

Molecular electronics

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Molecular electronics has grown as an interdisciplinary area with the object of micro miniaturization of electronics to the molecular level. There are various subfields in this—metal organics, organics, liquid crystals, electroactive polymers, L–B films and biological units. In this paper the present status of molecular electronics is briefly reviewed with the emphasis on the present scenario, molecular switching, typical molecular devices and potentials for future applications.

Molecular electronics is an emerging area of fundamental importance with tremendous technological potential¹. It encompasses many subfields. The basic idea is to use a single molecule or a set of molecules to perform electronic functions. The implementation of this idea has three basic steps: (a) Making an electrical connection to one molecule, (b) ability to firmly attach one molecule to desired supports, and (c) finding a molecule that performs desired functions.

The silicon based technology has certain limitations. Presently a 16 megabit chip works with 0.25 μ spacing. The problems encountered with silicon technology are due to quantum mechanical electron tunnelling between switching elements, photolithographic limit and the necessity for low temperatures.

Scenario of molecular electronics

Table 1 lists the emerging trends in molecular electronics. It also lists the different subareas, the problems currently tackled, and the directions in which the subject may develop in future.

In the metal organics, the porphyrins and phthalocyanines are good candidates for processing materials. The phthalocyanines are the flat organic molecules with metallic ions at their centres. They are good as dye materials. The metallic ions in the phthalocyanine systems are normally copper, iron and nickel. The metallic thread-like structure makes them as quasioone dimensional conductors. Haemoglobin with iron is present in blood protein and chlorophyll with magnesium is a good green pigment.

The quasi one-dimensional and two-dimensional materials have formed a very exciting class of molecular crystals. Many organic conductors fall under this class—the metal chain compounds (Krogman salts) like the

halogenated potassium platinum cyanate, the charge transfer complexes like TTF–TCNQ, the organic superconductors, and the fullerenes. Many molecular crystals have high nonlinear optical activity. The low dimensional organic conductors have been used as molecular switches, and have exhibited organic superconductivity. The low dimensional organic conductors have certain unique features—anisotropy in electrical property, charge density transport, and quantum tunnelling phenomena.

Liquid crystals form an important class of materials in molecular electronics. Cholesteric liquid crystals have been used for thermal imaging. Nematic liquid crystals are used for display. Their use for data storage and data processing is significant. Self-organized arrangement of liquid crystals are important candidates for molecular electronics.

Langmuir–Blodgett films offer an interesting structural system for molecular electronics. Such L–B films can be used as ultrathin dielectrics, nonlinear optical thin films, chemical sensors and as low-dimensional structures.

Perhaps the most important materials for molecular electronics are the biological molecules. Already it has been possible to synthesize biological molecules which mimic certain functions. Biological molecules can be used as chemical and biochemical sensors. It would be possible to develop biological molecules which can by themselves organize into suitable patterns, which can replicate, and which can repair their parts. The processing of biological molecules will turn out to be very interesting. It might be possible to have a molecular lattice network which can grow and reproduce. Parallel processing would be the feature of such biological systems. It might be possible to implant biochips which can perform certain specific functions. The functions which can be performed by such biochips are giving sight to the blind, hearing to the deaf, replacement of damaged spines, memory to human brain, and add the processing speed to the brain. This may eventually create a situation where a keyboard-operated brain could be visualized.

Let us see some specific applications of biological molecules in molecular electronics.

Protein as a potential candidate for molecular electronics

Proteins are independent three-dimensional structural units resulting from a large number of atoms. These

Table 1. Molecular electronics scenario

Biological molecules	Mimicking	Chemical biochemical sensors	Self-organization replication repair	Biological processing
Langmuir-Blodgett films	Ultrathin dielectrics	Nonlinear optical thin films	LB chemical sensors	Organic low dimensional structures
Electroactive polymers	Resists UV - e beam - X-ray - ion beam; Encapsulants dielectrics	Ultralithography	Polydiacetylene and other χ^3 materials electronic circuits Piezo-pyro-electrics semi-conducting polymers	High conductivity polymers Polymer electronics
Liquid crystals	Displays	Data storage Data processing		Self organization
Molecular crystals 1D, 2D conductors	Organic conductors	Nonlinear optics	Molecular switches 3D arrays organic super conductors	Organic HTSC technology
Organic molecules	Photochromics Electrochromics Laser processing			
Metal organics	MOCVD and ceramic precursors	Chemical sensors	Energy storage and converters	Porphyrins, phthalocyanines as processing materials Haemoglobin chlorophyll
Material	Current and near terms technologies	Advanced technologies	Hybrid systems	Molecular electronic materials and phenomena Molecular electronic devices Molecular electronic system
	Current and near term	Midterm	Long term	Further future
→ Time, Difficulty, Uncertainty, Complexity →				

patterns have sticky areas that adhere only to other sharply defined areas carefully built into the molecular chain (Figure 1). If the patterns of the two proteins are complementary, they stick nicely and this is how specific structures like viruses, humans and biochips are formed. It might be possible for the proteins to form structural units which will function as integrated circuits. It might be possible to attach nonprotein molecules to proteins and these might act as electronic devices. L-B techniques may come in handy for this.

Bioimplants

We can think of three types of applications from bionic implants. The first one is the prosthetic limbs. Here we can simulate the muscle action, coordination of muscle to mechanism movement by conventional electronics and also the nerve endings could be tapped by molecular scale circuiting. The second application is concerned

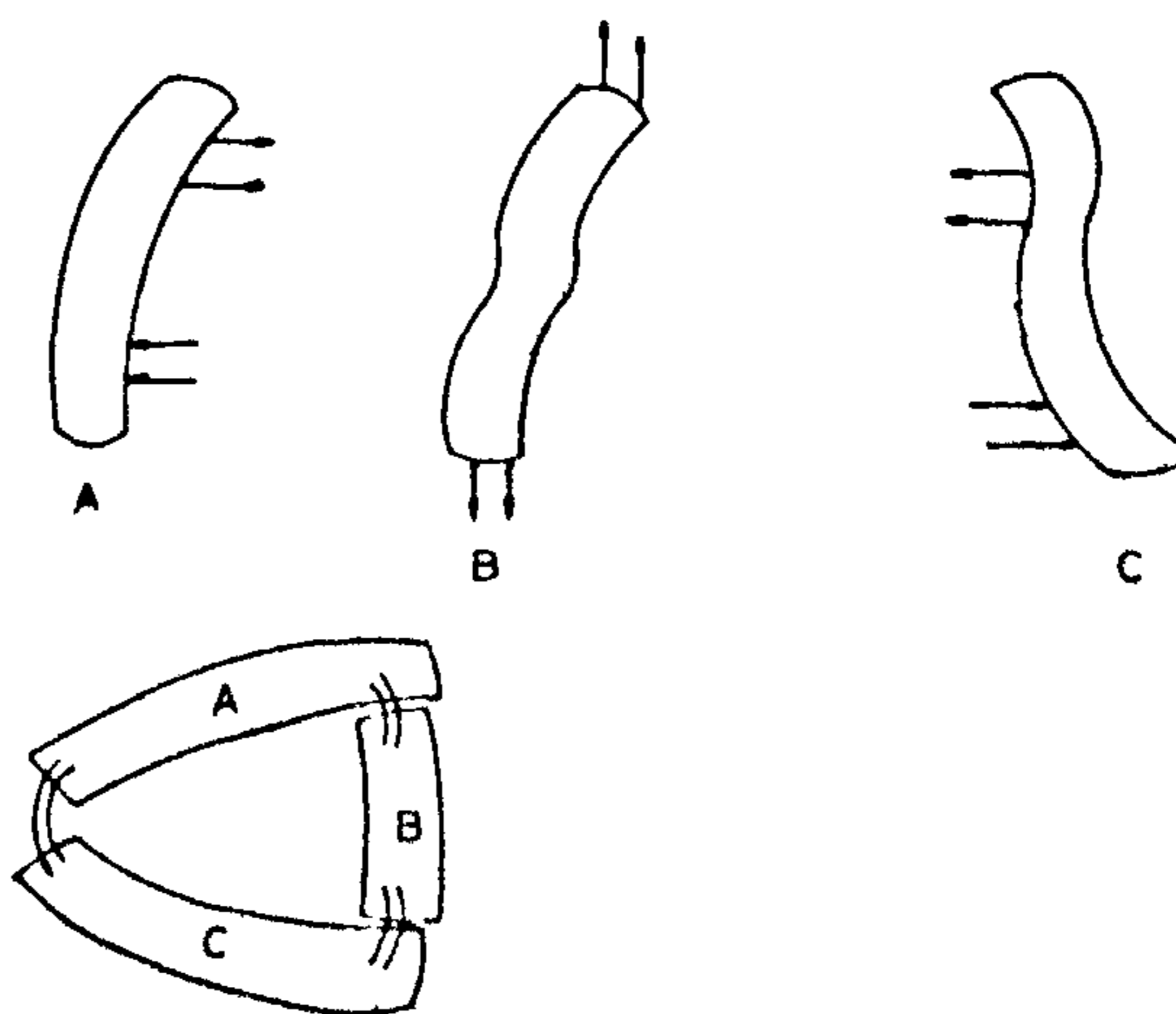


Figure 1.

with the vision for the blind persons. Here an array of ten thousand electrodes covered with protein and plastic with electron beam drilled-holes can be implanted into visual cortex and this can perform the function of an eye. The third application is concerned with the bio-electronic devices. We can have the bacterial cells which can monitor up to twenty parameters like temperature, pH, specific ion concentration, etc. Synthetic enzymes can act as biosensors.

Making connections to a molecule

This is a major problem in bioelectronic devices. The problem can be tackled in three ways. Firstly one can use multicore conducting strands drawn to fine dimensions. Secondly the contacts could be made using scanning tunnelling microscopy. Thirdly, we could avoid making electrical connections and use optical activation for signal input and signal output.

Fabrication of a molecular electronic device

Several alternate methods can be thought of to make a molecular electronic device.

Lithographic and vapour deposition technique

This is somewhat similar to the Molecular Beam Epitaxial method. In order to form silver lines on protein monolayer, one can initially apply polylysine onto glass. This can be covered with PMMA. A suitable pattern can be created on glass using electron beam lithography. The glass is then developed to show a pattern and this can be chemically reduced to metallic silver. By this process, silver lines can be formed on protein.

Chemical synthesis

A modular approach can be used for this. Molecular

size fragments are added to a textured and reactive substrate by a chemical reaction process (Figure 2). For example in perhydracoronena, the structure is shown in Figure 2 a. Here twelve C-H bonds project up and twelve C-H bonds project down. Suppose the five hydrogen bonds which are up are replaced by fluorine (Figure 2 b) and we form the conjugate of 2 b and this is represented in Figure 2 c. If the structures 2 b and 2 c are superimposed, they fit perfectly and form an insulating layer. If 2 b plus 2 c does not fit exactly, then the composite forms an active strand. This can become the basis of a molecular electronic device.

