11.1 Introduction

🗝 Balzani, V., Credi, A. and Venturi, M. *Molecular Devices and Machines*, Wiley-VCH: Weinheim, 2003.

11.1.1 Philosophy of Molecular Devices

The traditional goals of chemistry have centred on the idea of making molecules. If you can make molecules, then you can make new substances and materials, or make more of existing ones. Chemical substances – things like dyes and paints, metals and plastics, glass and ceramics, pharmaceuticals, synthetic textiles *etc.*– are useful things to have around. You can build things with them, wear them, change aesthetic and corrosion-resistance properties, consume them, make utensils and tools with them, and do whole host of other civilised things. In each case, only one main property of the chemical substance is being employed. This property can be something like colour (light absorption or emission), hardness and mechanical strength, cohesion and flexibility, therapeutic benefit (biochemical role), electrical or thermal conductance or insulating properties, and so on. Traditionally is has been left to the discipline of engineering, and latterly electronic engineering, to combine the bulk features of a number of different (chemical) substances, or at least mechanical components, in order to produce machines or devices.

We can define a machine as a functioning entity composed of a number of interacting components that collectively carry out a predefined task for (presumably) beneficial result. A machine, or device, differs from a chemical substance in that it is useful for what it *does*, rather than for what it *is*. Traditionally, because the components of a machine must be precisely orientated with respect to one another, and interact in a well-defined way, machines have been macroscopic structures that a human being can assemble through the use of keen eyesight and manual dexterity. In recent years, microscale machines (devices with components of the order of micrometres) have been produced in the electronics industry by other machines, which, metaphorically, have a vastly greater degree of manual dexterity and keener eyesight. Microscale machines take up less space, are subject to fewer external influences and, above all, are much faster and more sophisticated (in terms of the tasks they can perform) than their large ancestors. What has yet to be fully realised is the artificial production of nanoscale machines – machines the size of individual molecules – that have the potential to be yet faster and even more sophisticated. These kinds of nanoscale devices are exactly what Nature has evolved in living organisms and biochemical systems such as transport, signalling and recognition proteins, enzymes and the machinery of self-replication provide a lot if inspiration.

In Section 10.1, and throughout Chapter 10, we looked at methods by which large molecules or molecular-based systems on the nanometre scale might be assembled, or induced to self-assemble. Self-assembly addresses the fundamental problem of synthesising nanoscale structures in which components are placed in the correct orientations with respect to one another. In this chapter, we continue the theme of engineering large molecular structures, but with an emphasis on the properties of the individual components themselves and the ways in which they communicate, as a means towards the construction of molecular and supramolecular analogues of ‘real world’ devices, functioning on the nanometre scale.

11.1.2 When Is a Device Supramolecular?

So far we have focused on Lehn’s definition of a supramolecular compound as one involving non-covalent interactions (Section 1.1). Such a definition is entirely appropriate to host–guest chemistry,

Supramolecular Chemistry, 2nd edition J. W. Steed and J. L. Atwood
ISBN: 978-0-470-51233-3

and even to the templated and thermodynamic self-assembling systems discussed in Chapter 10. When we come to molecular devices, however, such a definition is not used by many workers in the field because the focus in the construction of supramolecular devices is on the functional interactions between the components rather than the chemical nature of their connectivity. This means that a 'supramolecular device' can be an entirely covalent molecule if it possesses characteristics of a supramolecular nature. Thus a supramolecular device may be defined as *a complex system made up of molecular components with definite individual properties*. These properties are intrinsic to a particular molecular component whether it is part of the device or not. Another way of saying this is that the *interaction energy* between the components of the supramolecular device must be small compared with other energy parameters relevant to the system. It does not matter, therefore, how the components are connected together in the device (covalently, hydrogen-bonded, coordination interaction *etc.*); all that matters is that each component should contribute something unique and identifiable with that component alone, within the system. If this rule does not hold true, and the functionality of the system is identifiable with the molecule as a whole, as opposed to the individual parts, then the complex is best thought of as a 'large molecule' and we will not consider it to be supramolecular.

Such a definition of a supramolecular device does not exclude the 'traditional' concept of host and guest or receptor and substrate. Molecular recognition events between host and guest may be an intrinsic part of the operation of a supramolecular device, which might, for example, be designed to bind and then signal the presence of a guest.

Common components within supramolecular devices as they are studied today are photochemically or redox active molecules, *i.e.* molecules capable of absorbing and/or emitting light and molecules capable of losing or gaining an electron. The definition of a supramolecular device made up from these components is illustrated in Figure 11.1. If light excitation of a molecule (♦↔•) results in the formation

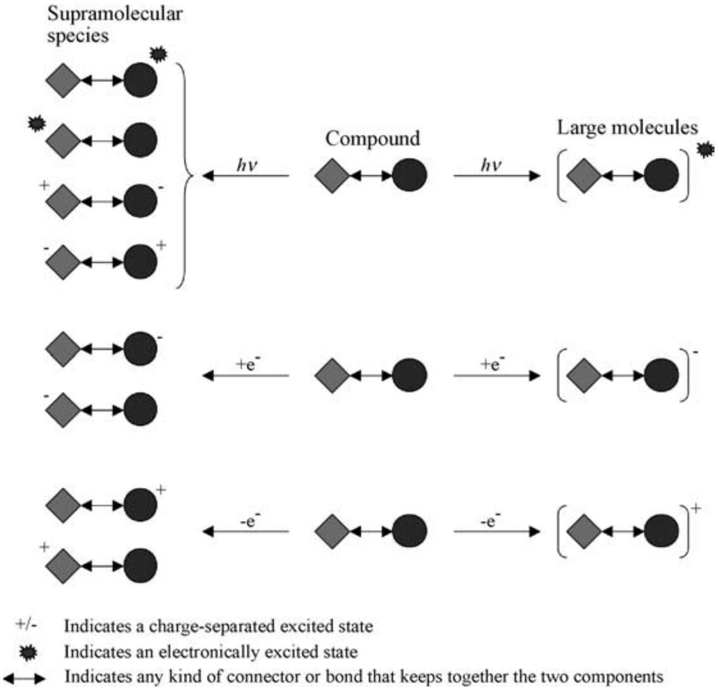

Figure 11.1 Photochemical and electrochemical criteria used to classify a complex chemical species as a supramolecular device or a large molecule.

