A comparison of potential molecular wires as components for molecular electronics

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Received 23rd August 2002
First published as an Advance Article on the web 4th December 2002

The field of electronics using single-molecule components has recently received much attention as a possible new design concept for the continued miniturisation of electronics. Molecular wires are the conceptually simplest components of such electronic systems and several different compound types have been used to produce molecular wires. Examples of some of the most promising families of molecular wires are presented, namely conjugated hydrocarbons, carbon nanotubes, porphyrin oligomers and DNA. Discussion centres around their potential use in functioning electronic architectures in terms of their electronic properties, ease and controllability of synthesis and potential for self-assembly.

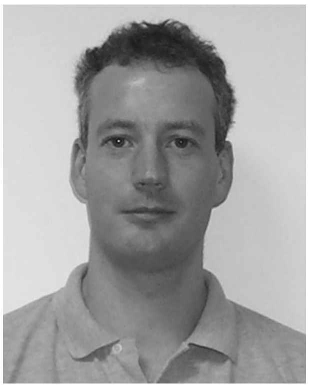
1 Introduction

The past decade has seen an increase in the need for more powerful computational devices. At present, this demand is accomplished with the miniaturisation of existing silicon-based chips, the top–down approach. It was predicted by Gordon Moore in 1968 that there would be a doubling of devices per chip every 18–24 months. This so-called 'Moore's Law' has held true over the past 34 years, however this approach will reach its physical limit in the next 5–10 years due to certain limiting factors. For example, when the oxide layers used in silicon chips reach a thickness of three atoms they become poorly insulating, resulting in charge leakage.[1] There are also financial implications such as the increasing costs for more complex production lines for the manufacture of ever-smaller devices on chips.

An alternative is the bottom–up approach, where molecules are synthesised to possess some inherent function, then assembled with other components to build the electrical device. Aviram and Ratner first suggested in 1974 that molecules could be used as alternatives to silicon chips,[2] but only more recently could significant progress towards this goal be realised through the advent of techniques such as scanning tunnelling microscopy, able to image and address single molecules. There are many different electrical components[3] that need to be considered, for example switches, logic gates, diodes *etc.* and this area has attracted much interest in recent years with several reviews written on the topic.[1,3,4] Wires are the simplest of electrical devices, and as such are particularly suited to the development of some fundamental understanding and techniques required for the realisation of molecule-scale electronics.

Several types of molecules have been suggested as 'molecular wires' and they all have the same key requirements. The most obvious is that they have to be electron or hole conducting in order to carry a current through the circuit. Thus the wire provides a pathway for transport of the electrons from one reservoir to another that is more efficient than electron transport through space. Quantification of the properties of a wire has been approached in different ways that generally depend on the technique used to analyse the wire properties. Measurements have been carried out of the rate of electron transfer across the wire using spectroscopic techniques and by techniques such as STM to obtain current–voltage characteristics and to classify wires as metallic or semiconducting. Conjugated molecules, comprising alternating single and double (or triple) carbon–carbon bonds, can conduct electrons through their π-system, and this has been the basis of many wires. The wire must also be linear and of a defined length in order to span the gap between two components in the circuit.

Once the wire has been synthesised a key problem is a method of attachment into a system in which it can be tested and



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DOI: 10.1039/b206919a

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eventually integrated into a circuit. This has proven to be difficult because, until recently, there has been no way of addressing individual molecules. It is also important to ensure that these connections are conducting otherwise current will be lost at the termini of the wire. Several methods have been investigated over the past few years.

One such approach to this problem is the integration of redox active metal centres at either end of the molecular wire (Fig. 1).

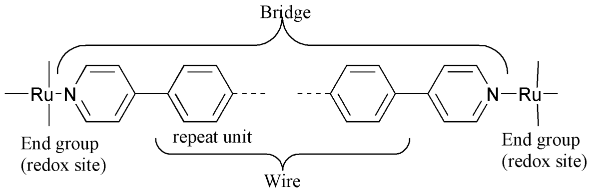


Fig. 1 Schematic illustration of a molecular wire incorporated into a mixed valence system. Redrawn from reference 5.

The metal centres act as donor and acceptor sites for the transfer of electrons across the bridge or wire. These donor–bridge–acceptor systems have the advantage of generating the electron *in-situ* so there is no need to connect the molecule to a macroscopic system. A key requirement is that there is good overlap between the d-orbitals of the metal and the π-orbitals of the bridging fragment, so that there is delocalisation from one metal to the other, allowing the transfer of the electrons. The rate at which the electrons are transferred can be related to the properties of the wire (such as length, degree of conjugation *etc.*).[5]

A variation of this method is to use two isovalent metal centres. If one of the metals is then oxidised the complex can show an inter-valence charge-transfer transition between the two end units. The timescale of the transition and intensity and shape of the absorption band provides quantitative information on the extent of coupling between the two metals, which can provide information related to the efficiency of the wire.

These methods have the advantage of generating the electron *in-situ* and providing an electron to test the conductivity of the wire. They have been studied extensively as a way of testing molecular electronic components for their suitability as candidates for future electronic devices.

There are however disadvantages, for example, one of the key requirements for these systems is a good overlap between the orbitals of the metal complex and the wire to allow conduction of the electrons. This consequently means that the compounds contain a contribution from the metal centres as well as the wire, and it is not possible to determine which favourable properties, *e.g.* fast electron transfer, are a result of the wire or the metal end groups. Related to this, the definition of where the wire actually begins in such systems can be difficult. The ‘bridge’ between the metal centres (Fig. 1) includes the primary coordination sphere of the metals whereas the ‘wire’ does not. Clearly such a definition is required for comparison between wires but must be regarded as an arbitrary choice.

There is also a difference between the transfer of an electron and the conductance of a current, which the wire would experience in an electrical circuit. It is not known if the molecular wire will carry the charge or simply decompose. This problem has become less of an issue with the design of molecular alligator clips and the use of scanning tunnelling microscopy (STM).

