcpower.com/fs/com/bin/fs\\_com\\_Page/0,5433,03540,00.html](http://www.utcpower.com/fs/com/bin/fs_com_Page/0,5433,03540,00.html)

Both alkanes and hydrogen are used in fuel cells to propel vehicles. A prototype Audi A2 has been built that runs on hydrogen, achieving 94 mpg, but with a limited range. Interestingly, the same car, with a diesel engine achieves the same fuel consumption.

Norwegian road construction giant Mesta aims to cut their CO<sub>2</sub> emissions from their vehicles in half by use of hydrogen powered vehicles. They took delivery of their first vehicle in March 2005, hydrogen is stored in three 115 dm<sup>3</sup> bottles at a pressure of 200 bar, giving the vehicle a 120 km range.

The Toyota Prius hybrid petrol/electric car has an electric motor that is driven by a bank of nickel-metal hydride batteries that recharge when the car is coasting down hill and switches to petrol when acceleration is required.

There are some obvious difficulties with running cars powered by hydrogen. Where does the hydrogen come from? How can it be stored safely?

### **Overcoming the hydrogen storage problem**

Hydrogen gas must be compressed in order for it to be stored at a small enough volume on a vehicle. This carries a significant risk of explosion.

An alternative approach is to find a solid material to absorb the hydrogen. The hydrogen is bonded to the material and is released by a chemical reaction when needed. The material itself can be recycled. So that the storage material doesn't make the fuel cell too heavy for the vehicle, the elements it is composed of should be in the first two rows of the Periodic Table. A team from the US Department of Energy and the New Jersey Institute of Technology are investigating sodium aluminium hydride NaAlH<sub>4</sub>, a solid known to reversibly absorb hydrogen molecules. High temperatures are needed and this hydride (and related hydrides) can only store about 5% by weight of hydrogen. The leader of the above team, Graetz, found that doping this compound with titanium made the absorption and release

of hydrogen much more efficient. It appears that, unexpectedly, the titanium acts as a catalyst, forming a compound called titanium aluminide on the surface of the  $\text{NaAlH}_4$ .

Another method is to use porous materials which have many molecular sized holes that can absorb hydrogen and release it when needed. Other researchers are investigating organic polymers that can form porous materials.

### **Sourcing hydrogen**

The issue of the hydrogen source for fuel cells is perhaps the biggest issue with this technology. It is attractive to think of the cars on our streets being replaced by cars that only emit water, but the processes used to produce hydrogen are not necessarily environmentally friendly. One option is electrolysis of water, but electricity is required for this process, and in most countries that electricity still comes primarily from power stations that burn fossil fuels. The electrolysis of water usually requires 50% more energy that is stored in the hydrogen produced. Another source of hydrogen is from methane in natural gas, but this process uses up natural resources and generates greenhouse gases. Further research is needed both into sources of hydrogen and into alternative fuel cells before this technology can truly be classed as green.

**SAQ 26.** Carry out some research on the web to find out about environmentally sustainable methods of producing hydrogen.

### **The future of nuclear power, potentially the greenest of fuels?**

The Australian Federal Education and Science Minister Brendan Nelson, has broken from his party's policy by arguing that use of nuclear energy is a way to cut down on greenhouse gases. Australia is a country with uranium mines.

Meanwhile the UK is again looking at introducing a new generation of nuclear power stations and Iran is looking at nuclear power. The French generate 80% of their electricity from nuclear power and other countries have shown interest in nuclear power.

Nuclear power has always been a controversial issue and there are many arguments both for and against. Some of the key issues for use of nuclear power are as follows.

- Nuclear fuel can be viewed as a clean source of energy with zero emissions of greenhouse gases. In contrast, coal or gas fired power stations may release carbon dioxide, sulphur dioxide and oxides of nitrogen. Only sulphur dioxide is being removed at present (producing a useful by-product of gypsum for plasterboard). Biomass has the same problem, it burns to release  $\text{CO}_2$ .
- Current use of fossil fuels amounts to 20 million 'fossil fuel years' per year. A teraWatt hour of electricity produces about 20 tonnes of nuclear waste compared to around 20 million tonnes of  $\text{CO}_2$  from fossil fuels.
- Nuclear power stations generate radioactive waste products and we must be sure that these can be stored safely well beyond our lifetimes. These can be contained most easily as solid waste and stored underground. The work of chemists has much to contribute in terms of cleaning up nuclear waste.
- There is concern that an accident at or a terrorist attack on a nuclear plant would have much more devastating and long-term consequences than an accident at or attack on a gas or oil-fired power station or pipeline. Unlike Chernobyl, modern nuclear power plants are designed to be fail-safe but opponents of nuclear power argue that the risks are still too great.

