

---

# Molecules to Materials

## 2. Liquid Crystals and Molecular Conductors

---

*T P Radhakrishnan*

T P Radhakrishnan is in the School of Chemistry, Central University of Hyderabad, Hyderabad, Hyderabad 500 046.

**Design and fabrication of molecular materials combines the versatility of synthetic chemistry and the fundamental insights into materials gained through condensed matter physics. This article presents several examples to illustrate the power of a molecular level approach to material properties. An overview of liquid crystals is presented followed by a brief account of molecular design for liquid crystal displays. The growth of organic semiconductors and metals, conducting polymers and organic superconductors is discussed next. Finally the basic aspects of the design of molecular conductors are analysed.**

### Introduction

<sup>1</sup> Previous article of this series was on the design and fabrication of functional molecular solids (April 1998).

We have outlined in Part 1<sup>1</sup> of this series of articles, the emergence of molecular solids as a fascinating class of materials. The variety of subtle solid state interactions which characterise these materials was discussed. It was also noted that the design and fabrication of molecular functional solids could be achieved through the clever manipulation of these forces. In the present article and the next, we unfold several of the interesting physical properties that may be realised in appropriately designed molecular materials. The logical extension of these investigations to the fabrication of molecular devices will be discussed in the last part of the series.

This article presents an overview of liquid crystals which may be considered as the earliest examples of molecular materials. The discovery of metallic conduction and superconduction in molecular materials is described next. The variety of molecular materials touched upon in this article include liquid crystals,

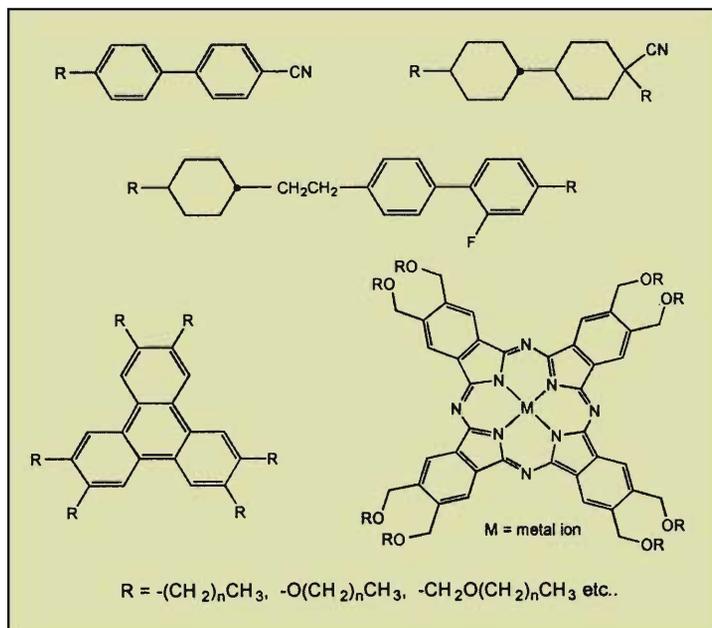


stacked metal complexes and organic charge transfer solids and  $\pi$ -conjugated organic polymers. Throughout the article we focus on the versatility of molecular material design and the fine-tuning of material properties achieved through the control of molecular characteristics.

## Early Examples of Molecular Materials - Liquid Crystals

Liquid crystals are stable and well-defined phases that exist between the isotropic liquid state and the perfectly 3-dimensionally ordered crystalline phase of some classes of molecules. They are also known as the mesophases and are usually formed by rod or disc shaped molecules. The hallmark of liquid crystals is their partial order which leads to simultaneous liquid and solid-like characteristics. Liquid crystals are known to exist in a variety of phases; the classification is based on the type of physical conditions that stabilise the liquid crystalline phase, the shape of molecules and the type of order present (*Box 1*). *Figure 1* provides some examples of molecules that form liquid crystals.

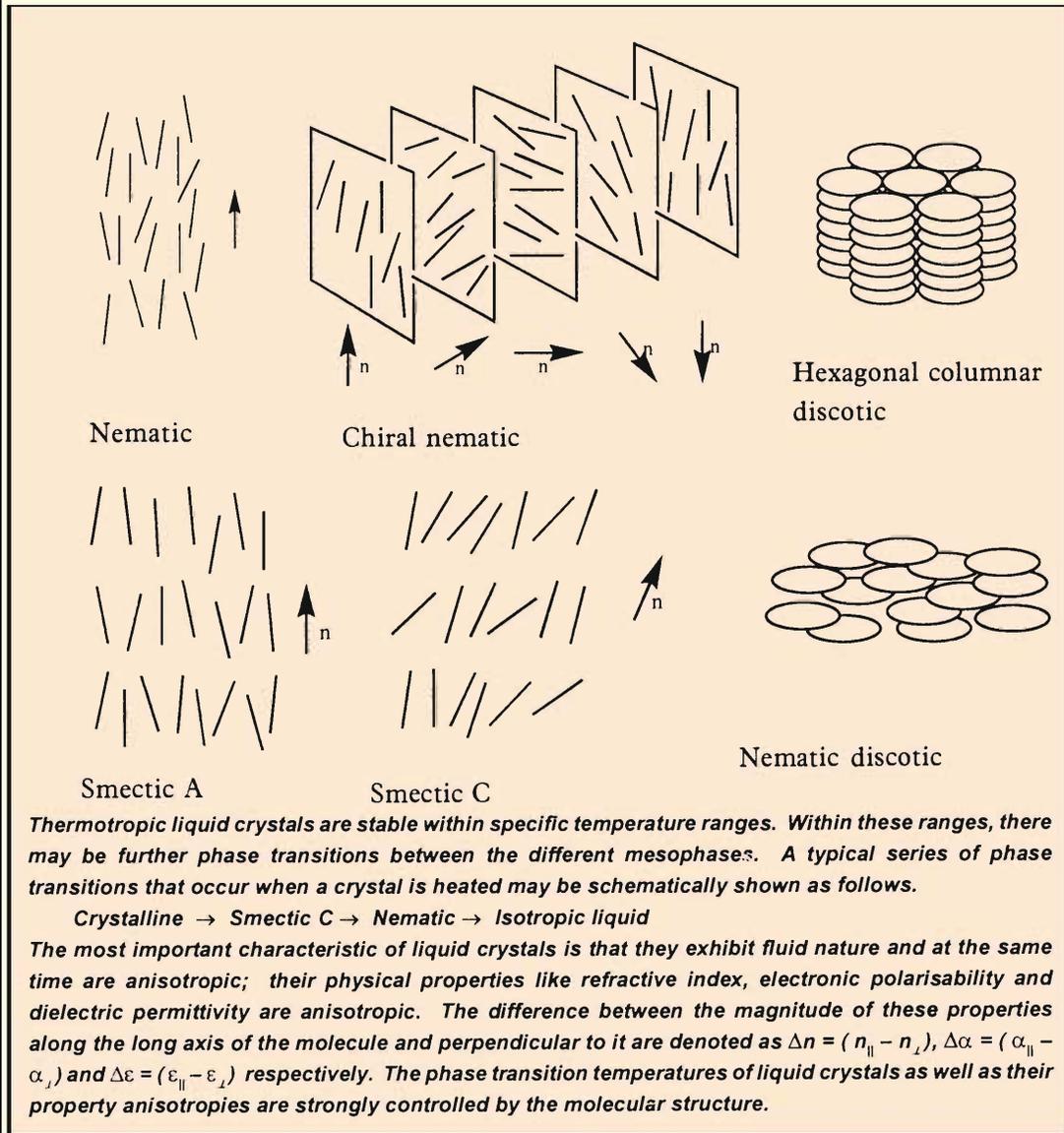
The hallmark of liquid crystals is their partial order which leads to simultaneous liquid and solid-like characteristics.