The attachment of ‘molecular alligator clips’ allows the wire to be attached to metal surfaces. One method of attachment is *via* thioacetates, which upon hydrolysis will form thiols. The thiols then form gold-thiolates on exposure to gold surfaces. However thiols are oxidatively unstable and the optimal method is likely to be *via* an *in-situ* approach. Some research has been carried out with arylformamides, which after coupling to oligomers can be converted to isonitriles, providing good adhesion to tungsten surfaces.[6] These alligator clips allow the molecular wire to be attached to two electrodes so that a current can be passed.

The direct measurement of the conductivity of a molecular wire has become possible with the development of the scanning tunnelling microscope (STM). The probe tip is small enough and precisely controllable so that it can interact with individual molecules absorbed onto a metal. Molecular wires have been inserted into an insulating layer of dodecanethiol molecules attached to a gold electrode. It was found that when the STM tip was manoeuvred along the surface of the monolayer the current flowing was significantly greater when in contact with the wire than when the tip was placed over the insulating layer (Fig. 2).[1]

Molecules studied as possible candidates for wires include conjugated hydrocarbons, carbon nanotubes, porphyrin oligomers and DNA strands and each of these will be considered in sections below.

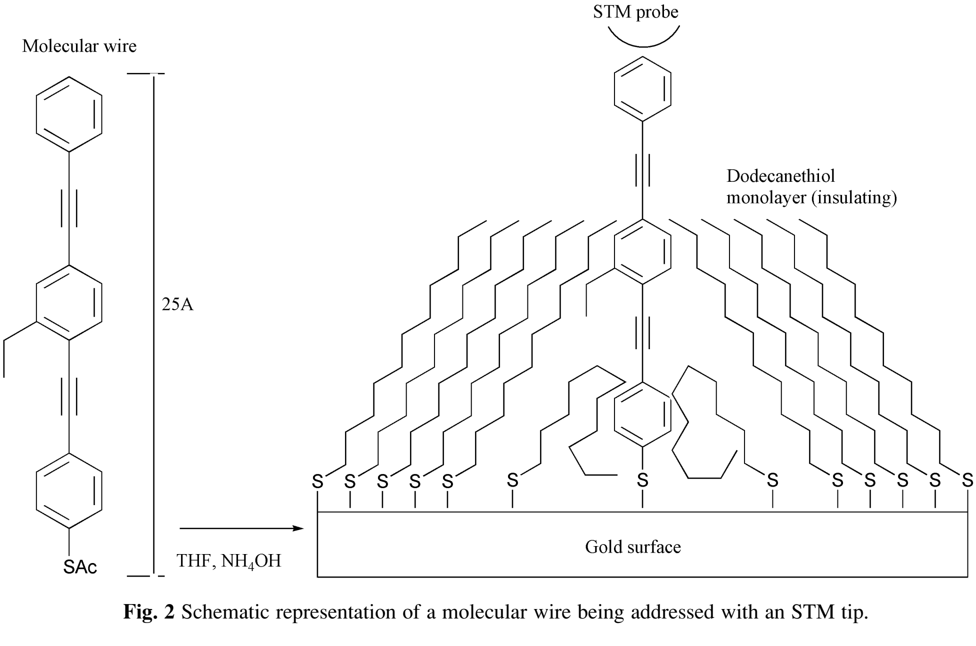


Fig. 2 Schematic representation of a molecular wire being addressed with an STM tip.

2 Conjugated hydrocarbons

The simplest hydrocarbon molecular wire is a carbon chain in which all of the atoms are linearly sp-hybridised, and therefore consist of alternating single and triple bonds, R-(C $\equiv$C)$_n$-R (where R is the terminating end group). Conjugated carbon chains, with lengths of up to twenty carbon atoms, have been synthesised with two chiral Rhenium end groups, (η^5-C_5Me_5)Re(NO)(PPh_3), (Fig. 3).[7] The presence of the metal groups allows the efficiency of the wires to be tested as described earlier.

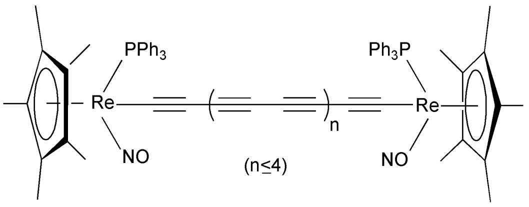


Fig. 3 Rhenium metal centres bridged by carbon chains.

It is also possible to have a chain of aromatic rings linked by acetylene units. By altering the groups attached to the rings it is possible to change other properties of the wires, for example, their solubility in particular solvents or use of 'linking' groups to fix the wire to a particular substrate. This has the advantage of 'tuning' the physical properties of the wire to complement its environment.

The most typical method of synthesising long molecules involves polymerisation. Any uncontrolled polymerisation leads to mixtures of molecules due to competing reactions, making it difficult to extract the molecule of required length and shape. Several alterations to polymerisation methods have been reported, which reduce side reactions and make purification of the desired molecule easier.

One example is the end capping polymerisation of *trans*-bis-(triisopropylsilyl)-protected tetraethynylethene (Fig. 4).[8] End capping reactions are used to control the average length of the polymers obtained. When the end capping reagent, phenylacetylene, was added to the oxidative polymerisation of the protected tetraethynylethene molecule a mixture of oligomers was obtained. These compounds were then separated by chromatography and it was discovered that their lengths varied from 19.4 Å to 49.2 Å. All these oligomers contain a persilylethynylated poly(triacetylene) backbone [–(C=C–CR–CR–C=C)$_n$–], making them linear. By varying the concentration and time at which pheneylacetylene was added it was possible to alter the average length of the polymerisation products.