Clearly there are arguments, both environmental and economic, for and against nuclear power. Some people believe that nuclear power is a cheap source of energy, others believe that the cost of cleaning up and securing nuclear waste is prohibitive. James Lovelock, a world famous ecologist, says that nuclear power is the environmentally friendly option. Other environmentalists take the opposing position. Chemists have a role both in optimising the process and in investigating waste disposal.



**SAQ 27.** Draw a table to compare the benefits and disadvantages to the environment of the technologies you have learned about. Include a column to list areas that require further research by chemists.

**Summary**

- Knowledge of chemical and physical properties of pollutants can inform the development of solutions to environmental problems.
- Increasing awareness of environmental issues had lead to increased chemical research into sustainable products and processes.
- The twelve principles of green chemistry summarise the aims for sustainability.
- Chemistry has a large role to play in the development of alternative energy sources.

### 3.6 – Key definitions

**allotrope:** an allotrope of an element is a different crystalline or molecular form of the same element

**asymmetric synthesis:** making one enantiomer of a chiral compound

**biodiesel:** diesel made from oilseed rape or other vegetable oil

**bioethanol:** fuel made by fermentation of sugar sources such as sugar cane or sugar beet

**buckminsterfullerene (or buckyballs):** the third allotrope of carbon

**graphene:** a single sheet of graphite

**'green chemistry':** the development of chemical processes of manufacture that do not harm the environment but provide sustainable routes for the synthesis of chemicals

**groundwater:** water that is below ground: such water provides a source of drinking water by drilling wells

**hydrophilic:** polar molecules that form hydrogen bonds with water and hence dissolve

**hydrophobic:** non-polar molecules that do not dissolve in water

**liposome:** an artificial microscopic vesicle consisting of an aqueous core enclosed in one or more phospholipid layers, used to convey vaccines, drugs, enzymes or other substances to target cells or organs

**nanotechnology:** science of the very small (with huge potential)

**nanotube:** a single sheet of graphite may be rolled to form a single walled nanotube (SWNT)

**scanning tunnelling microscope:** enables chemists to look at single atoms

**sorbent:** a floating porous material that is designed to absorb oil, but not water from a spillage on the sea

**targeting:** used in two different ways by chemists: (i) a compound is identified for synthesis; (ii) when using a liposome (or virosome) to carry a vaccine or a drug to cells or organs in the body

**remediation (of contaminated soils):** the improvement of disturbed land to achieve land that is the same as before the land was disturbed

**remediation (of groundwater):** removal of contaminants that are toxic

### 3.7 – Resources

#### Liposomes

<http://www.answers.com/>

<http://www.ingentaconnect.com/content/ben/cpd/>

#### Virosomes

<http://www.bernabiotech.com/rd/platforms/virosomes/>

#### Spider silk

<http://www.chm.bris.ac.uk/motm/motm.htm>

<http://www.xs4all.nl/~ednieuw/Spiders/Info/spindraad>

#### Kevlar

<http://www.dupont.com/afs/>

<http://www.lbl.gov/MicroWorlds/Kevlar/index.html>

#### Conducting polymers

<http://nobelprize.org/chemistry/educational/poster/2000/index.html>

#### Nanotechnology

<http://www.aip.org/pt/vol-57/iss-6/p30.html>

<http://www.kodak.com/eknec/>

#### Fullerenes

<http://www.lbl.gov/Science-Articles/Archive/fullerenes.html>

<http://www.vega.org.uk/schools/download/index.php>

<http://www.nanotech-now.com/nanotube-buckyball-sites.htm>

[http://www.lps.u-sud.fr/Collectif/gr\\_23/themes/fullnano/en\\_AC60.htm](http://www.lps.u-sud.fr/Collectif/gr_23/themes/fullnano/en_AC60.htm)