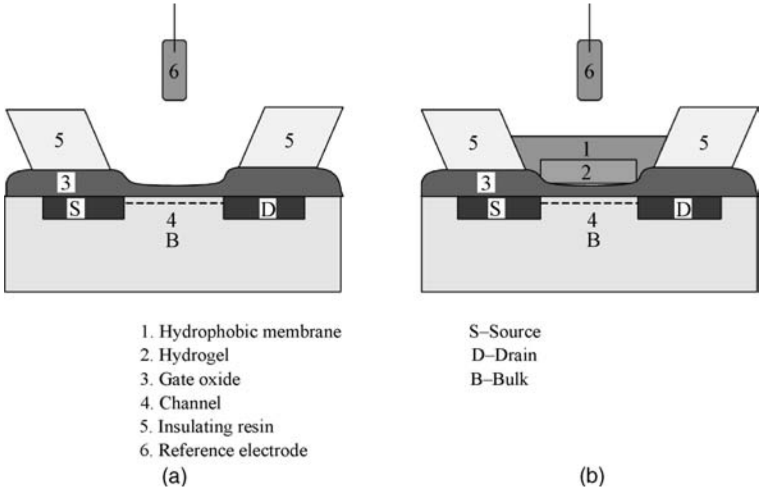

Figure 11.29 Schematic diagrams of (a) ISFET and (b) CHEMFET devices.

cryptands, and variously modified calixarenes.[43] CHEMFET devices may be improved further by the addition of a hydrogel layer that eliminates interference by CO_2 by incorporation of a salt buffer.

11.4 Molecule-Based Electronics

11.4.1 Molecular Electronic Devices

Petty, M., *Molecular Electronics: From Principles to Practice*, Wiley: Chichester, 2008.

Molecular electronic devices are, conceptually at least, those that most resemble electronic and computer components. If individual electronic components that may be coupled together, such as wires, switches, rectifiers *etc*., can be produced, then the conceptual basis exists to manufacturing molecule-sized (*i.e.* nanoscale) electronic devices with concomitant gains in speed, efficiency, capacity and reduced use of resources. The field of real world molecular computing is still in its infancy, although there have been some remarkable advances over the past five years. Chemically speaking, it is relatively straightforward to design and synthesise molecules that behave in an analogous way to individual electronic components, and we will look at a number of such examples in the sections below. However it is a far greater task to link such molecules together into a viable macroscopic device with input-output functionality, and the present state of the art still uses non-molecular (albeit often bordering on the nanoscale) read/write architecture as proof of principle of the functionality of the molecule-based components. We will look at recent progress in this regard in Section 11.4.6.

11.4.2 Molecular Wires

Ceccon, A., Santi, S., Orian, L., Bisello, A., ‘Electronic communication in heterobinuclear organometallic complexes through unsaturated hydrocarbon bridges’, *Coord. Chem. Rev.* 2004, **248**, 683–724.

The basic properties of a molecular wire are that it should connect to two components (generally an electron acceptor and an electron donor) and conduct an electrical signal or impulse between

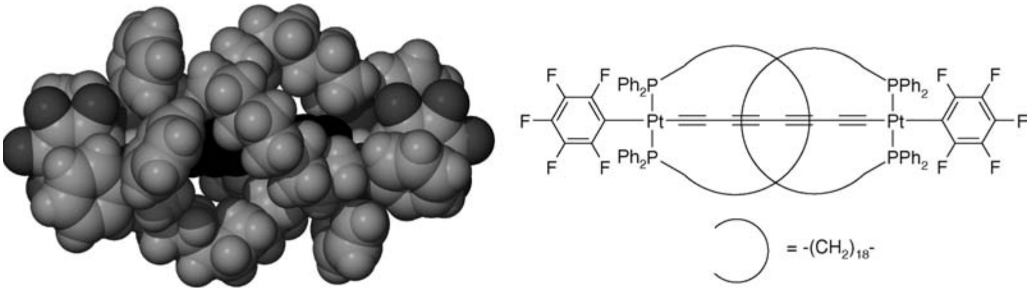

Figure 11.30 An insulated molecular wire based on a platinum(II) polyalkyne surrounded by two long-chain diphosphines. The polyalkyne wire (shown dark in the middle of the structure) is barely visible within the insulation.[45]

them. On a molecular scale, this may amount to a single electron. The electrical signal may have to be carried over a significant spatial distance, for example across a biological cell membrane (about 5 nm). The problem is analogous to the transmembrane current flow required for the transmission of nerve impulses in biochemistry (Section 2.2). In biological cells, the problem is solved by channel- and ionophore-mediated ion transport. The molecular wire concept is analogous to the channel-mediated mechanism, since it is expected to involve a rapid current flow, but the ideal electronic device would result solely in electron flow rather than the flow of alkali metal cations. It is generally believed that electron transfer within a molecule can be enhanced by providing a series of conjugated bonds allowing orbital overlap over a considerable distance (*cf.* Figure 11.6). In early work Lehn's group addressed this problem by the preparation of a number of carotenoid type compounds such as **11.45**, termed *caroviologens* because of the presence of the viologen-like bipyridinium moieties.[44] Using a technique called linear dichrosism spectroscopy (LD)*, Lehn *et al.* showed that the caroviologens were able to span lamellar model membranes of dihexadecylphosphate (flat liquid bilayer membranes, *cf.* Section 13.2.1) of thickness comparable to the length of the molecular wires. The hydrophilic pyridinium groups serve to interact with the aqueous phase either side of the vesicle wall as well as being electroactive groups. Transmembrane conductivity experiments were carried out in solution dihexadecylphosphate vesicles. When small amounts of the zwitterion **11.45** were used, conductivity enhancements of four to eight times background were observed between a internal oxidising phase containing potassium ferricyanide, $K_3[Fe(CN)_6]$, and an external reducing phase of sodium dithionite (Figure 11.31). In real electronic devices, some degree of redundancy may be required in case of damage, and hence triple wires have been prepared representing three-stranded molecular cables. Ingenious analogues of insulating cable coatings have also been developed, for example by threading cyclodextrins onto the wire to 'sheath' these delicate caroviologens molecular wires by 'molecular insulation'. An fascinating alternative kind of molecular insulation involves inducing an aliphatic diphosphine ligand to wrap around a polyalkyne molecular wire, Figure 11.30.[45]