Other substituents may be attached to the ends of these rods by changing the capping reagent, allowing the addition of 'alligator clips'. The lateral silyl groups can be exchanged for other substituents to allow attachment to substrates such as silicon wafers allowing an approach to the problem of fabrication into a functional system. The changing of these lateral substituents will also alter the solubility of the wire in different solvents.

These oligomers are amazingly stable with high melting points, and they remained unchanged for months at room temperature when exposed to air and light. These physical attributes have been assigned to the presence of the bulky (i-Pr)$_3$Si groups.

An alternative method of polymerisation is the Iterative Divergent/Convergent approach. The key advantage of this approach is that the molecular length doubles with each iteration. Another advantage is that any incomplete reactions lead to products half the length of the target molecule, making purification much easier. The ease of purification and rapid growth make this approach particularly attractive.[1] The steps themselves are very simple, involving only three sets of reaction conditions for the entire sequence. Thus, it is possible to produce a 16-mer molecule, with an approximate length of 100 Å, rapidly with very few conditions. The steps include an iodination, protodesilylation and a cross coupling with a Pd/Cu catalyst. The starting reagent (Scheme 1) is first split into two portions. One half is treated with methyl iodide to convert the triazene into the aryl iodide. A protodesilylation is carried out on the alkynyl end of the second half. The two portions are then mixed together with a soluble Pd/Cu catalyst, which couples the aryl iodide to the terminal alkyne, thus generating the dimer. This dimer has the same end groups as the monomer so the entire process can be repeated, *i.e.* the second iteration. This produces the tetramer on which the third iteration is carried out to produce the octamer. Finally, a fourth iteration produces the

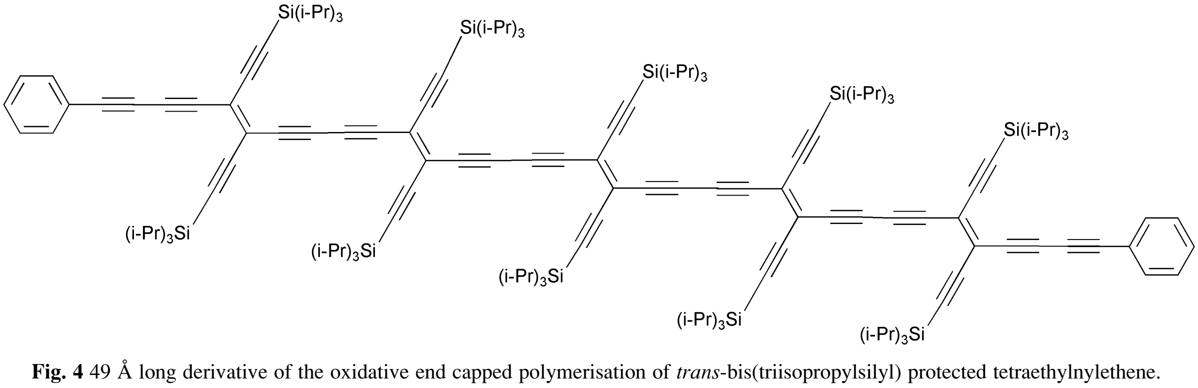
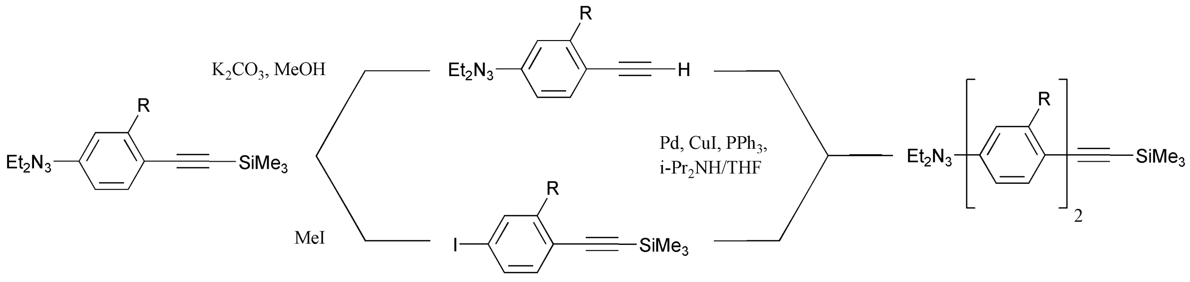


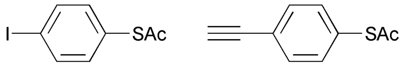
Fig. 4 49 Å long derivative of the oxidative end capped polymerisation of *trans*-bis(triisopropylsilyl) protected tetraethylnylethene.



Scheme 1 Synthesis of oligo(1,4-phenylene ethynylene)s using the iterative divergent /convergent approach.

16-mer. When R is 3-ethylheptyl the obtained 16-mer is 128 Å long (Scheme 1).[9]

Once all the iterations have been carried out thiol end groups can be added ready for attachment to the gold electrodes. This is easily achieved with molecules A and B, which can be attached with the same conditions used in the synthesis (Fig. 5).



Molecule A Molecule B

Fig. 5 Molecular alligator clips used for the end functionalisation of oligo(1,4-phenylene ethynylene) oligomers.

The aryl iodide (molecule A) is coupled to the alkynyl end of the oligomer while the alkynyl arene (molecule B) is coupled to the other end. These end groups are then deprotected with sodium hydroxide under reductive conditions to form the thiols for attachment to the electrodes.