#### Manipulating atoms

<http://www.che.utoledo.edu/nadarajah/webpages/whatsafm.html>

#### Mining

<http://www.ias.ac.in/resonance/Aug2004/Aug2004p27-34.htm>

#### Green chemistry

[http://www.uyseq.org/greener\\_industry/index.htm](http://www.uyseq.org/greener_industry/index.htm)

<http://www.uyseq.org/sustain-ed/index.htm>

<http://www.uyseq.org/sustain-ed/pages/Process/ProcessFrameset.htm>

#### Fuel cells

[http://www.utcpower.com/fs/com/bin/fs\\_com\\_Page/0.5433.03540.00.html](http://www.utcpower.com/fs/com/bin/fs_com_Page/0.5433.03540.00.html)

<http://www.rsc.org/chemistryworld/Issues/2006/March/HydrogenOnBoard.asp>

<http://www.rsc.org/chemistryworld/Issues/2006/March/FuelCells.asp>

#### General

<http://www.rsc.org/chemistryworld/>

<http://www.chemsoc.org/networks/learnnet/index.htm>

<http://pubs.acs.org/cen/science/science.html>

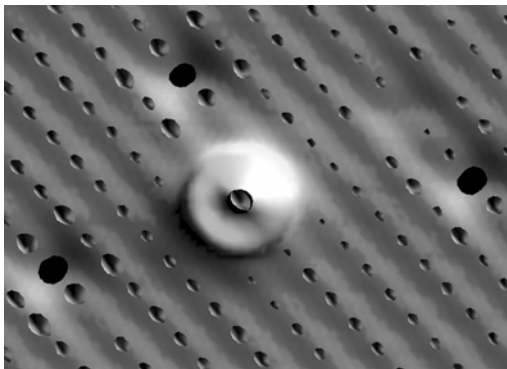
<http://www.chemistry.org/portal/a/c/s/1/enthusiasts.html>

## Nanotechnology worksheet

In this activity you will look at pictures of atoms. See how scientists can move atoms around to make pictures. Look at the pictures of atoms and read their descriptions. Make as many observations as you can and answer the questions about each picture.

### Seeing atoms

#### Seeing is believing



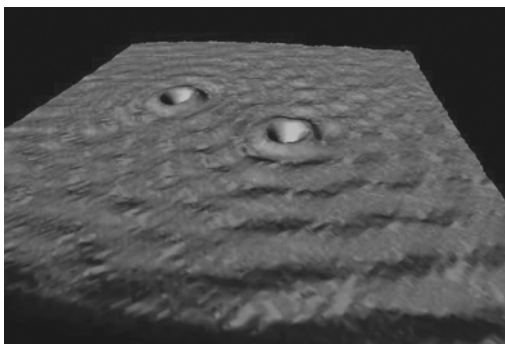
This picture is made from two images laid one on top of the other. This can be done using a computer. The lower picture is of nickel atoms. The big bump is a xenon atom. The tip of the pimple is a peek through to the nickel atom underneath. In a coloured picture produced by a computer, nickel is orange and xenon is blue.

#### *The zit*

Reproduced with kind permission from Mike Ross, IBM Almaden Research Center, California USA.

#### Questions

1. What are the symbols, atomic number and relative atomic mass values of the elements: nickel; xenon?
2. Why is the xenon atom much bigger than the nickel atom?
3. If you could see the nickel and xenon atoms, would they be these colours?



This is a sample of copper which is not perfect – the two dents are probably caused by atoms of another chemical element. The 'foreign' atoms have electron arrangements which are not the same as those of the copper atoms. The copper electrons on the surface are scattered, making patterns.

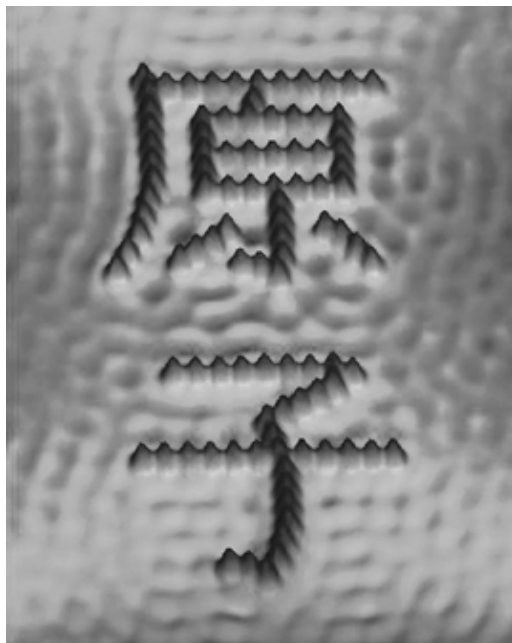
#### *The dents*

Reproduced with kind permission from Mike Ross, IBM Almaden Research Center, California USA.

