Molecules to Materials

1. An Overview of Functional Molecular Solids

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With the advent of modern physics and chemistry, fundamentally new types of materials have been created in this century. Various types of forces operating in different classes of solids are exploited in the design of molecular materials. A variety of fabrication techniques have been developed to make materials with the desired properties. An overview of these aspects is provided in this article.

Historical Perspective

The kinds of materials that have been developed and used over the course of history serve as excellent indicators of the evolution of technology, and civilisation at large. For instance, the early growth of civilisation has been described in terms of the stone, copper, bronze and iron ages. The earliest materials were those which were readily available in nature, like stone, clay and wood and the technology consisted in reshaping and restructuring physically these materials to suit specific purposes such as weaponry and utensils. The most intricate process at this stage perhaps involved the fabrication of ceramics such as porcelain by baking clays, a practice that dates back to the eighth millennium BC. Discovery of procedures for extraction of metals from their ores and fabrication of alloys was a major revolution in the history of materials. Here was a case of complete transformation of the physical and chemical properties of a material. Equally fantastic was the discovery of glass-making, a process in which the optical properties of the starting substance, sand, are completely and drastically modified. Though not known at that time, these fabrication methods involve chemical reactions in addition to physical transformations; the chemical

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changes often brought about by the application of heat lead to the new physical properties of the materials.

The early utilisation of materials was partly or wholly based on their structural, mechanical, optical or thermal properties. Strength of materials was of paramount concern when used for the construction of weapons, utensils and buildings. Thermal attributes were exploited for reshaping the materials and moulding them into desired shapes. Since the earliest known deliberate use of materials, none of their other properties were exploited extensively for several thousands of years. For the appreciation and utilisation of other properties we had to wait until the latter part of the second millennium AD when advances in physics unraveled the wonders of electricity and magnetism.

Many materials which are naturally available, like cellulose and natural rubber, are polymeric in nature. The discovery of synthetic polymers in the nineteenth century AD, one of the major achievements of synthetic chemistry, added a whole new dimension to the world of materials. The electrically insulating nature coupled with the light weight and wide choice of mechanical properties they offer, made plastics extremely versatile materials, unparalleled in the domain of metal-based compounds and ceramics.

Thus we see that till the advent of modern physics and chemistry in the beginning of the twentieth century, the world of materials was dominated by just a handful of general classes of materials, namely metals and their alloys, metal compounds such as oxides and sulfides, ceramics and glasses and finally plastics. The application of these materials was based primarily on their electrical, magnetic, optical and mechanical properties. A sea change in the science and technology of materials was to follow with the development of a deeper understanding of the microscopic nature of matter in the form of quantum theory.

The development of a clear picture of the phenomenon of semiconduction during the first half of the twentieth century

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The growth of the electronic industry, propelled primarily by the advances in semiconductor physics, made unprecedented and challenging demands on the specificity and precision of material properties.

leading to the fabrication of the first transistor in 1948, as well as the discovery of superconductivity in 1911 and the explanation of this amazing phenomenon in 1957, marked the beginnings of a new era in the history of materials. The pace at which new developments took place in fundamental physics and chemistry was reflected in the progress in the fabrication of new materials. The growth of the electronic industry, propelled primarily by the advances in semiconductor physics, made unprecedented and challenging demands on the specificity and precision of material properties. Concepts like purity and method of fabrication emerged as key factors that determined the properties and applications of the materials. The stringent demands on materials made by the emergence of a wide variety of new applications such as fast switches for communication devices and sensors and novel concepts such as quantum confinement have led to extensive exploration of new types and classes of materials. Some of the new types of materials that exhibit unusual phenomena and promise interesting applications are composites, nanostructured materials, thin films and amorphous solids.