One of the disadvantages to the iterative convergent/divergent sequence mentioned above is the use of methyl iodide, which is a volatile carcinogen. An alternative approach has been developed based on the halogen metal exchange of bromine and iodine.[10]

A similar approach has also been developed where the molecular system grows bi-directionally *i.e.* from both ends after each iteration. This method also has the advantage of only requiring two reaction conditions, Pd catalysed cross coupling of trimethylsilyacetylene with an aryl halide and an *in-situ* desilylation/Pd-catalysed coupling with an aryl iodide. This two-step process is achievable because masking of the aryl iodides is no longer required due to the selectivity of iodides over bromides. Some insoluble by-products are formed which increase as the length of the oligomer increases, making this method best suited to shorter oligomeric systems rather then longer molecular wires.[11]

This iteration approach has also been adapted to work on solid phase methods. There are several advantages to this over the solution phase synthesis. The reaction procedures are considerably simplified because time-consuming chromatography is not required for purification, the product can simply be washed with an appropriate solvent. The reactions can also be driven to completion using large amounts of reagents, which can then be easily recovered by filtration, preventing wastage. There is also no need to protect the end groups in the reaction cutting down on the number of toxic reagents required in these steps. This solid supported iterative convergent/divergent approach is expected to be suitable for automation and combinatorial chemistry.

The monomer is attached to a solid support such as polystyrene beads or Merrifield's resin *via* triazene functional groups.[12] The convergent/divergent iteration process can then be carried out with the same steps as the solution phase synthesis, except for the protection of the functional end groups. This solid phase sequence also gives increased yields, as all the impurities are in solution and easily removed.[9]

This solid phase synthesis has also been adapted to triple the length of the molecules at each iteration (Scheme 2).[13] The process is very similar but rather than attaching the monomer to the resin *via* an end group, it is attached at its centre. The molecule therefore contains two terminal iodides, one at each end, allowing the growth of the oligomers in both directions. The polymer supported *n*-mer bearing the terminal iodides is split into two portions. The first portion is converted into the (*n* + 2)-mer with the addition of 1,4-diethylnylbenzene to each end. The second portion is then liberated from its polymer support and coupled with the first portion to generate the (3*n* + 2)-mer, which also contains terminal iodides, ready for the next coupling reaction.

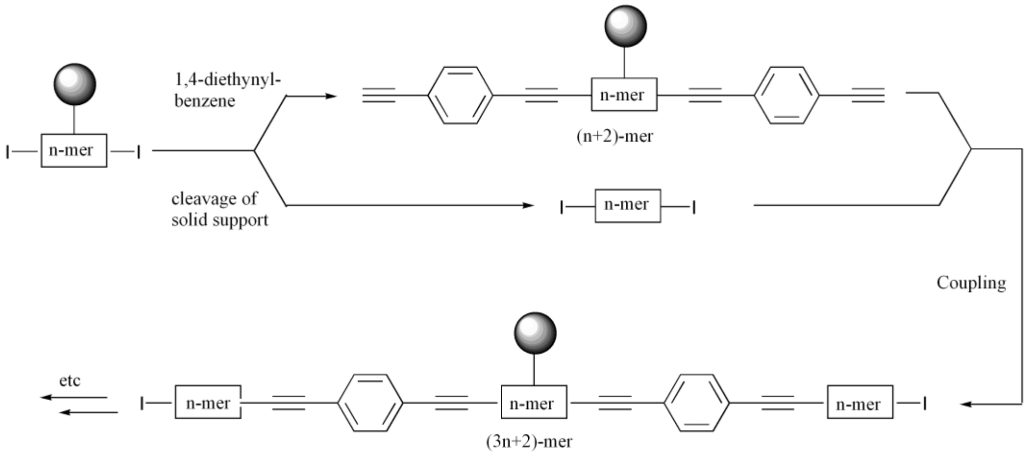
These are exciting results, which indicate that the production of suitable molecular wires on a large scale is not too far away.

Conjugated hydrocarbons can also be used as a ligand bridging two metal centres, which have the general formula $L_nMC_mM'L'_n$ (where C_m is the molecular wire, L_n,L_n' are auxiliary ligands and M,M′ are metal centres). It has previously been discussed how these complexes can act as a method for evaluating the conductivity of the wires by generation of an electron *in-situ*. They can also act as molecular alligator clips for integration into molecular systems as the metal groups can connect the different components required in an electrical circuit *via* their ligands. It has however been shown that the electronic coupling between the two metals decreases considerably as the hydrocarbon chain increases *i.e.* resistance increases with length. It has therefore been suggested that small bimetallic compounds could be synthesised and then joined *via* their terminating metal groups to construct a wire of desired length. The integrated metal centres will therefore prevent the conductance of the wire decreasing.

Bimetallic compounds may also provide a solution to the problem of connecting molecules into macroscopic environments by using light as a current carrier rather then electrons. In such molecules the donor and acceptor sites are photoactive, allowing the generation of an electron upon specific interactions with light. These so called 'photonic wires' are being studied as possible candidates for information transfer and data storage (Fig. 6).[14]

3 Carbon nanotubes

Ever since their discovery back in 1991[15] carbon nanotubes have been regarded as possible candidates for potential



Scheme 2 Solid phase iterative divergent/convergent approach with (3*n* + 2) molecular growth.

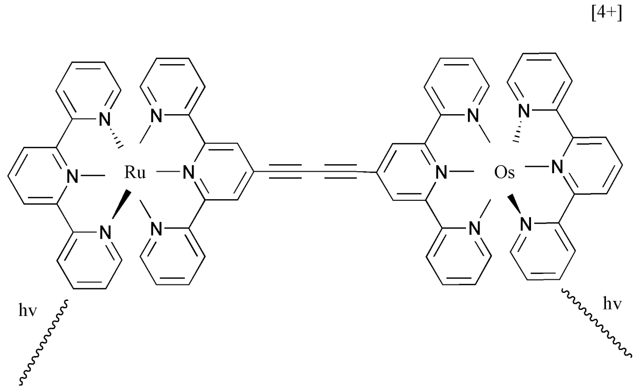


Fig. 6 A candidate for a possible 'photonic' molecular wire.

molecular wires[16] and other nanoelectronic devices as their electrical properties and high mechanical stiffness make them ideal.