#### Questions

4. What do the patterns on the surface look like?
5. In what other substances have you seen this kind of pattern?
6. What does this tell you about how electrons can behave?

### Atomic art



Iron atoms have been arranged on a surface of copper to make two Kanji characters which together mean 'atom'. On their own, the characters mean 'original' and 'child' in Japanese and Chinese, giving the title for the picture.

This is how to pronounce the characters:

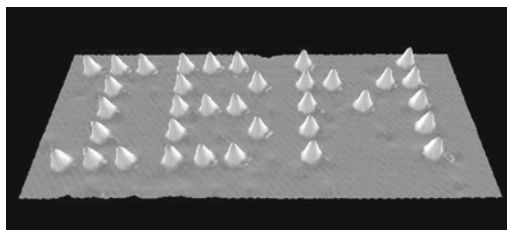
yuan zi ('you-an zee')	Mandarin Chinese
gen shi ('hard' g, like in 'gun')	Japanese
yuen ji ('you-en jee')	Cantonese Chinese

*An 'original child'*

Reproduced with kind permission from Mike Ross, IBM Almaden Research Center, California USA.

### Questions

- How many iron atoms have been used in the picture?
- One iron atom has a diameter of 248 pm. What is the distance across the top of the upper character in nanometres?
- Is 'original child' a good name for 'atom'? Explain your answer.



Xenon atoms have been arranged on the surface of nickel atoms to make the letters IBM. This was the first time that individual atoms were moved in a controlled way to make a new arrangement. The picture was taken in 1989.

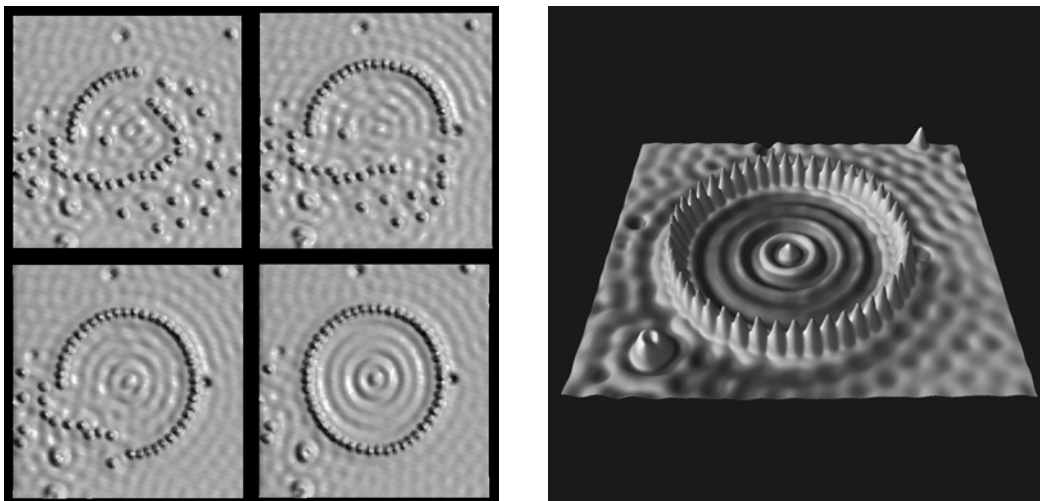
*In the beginning....*

Reproduced with kind permission from Mike Ross, IBM Almaden Research Center, California USA.

### Questions

- Why would the computer company IBM (International Business Machines) invest in nanotechnology?
- Explain how this picture is a good advert for IBM and for nanoscience.

## Making rings



*Ironing the perfect circle*

*The birthday cake*

Reproduced with kind permission from Mike Ross, IBM Almaden Research Center, California USA.

The four pictures show 48 iron atoms being moved into a circle 7.13 nm in diameter on the surface of copper. The tip of an STM is used to move the atoms. The finished ring looks like a birthday cake with candles. A pattern is seen in the centre of the finished ring.