An alternative approach to molecular conductors has been pioneered by Marye Fox of the University of Texas, USA, using block copolymers comprising electron donor and acceptor units, separated

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* LD is a spectroscopic technique that can be used with systems that are either intrinsically oriented, or can be oriented during an experiment by external forces. The technique gives information about conformation and orientation of structures within molecules. The linear dichroism of a sample is measured by orientating the sample along its axis and recording the difference in absorption of light linearly polarized parallel and perpendicular to the orientation axis. The LD signal is the difference in these two measurements (*cf.* circular dichroism, Box 6.2).

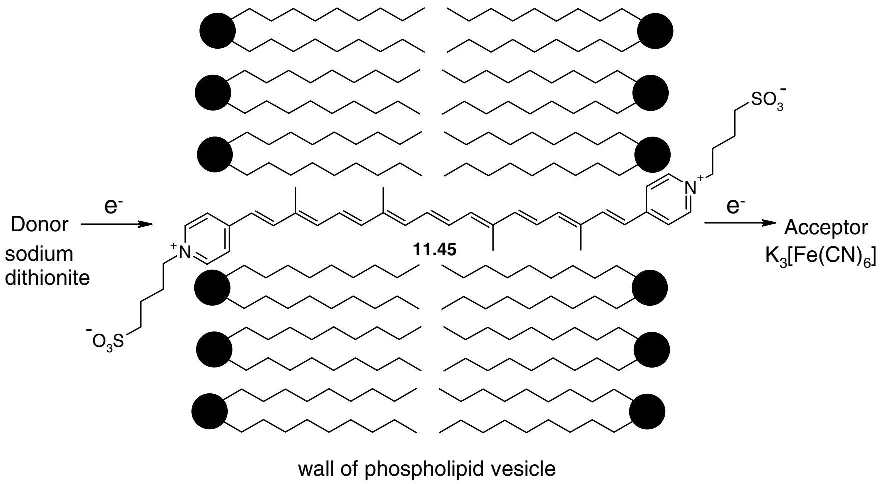
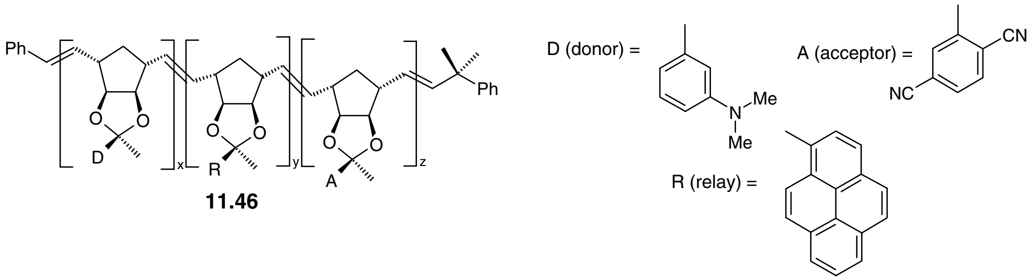


Figure 11.31 Molecular conductivity through a phospholipid vesicle by caroviologen **11.45**.[44]

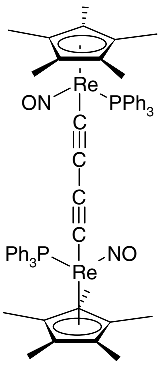
by conducting relays, as in **11.46**.[46] The block copolymers are prepared by ring opening metathesis polymerisation (ROMP), which allows highly monodisperse (narrow molecular weight range) materials to be prepared under mild conditions. The polymerisation is metal-catalysed and is an example of living polymerisation, *i.e.* once polymerisation is complete, addition of further monomer units (even structurally different ones) will restart the reaction. In this way, excellent control may be achieved over not only the overall polymer length, but the number of monomer units that comprise each polymer block. The polymers are also rigid (on the electron-transfer time scale), and hence display well-defined electrical characteristics and exhibit vectorial electron transfer from donor to acceptor. We will look at more block co-polymers in Section 14.3.1.



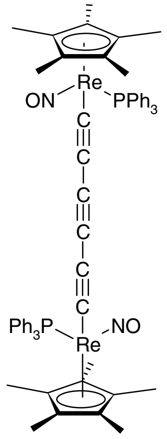
11.46

Interestingly, related polypeptide-based materials display differential electron-transfer rates depending on the orientation of the dipole of the peptide helix. This suggests that electron transfer in such systems may be controllable by externally applied potentials. Such results represent the beginning of the kind of long-range control and electron-transfer characteristics necessary for functional nanoscale optoelectronic devices.