Most of the classes of materials mentioned above are built up as an assembly of atoms or ions. Polymers are exceptional in the sense that they have very long chain molecules as their basic building blocks. A significant departure from the course taken in the development of materials is the growth of a new family of materials which have small molecules and molecular ions as their fundamental building blocks. We develop in this series of articles, a broad overview of this new class of materials, which we will henceforth refer to as molecular materials. In some sense, polymers, which are built up from macromolecules (a term preferred these days for long chain molecules) can also be classified as belonging to this family of materials.
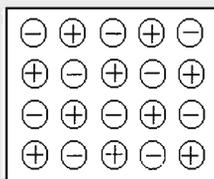
Molecular Solids

A molecule is an entity wherein strong covalent or coordination bonds hold a group of atoms together in a stable state, in solid,
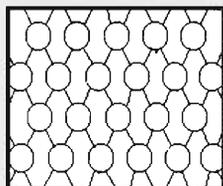
in solution/liquid and in several cases, even in the gaseous state. We are thus referring to typical organic or organometallic molecules and coordination complexes. When a solid built up of such molecular units is dissolved in an appropriate solvent, or in some cases even when melted or sublimed, it breaks down into its constituents which retain to a large extent the individual characteristics they exhibited in the solid state; for example, their vibrational spectrum. This picture may be contrasted with the case of traditional solids like inorganic salts and metal oxides, covalent solids like graphite and silicon, and metals and their alloys wherein the characteristics of the constituent atoms/ions are very different in the isolated and in the bulk states. In standard textbook parlance, the latter groups constitute the ionic, covalent and metallic solids, whereas the molecular solids are referred to as van der Waals solids (*Box 1*). However, it is

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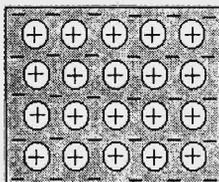**Box 1. Classification of Crystalline Solids**

Crystalline solids are traditionally classified into four groups, ionic, covalent, metallic and van der Waals, based on the type of forces that keep the bulk solid together. Ionic solids are made up of positive and negative ions which are held together by strong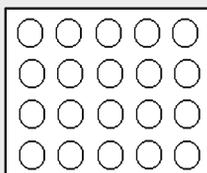 electrostatic (coulombic) forces. The strong interatomic interactions lead to the high melting points of these solids. Typical example of an ionic solid is common salt (Na^+Cl^-). Covalent solids on the other hand have strong covalent chemical bonds between the constituent atoms. Elemental silicon is a good example. Metallic solids like copper, have a periodic array of the positively charged metal ions; the valence electrons of the metal atoms are relatively free to move around and provide the binding force that holds the metal ions together. The sea of free electrons leads to the high conductivity of metals. Finally, the so-called van der Waals solids have atoms or molecules held together by relatively weak interactions. These are usually dispersion forces like induced dipole–induced dipole, dipole–induced dipole or dipole–dipole attractions. These solids usually have relatively low melting points. Typical examples are the solid state of noble gases like helium and several organic solids such as naphthalene.

IONIC

COVALENT

METALLIC

VAN DER WAALS

The design and fabrication of molecular materials effectively exploits the enormous power and flexibility of synthetic chemistry.

important to recognise that the latter is a very limited description of the molecular solids known today. As we shall see below, the class of molecular materials (functional molecular solids) utilise ionic and covalent interactions and in addition a wide variety of novel weak interactions not found anywhere in the traditional solid state.

The design and fabrication of molecular materials effectively exploits the enormous power and flexibility of synthetic chemistry. The unique electronic structural features such as delocalised π-electrons of molecular materials make them superior candidates for several technological applications. These aspects will be discussed in the articles that follow in this series. We present below some general features of molecular materials. First we look at the variety of interactions that are crucial to the design of molecular materials. Subsequently we outline the different 'fabrication techniques' relevant to these materials.

As per our definition above, the building blocks of molecular materials can be purely organic molecules or metal containing systems such as organometallic compounds and coordination complexes. Polymers are also often treated as belonging to this general class; in particular, organic polymers with extended delocalised π-electrons and metal coordination polymers qualify in this respect because of the novel electronic and optical properties and low dimensional magnetic phenomena they exhibit. Extensive research efforts have gone into the study of each of these types of molecular materials. To provide a coherent overview of the versatility of molecular materials, we have chosen to focus on purely organic systems in these articles. However to put things in the right perspective, we will often refer to the metal containing molecular materials as well.