These carbon structures can be thought of as graphitic sheets with a hexagonal lattice that have been wrapped up into a seamless cylinder. It is possible to obtain single-walled nanotubes (SWNTs) or multi-walled nanotubes (MWNTs), which vary in thickness from 2 to 50 layers. In the case of MWNTs it has been discovered that the electrical properties of individual tubes can vary greatly from tube to tube due to interactions between neighbouring layers. SWNTs are therefore better suited for use as potential molecular wires.

Several methods have been employed to determine the electrical properties of carbon nanotubes. The earliest of these experiments involved connecting the two ends of a tube to electrodes and measuring the current flowing through it. The connection to the electrodes may however have some effect on the reading. Experiments have recently been carried out with scanning force microscopy (SFM).[17] This method allows the total resistance of the tube to be split into two contributions: the contact resistance (that from the electrode and the SFM tip) and the resistance from the SWNT.[18]

One interesting electrical property is that their conductivity depends on tube diameter and wrapping angle, with only slight differences in these parameters causing a shift from a metallic to semi-conducting state. By using scanning tunnelling microscopy it has been possible to relate these changes to the structure of SWNTs and hence predict the electronic state of a particular wire.[19] Thus carbon nanotubes can be categorised into three classes based on the changes in physical properties: The first class consists of metallic tubes, the second class semi-conducting with narrow band gap, and the third class are semi-conducting wires which have a moderate band gap. The band gap is therefore tuneable by choosing the structure of the wire.[21]

There are four main methods for the production of carbon nanotubes (1) d.c. carbon arc discharge; (2) pyrolysis of hydrocarbons or other carbon containing molecules over metal catalysts; (3) laser vaporisation of graphite and (4) electrolysis using graphite electrodes immersed in molten ionic salts.[22] These methods do not allow selective growth and/or assembly of semi-conducting and metallic nanotubes as there seems to be no way to reliably design tube diameter or wrapping angle, leading to a wide range of conductivities. This makes constructing electronics from nanotubes difficult, as there is no control over the electrical properties. The desired tube has to be extracted from a bundle of varying sizes and thicknesses, this is time consuming and impractical on a large scale.

Problems with electrical conduction occur when impurities or defects are present within the tubes. For example, the presence of pentagon–heptagon defects, called elbow connections, result in the charge passing in only one direction. This leads to abrupt changes in current along the wires. This can however have advantages, for example, it is expected that doping the nanotubes with other metals could lead to some interesting electrical properties, which may improve their suitability for molecular electronics. It has also been suggested that two nanotubes could be used to construct the wire. The first one would be metallic and carry the charge. The second would fit around the first and be semi-conducting or insulating in nature. This would provide a protective sheath around the wire protecting it from nearby charges, such as other wires.

Carbon nanotubes make good molecular wires because of their electrical properties and rigid structure. They have very little resistance and it is possible to 'tune' their conductance by changing the diameter and wrapping angle. The disadvantages are clearly the current inability to selectively and cleanly synthesise particular nanotubes and the lack of sites for further functionalisation that could allow tuning of, for example, assembly properties.

The unique electrical properties and mechanical rigidity associated with carbon nanotubes has led to the construction of a device that indicates one possible way in which integrated molecular electronics might operate. The proposal for the device involved an array of SWNTs consisting of a set of parallel nanotubes on a substrate and a set of perpendicular nanotubes that have been suspended on a periodic array of supports (Fig. 7).[23] Each point on the array where two nanotubes cross represents a device element that can be switched between two positions. The OFF state is given when the two SWNTs are separated by the gap created by the supports and resistance between the two separated wires is high. Transient charging of the nanotubes produces an attractive force that causes them to move so that they are touching leading to a higher conductivity between the wires and an ON state. This configuration remains stable due to van der Waals forces, until the former state is recreated by the transient generation of repulsive electrostatic forces. The advantage of this approach is that the integrated system need only be addressed at the end of each wire, as this is sufficient to allow control of each individual crossing point in a large array of switches. Thus alteration of the state of the switch and measurement of the position of the switch through conductivity measurement can both be readily achieved. Calculations have suggested that the SWNTs possess the correct mechanical properties for such an array to function whereas the strain induced due to the bending angle in the ON state would exceed the failure limit of most other materials. These proposals have been demonstrated to be feasible through measurements on a device involving one pair of crossed nanotubes assembled through mechanical manipulation and comprising a single switch. A difference in conductivity of

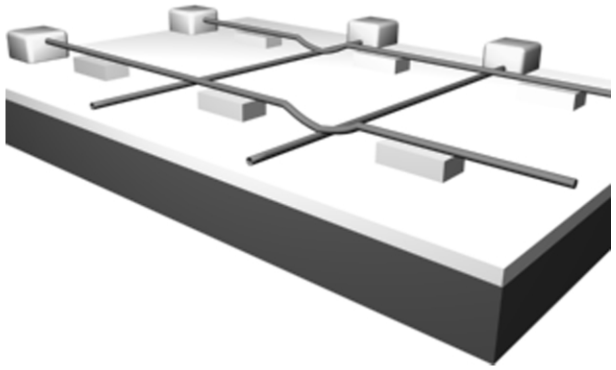


Fig. 7 3D view of a suspended cross bar array of carbon nanotubes, showing four junctions with two elements in the ON (contact) state and two elements in the OFF (separated) state. The substrate consists of a conducting layer [*e.g.*, highly doped silicon (dark grey)] that is covered with a thin di-electric layer [*e.g.*, SiO_2 (light grey)]. The lower nanotubes are supported directly on the di-electric film, whereas the upper nanotubes are suspended on periodic inorganic or organic supports. A metal electrode contacts each nanotube. Redrawn from reference 23.

around 10 was observed between the ON and OFF states in a device where reversible switching between the states was achieved. A device showing irreversible switching from OFF to ON gave a conductivity difference of 10^5 between the two states. These measurements are important as they identify a method whereby some of the requirements concerning integration of wires (and switches) into addressable devices can be achieved. The problem to be tackled however, is the reliance on mechanical manipulation of individual wires to assemble the device, a method clearly inappropriate for construction of larger devices or automated fabrication.