Biotechnology method

It is possible to use the biotechnology method to form a 'biochip'. Here one can use a molecular epitaxial superstructuring. We can start with 100 silicon surface and deposit large molecules of B proteins on its surface (Figure 3 a). This can be repeated to form a pattern in which there are voids present (Figure 3 b). The void regions can then be filled and the starting molecules B removed (Figure 3 c). Hence a pattern develops in which the molecules *b* are spaced at about 200 Å apart. The filling of the void region can be done by electrochemical transport technique, cytochemical staining, sputtering or vapour deposition. The initial mask of protein molecules can be removed by digestion or photolysis, leaving behind a submicroscopic, on which biochip might be constructed.

Signal transport for molecular electronic devices

This is a major problem which has to be tackled carefully. In normal electronic circuits, electrons are the signal transporters. In molecular electronic devices, we can have electrons as the carriers of signals and also we can have solitons, polarons and bipolarons to transport

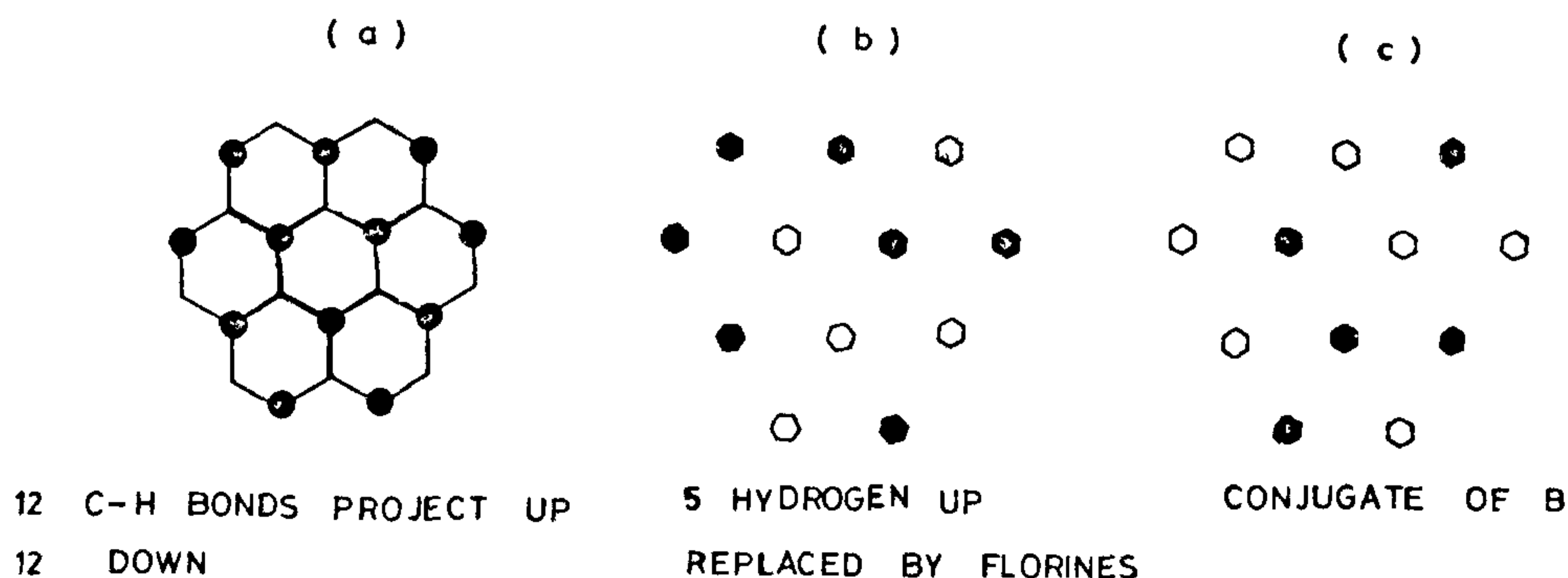


Figure 2. Chemical synthesis of a molecular electronic device.

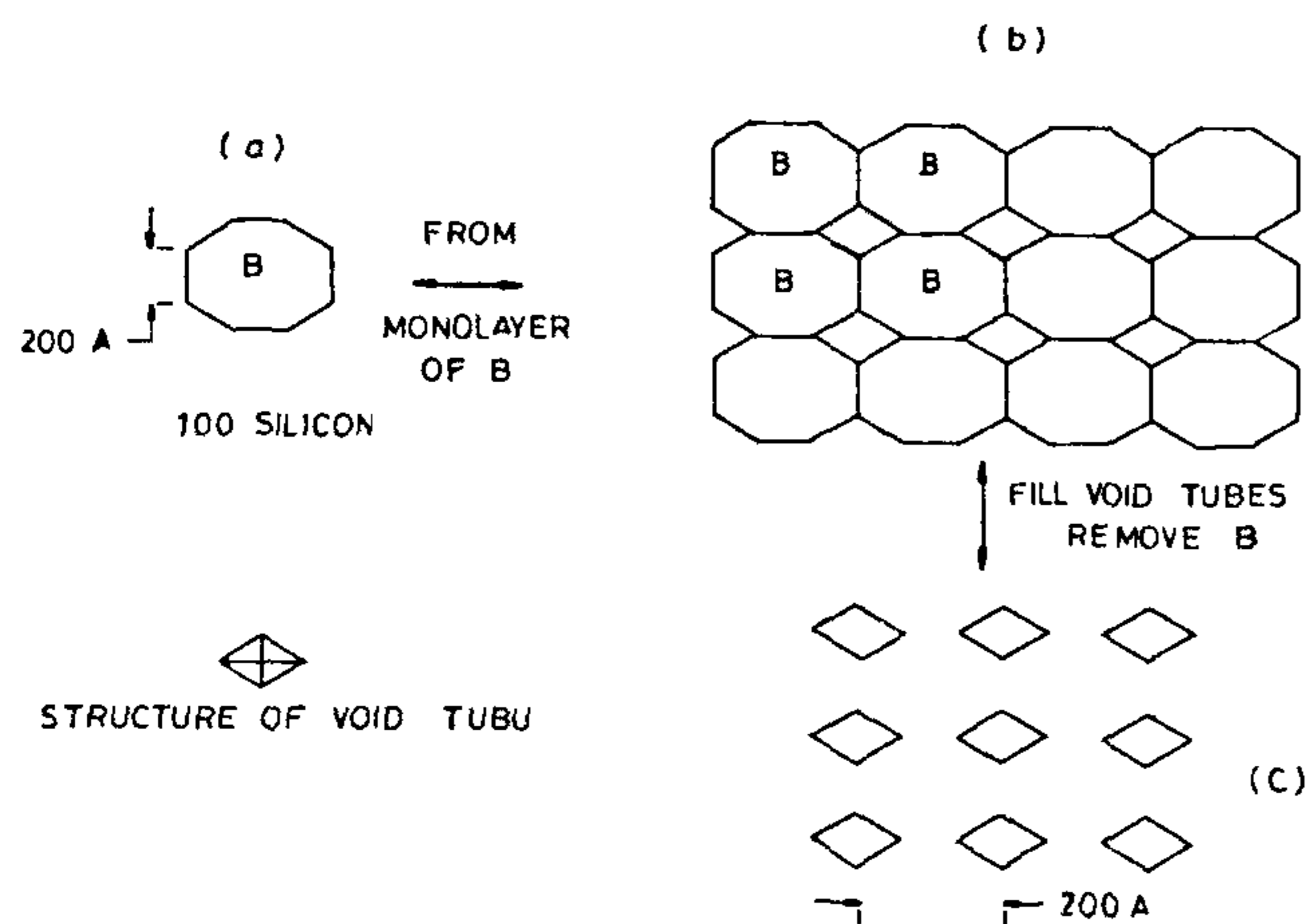


Figure 3. Biotechnology method.

signals. In conducting polymers, solitons become the major signal carriers. Solitons are the solitary nonlinear disturbances (Figure 4). In the polyacetylene chain, a soliton becomes the kink in the charge distribution. We can have the neutral soliton, the positive soliton and the negative soliton. It is possible for the soliton to move forward or backward. Under an electric field, solitons move just like electrons. When the soliton reaches the positive terminal, it gives up an electron to the terminal. It is interesting to study the electrical transport in conducting polymers to understand the role of solitons, polarons and bipolarons.

Electrically conducting polymers

Conducting polymers form a very important class of polymeric materials. The earliest conducting polymer which has been studied extensively has been the polyacetylene. The conductivity of polyacetylene increases with dopant addition by almost twelve orders of magnitude, from almost insulating phase to near metallic phase. We can also have either *n*-type or *p*-type semi-conducting phase with a suitable choice of dopant. In addition to polyacetylene, a number of other polymers have been prepared and studied. Some of these are listed in Table 2. Some specific features of polypyrrole and pyrolytic carbon films will be discussed below.

Polypyrrole has the special feature that bipolarons are the major charge carriers in doped systems. Bipolarons are formed by the combination of two adjacent polarons (Figure 4). The concentration of bipolarons can be varied by varying the dopant concentration. Thus one can form polypyrrole with light doping, medium doping and heavy doping. The bipolarons vary from independent ones to strongly interacting ones. For heavily doped polypyrrole, the interacting bipolaron systems can lead to a tunnelling conduction between the bipolaron states. When this