**Figure 1.** Some examples of molecules that exhibit liquid crystallinity.

**Box 1. Classification of Liquid Crystals**

Liquid crystals are broadly classified as thermotropic and lyotropic based on whether temperature or presence of solvent stabilises the liquid crystalline phase. Thermotropic liquid crystals which are the more popular ones, may be grouped into calamitic and discotic types based on the molecular shape. Calamitic liquid crystals are those formed from rod-shaped molecules. They are further classified on the basis of the type of order present. Though a large number of different phases have been identified



Box 1 continued...



the most basic types are the nematic, chiral nematic and smectic phases. The nematic phase (N) is the least ordered mesophase. It is characterised by the long axes of the molecules being oriented on an average in the same direction; this net direction is usually defined by a parameter known as the director,  $n$ . There is no positional ordering in the nematic phase. When a nematic mesophase is made up of chiral molecules or if it is doped with chiral molecules, the director precesses through the phase describing a helix. Such phases are known as chiral nematic (N\*) or cholesteric phases. When, in addition to the orientational correlation of molecules present in the nematic phase, a positional correlation of molecules into layers also occurs, the phase is known as the smectic phase. If the director is perpendicular to the layer the phase is denoted as  $S_A$ ; if the director is tilted from the normal to the layer, it is denoted as  $S_C$ .

Discotic liquid crystals are generally formed by molecules with an aromatic core unit surrounded by long alkyl chain substituents. Nematic discotics ( $N_D$ ) possess only orientational ordering of the molecular short axes. The more common phases are the columnar phases which are characterised by the symmetry of the side-to-side molecular arrangement and the presence or absence of order within the columns.

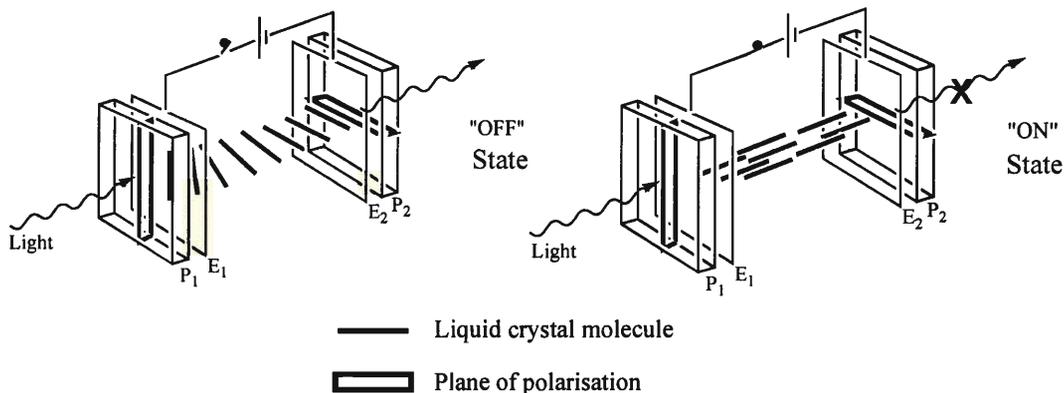
Liquid crystals are perhaps the finest examples of molecular materials which have found extensive technological application. The sensitive response of the liquid crystalline order to applied electric fields has been exploited in a wide variety of ways to fabricate displays, switches and other devices. The nature of the mesophase order is strongly correlated to the molecular structure and the nature of the substituent groups on the molecule. Often mixtures of different liquid crystalline molecules are formulated to achieve specific mesophase properties. The temperatures of the various phase transitions: crystal→mesophase, mesophase → liquid and also those corresponding to the transformation of one type of mesophase to another are strongly influenced by the molecular structure and composition.