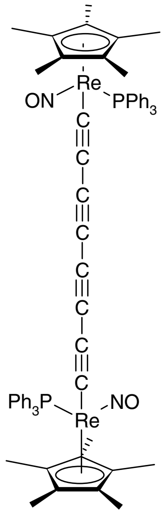
As we saw in Figure 11.6 molecular wires are not limited to organic conductors. The incorporation of metal ions with their variable redox states and photochemical activity, not to mention widely tuneable electronic and geometric properties, gives ample scope for the synthesis of novel metal-containing molecular conductors. For example, the rigid rod oligomers **11.47a–c** all undergo two reversible one-electron oxidations with the electrode potential separation between them increasing with decreasing bridge length (the separation is as much as 0.44 V in **11.47a**). The fact that two oxidation processes are noted (both formally transitions from Re(I) to Re(II)) indicates that the electronic environment about the second metal centre is influenced by the oxidation of the first *via* the conjugated polycumulene ligand. Indeed, in the case of **11.47a**, the mixed valence Re(I)/Re(II) species may be isolated and shown to be a class III mixed-valence compound (*i.e.* the 'extra' electron from the Re(I) side is delocalised fully over both metal centres).[47] These kinds of small molecule systems have been extended to form conducting metal–acetylide polymers such as **11.48**, which are also of interest for their electrical conductivity as well as nonlinear optical properties.



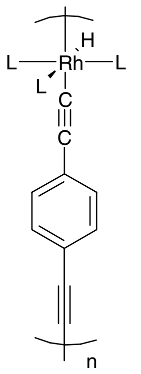
11.47a



11.47b



11.48c



11.48

A fascinating series of fully conjugated porphyrin-based molecular wire has been reported by the group of Osuka (Kyoto, Japan).[48] The molecules are tape-like and exhibit extremely red-shifted absorption bands as a result of their extensively π-conjugated electronic systems which give rise to a low π–π^* separation. The electronic absorption maximum for the dodecamer shown in Figure 11.32 is only *ca.* 3500 cm^{-1}, a similar energy to the vibration of an O–H bond! Understandably the compounds are also increasingly readily oxidised as the number of porphyrin units increases.

Finally the longest single molecular wire reported to date has been prepared by Martyn Bryce and coworkers from Durham University, UK. The rigid, conjugated molecule (Figure 11.33) is 7 nm long and is equipped with terminal thiol groups allowing it to dock between gold electrodes.[49] The central dipyridyl group can be protonated making it electron deficient and allowing coupling with an electron rich donor. This arrangement leads to the wire exhibiting rectification behaviour. We will look at molecular rectification in the next section.

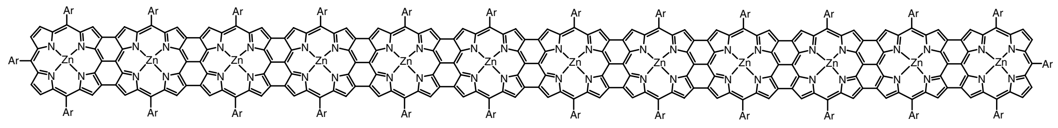


Figure 11.32 A fully conjugated porphyrin-based molecular wire.[48]

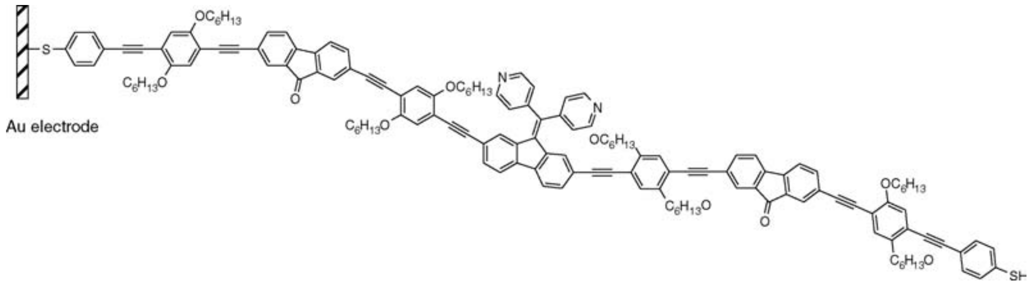


Figure 11.33 A 7 nm long protonatable molecular wire.[49]

11.4.3 Molecular Rectifiers

Metzger, R. M., 'Unimolecular electrical rectifiers,' *Chem. Rev.* 2003, **103**, 3803–3834.

Electrical rectification by a single molecule was first seriously proposed in 1974 by Ari Aviram and Mark A. Ratner who proposed (but never synthesised) compound **11.49**. Their visionary ideas have since stood the test of experimental verification in other systems.[50] A rectifier is a device that allows only one-way flow of electrons. In bulk electronic devices, it is used to convert an alternating current into a direct current. Conventional rectifiers are made up of a contact between a p-type (electron-poor) and n-type (electron-rich) semiconductor. The rectifier operates by causing the build-up of an insulating layer in the contact region (Figure 11.34). When the p- and n-type junction is formed, electrons flow from donor to acceptor until the charge is neutralised within the contact region and no further current flow is possible. If an external voltage is applied to the rectifier, then one of two possible situations develops, depending on the polarity of the applied voltage. If the applied potential is such that the cathode (negatively charged electrode) is placed in contact with the n-type side and the anode in contact with the p-type side, the insulating layer will grow as a consequence of additional electron flow until, once again, no current flow is possible. Conversely, if the polarity is reversed, then the insulating layer will shrink, allowing current flow. If an alternating current is applied, the result is current flow only when the alternating cycle is of the correct polarity, *i.e.* the conversion of alternating current into direct current.

On a molecular level, exactly the same characteristics are required of supramolecular components and hence a molecular rectifier should comprise an electron donor and an electron acceptor, separated by an insulating spacer. Compounds **11.49** and **11.50** are based on σ-insulating framework, while donor–acceptor carotenoid derivatives such as **11.51** are separated by a more conducting π-system.