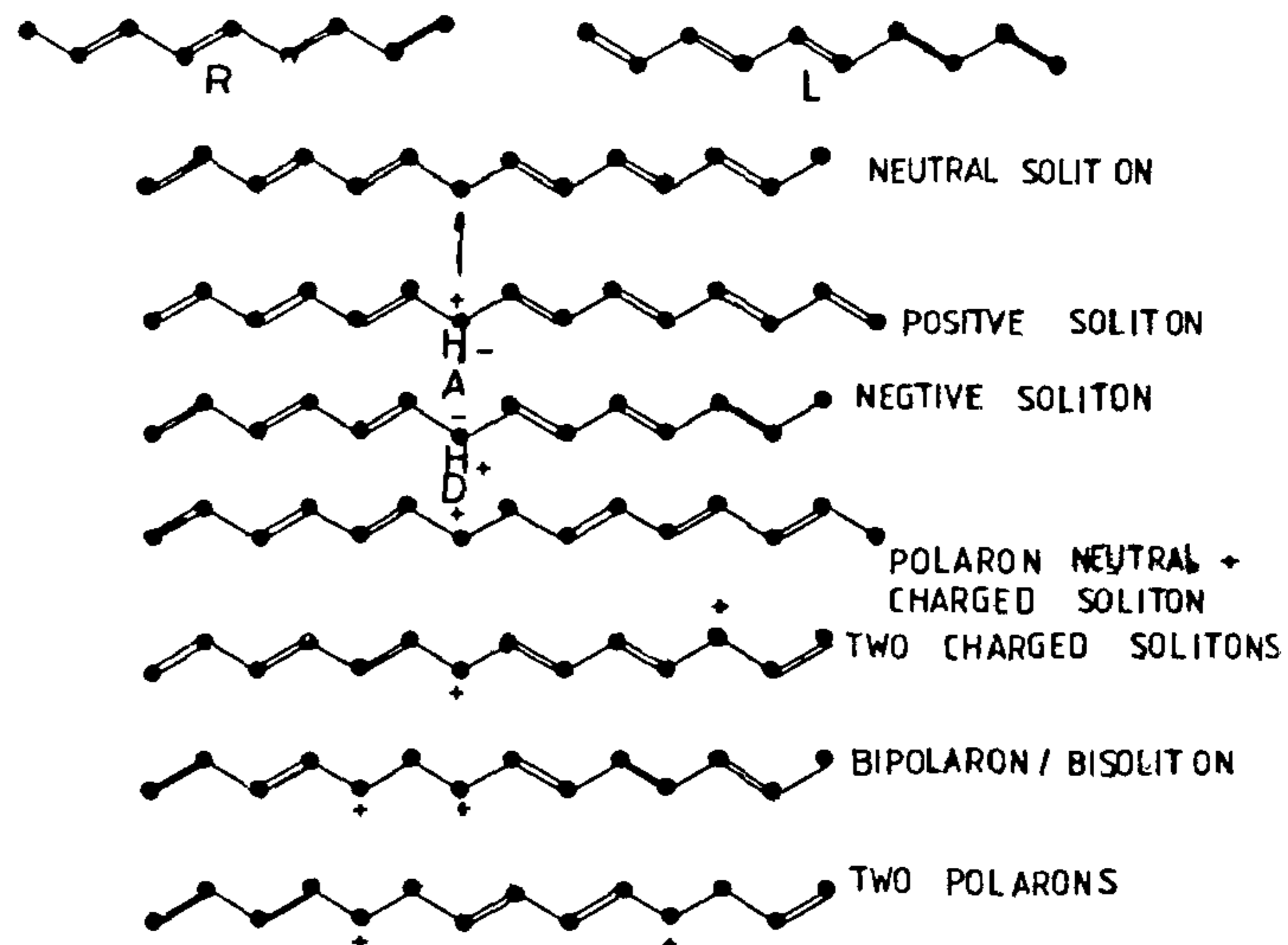


Figure 4. Solitons, polarons, bipolarons.

Table 2. Electrically conducting polymers

Polymer	Dopant	σ (S cm ⁻¹ at 25°C)
Polyacetylene	I, AsF ₅ , ClO ₄	500
Polysulphur nitride		
Polyparaphenylene	AsF ₅	500
Polythienylene	ClO ₄	1000
Poly- <i>p</i> -phenylene sulphide	AsF ₅	1
Polythiophene	AsF ₅	10
Polykapton	AsF ₅	100
Polypyrrole	ClO ₄	40
Polyvinylchloride	SO ₃	10 ⁻³
Pyrolytic carbon		100-1000

happens, a small peak in conductivity can be seen. While this was predicted theoretically by Bryksin² in 1986, this tunnelling conductivity was seen experimentally³. In suitably controlled ac conductivity experiments, one can also see the dissociation of bipolarons into polarons⁴. The conduction due to bipolarons can be reduced by the application of a magnetic field on the sample.

The pyrolytic form of carbon has some very striking structural and transport properties. The high conductivity of graphite is due to the layered structure and the *sp*² bonding. The insulating nature of the diamond is due to its tetrahedral structure and *sp*³ bonding. Pyrolytic carbon can be graphitic, can be diamond like and can also be amorphous. Pyrolytic forms of carbon obtained from derivatives of certain aromatic compounds have some very interesting transport behaviour. In particular pyrolytic carbon films obtained from perylene tetracarboxylic dianhydride and maleic anhydride show conductivity in the range of 100 to 1000 S cm⁻¹, nearly temperature independent conductivity in the temperature

range 4 K to 1000 K and an increased conductivity at higher pressures⁵⁻⁷.

Molecular switching

Electrical switching from a nearly insulating state to a semiconducting or metallic state has been observed in a number of systems.

Donor-acceptor complexes. Here the donor molecule can be such as tetrathiofulvalene and the acceptor can be like tetracyanoquinodimethane. The bridge linking the donor and acceptor molecules can be a covalent sigma bridge (Figure 5). If the circuit is complete, current flows from M_2 to M_1 and no current flows from M_1 to M_2 (ref. 8). The reason for this is that the energy $D^- - \sigma - A^+ \gg D^+ - \sigma - A^- \gg D - \sigma - A$.

Hemiquinone switch. A hemiquinone molecule can exist in two different forms (Figure 6), which are really equivalent. By the application of a voltage, the molecule switches from one form to the other. By embedding the molecule in a suitable environment, the switching can be controlled⁹.

Metal-acceptor composite can also show an insulator to metal transition. A good example of this is the copper-TCNQ system¹⁰. An application of a voltage across the copper-TCNQ can bring about such a transition (Figure 7). The transition is sharp and the switching time is about 5 ns. The transition probably occurs because of the formation of a structure composed of neutral copper, TCNQ and the radical ions of the copper-TCNQ.

A metal-acceptor composite can also be triggered by an optical process (Figure 8). An insulator-metal transition can be induced in copper-TCNQ system by a

photoinduced process.

Molecular switching can also be brought about by an optical process as in copper phthalocyanine. A circularly polarized yellow light can alter the conductivity substantially.

Push-pull switch. An organic chromophore which can be olefin derivative is basically a light sensitive molecule. This can be embedded in a polyacetylene chain. The olefin can be activated by light and an electron is transferred from one nitrogen atom to another, changing the charges and double bonds within the molecule (Figure 9). A soliton which moves along the polyacetylene chain will eliminate the carbon to carbon double bond in the olefin. This makes it impossible to photoactivate the olefin. In this way, a soliton can be

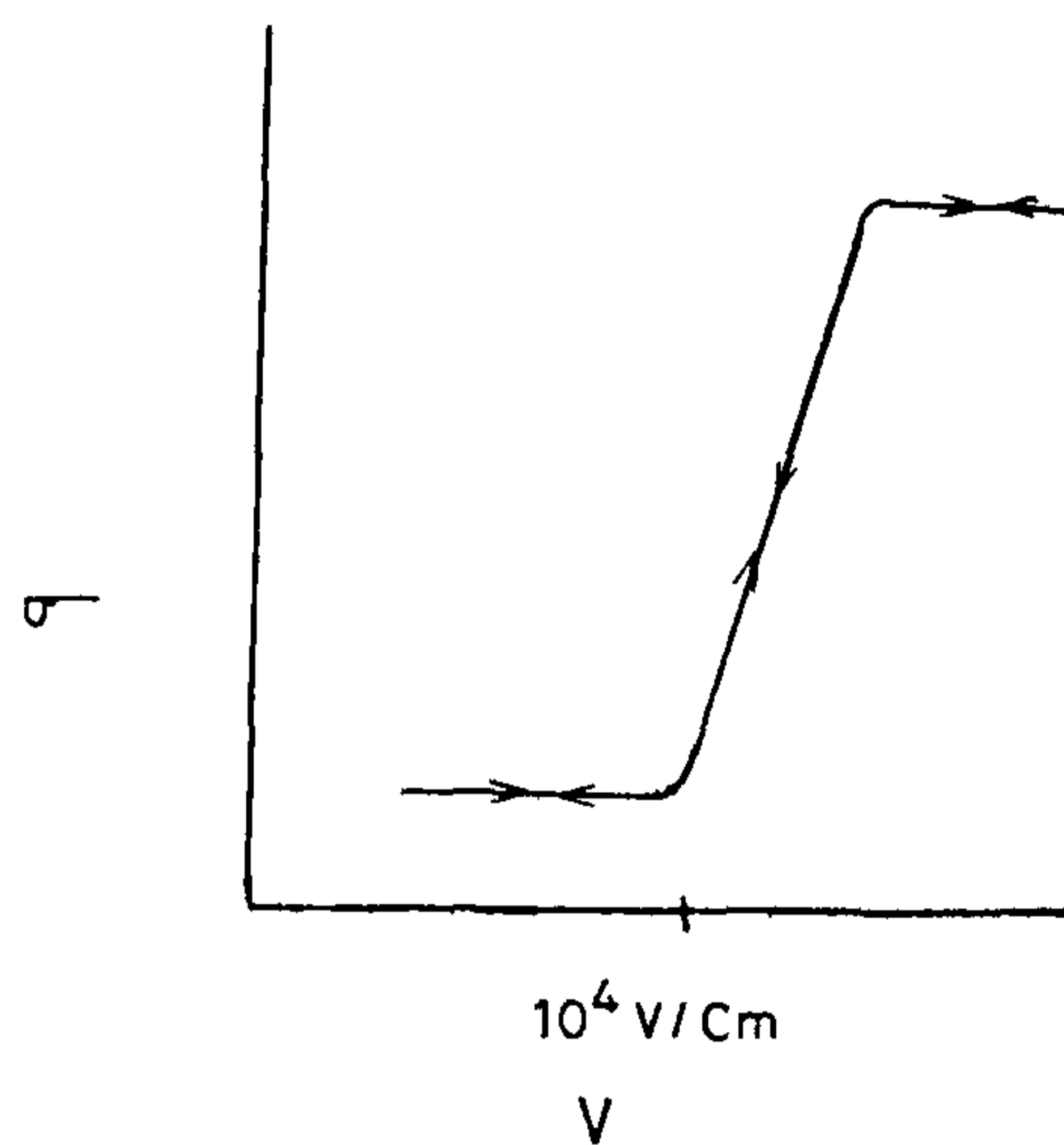


Figure 7.