4 Porphyrin oligomers

The porphyrins are a group of naturally occurring pigments and a typical example is zinc octaethylporphyrin (Fig. 8). It has been discovered that if these molecules are joined to form conjugated oligomers, they possess some extraordinary electrical properties. This has been attributed to the fact that their π-systems merge to form giant supramolecular chromophores.[24,25]

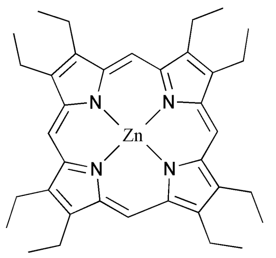


Fig. 8 Zinc octaethylporphyrin ZnOEP.

The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of conjugated porphyrin arrays are generally separated by only 2 eV. If this gap is narrowed slightly then the molecules will have useful electrical properties required for molecular wires. The metal chelation of porphyrins allows considerable control over the redox properties of such systems, since 56 different metals are known to complex with porphyrins.

Another key advantage to the use of porphyrins as molecular wires is the large size of the monomeric unit, which is *ca.* 16 Å. Therefore, the linear tetramers have a span of *ca.* 56 Å. This in itself is large enough to span the expected gap in an electrical circuit. Synthesis allows for a doubling of size at each extension, so the next molecule, the octamer, is expected to be *ca.* 120 Å. This means that long rigid wires can be synthesized relatively easily.

There are two methods of linking these giant ring structures together. The first method involves directly 'fusing' porphyrins together *i.e.* each porphyrin structure is directly linked to the next. This forces a coplanar geometry that should be favourable for electronic π conjugation. Porphyrins can be fused either at the *meso* or the β-pyrrolic carbon atoms. Fused porphyrins have been synthesised through the oxidation of metallo-porphyrins with tris(4-bromophenyl)aluminium hexachloroantimonate, where the two porphyrin units are doubly or triply linked through ring carbon atoms. The structures of these diporphyrins have been characterised and their optical and electrochemical properties have been reported.[26] The triply-linked diporphyrin structures showed the greatest conjugation, which is likely to be the result of more planar geometries, leading to better π-overlap (Fig. 9). They also showed stronger electronic interactions and smaller optical HOMO–LUMO gaps (1.14–1.33 eV) compared with the doubly fused diporphyrins.

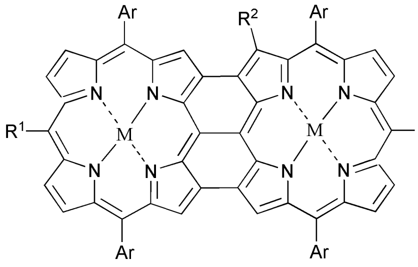


Fig. 9 Triply linked (*meso-meso* β–β β–β) diporphyrin.

The second method is to bridge the porphyrin arrays *via* delocalised coplanar structures such as aromatic systems or simple alkyne molecules. An example of this is the tetrakisporphyrin system (Fig. 10), which is about 65 Å long, and has a sheath of *tert*-butyl groups in the *meta* positions along the backbone.[27] This sheath insulates the wire from its surroundings and protects it from nearby electric fields. By control of these substituents it is also possible to alter the solubility properties of the wire making it more or less soluble in different solvents.

Porphyrin oligomers, which contain a photoactive unit, have also been synthesised. Such 'photonic molecular wires' based on side-to-side oligomerisation of *meso*-functionalised porphyrins have been studied and have been shown to absorb light at one end of an array of porphyrins and then emit a different photon at the other end.

This is a new area of exploration, and it is still easy to design new highly conjugated structures. For example, the azo link is almost as sterically unencumbered as an alkyne, and has less bond length alternation. Azo-linked dimers are likely to show strong conjugation and related structures are predicted to be good molecular wires.

5 DNA

The use of DNA molecules as wires in electronic circuits potentially offers some attractive advantages. The largest problem yet to be solved with molecular electronics is inter-element wiring and positioning at a nanometer scale. The use of molecular recognition processes and the self-assembly of molecules into supramolecular structures might help overcome these difficulties and, in this context, DNA has the appropriate

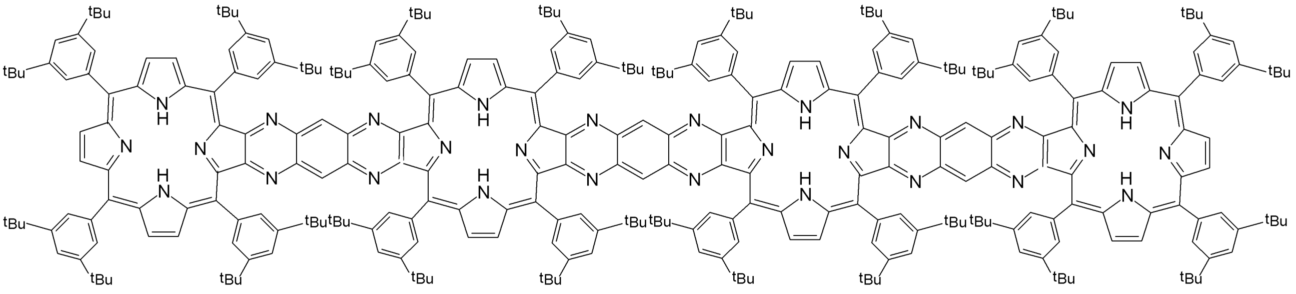


Fig. 10 Tetrakisporphyrin system.

molecular recognition and mechanical properties. Although this potential has been recognised, to date studies have focused on more fundamental questions concerning the ability of DNA to act as a wire and the mechanisms involved.