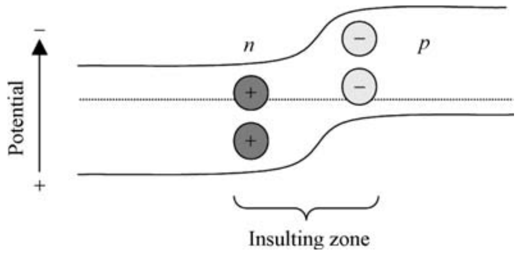
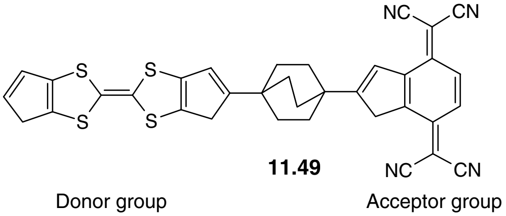
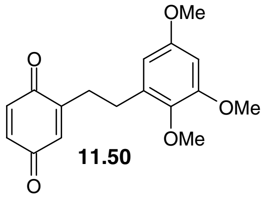


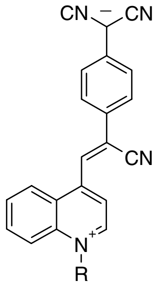
Figure 11.34 Semiconductor p–n junction in a conventional rectifier.



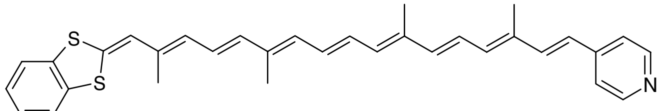
11.49



11.50



11.52



11.51

The operation of the molecular rectifiers may be explained with the help of Figure 11.35, which represents a molecule such as **11.49** attached *via* its donor and acceptor components to an anode and cathode with each possible polarity. The configuration shown in Figure 11.35a allows current to flow because the driving potential, V, required to overcome the insulating layer is relatively small, implying a small insulating layer. The required driving potential in Figure 11.35b is much larger, hence current flow is more difficult. The magnitude of V is determined by the relative energies of the donor and acceptor orbitals. In the case shown in Figure 11.35a, electrons from the cathode are transferred into acceptor orbital B as soon as the potential is large enough to cause overlap of donor and acceptor orbitals. Similarly, electrons are transferred from donor orbital C to the anode. Because the energy difference between B and C is small, electrons can

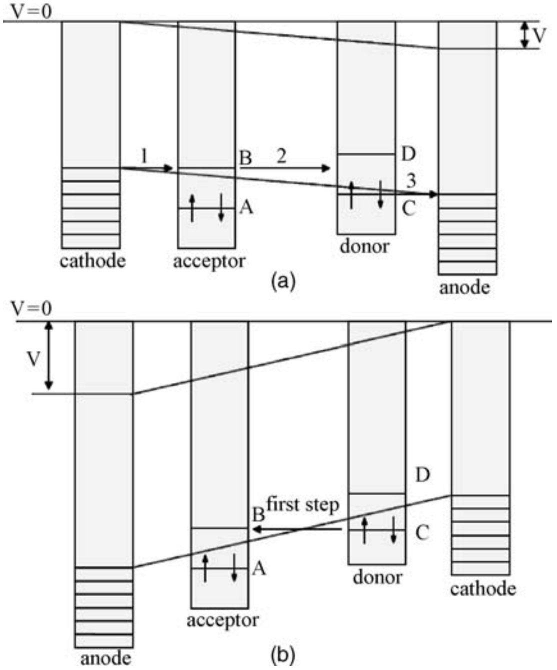


Figure 11.35 Molecular rectification (a) Flow of electrons. (b) No current unless V is sufficiently large. Steps 1, 2 and 3 are tunnelling processes.

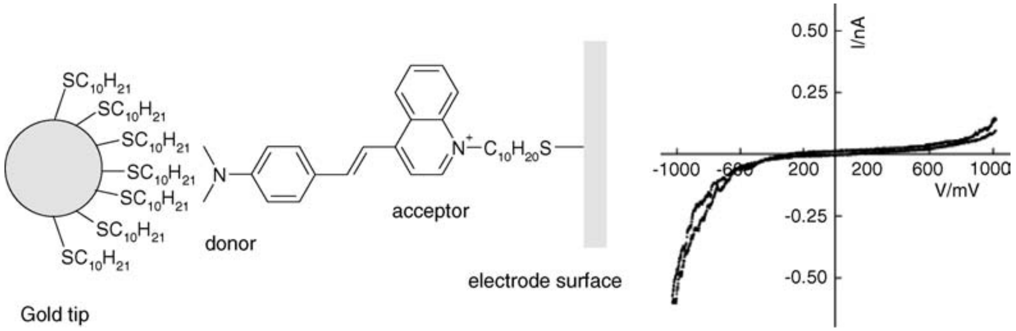


Figure 11.36 A single molecule rectifier attached to a gold electrode surface and probed by a coated gold STM tip. The thickness of the coating allows control of the distance between the two gold electrodes. The resulting current-potential (I – V) curve is shown right (reproduced with permission from [52] © 2004 American Chemical Society).

tunnel through the insulating spacer. The electron from B tunnels into the donor manifold in an excited Franck–Condon state and decays back to the ground state, C, by radiationless relaxation, and the electrical circuit is closed. The process is irreversible as long as the energy of B is above that of C. In the reverse situation (Figure 11.35b), a continuous flow of electrons is achieved only if level D is below the Fermi level of the cathode, allowing electrons to flow from cathode to D. Similarly, the Fermi level of the anode would need to be below the level of A. The necessary potential to achieve this is much larger than in the former case. A great deal of work has been carried out on molecular rectifiers because they offer the possibility of being part of a molecular electronics system allowing very densely packed electronic circuitry.