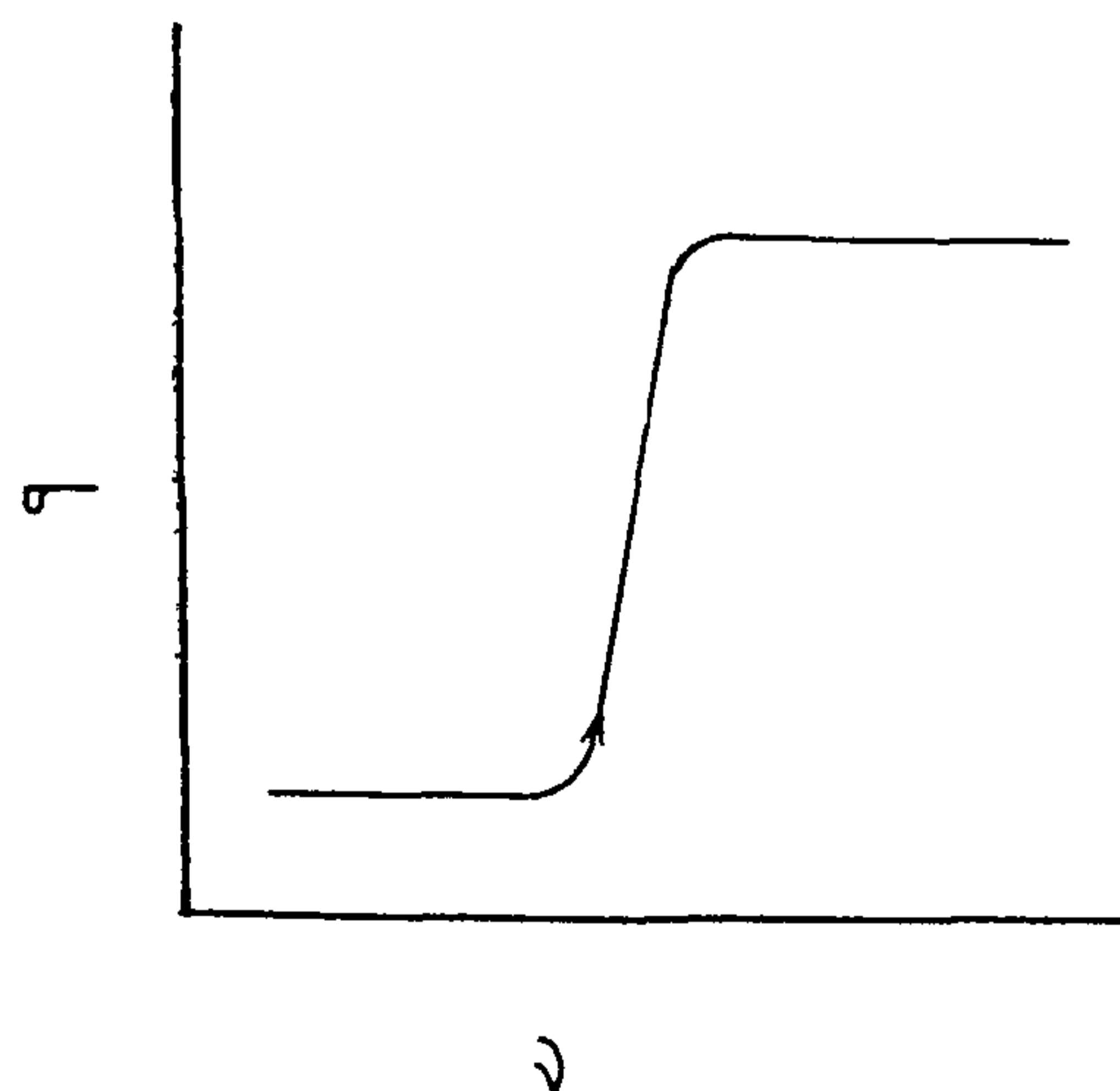


Figure 8. Photoinduced switch

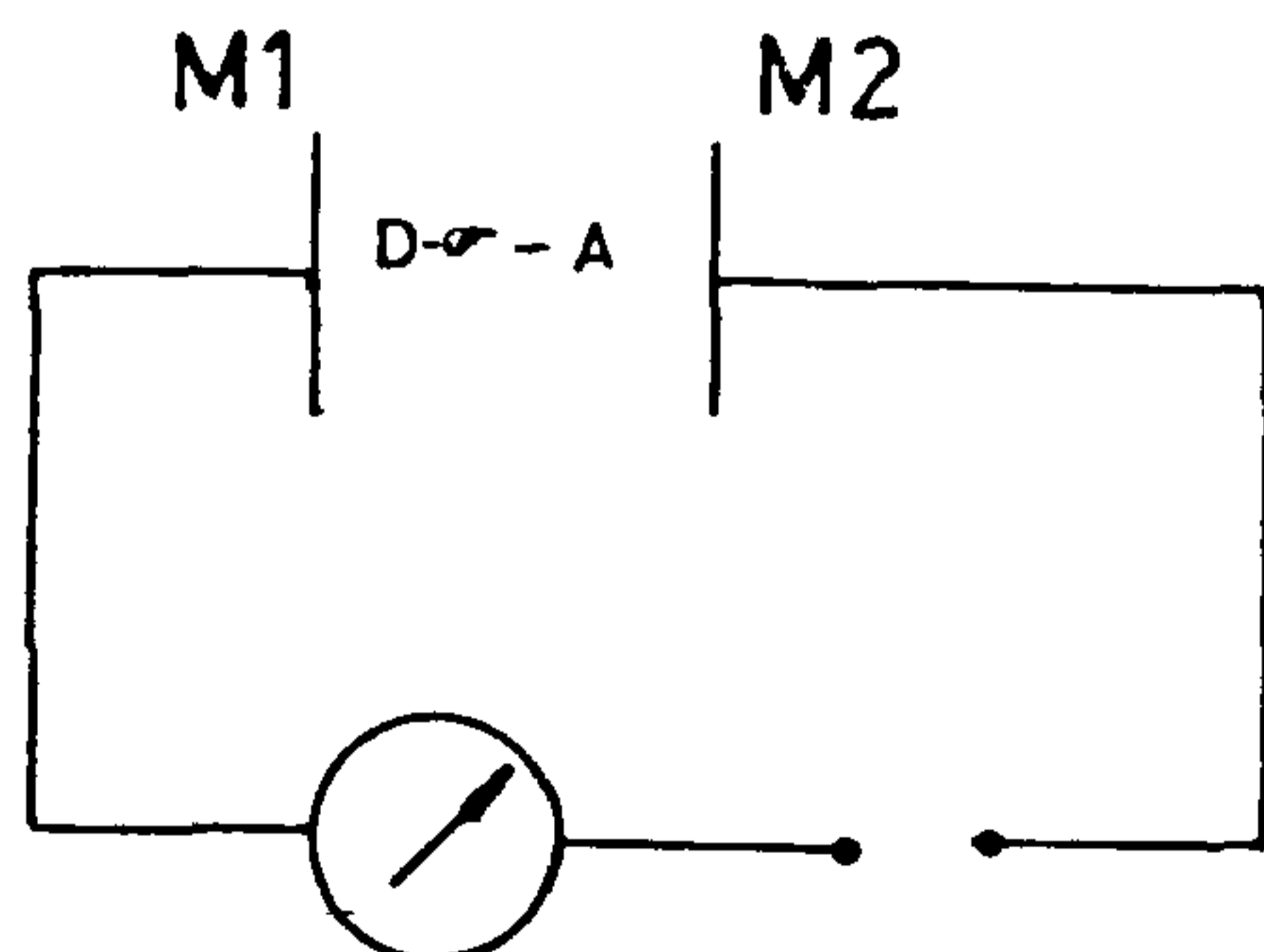


Figure 5. Donor-acceptor molecular rectifier

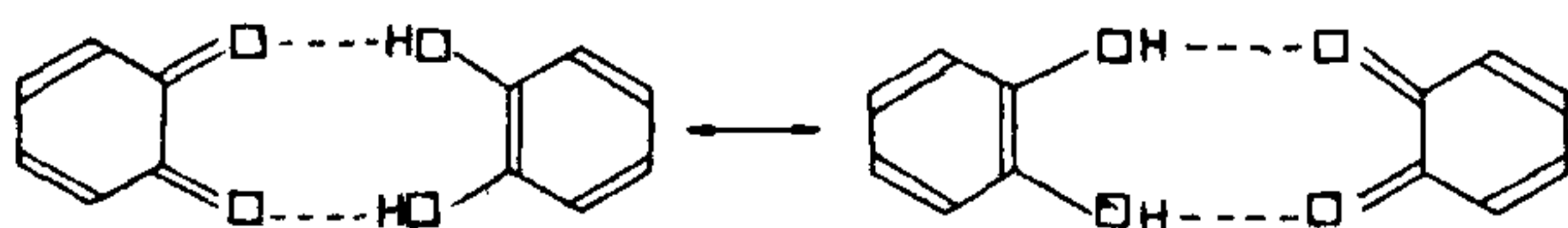


Figure 6. Hemiquinone switch

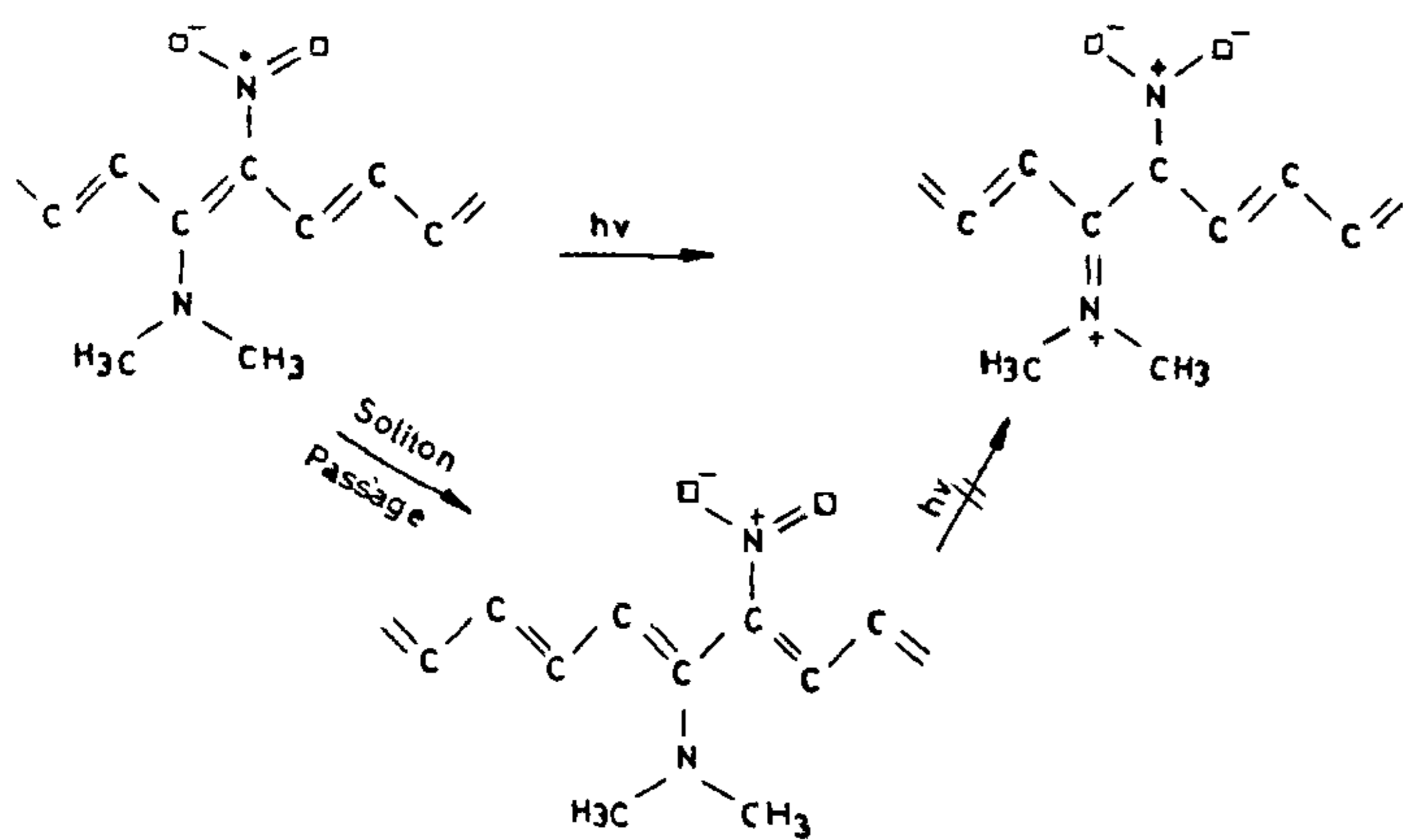


Figure 9. Push-pull switch.

used to switch off the capacity of the molecule to act as a photoactivated switch.