Design of Molecular Materials

The fundamental difference between the fabrication of molecular materials and other kinds of materials may be schematised as
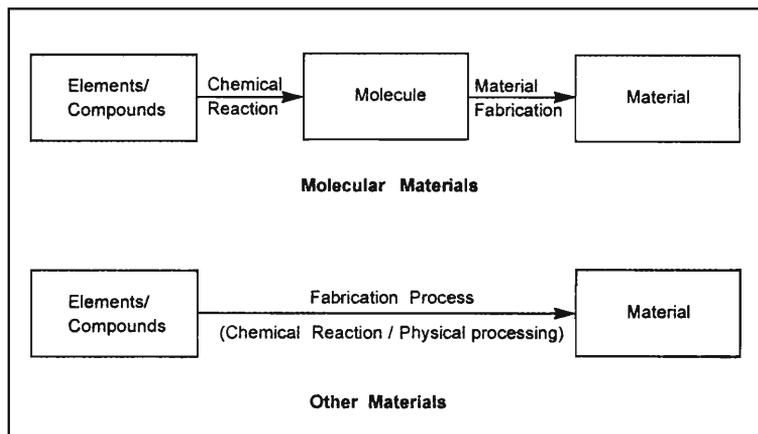
Figure 1. The two-level synthesis of molecular materials compared with the conventional procedure of making materials.

follows (*Figure 1*). The latter are usually fabricated starting from suitable precursor materials and employing techniques such as ceramic methods, soft chemical methods (*chemie douche*), melt-quench process, chemical vapour deposition and so on. The chemical composition of the product material is determined by the chemical reactions involved in the fabrication process. The fabrication procedure which may consist of one or more steps will also determine the final physical properties of the material. In the case of molecular materials an additional stage is involved which effectively separates the chemical reaction from the material fabrication process. The first step determines the chemical composition of the final material and the second step, together with the chemical composition, controls the material properties. This intermediate stage is simply the molecules or molecular ions from which the material is assembled. The molecules can be clearly identified and studied by the panoply of spectroscopic and other analytical tools available today. This provides for a systematic approach to the problem of assembling the bulk material. In most cases, the bulk material once assembled can be taken apart into its molecular constituents and reassembled in another fashion, if one so desires. The extra handle that this intermediate stage provides in fine-tuning the material properties is of enormous advantage as we shall see.

An appreciation of the nature of forces that exist in molecular materials is essential for their design. As noted earlier, molecular

Molecular solids are held together by several non-covalent interactions, such as electrostatic forces, intermolecular charge transfer, hydrogen bonding, π-stacking and dispersion forces.

materials possess binding forces arising from covalent interactions, and in several cases from ionic interactions as well; these are features they share with different traditional solids. However, there are significant differences in the distribution of these forces in the two types of solids. The covalent interactions in solids such as silicon or diamond extend through the bulk of the material. However, in molecular materials, the covalent forces are confined to within the molecular entities. Polymeric solids with extended covalently bonded macromolecular building blocks are, in this sense, half-way between small molecule based molecular solids and traditional covalent solids. Molecular solids built from π-electron donor and acceptor molecules are stabilised by intermolecular charge transfer interactions. When the molecules are strong donors and/or acceptors they exist as molecular ions in the solid. Molecules with strong electron donating and accepting groups show intramolecular charge transfer which results in a large dipole moment. Dipole-dipole interactions between such molecules will be quite significant. The electrostatic forces that exist in these molecular materials may be contrasted with similar forces in solids such as the inorganic salts (e.g. NaCl). In the latter, these forces exist between nearly point-like charges (Na^+ and Cl^-) and hence are very strong. However, the electrostatic forces in ionic molecular materials are relatively weaker, since the charges are usually delocalised over several atomic sites in a molecular ion and the electrostatic interactions occur over larger distances. *Figure 2a* provides examples of some compounds that form ionic molecular solids; they may contain metal ions as in 1 (benzoate salt, M^+ = Na^+, K^+ etc.) or could be purely organic systems like 2 (N-methylphenazenium tetracyanoquinodimethanide, NMP^+ $TCNQ^-$). The atomic charges on NMP^+, derived from semiempirical quantum chemical computations are also shown in *Figure 2a* to illustrate how charge is distributed in a molecular ion. *Figure 2b* presents a simple calculation that contrasts the electrostatic interactions between localised charges and that between distributed charges exemplified by molecular ions with two sites; E represents the electrostatic energy. This figure
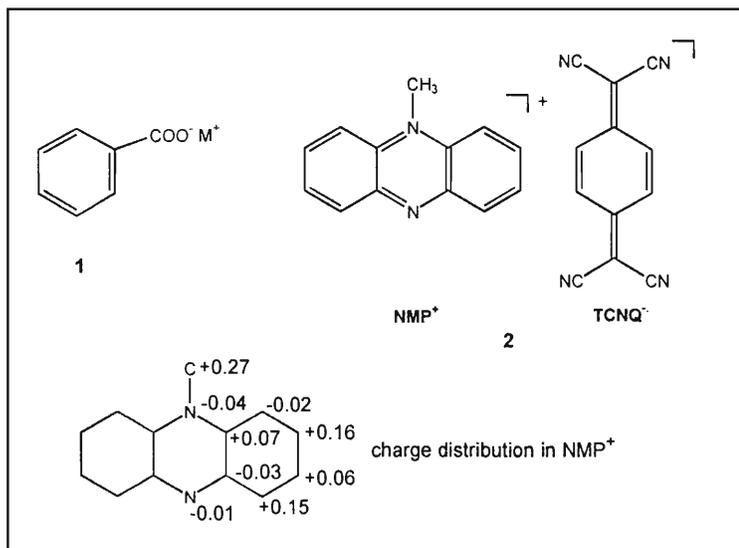
demonstrates that electrostatic interactions in molecular solids are generally weaker than in traditional ionic solids.