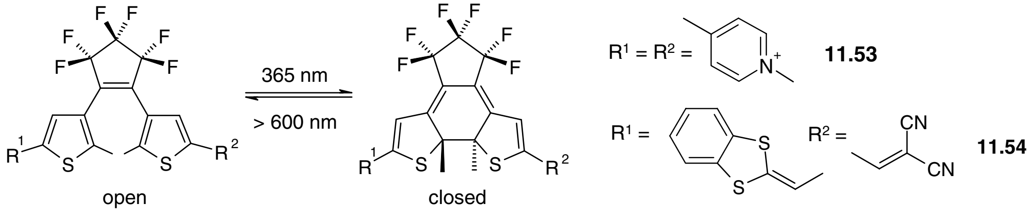
There have been some impressive, relatively recent examples of molecular rectification. Compound **11.52** has proved to be an extremely efficient molecular rectifier, able to actually function as a rectification device by intramolecular tunnelling either as a monolayers or multilayer macroscopic film or on a nanoscopic level.[51] Switchable rectification has been demonstrated for a related dye shown in Figure 11.36. The electrical asymmetry can be chemically switched, off and then back on, by treatment with acid and base, respectively. Protonation disrupts the intramolecular charge-transfer axis, destroying the rectification effect.[52] Recent calculations, however, suggest that there may be relatively unpromising theoretical limits on the rectification possible by a single molecule.[53]

11.4.4 Molecular Switches

Otsuki, J., Akasaka, T. and Araki, K., 'Molecular switches for electron and energy transfer processes based on metal complexes', *Coord. Chem. Rev.* 2008, **252**, 32–56.

In principle any molecule able to exist in two reversible, switchable states can represents a molecular switch (bistable device) with potential to form part of molecular circuitry or act as molecular memory. An excellent component for switchable molecular devices is the 1,2-dithienylethene system, which has been exploited ingeniously by Lehn in a number of bistable systems.[54] The core switching element is the transformation of the dithienylethene unit between two stable states as a function of the wavelength of incident radiation (Scheme 11.8).

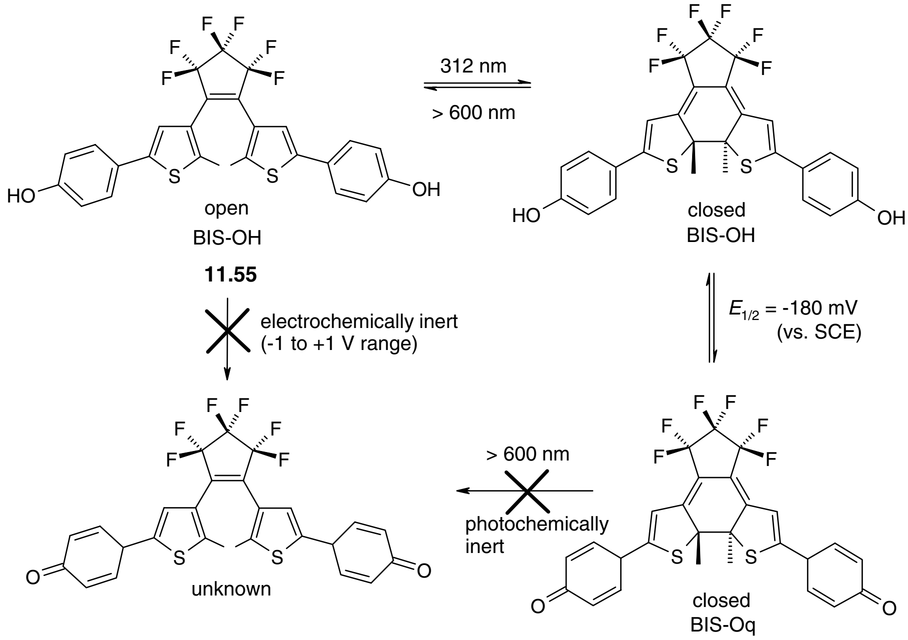
This switching ability is highly reversible simply by alternating between irradiation by ultraviolet (about 300 nm) and visible (>600 nm) light. Furthermore, the two states, 'open' and 'closed', have very different electronic properties. The closed state contains a fully conjugated π-system across the bridge, allowing effective electronic communication from substituent R^1 to R^2 *via* the delocalised π-system.



Scheme 11.8 States of the bistable 1,2-dithienylethene switch unit.

The open state effectively insulates R^1 from R^2. Lehn's group have put this functional switching system to a number of different uses, highlighting its 'component' nature, which, by definition, must have intrinsic, transferable properties. In **11.53**, the two substituents linked by the switch are identical electroactive groups. In the closed form, compound **11.53** is easily reduced electochemically, whereas the open form is not. Thus we have a prototype switchable molecular wire. In the case of **11.54**, R^1 is an electron-donating group, while R^2 is an electron-poor acceptor. The resulting molecule in the closed form is an electronically communicating 'push–pull' system with marked nonlinear optical (NLO) properties, as characterised by a large hyperpolarisability (β coefficient). Opening the switch by irradiation by visible light destroys the communication between the two ends of the molecule, and the hyperpolarisability is markedly decreased. An explanation of NLO properties may be found in Section 11.6.

Perhaps the most remarkable photoswitchable system based on this concept is that shown in **11.55** (Scheme 11.9), which represents a system that is both photo- and electroswitchable. As with **11.53**, the open BIS-OH form is electrochemically inert. Photoswitching to the closed form enables the molecule to be oxidised easily to the bis(quinone) BIS-Oq. The quinone form is photochemically inert and cannot revert back to an 'open' form until re-reduced. The system is of interest in the context of information storage applications. It represents a chemical approach to the EDRAW (erase direct read after write) mode



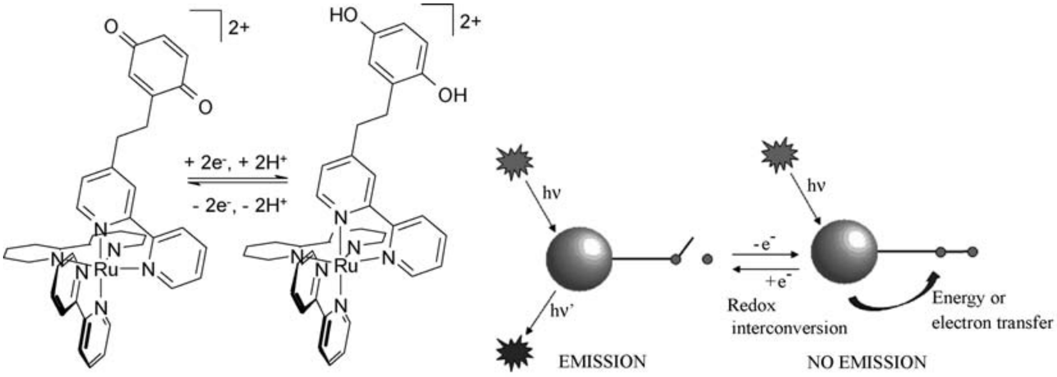
Scheme 11.9 A photo- and electroswitchable system based on **11.55**.