Three chain junction soliton switch. Let us consider three transpolyacetylene chains terminating at a single carbon atom. A soliton which changes single bonds into double bonds and vice versa moves along the A chain towards the junction. Then it can move either to B or C chain (Figure 10). However a soliton moving along the C chain can transfer only to the A chain. It cannot go to the B chain because of the mismatch of the bonds at the junction. When a soliton moves from A to B, the configuration shifts as shown in the figure. In this configuration (Figure 10 b), a soliton can move from A to B, from B to A, C or from C to B, (and not to A). This gives the third possible configuration (Figure 10 c). This three chain polyacetylene molecule can be used as a switching device. When it is used in a network of three chain switches, it could possibly be used in parallel processing (Figure 11).

NOR gate. A molecular electronic device can also be used as a NOR gate. Here a true result will occur only if all inputs are false. And a false input occurs if any input condition is true. A molecular electronic circuit to function as a NOR gate can be easily visualized (Figure 12). This is based on gallium phthalocyanine ring molecules in the chain with nickel polysulphur nitride molecules attached to the nickel phthalocyanine molecules. The voltage input is at the polyacetylene molecule. An electron moving down the (SN) cuts off the main flow of the electrons down the stack. The flow of electrons is by periodic tunnelling. Hence the current now flows out through the output lead and the gate is switched off.

Electrical switching with memory. This has been studied extensively in many donor-acceptor complexes¹¹. The material can be made to undergo a transformation from

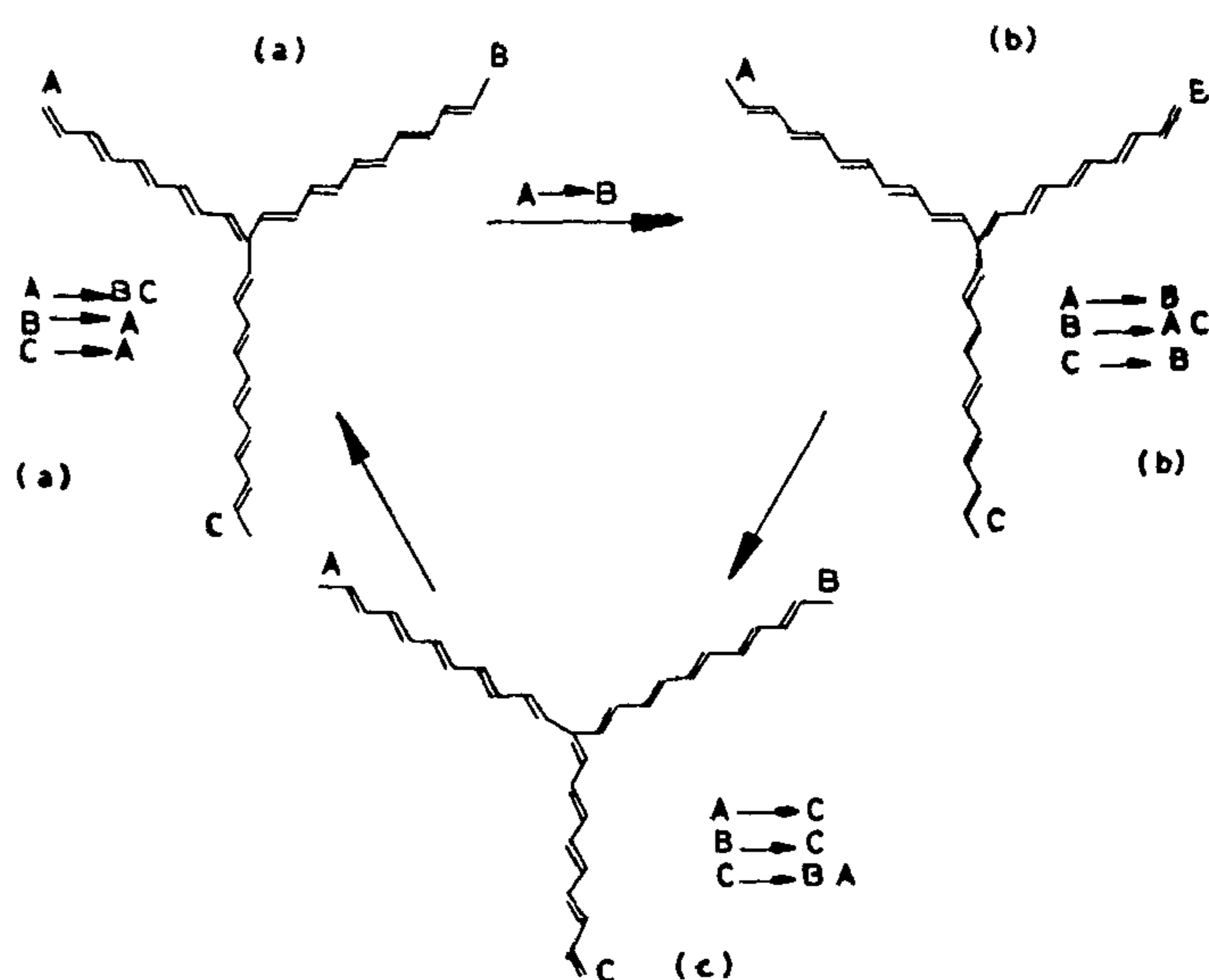


Figure 10. Three chain function soliton switch.

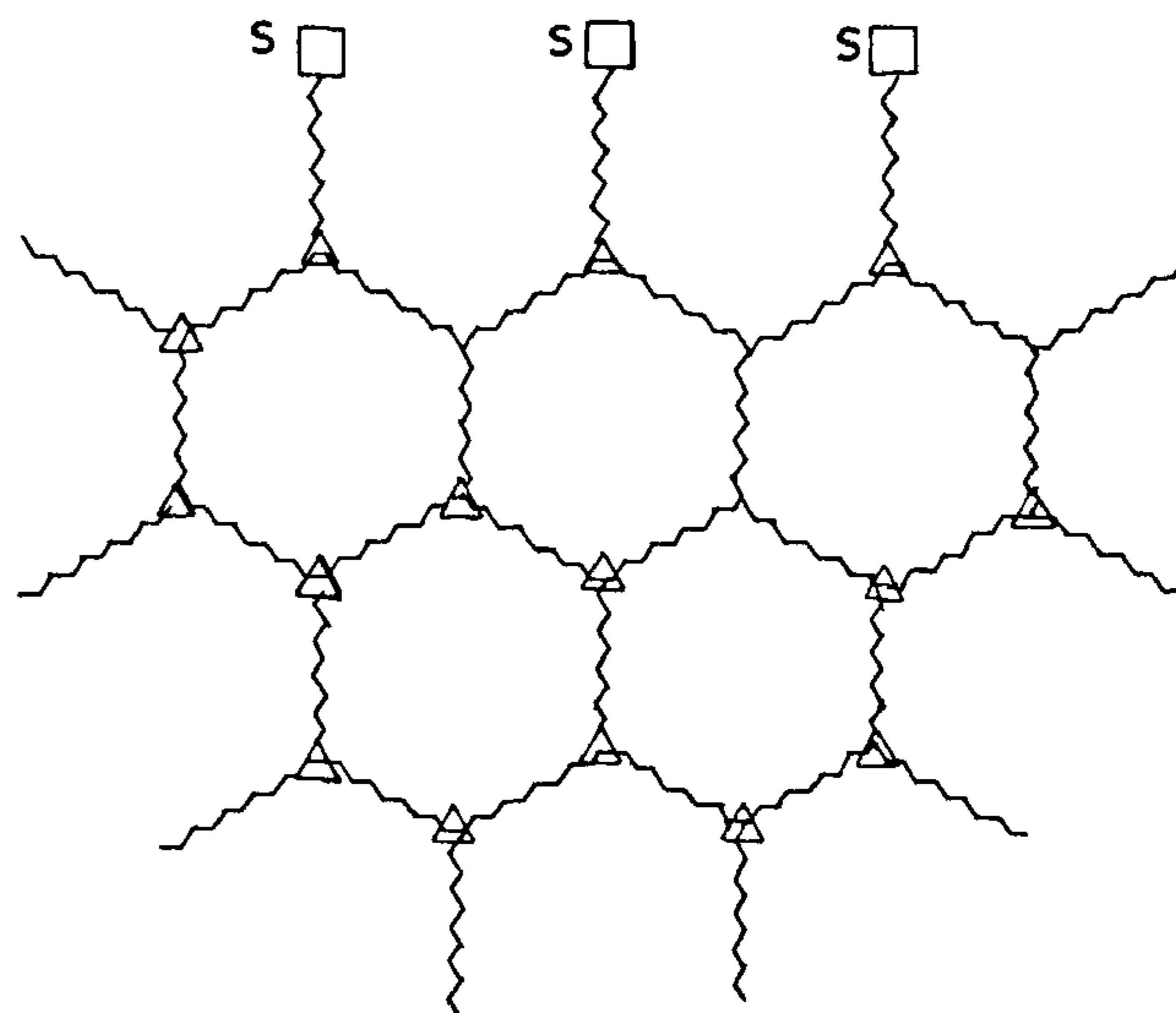


Figure 11. Parallel processing of soliton switches.

a resistive state to a conducting state. The transition can be reversible or irreversible. Many memory effects are associated with this. Such electrical switching has been studied in detail in tetramethyl benzidine-TCNQ, tetramethylphenylene-TCNQ, CS-TCNQ, benzidine-DDQ, methyltriphenylarsonium-TCNQ, and tolidine-iodine. A typical electrical switching behaviour is shown in Figure 13, for tolidine-iodine. These are quasi one dimensional crystals with anisotropy in electrical conductivity ($\sim 10^3$). Along the high conductivity axis, the transport behaviour is studied. In order to increase the conductivity, the transport is studied at high pressures. The I-V characteristics show an initial ohmic behaviour, and then a pronounced nonohmic behaviour. The nonohmic conduction in quasi one-dimensional conductors is normally due to several processes, charge density wave propagation, zener tunnelling, etc. At a suitable driving field, the crystal of *o*-tolidine-iodine almost tends to an in-