A detailed survey of liquid crystals is beyond the scope of this article. We discuss here, only an illustrative example of how molecular design influences material properties in liquid crystals. The story of cyanobiphenyl based systems clearly demonstrates how a series of chemical modifications have led to the



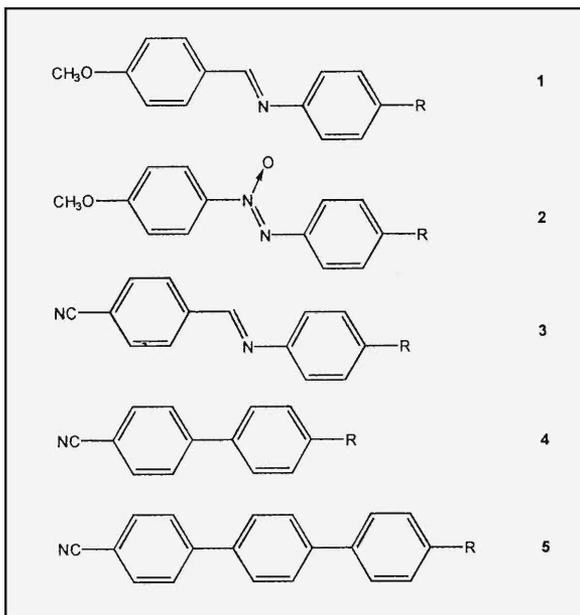
**Box 2 The Twisted Nematic Effect in Liquid Crystals**

The twisted nematic (TN) effect utilises the efficient, fast and reversible response of liquid crystal molecular alignment to an applied electric field. This effect is exploited in liquid crystal displays such as those on pocket calculators and wrist watches. A signal is usually indicated by a dark region contrasted against a light background; the 'switching on' of the dark region is effected as follows.



*The TN cell has the liquid crystal molecules held between two transparent electrodes  $E_1$  and  $E_2$ . These are usually glass coated with transparent conducting material such as indium tin oxide. Special treatment of the electrode aligns the liquid crystal molecules in their neighbourhood in such a way that as one moves across the cell from one electrode to the other, the alignment changes smoothly through  $90^\circ$  i.e. through a quarter helix. Plane polarised light produced at the polariser  $P_1$  enters the cell through electrode  $E_1$ . Its plane of polarisation undergoes a  $90^\circ$  rotation as it is transmitted through the liquid crystal molecules and passes through the other electrode  $E_2$ . A cross-polariser  $P_2$  kept at this end, therefore allows the full intensity of the light to come out. This leads to the 'light' or 'off' situation of the display. If an electric field is now applied across  $E_1$  and  $E_2$ , it aligns the liquid crystal molecules along an axis perpendicular to the electrodes and the rotation of the plane polarised light is inhibited. Therefore no light exits through the cross-polariser,  $P_2$ . Thus the 'dark' or 'on' state of the display is effected. Removal of the applied field immediately pulls the liquid crystal molecules back into the quarter helix arrangement and reverts the cell to the 'off' state.*

development of commercially successful liquid crystal displays. The twisted nematic effect (Box 2) discovered in 1969 provides an ingenious technique to produce displays utilising very low voltages sourced from small batteries or solar cells. However, most of the liquid crystals that were known around the time of the discovery of this effect are not stable at ambient temperatures. The ones which form stable phases at room temperature were mostly based on Schiff bases (e.g. 1 in Figure 2); the high purity



**Figure 2. Molecular structural evolution of stable liquid crystalline molecules.**

required for applications is difficult to achieve with these systems because of hydrolytic and oxidative instability. Though azoxy bridged systems like **2** are chemically more stable, they are again strongly coloured and sensitive to ultraviolet light. Another difficulty with these molecules is the negative permittivity anisotropy,  $\Delta\epsilon$  (*Box 1*) which is unsuitable for the twisted nematic cell.  $\Delta\epsilon$  determines how easily an applied electric field can alter the alignment of the liquid crystals. Higher  $\epsilon_{||}$  and hence positive  $\Delta\epsilon$  can be achieved by the introduction of chemical groups with strong dipole moments at suitable positions in the molecule. In this case, it was achieved by the introduction of cyano groups as in **3**. However the problem of colour persisted, which was solved by the removal of the bridging groups leading to molecules such as the cyanobiphenyls (**4**) and terphenyls (**5**). These molecules turn out to be some of the ideal candidates to exploit the twisted nematic effect at ambient temperatures. These and related systems have become highly successful commercially

Extensive research in this area has led to the development of novel molecules which form the nematic phase over wide ranges

Liquid crystalline materials and devices provide an excellent example of molecular materials research that has paid rich dividends and continues to do so.

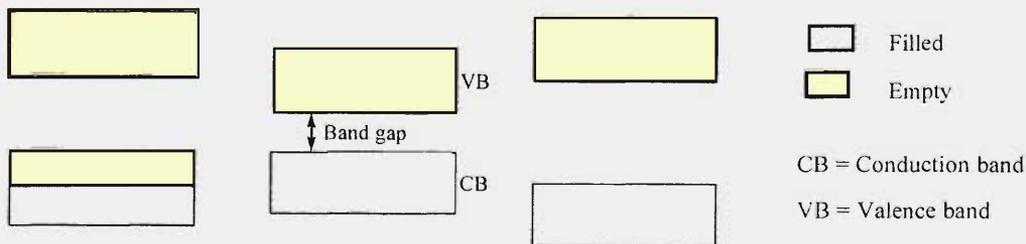
of temperature. Optical properties of liquid crystals are sensitive to their birefringence,  $\Delta n$ . Chemical modification of molecules and utilisation of combinations of several liquid crystalline molecules in the same device can lead to the optimisation of properties such as  $\Delta n$  and  $\Delta \epsilon$  so that the device characteristics can be chosen almost at will. Thus liquid crystalline materials and devices provide an excellent example of molecular materials research that has paid rich dividends and continues to do so.

### Molecular Semiconductors, Conductors and Superconductors

The first molecular conductor was synthesised as early as in 1842, when Knop prepared some crystals with the sheen of metallic copper by oxidising the metal complex,  $K_2[Pt(CN)_4]$  using chlorine or bromine. However he could not ascertain the composition of the product and perhaps never suspected that it

#### Box 3. Semiconductors, Metals and Superconductors

Materials are often classified on the basis of their electrical conductivities. Those which offer strong resistance to electrical transport are called insulators; metals on the other hand display facile conduction of electricity. Semiconductors behave as insulators at a temperature of absolute zero, but at finite temperatures show conductivities intermediate between metals and insulators. The conductivities ( $\sigma$ ) of insulators, semiconductors and metals are typically of the order of  $10^{-22} - 10^{-14}$ ,  $10^{-9} - 10^3$  and  $10^5 - 10^6 \text{ S cm}^{-1}$  respectively. S stands for Siemens or  $\text{Ohm}^{-1}$  ( $\Omega^{-1}$ ), sometimes also denoted as mho; resistivity ( $\rho$ ) is usually expressed in  $\Omega \text{ cm}$ . Increase in temperature leads to a decrease in the conductivity of metals whereas it causes an increase in the conductivity of semiconductors. These aspects are explained by the band theory of solids.