It has been proposed that electrons or holes can travel through the π-orbitals of the stacked aromatic bases in DNA, and several methods have been investigated to determine the nature of charge transport through DNA strands.[28] The earliest studies involved physical measurement of current flowing through DNA fibres and these experiments gave a mixture of results, suggesting that DNA is semi-conducting or even metallic[29] in nature. These variations in results are likely to be due to the connections of the strands to the electrodes and the physical properties of the DNA once exposed to high voltages.

There are also, however, reports which state that DNA is an insulator. A series of experiments carried out by Dekker *et al.*, in which a number of key parameters were changed, for example the base-pair sequence of the DNA, the type of substrate, the distance between the electrodes and the contact material, concluded that there was no evidence of any electronic conductivity in DNA molecules.[30]

Photochemical and photophysical studies have also been employed to determine the electrical properties of well-defined oligonucleotide assemblies in solution. These assemblies contain an electron donor and acceptor. Electron transfer is then measured through fluorescence quenching as a function of distance. These studies also yielded a range of conclusions, which again was probably dependent on the connection of the donor and acceptor groups as well as coupling between them in the base pair stack.

Biochemical studies of DNA have so far been the most successful in identifying charge transport through DNA over long distances. In these studies photo-oxidants are attached to a DNA strand at a given site separated from guanine doublet or triplet sites, which are the targets of oxidants, as guanine has the lowest ionisation potential of the four bases in DNA. The first step in the oxidation process is the formation of a guanine radical cation (G^+), by UV irradiation in the presence of oxidants. GG and GGG sequences have lower ionisation potentials than single G's, so the positive charge should migrate to these G clusters if long distance electron transport is possible.

Two theories have been proposed for the mechanism by which charge is transported from the donor to the acceptor through the DNA strand. The first theory is superexchange, or tunnelling. This mechanism predicts that the rate of charge transport will decrease exponentially with increasing distance between the donor and acceptor. The second mechanism involves charge hopping between discrete base orbitals.[31] It is predicted that the distance dependence will be much shallower than the tunnelling mechanism. Experimentally an intermediate distance dependence of charge transport is observed. Based on these observations, new theories have been proposed in which the charge transport involves a combination of tunnelling and hopping. It is also clear from the experiments carried out that the electron transfer properties of DNA strands are also base sequence dependent.

Schuster and co-workers have proposed the phonon-assisted polaron hopping mechanism, which occurs, between guanine bases in DNA. In this mechanism, upon hole injection, a transient polaron is formed, which causes base pairs in and near the structural distortion to leave or join the polaron. Charge is then transported along the DNA by polaron hopping assisted by phonons.[32]

Research has been carried out on ways to engineer DNA to enhance its conductivity. For example, modification has been carried out involving substituting the imino proton of each base pair with a metal ion, such as Zn^{2+}, to alter the electronic properties (Fig. 11).[33] This modified DNA is known as *M*-DNA.[34] Conductivity measurements were carried out by placing the DNA between two electrodes, separated by a deep physical gap. A comparison of unconverted *B*-DNA with the modified *M*-DNA showed metallic conductivity for the latter compared with semi-conducting behaviour for the former. The easy conversion of normal DNA into *M*-DNA means that the conductivity can be increased after integration into electronic circuits and this indicates how the unique properties of DNA may be used to advantage in the design of molecular electronics.

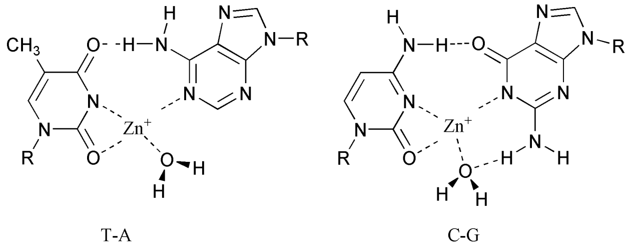


Fig. 11 Base pairing schemes for *M*-DNA. The imino protons with coordination to the N3 position of thymine and the N1 position of guanine are replaced by the Zn^{2+} ion.

This method utilises the properties of DNA that allow it to be altered and also undergo self-assembly, and it is this aspect which may offer a unique advantage over other potential wires in constructing nanoscale electronics. Using the self-assembly potential to practical advantage in constructing nanoscale devices however, has yet to be seriously addressed and studies have largely focused on the basic understanding of conductivity within DNA molecules. Charge transport within DNA helices clearly shows dependence on DNA base sequence, defects and local flexibility in addition to consideration of the interaction of the charge donors and acceptors with the DNA molecule. Clear evidence now exists, however, that in appropriate circumstances, charge transport over as much as 200 Å can occur under the appropriate circumstances.[28] Much of the interest in the charge-transporting abilities of DNA has so far been motivated by the need to understand biological processes such as oxidative damage. Such interest, however, also fuels the possibility that DNA may be able to act as a functioning molecular wire. The complexity of DNA molecules and the infinite possibilities for variation have so far led to difficulty in establishing the fundamental electronic properties. As the basic understanding improves however, this very complexity and ability to be modified may prove to be an advantage in the construction of electronic devices.

6 Conclusion

The aim of this review is to identify the key advances in the synthesis and understanding of molecular wires for use in nanoscaled electronics. Current down-sizing of silicon chips will reach a physical limit in the near future and an alternative system needs to be found.