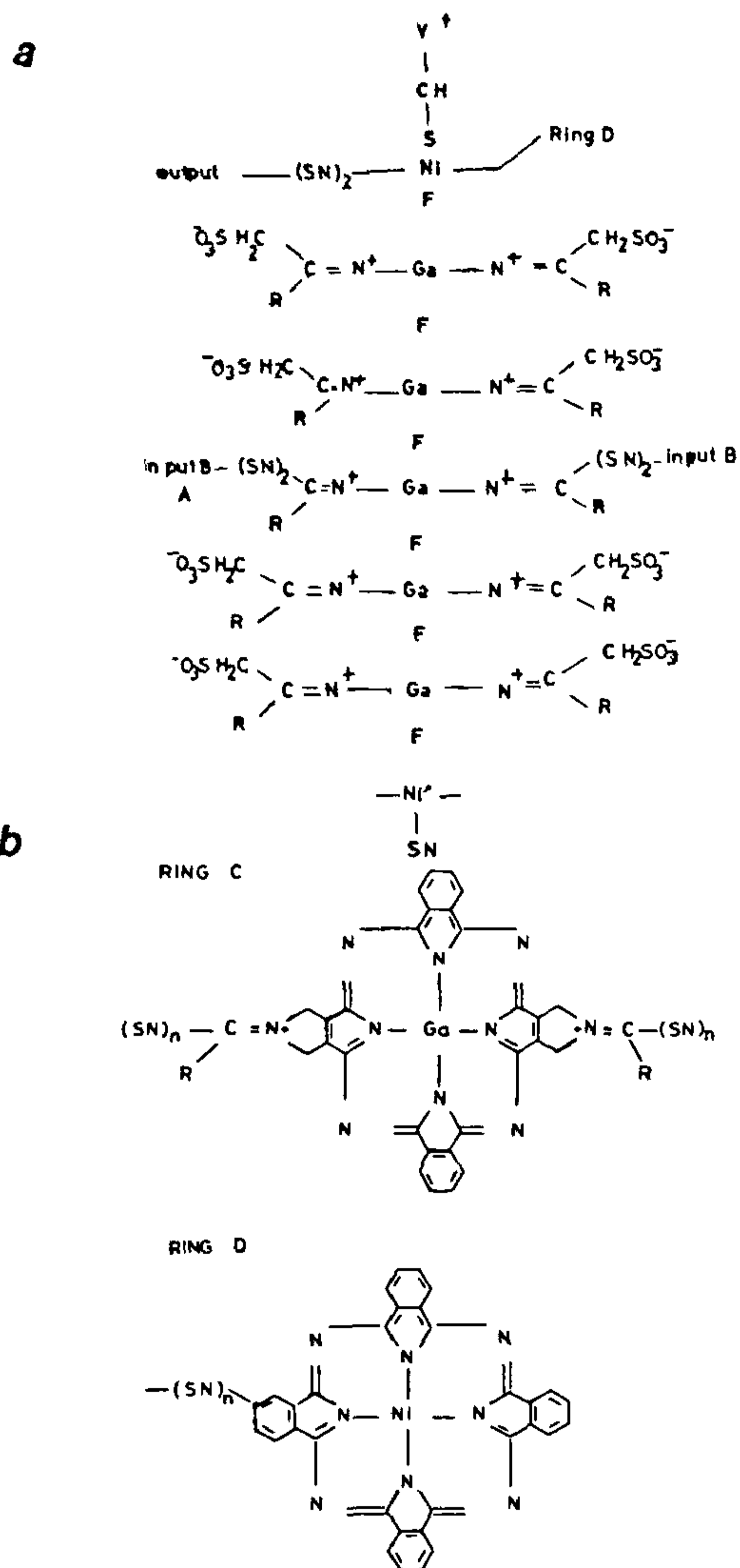


Figure 12.

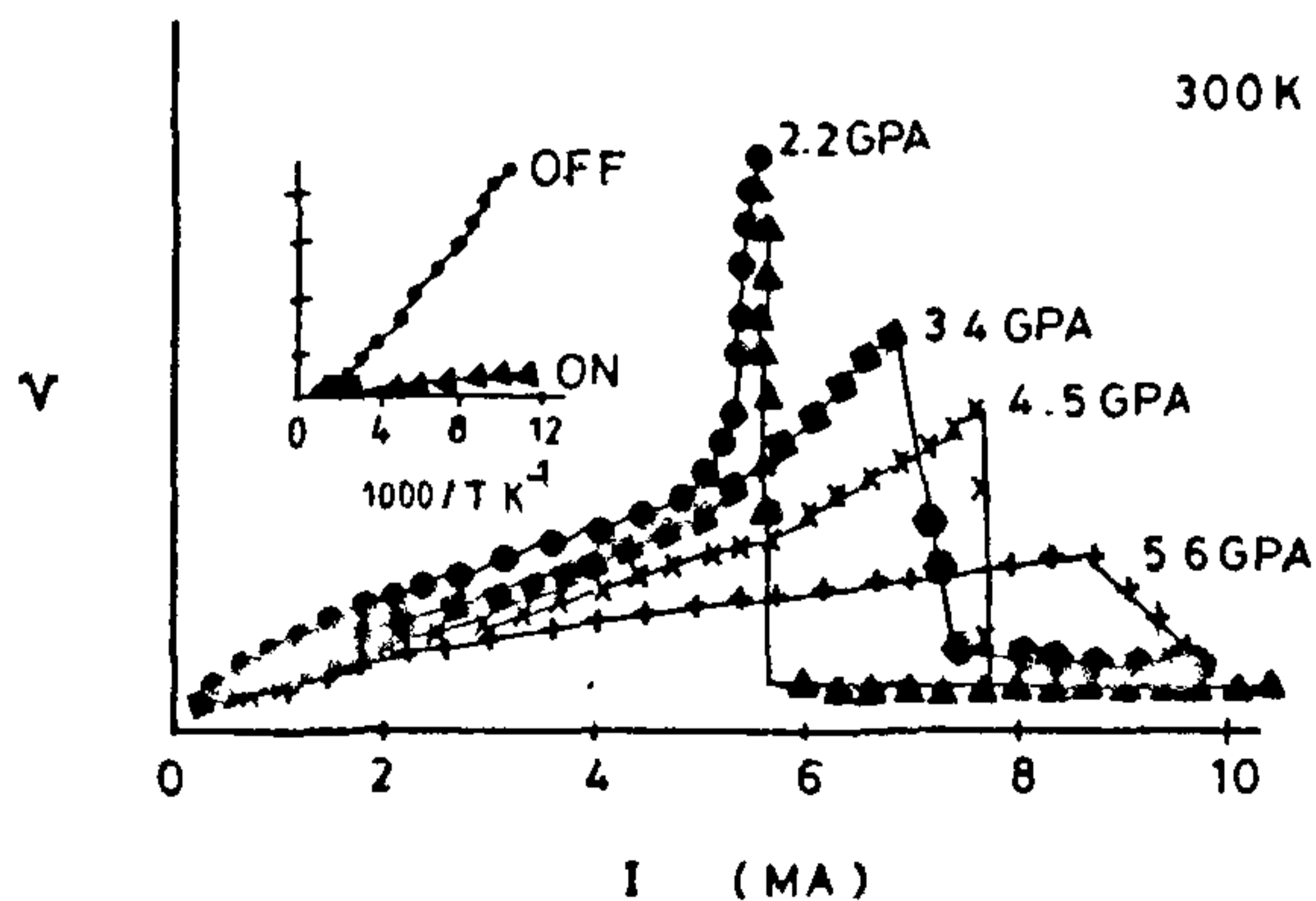


Figure 13.

ulating state and immediately thereafter, it switches into a high conducting state. Earlier to switching, the material is semiconducting with an activation energy of 0.04 eV. We call this the OFF state. After switching, the material is nearly metallic with an activation energy of 0.003 eV. On removal of the applied field, the ON state is retained. Application of an *ac* pulse of suitable frequency switches the material back to the OFF state. The switching field is approximately 10^3 V/cm. The electrical switching with associated memory effects conforms to the model of the depinning of charge density waves proposed by Bardeen¹². This can become an effective molecular electronic switch.

Biological switch with memory. An optically activated voltaic biochip device has been visualized by many workers. Consider the situation shown in Figure 14. K_2 and K_1 are enzymes, for example a kinase. A stimulus activates K_2 which in turn can switch on K_1 . Then even if K_2 stops, K_2 will be in switched state. K_1 therefore influences neurons via K_1^*P . Long term information can be stored by this switch even though molecules switch over rapidly and completely.

Typical molecular electronic devices

Schottky diode. Polyaniline doped with polyacrylic acid shows typical behaviour of a Schottky diode (Figure 15).

Molecular microlaser. As mentioned earlier, an optically driven switch can be used for communication. We can combine this switch with an excitable system, which has an optically pumped metastable state. It is possible to have stimulated emission in this process leading on to a molecular microlaser. Consider the operation schematically shown in Figure 16. *a* to *b* denotes a process of photoactivation of a chromophore to excited Zwitterionic state. *c* to *d* signifies excitation of chromophores by two solitons. Then there is an internal rearrangement of bonds as shown in *d* to *b*. Then the process *b* to *a* illustrates the return of the excited chromophore to the ground state by the emission of a photon. Thus the

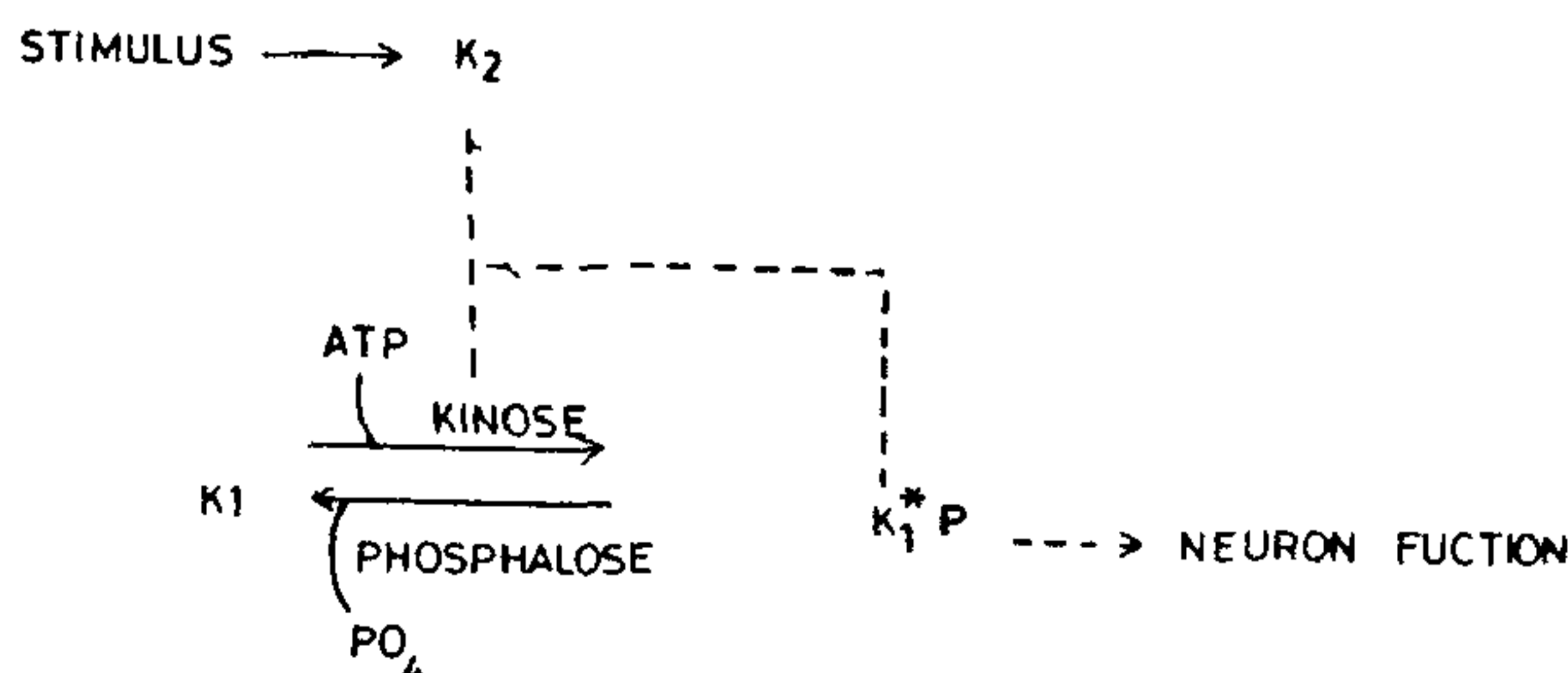


Figure 14.