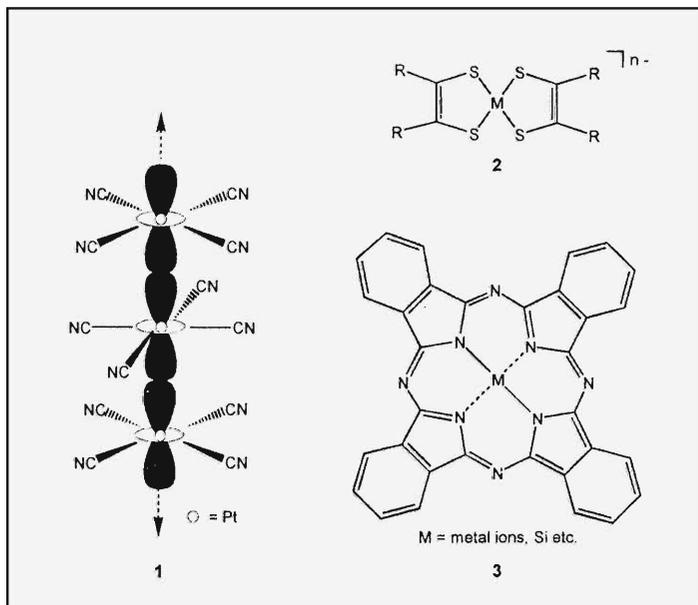
*Box 3 continued ...*

Just as atomic orbitals combine to form molecular orbitals in molecules, in solids they combine to form a very large number (of the order of Avogadro number) of states. The energy levels corresponding to the states formed from a given type of orbital can be treated as a continuous band of energy. Since the atomic orbitals are discrete levels with energy gaps in between, the energy bands formed from the different atomic orbitals leave regions of energy in between where the entry of electrons is forbidden. Depending on the structure of band formation and the number of electrons that are packed into these bands, primarily two situations are possible. In one case, packing of available electrons from the lowest energy band upwards, leads to the final band containing electrons to be partially filled (a); the highest level occupied by electrons is called the Fermi level. The other possibility is that one ends up with a completely filled band (valence band) and a higher energy empty band (conduction band), the two being separated by an energy gap (b). Case (a) allows unactivated electron transport and is characteristic of metals whereas case (b) leads to thermally activated conduction, characteristic of a semiconductor. When metals are heated the resistance increases because of enhanced lattice vibrations which impede electron flow. Heating causes increased lattice vibrations in semiconductors as well, however it simultaneously leads to higher population of charge carriers in the conduction band and hence a net increase in conductivity; at absolute zero of temperature the conduction band is completely empty and the semiconductor behaves as an insulator. When the energy gap is very large compared to thermal energies (c) the material is an insulator which shows negligible improvement in conductivity with heating. Metals like gold, silver and copper are excellent conductors. Semiconductors based on pure materials such as silicon or gallium arsenide are called intrinsic semiconductors; those based on doped materials such as silicon (IV group) containing small amounts of arsenic (V group) or boron (III group) are known as extrinsic semiconductors. Some of the best insulators are organic polymers such as teflon or bakelite.

In 1911, Kamerlingh Onnes discovered that mercury loses its electrical resistivity completely at about 4K. Soon it was found that many other materials display this amazing phase transition at low temperatures. Associated with the loss of electrical resistivity was the interesting magnetic property of perfect diamagnetism, i.e. complete expulsion of a sufficiently low applied magnetic field from within the bulk of the material. This effect is known as the Meissner effect. This marvellous phenomenon of infinite conductivity and perfect diamagnetism is known as 'superconductivity' and the temperature at which this phase transition occurs is called the critical temperature,  $T_c$ . Several metals, alloys and metal compounds were discovered to be superconducting with  $T_c$ 's typically below 25K; the highest  $T_c$  for a long time was 23.2K discovered in  $Nb_3Ge$ . The phenomenon of superconductivity was explained by Bardeen, Cooper and Schrieffer in 1957, on the basis of the close interaction between electrons and lattice vibrations that leads to an unusual pairing of electrons (known as Cooper pairs) that enables them to transport electricity without being scattered by lattice vibrations in solids. Continuous efforts to increase the  $T_c$  resulted in the discovery of the so-called 'high  $T_c$  superconductors' based on oxide materials in 1986. Some examples are Sr doped  $La_2CuO_4$  ( $T_c = 37K$ ) and  $YBa_2Cu_3O_{7-x}$  ( $T_c = 95K$ ). The emergence of organic superconductors and fullerene based superconductors is discussed in the text.