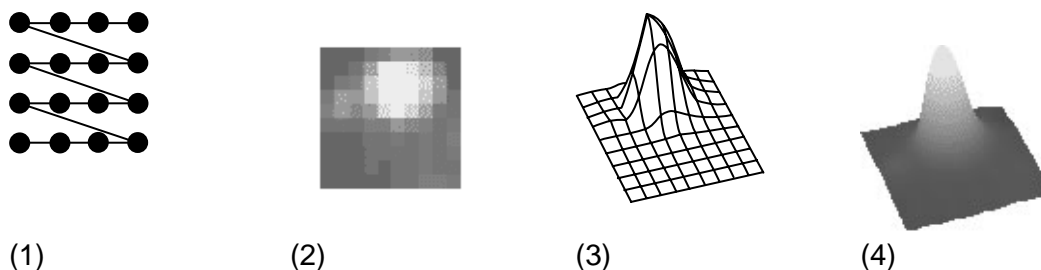
## Questions

12. What is the shape of the iron atoms? Is this shape that might be expected?
13. What might the central pattern be caused by?
14. Why is it useful to be able to move atoms individually?

## How STM pictures are made

The computer connected to the STM makes a grid of the surface of the substance. The tip of the STM scans the surface at points on the grid. The tip records a tiny electrical current, called the 'tunnelling current', at each point. The current changes as the tip moves up and down depending on the atoms present on the surface. A system inside the STM adjusts the tip movement, keeping it at a constant height. The adjustments are recorded and processed by the computer into an image, showing the changes in the surface of the substance.

The pictures show the process: (1) scanning; (2) the original image showing light areas as small adjustments; (3) the processed image changing light areas into heights; (4) the processed image coloured in shades of grey.



*Producing an STM picture*

Reproduced with kind permission from Mike Ross, IBM Almaden Research Center, California USA.  
Then the image is coloured to show different features of the atoms.

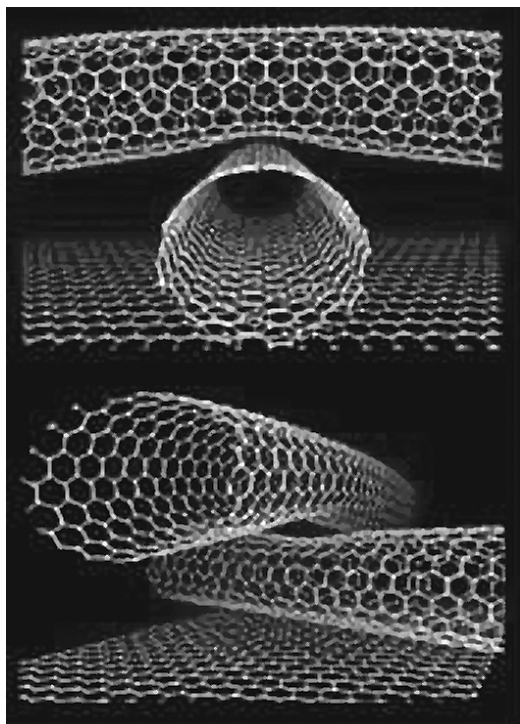


### Carbon and its various forms

Diamond and graphite are two well-known forms of carbon. In 1985 scientists discovered a third form of carbon based on 60 atoms bonded in a football-like structure. Scientists called this 'buckminsterfullerene', or 'buckyball'. This started a search for other carbon structures.

In 1991 a Japanese scientist called Sumio Iijima found carbon nanotubes. These are about 10 000 times thinner than a human hair, made from carbon atoms bonded in sheets and rolled into tubes. A carbon nanotube is about 1 nm in diameter and 1–10  $\mu\text{m}$  long. The tubes are often capped at each end with a half-buckyball structure. Scientists are working to find out more about carbon nanotubes and what they could be used for.

#### *What do nanotubes look like?*



#### *Piled high*

Reproduced with kind permission from Mike Ross, IBM Almaden Research Center, California USA.

#### Questions

15. Describe the appearance of the nanotubes in the figure Piled high. What do they remind you of?
16. Name the chemical element from which nanotubes are made.
17. Name another form of this element which has a structure similar to nanotubes. How are nanotubes different from this substance?
18. Explain in terms of chemical bonding why this chemical element exists in several different forms, each with different properties.