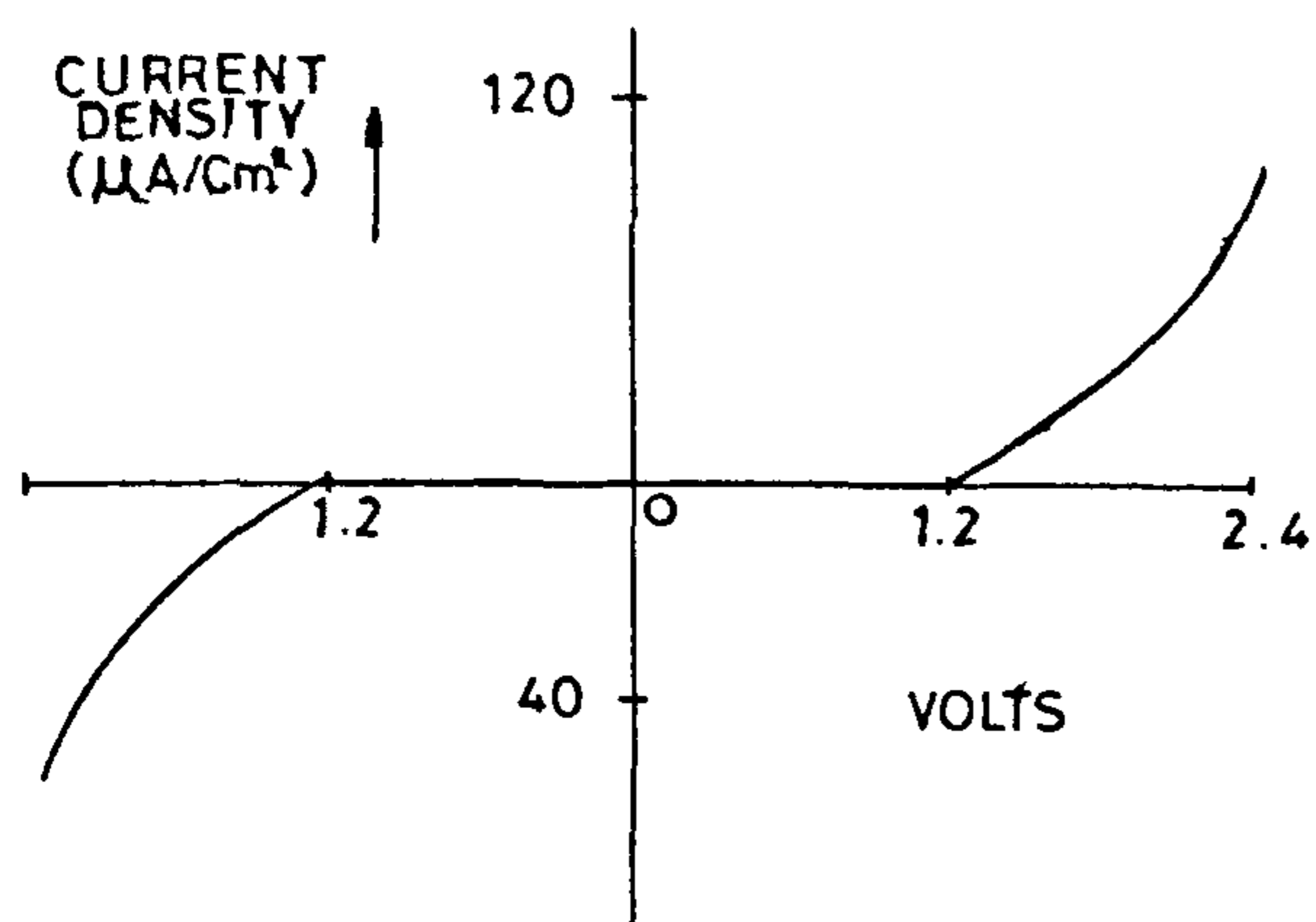


Figure 15.

chromophores are excited by two charged solitons and the release of the photon is triggered by a radical soliton. The laser action is by a photon tunnelling mode. This becomes the building block of a molecular laser (Figure 17). The chromophore shown in Figure 17 is different from the one shown in Figure 16. This system can behave like a highly directional microlaser.

Signal amplification at molecular level. Here there are two possibilities. Firstly we may have electron tunnel switches with periodic arrays. Secondly we can have soliton amplification. This is the inverse of molecular microlaser. A chromophore embedded in the trans-polyacetylene chain (Figure 18 a) is photoactivated to that in Figure 18 b. If a soliton propagates, a portion of the conjugated chain is reactivated as in Figure 18 c. This emits a positive and negative soliton propagating left and right, while the chromophore returns to the ground state. (Compare Figures 18 a and 18 d.) Thus the soliton propagating from left to right gives rise to two or more solitons as shown in Figure 18 d. The

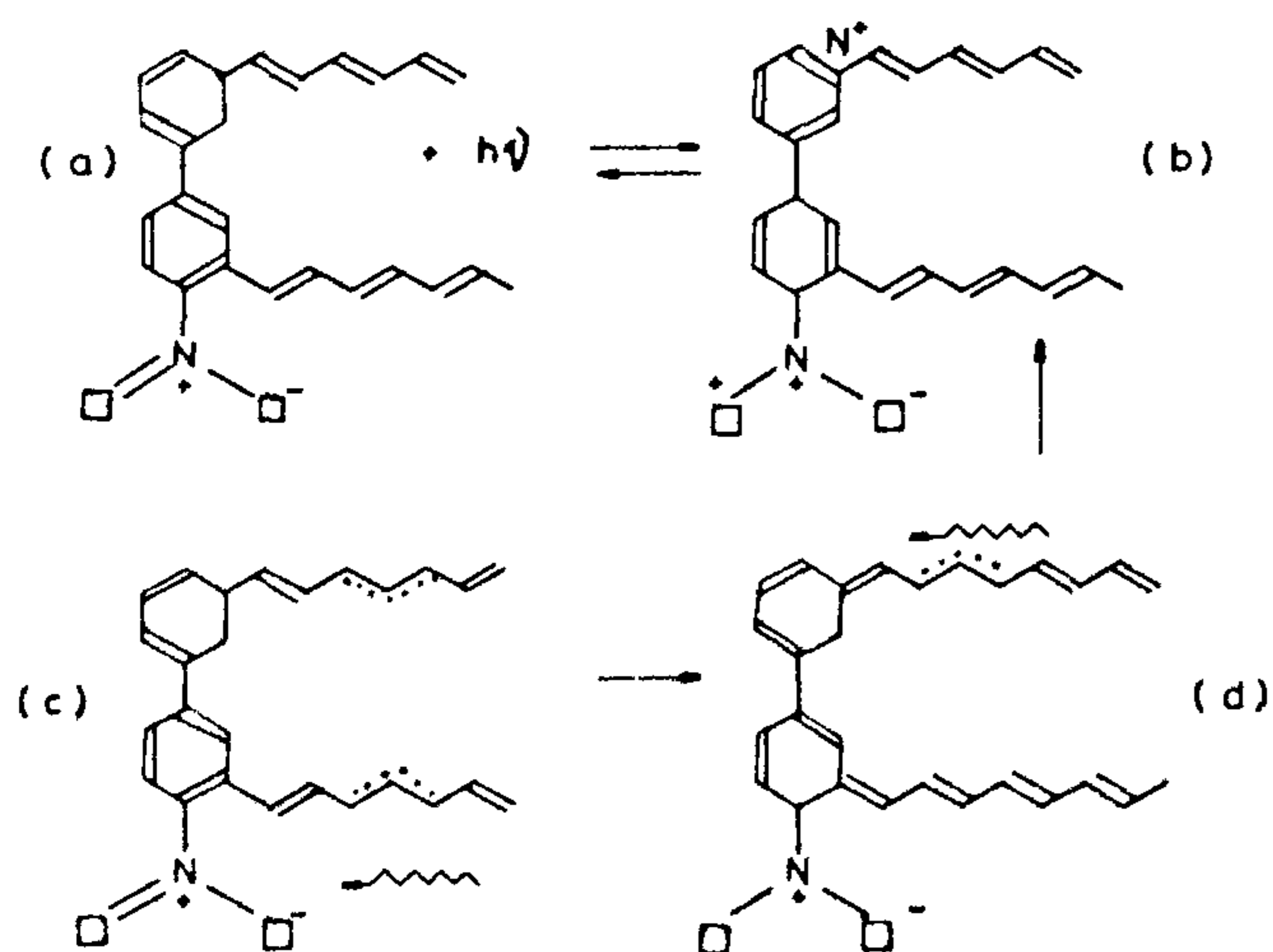


Figure 16. Molecular microlaser.