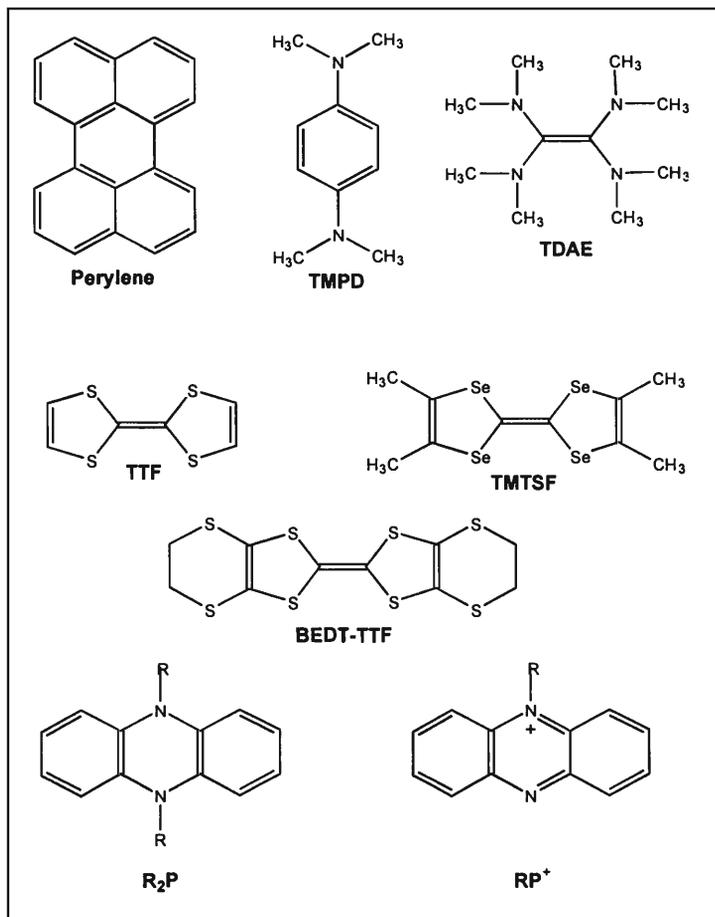
Figure 3. Examples of metal containing molecular conductors.



would show the conducting properties of a metal ! Later it was realised that this material has stacks of  $[\text{Pt}(\text{CN})_4]^{2-}$  (1 in Figure 3) which enabled close contact between  $\text{Pt}^{2+}$  ions and electronic energy band formation from the overlapping  $d_z^2$  orbitals. Oxidation by chlorine or bromine leads to a nonstoichiometric composition,  $\text{K}_2[\text{Pt}(\text{CN})_4]\text{X}_{0.3}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) with a partially filled band and metallic conductivity. More recently, several metal complexes, primarily based on the bis(dithiolene) ligand (2 in Figure 3) and phthalocyanines (3 in Figure 3) have been shown to possess metallic conductivities; some of the former systems even attain a superconducting state at very low temperatures. Molecular conductors are often described as ‘synthetic metals’ to highlight the fact that these materials with metallic properties are prepared through normal synthetic chemistry protocols.

The development of purely organic conductors *i.e.* molecular conductors containing no metal atoms/ions, is quite fascinating. In the early 1950’s a group of Japanese researchers observed that a polybenzenoid aromatic hydrocarbon, perylene (Figure 4a), when treated with bromine vapours gave a dark coloured material that showed low electrical resistivity of about  $8 \Omega\text{cm}$ , a rather

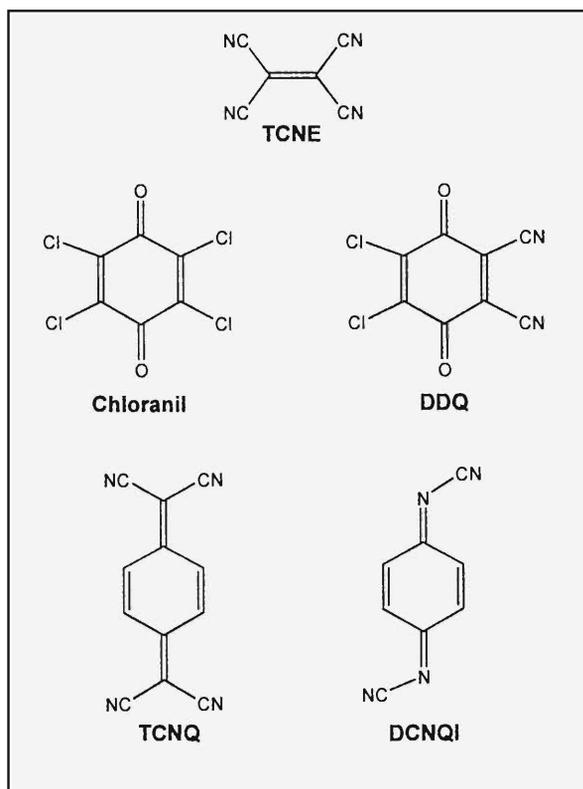
Molecular conductors are often described as ‘synthetic metals’ to highlight the fact that these materials with metallic properties are prepared through normal synthetic chemistry protocols.



**Figure 4a.** Examples of electron donating molecular constituents of organic molecular conductors.

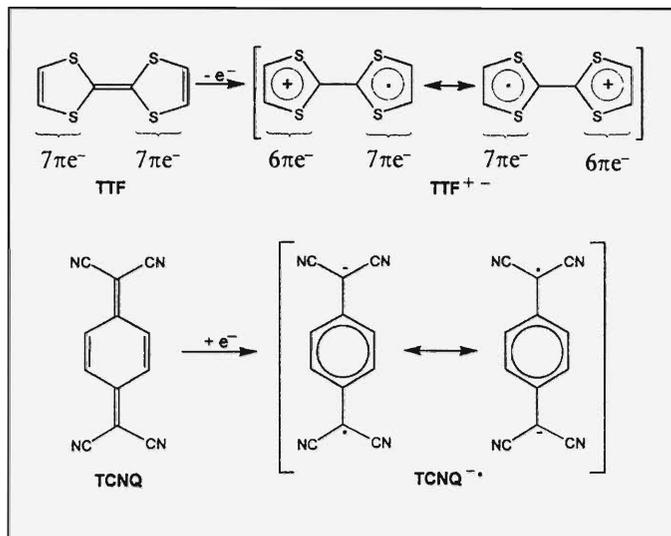
unexpected property for an organic solid. It was soon realised that perylene was being partially oxidised by bromine to create unpaired electrons in its delocalised  $\pi$ -system. These unpaired electrons were responsible for the low electrical resistance. Strong  $\pi$ -electron donor and  $\pi$ -electron acceptor organic molecules, soon became the focus of attention; several new ones were synthesised as well. Molecules like *N,N,N',N'*-tetramethyl- $\pi$ -phenylenediamine (TMPD), tetrakis (dimethylamino) ethylene (TDAE), tetrathiafulvalene (TTF) and related systems, like tetramethyltetraselenafulvalene (TMTSF) and bis (ethylenedithio) tetrathiafulvalene (BEDT-TTF), and also *N,N'*-dialkylphenazines ( $\text{R}_2\text{P}$ ) (Figure 4a) are very good  $\pi$ -electron donors and have ionisation potentials in the range 6 – 7eV. We