The intermolecular interactions in molecular materials can come about in a wide variety of ways besides the covalent and ionic interactions discussed above. Dispersion and repulsive (the so-called steric interaction) forces exist in all molecular materials. These interactions are quite weak, but often play a crucial role in determining the bulk structure of the molecular solid. For instance, the shape anisotropy of some molecules and the interactions between the alkyl chains attached to them lead to the formation of liquid crystals, and the 3-dimensional lattice structure of several crystalline materials is controlled by the steric interactions between their molecular building blocks. These are usually the only intermolecular interactions present in several neutral aliphatic and aromatic molecular solids. In materials based on planar aromatic molecules and molecular ions, weak bonding interactions between the delocalised π-electrons of adjacent molecules often leads to the so-called 'π-stacking'. These stacks are columnar structures wherein the flat molecules are stacked like plates one on top of the other, though often with a slight tilt and a slip. The structure of tetrathiafulvalenium tetracyanoquinodimethanide, TTF-TCNQ, containing

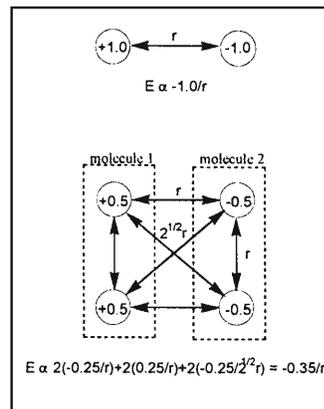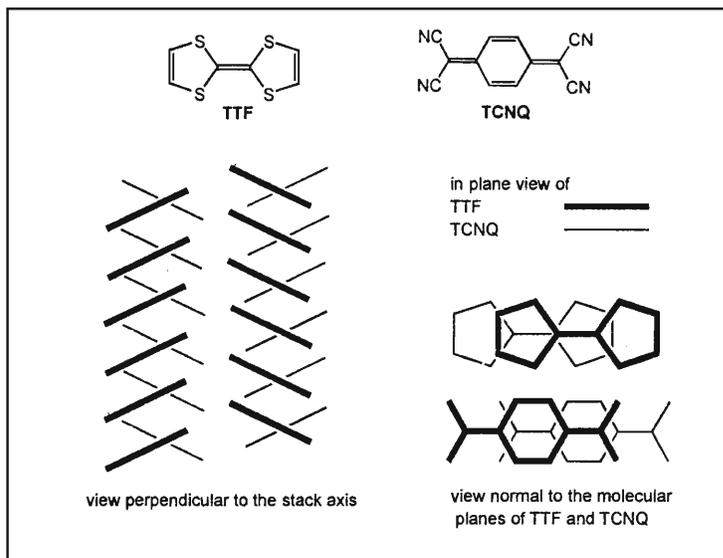Figure 2b. Magnitudes of electrostatic interactions in localised and molecular ionic systems.