of information storage in which information is written optically by irradiation with UV light and is then safeguarded by oxidation. The information may then be read many times without destruction before finally being erased after reductive unlocking (*cf.* the WORM (write once read many) type, in which information is written to media such as CD-ROM and may then be read a large number of times as required).

The 1,2-dithienylethene unit has also been used to link together metal tris(bipyridyl) moieties including an unsymmetrical Ru(II)/Os(II) complex. In the 'open' form luminescence from the MLCT state is observed with efficient energy transfer from ruthenium to osmium. However, the emission is quenched upon conversion to the closed form because of energy transfer to the photochromic 1,2-dithienylethene orbitals.[55]

Another example of a combined, switchable electro-optical molecular device is the couple **11.56** and **11.57**, which are readily interconverted electrochemically since oxidation of the hydroquinone moiety occurs before the oxidation of the Ru(II) centre. In the reduced hydroquinone form, the Ru(bpy)$_3^{2+}$ moiety is highly luminescent from its MLCT state, as described in Section 11.2. Electrochemical oxidation to the quinone form, however, results in complete switching off of the luminescence because of the quinone's ability to quench the MLCT state by extremely fast metal-to-ligand electron transfer. The quinone is an excellent electron acceptor, and indeed quinones play a significant role in charge separation in photosynthesis because of their low-lying π* acceptor orbitals (Section 2.4): hence the compound acts as an efficient bistable electrophotoswitch (Figure 11.37). Both oxidised and reduced forms of the compound are isolable and the redox couple is entirely reversible and stable. Luminescence quenching is complete.[56]

The mechanical nature of the connectivity between rotaxane and catenane components (Section 10.7) resembles strongly the mechanical connectivity in macroscopic machines and has inspired a great deal of work on photo-, redox- and pH-switchable systems. Initially, as part of attempts to produce [3]rotaxanes, long, terminated, dumb-bell-shaped threads were produced by Stoddart *et al.*, incorporating two or more electron-rich aryl and biaryl residues. However, in most cases, only [2]rotaxanes resulted. The occurrence of a [2]rotaxane with two possible electron-rich binding sites raises the interesting possibility of the 'shuttling' of the 'blue box' macrocycle **6.81** (Section 6.5.8) back and forth between the two points of attachment, rather like a train on a railway line with two stations. As a result, the [2]rotaxane shown in Figure 11.38 was prepared *via* a threading approach in 19 % overall yield. Because the two 'stations' are different from each another, there is a significant energetic preference for the more electron-rich benzidine unit (nitrogen station). ^{1}H NMR spectroscopy gives a ratio between the two translational isomers of 84:16 in CD$_3$CN solution at –44°C. However, protonation with trifluoroacetic acid decreases dramatically



11.56 **11.57**

Figure 11.37 Electrophotoswitching in a real system and cartoon representation.[56]

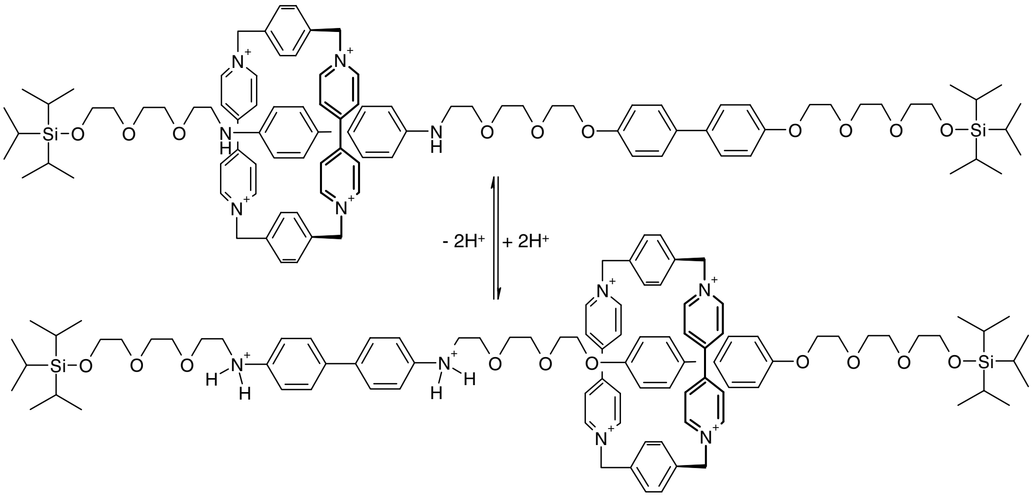
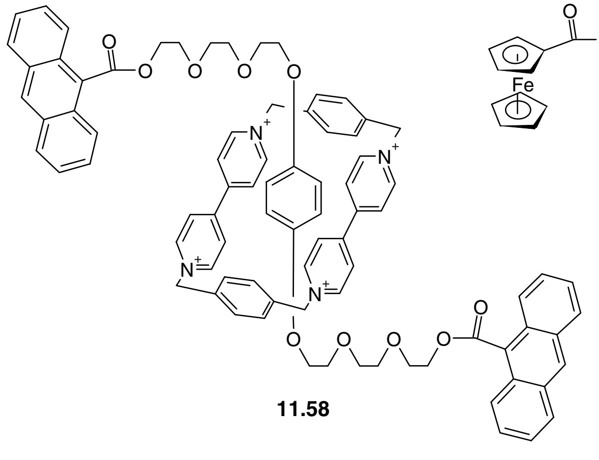