**Figure 4b. Examples of electron accepting constituents of organic molecular conductors.**



note that the ionisation energies of alkali metals, the lowest found among elements, are typically  $\sim 3 - 4$  eV. Molecules like tetracyanoethylene (TCNE), tetracyanoquinodimethane (TCNQ), 2,3-dichloro-4,5-dicyanobenzoquinone (DDQ) and dicyanoquinodimethane (DCNQI) (Figure 4b) are excellent  $\pi$ -acceptors with electron affinities in the range  $2 - 3$  eV. These may be compared with halogens which have the highest electron affinities among elements, typically  $\sim 3 - 4$  eV. The strong electron donating and accepting capability of these molecules arise due to the stability of the aromatic cation and anion radicals that form respectively upon donation or acceptance of electrons (Figure 5). These resonance-stabilised ion radicals form stable salts with inorganic counterions (e.g.  $K^+TCNQ^-$  and  $TTF^+BF_4^-$ ). Many of these salts are found to be good semiconductors. The semiconductivity arises from the activated hopping of electrons along stacks of these ion radicals (Figure 6a).

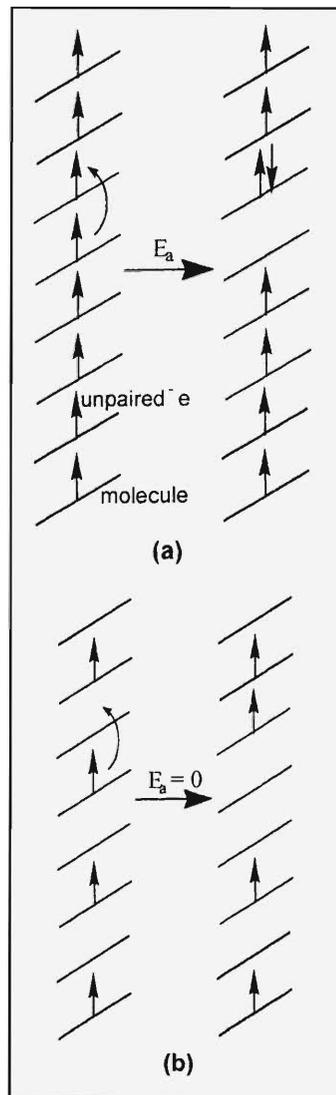
The semiconductivity in such charge transfer salts arises from activated hopping of electrons along stacks of these ion radicals.



**Figure 5.** Formation of aromatic species as a result of charge transfer between the donor and acceptor.

**Figure 6.** Mechanism of conduction in charge-transfer salts.

It is an obvious extension at this point to consider the formation of an all-organic charge transfer complex by the combination of a strong  $\pi$ -electron donor molecule with a  $\pi$ -electron acceptor molecule. This was indeed carried out quite some time ago and gave rise to the amazing situation where a purely organic material conducted electricity like a semiconductor or a metal. The most popular example of an 'organic metal' is the complex between TTF and TCNQ first prepared in 1973; see *Figure 3* of Part 1 of this series of articles for a schematic drawing of the crystal structure of TTF-TCNQ. The oxidising and reducing capabilities of TCNQ and TTF respectively are so matched that a full electron transfer between them does not take place; on an average only about 0.6 electron is transferred. Therefore complete ionisation of all the molecules in a stack as seen in *Figure 6a* does not occur. The situation now can be schematised as in *Figure 6b* wherein several molecules within a stack remain unionised leading to an unactivated *i.e.* free electron transport, which is the hallmark of metals; hence the name 'organic metals'. In TTF-TCNQ, both TTF and TCNQ stacks contribute to this metallic conduction giving rise to an appreciable conductivity of  $10^3 \text{ S cm}^{-1}$  at room temperature which increases to about  $10^4 \text{ S cm}^{-1}$  below 100 K. It is instructive to compare this with the case of copper metal for which the respective values are about



temperatures, copper remains a metal whereas many organic metals including TTF-TCNQ undergo phase transitions to semiconducting or insulating phases; in the case of TTF-TCNQ the metal-semiconductor transition occurs near 60 K. We take a closer look at this problem later.

Polymers with extended  $\pi$ -electron conjugation are another class of organic materials which show high conductivity (see S Ramakrishnan in Suggested Reading). Polyacetylene (PA) in its all-*trans* form (Figure 7) is an insulator with resistivity of  $10^6 - 10^8 \Omega \text{ cm}$ . When PA is doped with small quantities of electron acceptors like iodine, an astounding enhancement of the electrical conductivity is observed. In highly oriented films of doped polyacetylene the conductivity can be as high as  $10^4 - 10^5 \text{ S cm}^{-1}$ ! Interestingly, doping by small amounts of electron donors like potassium metal also leads to an enhanced conductivity. Some of the other popular conducting polymers are based on polythiophene (PT), polyaniline (PAn) and polypyrrole (PPy) (Figure 7). The conduction in these polymers