There are four main types of molecules studied as potential wires, each with advantages and disadvantages. The most studied family of molecular wire is that constructed of conjugated hydrocarbon chains with conduction through their π-systems. Several approaches have been adapted to construct these wires fast and efficiently. They have been extensively tested and proved to be conducting. The major problem is that there is no method of positioning these molecules on a nanometer scale, in a manner that is required for fully functional electronics. One-way to overcome this problem is to utilise the self-assembly properties of DNA, but the variety and complexity of DNA has led to controversy over whether or not it is conducting. Several methods have been investigated to deal with this problem and better understanding has emerged of the circumstances in which DNA shows high conductivity and how to modify this. Carbon nanotubes are also promising candidates as they have some of the most attractive electrical properties, which can also vary, depending upon the topology of the nanotube. It is however not possible to synthesise specific tubes and current methods involve selection of a particular nanotube for study from a collection of mixed sizes. Thus, although carbon nanotubes have given rise to some exciting properties and demonstration devices, it is not clear how large-scale production and integration of these molecules and devices could be achieved.

Progress has been made in all these areas, but there is still a long way to go before single molecule electronic devices become practical. The next key step is to continue to find methods of integrating these molecules into useable systems. This involves solving several problems that go beyond the production and assessment of wires (and other functional molecules) described here. For example, methods of addressing these systems in a macroscopic environment must be addressed and heat dissipated from existing technology could be sufficient to cause the molecules to decompose. This is a fast moving area of research which is increasing in pace as the bottom–up approach is becoming exhausted.

7 References

1 J. M. Tour, *Acc. Chem. Res.*, 2000, **33**, 791.
2 A. Aviram and M. A. Ratner, *Chem. Phys. Lett.*, 1974, **29**, 277.
3 M. D. Ward, *J. Chem. Educ.*, 2001, **78**, 321.
4 J. M. Tour, A. M. Rawlett, M. Kozaki, Y. Yao, R. C. Jagessar, S. M. Dirk, D. W. Price, M. A. Reed, C. Zhou, J. Chen, W. Wang and I. Campbell, *Chem. Eur. J.*, 2001, **23**, 5118.
5 J. Launay, *Chem. Soc. Rev.*, 2001, **30**, 386.
6 J. S. Schumm, D. L. Pearson and J. M. Tour, *Nanotechnology*, 1996, **7**, 430.
7 R. Dembinski, T. Bartik, B. Bartik, M. Jaeger and J. A. Gladysz, *J. Am. Chem. Soc.*, 2000, **122**, 810.
8 A. M. Boldi, J. Anthony, V. Gramlich, C. B. Knobler, C. Boudon, J. Gisselbrecht, M. Gross and F. Diederich, *Helv. Chim. Acta*, 1995, **78**, 779.
9 L. Jones II, J. S. Schumm and J. M. Tour, *J. Org. Chem.*, 1997, **62**, 1388.
10 U. Ziener and A. Godt, *J. Org. Chem.*, 1997, **62**, 6137.
11 S. Huang and J. M. Tour, *Tetrahedron Lett.*, 1999, **40**, 3347.
12 J. K. Young, J. C. Nelson and J. S. Moore, *J. Org. Chem.*, 1994, **116**, 10841.
13 S. Huang and J. M. Tour, *J. Org. Chem.*, 1999, **64**, 8898.
14 F. Barigeletti and L. Flamigni, *Chem. Soc. Rev.*, 2000, **29**, 1.
15 S. Lijima, *Nature*, 1991, **354**, 56.
16 S. J. Tans, M. H. Devoret, H. Dai, A. Thess, R. E. Smalley, L. J. Geerligs and C. Dekker, *Nature*, 1997, **386**, 474.
17 M. Ouyang, J. Huang and C. M. Lieber, *Annu. Rev. Phys. Chem.*, 2002, **53**, 201.
18 P. J. de Pablo, C. Gómez-Navarro, M. T. Martínez, A. M. Benito, W. K. Maser, J. Colchero, J. Gómez-Herrero and A. M. Baró, *Appl. Phys. Lett.*, 2002, **80**, 1462.
19 T. Wang Odom, J. Huang, P. Kim and C. M. Leiber, *Nature*, 1998, **391**, 62.
20 J. W. Wildöer, L. C. Venema, A. G. Rinzler, R. E. Smalley and C. Dekker, *Nature*, 1998, **391**, 59.
21 N. Hamada, S. Sawada and A. Oshiyama, *Phys. Rev. Lett.*, 1992, **68**, 1579.
22 P. R. Birkett and M. Terrones, *Chem. Br.*, 1999, **35**, 45.
23 T. Rueckes, K. Kim, E. Joselevich, G. Y. Tseng, C.-L. Cheung and C. M. Lieber, *Science*, 2000, **289**, 94.
24 H. L. Anderson, *Chem. Commun.*, 1999, 2323.
25 A. Tsuda and A. Osuka, *Science*, 2001, **293**, 79.
26 A. Tsuda, H. Furuta and A. Osuka, *J. Am. Chem. Soc.*, 2001, **123**, 10304.
27 M. J. Crosley and P. L. Burn, *J. Chem. Soc., Chem. Commun.*, 1991, 1569.
28 E. M. Boon and J. K. Barton, *Curr. Opin. Struct. Biol.*, 2002, **12**, 320.
29 H. Fink and C. Schönenberger, *Nature*, 1999, **398**, 407.
30 A. J. Storm, J. van Noort, S. de Vries and C. Dekker, *Appl. Phys. Lett.*, 2001, **79**, 3881.
31 B. Giese, *Acc. Chem. Res.*, 2000, **33**, 631.
32 G. B. Schuster, *Acc. Chem. Res.*, 2000, **33**, 253.
33 P. Aich, S. L. Labiuk, L. W. Tari, L. J. T. Delbaere, W. J. Roesler, K. J. Falk, R. P. Steer and J. S. Lee, *J. Mol. Biol.*, 1999, **294**, 477.
34 A. Rakitin, P. Aich, C. Papadopoulos, Y. Kobzar, A. S. Vedeneev, J. S. Lee and J. M. Xu, *Phys. Rev. Lett.*, 2001, **86**, 3670.