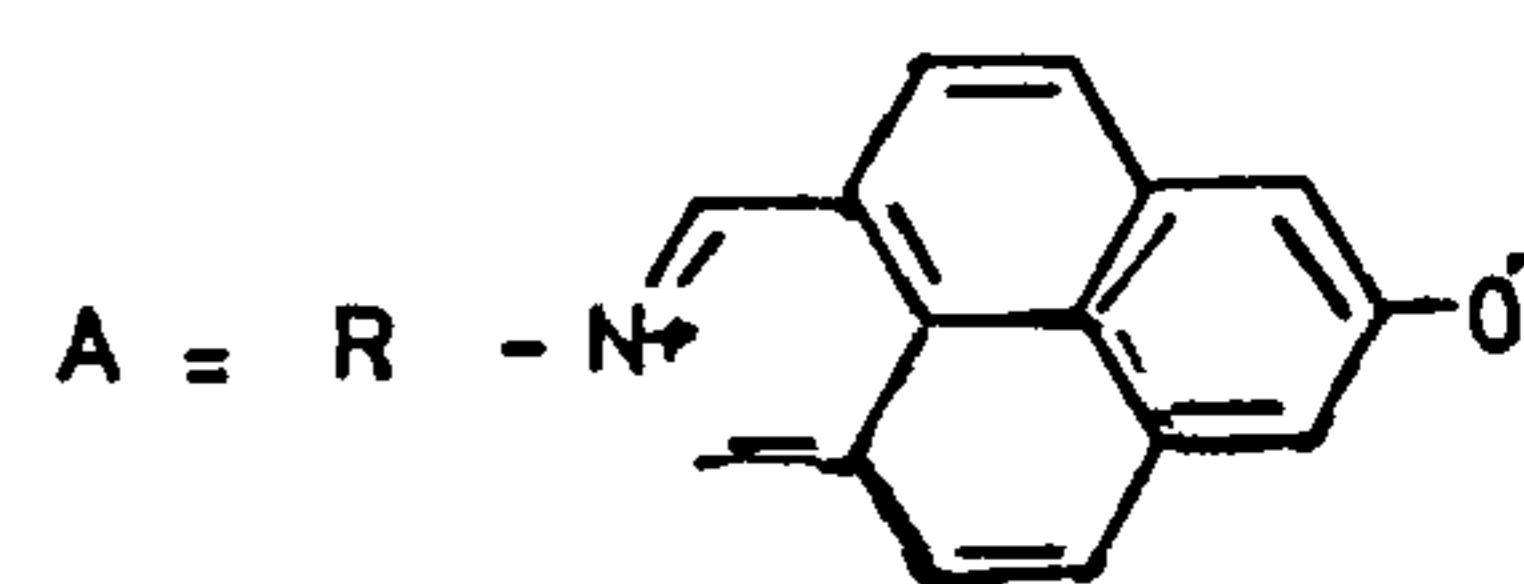
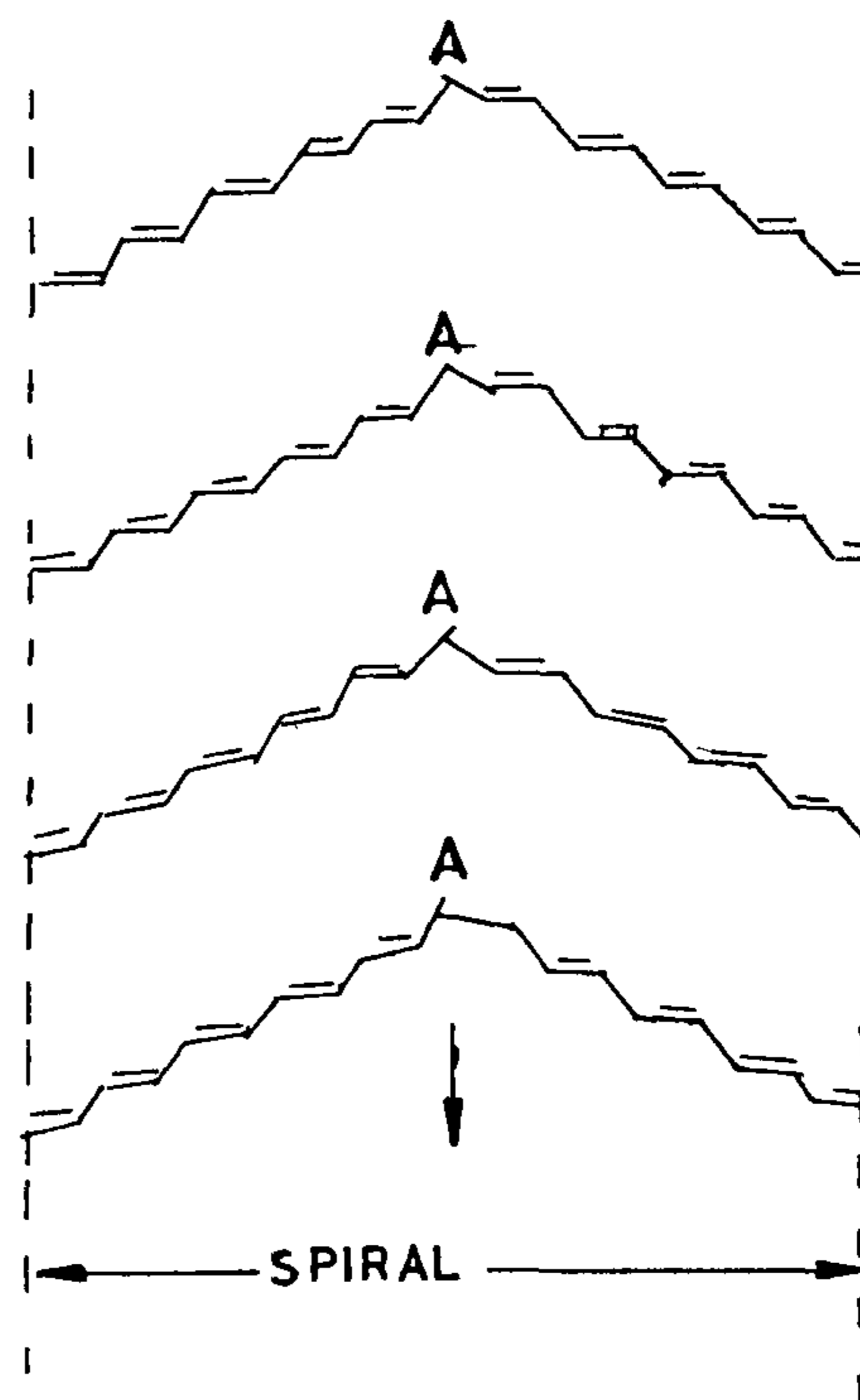


Figure 17.

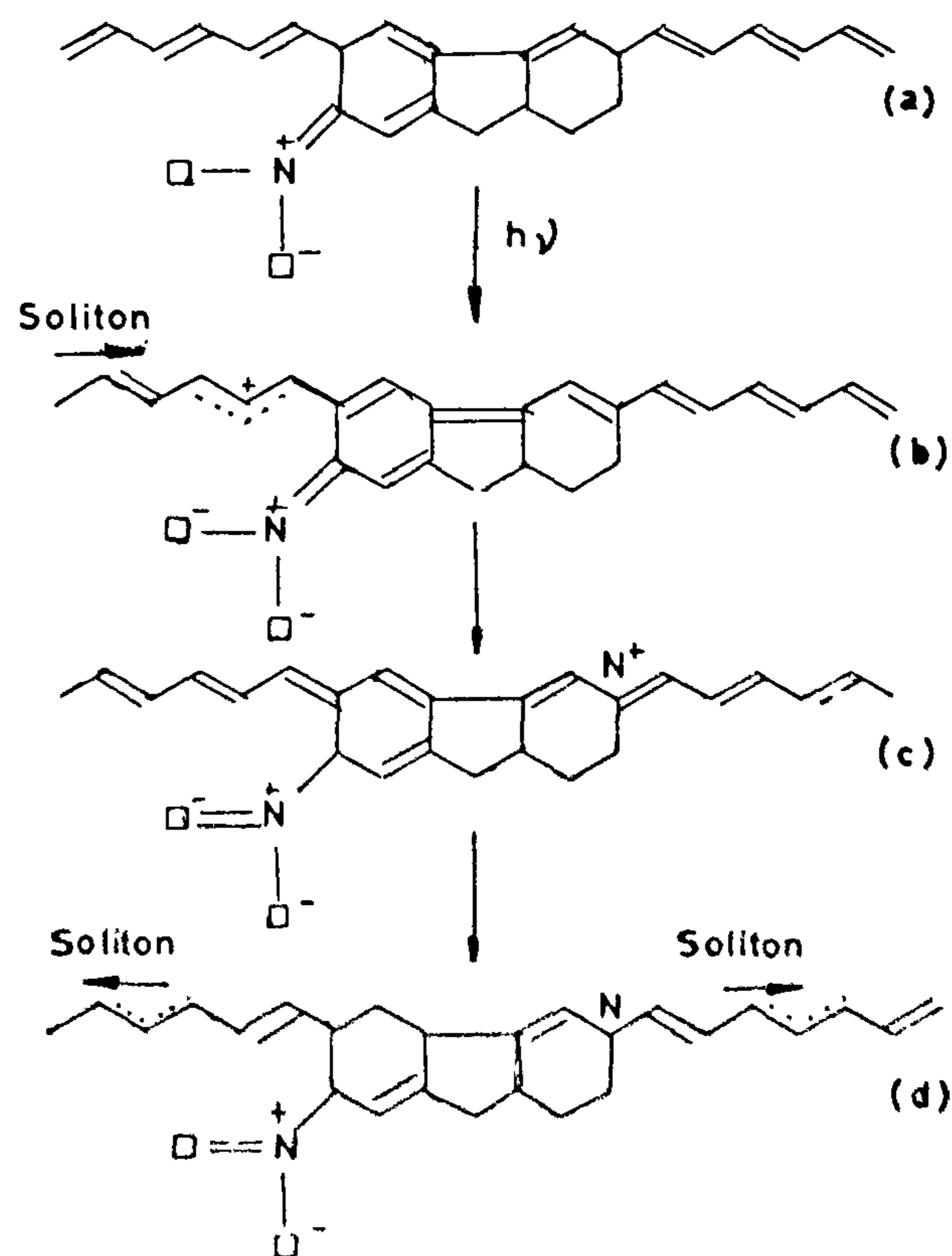


Figure 18. Signal amplification

energy for this amplification is the photon. Further amplification can be achieved by an array of photochromes embedded in the polyacetylene chain. This is a schematic process of soliton amplification.

Technological applications of molecular electronics

The following is a partial listing of some of the applications of molecular electronics.

1. Analogue and digital computers.
2. Interfacing with biosensors
 - artificial intelligence
 - pattern recognition
 - robotics.
3. Quantum mechanical electron tunnelling.
4. Molecular state elements.
5. Molecular switches
 - organometallic
 - molecular/intramolecular rearrangement
 - donor/acceptor complexes.
6. Molecular switching and proton engineering.

Possibility

The subject of molecular electronics is not just an extension of electronics. It is in fact, the future of electronics. When electronic devices can be conceptualized at molecular levels and when such chips can be interfaced with biological items, it will be almost like

keying on to the functions of the brain. The bioprocessor can not only perform, but it can also regenerate itself. The biochip implants can take over the functioning of the nervous systems. When these things happen, they may be the limits of technology.

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Semiconductor physics—Where do we go?

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The current trend in semiconductor physics and devices are reviewed. The Indian scenario and its limitations are pointed out.

Semiconductor materials form the heart of electronics. Semiconductor devices perform the functions of rectification, detection, mixing, amplification, blocking and switching. These also act as sensors for converting physical parameters like temperature, pressure, light into electrical signals and innumerable others. The advancements in semiconductor technology are responsible for the fast growth of electronics industry with improved

reliability, efficiency and convenience of electronics systems used in communications, computers, defence, entertainment, medical, etc.

Current trends in research in the area of semiconductor physics involve tailoring of properties by combining different materials. Such heterostructures allow bandgap engineering resulting in devices with increasing frequency for microwave devices, increasing power handling for industrial applications and improved line shapes for lasers, in addition to improved reliability and performance. This has required multidisciplinary research in materials, basic physics, device physics, epitaxial technology, process instrumentation, characterization techni-