Figure 3. Examples of ordered structures resulting from π-stacking interactions.

stacks of TTF and TCNQ shown schematically in *Figure 3* is a good example. π-Stacking is a unique feature found in molecular materials that has considerable relevance in connection with their electrical properties. Another special feature found in many molecular materials, namely intermolecular hydrogen bonding, plays a very prominent role in shaping their bulk structure. Though once again weak compared to typical ionic or covalent bonds, these interactions are highly directional and their cooperative influence can be quite overwhelming. Crystal structure of urea schematically shown in *Figure 4* is an illustrative case. Besides the usual H-bonds between strongly electronegative atoms like oxygen or nitrogen, those involving atoms such as carbon or halogens can play a decisive role in the formation of molecular crystals. Yet another factor that exerts a subtle influence on crystal packing is molecular chirality; this effect arises from fundamental symmetry considerations.

The tunability of the subtle and relatively weak interactions listed above is at the heart of the versatility of molecular materials. Molecular material design can be achieved by the clever manipulation of these forces. The synthesis of the appropriate molecular building block is the first step in this process. This aspect is best described using several illustrative examples;
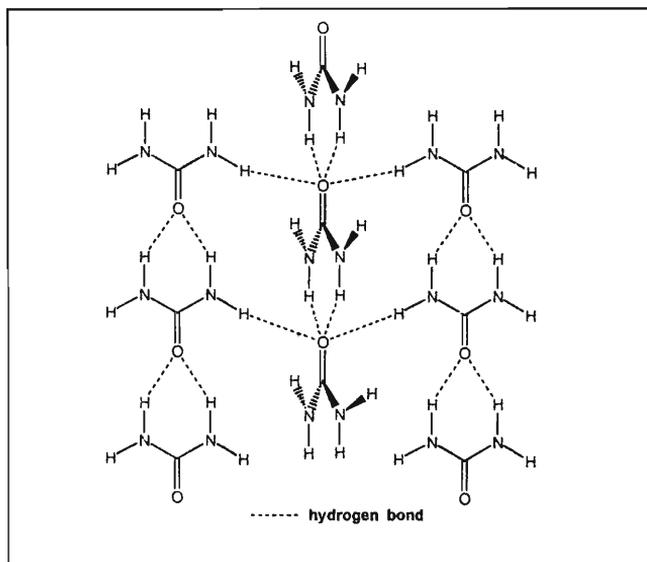
Figure 4. Schematic representation of the hydrogen bonding network in solid urea.

hence we take them up in the later articles in the series. Once the appropriate molecule is synthesised, a suitable procedure has to be adopted to assemble them into the required functional molecular solid in the form of crystals, thin films etc. We summarise below the popular fabrication techniques that form this second step.

Material Fabrication Techniques

Crystallisation from organic or aqueous solvent medium is perhaps the most common technique employed for the fabrication of molecular materials. The choice of the solvent can be important in some cases since different polymorphic forms of the crystal can be grown depending on the nature of the solvent. The most common methods of crystallisation include slow evaporation and cooling. Sometimes vapours of a second liquid which is a poor solvent for the compound of interest are slowly diffused into the solution leading to the growth of crystals. Crystallisation from the melt and sublimation techniques can be used in the case of thermally stable materials. Electrocrystallisation is a popular technique in the case of molecular conductors and superconductors; when the molecule of interest is oxidised or reduced in the presence of appropriate counterions, crystals of

Figure 5. Alignment of molecular dipoles using the poling technique.
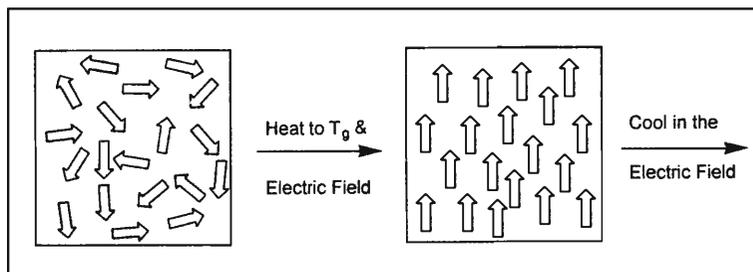
the molecular ion complex grow off the electrode surface. Logical design and generation of predefined crystal architectures through chemical modification of the molecules and simple crystallisation techniques is an area being extensively explored today. However, in many cases, simple crystallisation procedures do not provide much control on the final bulk structure. Some of the alternative techniques that may be adopted for the directed assembly of molecular materials are the following.