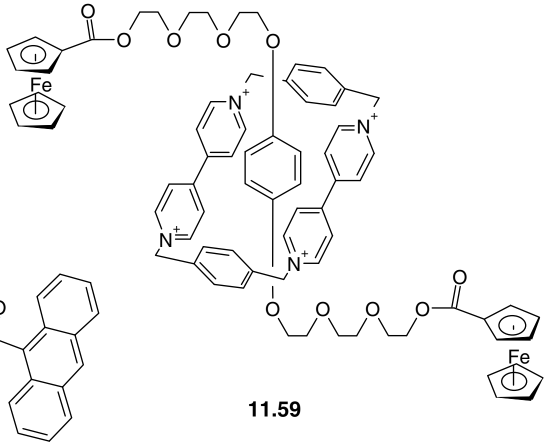
Figure 11.38 A [2]rotaxane-based, pH- and redox-switchable molecular shuttle.

the electron density at the basic benzidine unit, causing the macrocycle to shunt completely to the 4,4′-biphenolate unit. A similar result is obtained by electrochemical oxidation of the benzidine station to the analogous radical cation. Both pH- and electrochemically driven processes are entirely reversible, giving a rotaxane-based molecular switch.

A great deal of work has gone into the production of further redox- and photoswitchable rotaxanes.[57] In particular, the use of photoactive terminator groups incorporating anthracene substituents, or redox active ferrocenyl groups, instead of Si(i-Pr)$_3$ groups, have been found to control the rate of charge recombination upon photoexcitation in rotaxane **11.58**. Photoexcitation by a laser pulse at 437 nm affords a radical ion pair by electron transfer from the electron-rich thread to the macrocyclic shuttle. In the case of the ferrocenyl derivative **11.59**, very long-lived charge-separated states, somewhat analogous to those occurring in photosynthesis, are observed. The photoexcited [2]rotaxane is quenched by rapid oxidation of the ferrocenyl stopper by the oxidised 4,4′-biphenol moiety. Charge recombination is very slow because of the repulsion of the cationic macrocycle away from the positively charged ferrocene-derived terminator group (Figure 11.39). In contrast, the analogous anthracenyl-stoppered analogue exhibits very rapid charge recombination.



11.58



11.59

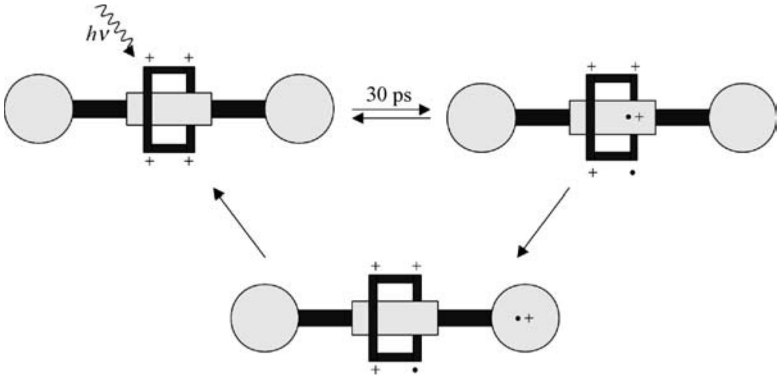


Figure 11.39 Long-lived charge separation using **11.59**.

Work on pseudorotaxanes has resulted in a system that is switchable between two different colours (a chromophoric switch) as a function of the binding of two different rotaxane threads. The colour of the complex, which switches between red and purple, depends strongly upon which thread, **11.60** or **11.61** is bound. In the resting state of the switch, the more-electron rich 1,5-dioxynapthalene group of **11.60** is complexed preferentially, giving a purple colour to the complex in MeCN solution. Thread **11.60** is ditopic, however, and can act as a host for alkali metal cations, particularly K^+, by virtue of the appended [18]crown-6 ring. On binding of K^+ ions by the crown ether portion of **11.60**, there is immediate electrostatic repulsion between the thread and the cationic cyclophane paraquat macrocycle **6.81**. Because the complex is only a pseudorotaxane (there are no end stopper groups), this repulsion causes immediate dethreading, allowing complexation of the other thread, **11.61**, which imparts a red colour to the solution. The inference is that the presence of colourless K^+ salts may be detected by a simple visual examination of the solution (Scheme 11.10).

Just like the rotaxane-based shuttle shown in Figure 11.38, unsymmetrical catenanes can also undergo translational isomerism. A [2]catenane has been constructed based on a desymmetrised tetracationic cyclophane containing two different recognition sites, or 'stations': a bipyridinium unit and a *trans*-bis(pyridinium)ethylene moiety, **11.62**. This tetracationic cyclophane may be prepared interlocked with bis(*p*-phenylene)[34]crown-10 in the same fashion as the [2]catenane **10.76** (Section 10.7). The ^1H NMR spectrum of the catenane in acetone shows that the smaller bipyridinium unit resides within the electron-rich crown component. Electrochemical reduction of **11.62** to produce a radical trication also occurs on the bipyridinium moiety because of its high π-acidity. The reduction reduces dramatically the electron-acceptor characteristics of the bipyridinium unit, however, and as a result it undergoes circumrotation to the outside of the crown, placing the now better π-accepting *trans*-bis(pyridinium)ethylene unit within the crown ether cavity. Upon reoxidation, the process is reversed (Scheme 11.11).[57]

11.4.5 Molecular Logic

Pischel, U., 'Chemical approaches to molecular logic elements for addition and subtraction', *Angew. Chem., Int. Ed.* 2007, **46**, 4026–4040.

In order to carry out sophisticated computation the molecular computers of tomorrow will need not just basic elements such as switches, memory and connectors but also more sophisticated components, particularly logic gates. A logic gate is an element of a computer that gives a particular output for a