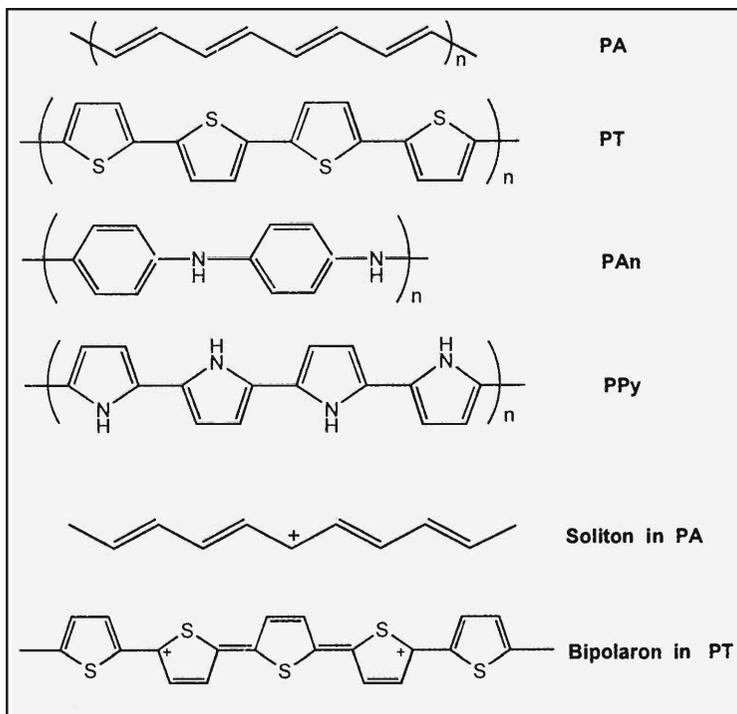


Figure 7. Examples of some conducting polymers.

is believed to be due to such exotic species as solitons and bipolarons (schematically illustrated in *Figure 7*) which are formed as a result of the oxidation or reduction of the  $\pi$ -electron system by the dopants. Conducting polymers like PAn have found several applications, for example in light weight batteries and electrochromic displays. The unique combination of light weight and mechanical properties in polymers and high conductivity characteristic of metals is likely to bring about a great demand for conducting polymers for use in future technologies.

The observation of semiconduction and metallic conduction in organic materials instigated a hectic search for superconductivity in purely organic systems. Some theoretical models suggested that high critical temperatures could be achieved in such superconductors based on light non-metallic atoms. Though the latter predictions have never been realised, superconductivity was indeed discovered in organic charge transfer complexes. The first organic superconductor, the hexafluorophosphate salt of TMTSF (see *Figure 4a* for its structure),  $(\text{TMTSF})_2\text{PF}_6$  was discovered in 1980; it becomes superconducting at 1.4 K under 6.5 kbar pressure. Ambient pressure superconductors were discovered soon after this and more than fifty organic superconductors are known today. Majority of these are based on the donor molecule, BEDT-TTF (see *Figure 4a*); a polymorph designated as  $\kappa$ , of the complex  $\{\text{BEDT-TTF}\}_2\{\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}\}$  has the highest  $T_C$  of 12.8 K (at 0.3 kbar) in this series. An interesting recent entry into the world of molecular superconductors is the alkali metal salts of buckminsterfullerene,  $\text{C}_{60}$ .  $\text{K}_3\text{C}_{60}$  has a  $T_C$  of 18 K and the highest  $T_C$  found in this group is 33 K in  $\text{Cs}_2\text{RbC}_{60}$ . It is interesting to note that none among the polymeric conductors discussed above become superconducting. A notable case however, is the polymer  $(\text{SN})_x$  which shows superconductivity below 0.9 K.

### Design of Molecular Conductors

Thus the world of electrical conductors, superconductors and semiconductors which was dominated by metals, their

The unique combination of light weight and mechanical properties in polymers and high conductivity characteristic of metals, is likely to bring about a great demand for conducting polymers for use in future technologies.

One can fine-tune the molecular ionisation potential and electron affinity by tailoring the molecular skeleton and introducing appropriate functional groups.

compounds and alloys and covalent solids like silicon was thrown open to molecular materials based on strong electron donors and acceptors and  $\pi$ -conjugated polymers. At this point it is worthwhile to look back and analyse how molecular design plays a crucial role in defining the solid state property in these conducting materials. In the context of TTF-TCNQ, we have briefly mentioned that the key factor that enables metallic conduction in molecular charge transfer complexes is the partial electron transfer between the donor and acceptor molecules. This results in a fractional charge on the donor and acceptor components of the complex which is termed the 'partial ionicity' of the complex. The partial ionicity depends on the ionisation potential of the donor, the electron affinity of the acceptor and the electrostatic stabilisation energy of the ions resulting from electron transfer. If the ionisation potential of the donor is very low and the electron affinity of the acceptor is very high, complete electron transfer occurs leading to the situation shown in *Figure 6a*. At the other extreme, if the ionisation potential of the donor is high and the electron affinity of the acceptor is low negligible electron transfer is effected. These cases result in semiconducting or insulating state of the bulk material. One can fine-tune the molecular ionisation potential and electron affinity by tailoring the molecular skeleton and introducing appropriate functional groups. Thus an optimal match of the electron donating and accepting capabilities of the donor and acceptor molecules respectively can be realised leading to partial ionicity and metallic conduction (*Figure 6b*). The case of two complexes of hexamethylenetetraselenafulvalene (HMTSF) provides a graphic illustration of this concept. HMTSF-TCNQ complex has a room temperature powder conductivity of about  $25 \text{ S cm}^{-1}$  and remains highly conducting down to the lowest temperatures studied. However HMTSF-TCNQF<sub>4</sub> (TCNQF<sub>4</sub> is the tetrafluoro derivative of TCNQ) with virtually identical crystal packing as HMTSF-TCNQ, has a conductivity about  $10^6$  times lower and displays typical semiconductor behaviour. This drastic difference arises from the fact that the TCNQ complex exhibits partial ionicity and the complex containing the stronger



acceptor TCNQF<sub>4</sub> is fully ionic. Besides the matching of ionisation potentials and electron affinities there are several strategies to achieve partial ionicity in molecular conductors. For example, in (TMTSF)<sub>2</sub>PF<sub>6</sub> and  $\kappa$ -{BEDT-TTF}<sub>2</sub>{Cu[N(CN)<sub>2</sub>]Cl} mentioned above, the 2:1 stoichiometry and the -1 charge on the inorganic counterion lead to an ionicity of 0.5 on the organic donor.

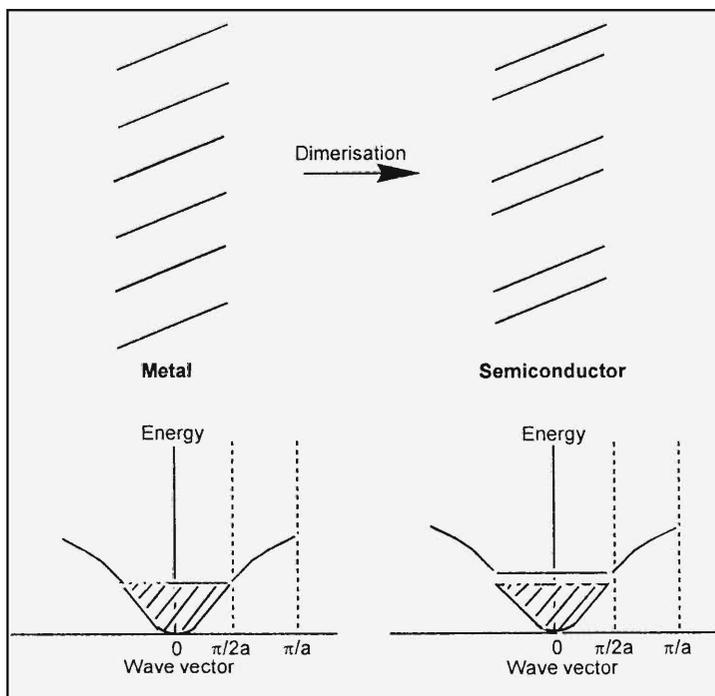
Another important criterion to achieve conductivity is that molecules of the same kind should stack upon one another to form what is commonly referred to as the 'segregated' or homomolecular stack. If the donors and acceptors alternately stack to form the so-called 'mixed' stack, then metallic conductivity cannot be achieved since electrons tend to localise on the acceptors sandwiched between the donors. An interesting case of the influence of molecular structure on stacking is provided by the TCNQ complexes of alkylphenazinium (RP<sup>+</sup>) ions (*Figure 4a*). It is found that the N-methylphenazinium complex, MeP<sup>+</sup>TCNQ<sup>-</sup> shows a room temperature conductivity of  $\sim 10^2$  S cm<sup>-1</sup>. When a minor change of the alkyl group is effected, *i.e.* in the case of the N-ethylphenazinium complex, EtP<sup>+</sup>TCNQ<sup>-</sup>, the conductivity drops to  $\sim 10^{-9}$  S cm<sup>-1</sup>! This dramatic change in the conductivity arises due to the fact that the first complex has a segregated stack structure whereas the second one goes into a mixed stack structure. Though no clear rules are known in this game of stacking preferences, experience shows that the TTF family of donors have been singularly successful in this regard. Even when segregated stacking is achieved, it is essential that the interplanar distance between molecules is short enough for good  $\pi$ -orbital overlaps and easy electron transport. Recall the discussion of  $\pi$ -stacking interactions in Part 1 of this series of articles; we now see that these interactions play a crucial role in achieving high conductivity in molecular materials.

Another important criterion to achieve conductivity is that molecules of the same kind should stack upon one another to form what is commonly referred to as the 'segregated' or homomolecular stack.

The  $\pi$ -conjugated polymers as well as the stacked charge transfer solids discussed above possess strong orbital overlap

Molecules that give rise to inter-stack interactions tend to suppress the low dimensional character and circumvent the low temperature instability.

along one direction that facilitates transfer of electrons in that direction; the interactions along the orthogonal directions are usually several orders of magnitude weaker. Therefore these are highly anisotropic materials and are often described as quasi one-dimensional solids. A problem that arises due to the low dimensional nature of these molecular conductors is the possibility of low temperature phase transitions that convert them into semiconductors or insulators. This has frustrated researchers trying to achieve high conductivity or superconductivity in molecular materials at low temperatures. A commonly encountered instability is the Peierl's distortion (named after the physicist who predicted such instabilities in low-dimensional conductors). In the context of the stacked organic conductors, this instability is usually associated with the dimerisation (pairing up) of neighbouring molecules in the stack at low temperatures. This is driven by the electronic energy stabilisation resulting from the splitting of the energy band at the Fermi level (*Figure 8*). The consequence of this crystallographic phase transition and the electronic band



**Figure 8. Evolution of band structure as a result of pairing.**

splitting is the changeover from metallic to semiconducting behaviour. Appropriate design of molecules that gives rise to interstack interactions tends to suppress the low dimensional character. Thus the low temperature instability is circumvented and the metallic nature is retained to low temperatures. This strategy has been employed particularly successfully in the design of superconductors by the incorporation of large Se atoms or several S atoms in the molecular skeleton that gives rise to intermolecular Se $\cdots$ Se or S $\cdots$ S contacts and leads to a quasi two-dimensional nature of the crystalline lattice. TMTSF and BEDT-TTF (*Figure 4a*) were born out of such considerations.

## Conclusion

This article provides an overview of molecular control of material design with specific reference to liquid crystals and molecular semiconductors, conductors and superconductors. A brief introduction to liquid crystals is provided followed by a specific example of molecular design for liquid crystal displays. The emergence of 'synthetic metals' is outlined next, followed by an overview of organic superconductors. The important strategies that have evolved for the design of molecular conducting materials is also summarised. The next article in this series will focus on the design of molecular materials which exhibit interesting magnetic and non-linear optical phenomena.

## Suggested Reading

- ◆ S Chandrasekhar. *Liquid Crystals*. Cambridge University Press. London, 1977.
- ◆ P Day, D C Bradley, D Bloor (Eds.), *Molecular Chemistry for Electronics. Proceedings of the Royal Society Discussion Meeting*, Royal Society. London, 1990.
- ◆ T Ishiguro and KYamaji. *Organic Superconductors*. Springer Series in Solid State Sciences Springer-Verlag, Berlin. 88, 1990.
- ◆ S Ramakrishnan. *Resonance*. 2. 11.48–58, 1997.
- ◆ T A Skotheim. R L Elsenbaumer and J R Reynolds (Eds.). *Handbook of Conducting Polymers*. Marcel Dekker. New York. II Edition, 1998.

*Address for Correspondence*

T P Radhakrishnan  
School of Chemistry  
University of Hyderabad  
Hyderabad 500 046, India