Thin films of polymers or polymer matrices embedded with small molecules can be prepared by spin coating techniques. In this process, solutions are spread on suitable substrates such as a glass slide and the solvent is evaporated off while spinning the substrate to achieve uniform film formation. Specific orientation of molecular dipoles physically trapped in the polymer matrix or chemically bound to the polymer chains can be achieved by electric field poling techniques (*Figure 5*). First the polymer matrix is softened by heating it to above its glass transition temperature (T_g). A strong electric field is simultaneously applied, which aligns the molecular dipoles which were earlier randomly distributed in the polymer film. Subsequently the system is cooled in the presence of the field to lock the orientation of the dipoles into position. Randomisation of the dipole orientation upon removal of the applied field (depoling) poses a serious problem. In systems where the dipoles are chemically attached to the polymer, this may be prevented by cross-linking of the polymer matrix, usually achieved photochemically.

Another method for orienting molecules in thin films is the Langmuir-Blodgett technique. In this procedure (*Figure 6*),

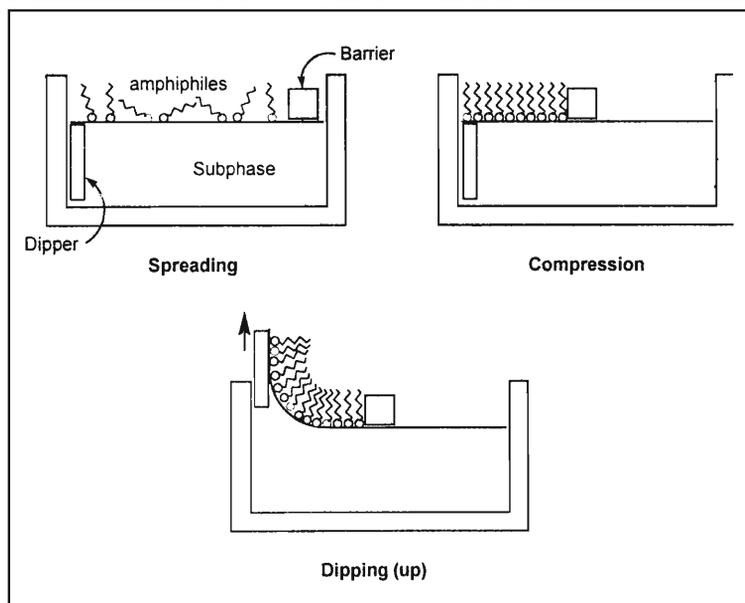Controlled crystallisation, electric field poling, formation of L–B films, and sol-gel technique are means of making materials with desired structural arrangements of molecules.

amphiphilic molecules (having hydrophilic polar groups and hydrophobic long hydrocarbon chains) are spread on the surface of a suitable subphase, usually water. When a barrier is moved over the surface, these molecules are compressed to form an ordered monolayer. The monolayer is then transferred onto suitable substrates, typically a glass plate, by a dipping process. Multiple layers can be coated on the substrate by repeated dipping. The preferential orientation of the molecules at the air-water interface ensures specific orientation of the molecules in the bulk thin film deposited on the substrate. Depending on the mode of dipping and the molecular structure of the amphiphile, head-to-tail or head-to-head orientation may occur between the neighbouring layers deposited.

Sol-gel technique is widely used to prepare composite materials which incorporate organic molecular entities in an inorganic matrix. Hydrolysis of compounds like alkyl silicates and aluminates yields extended covalently bonded networks. These may be utilised to assemble the molecules of interest into a material with desired properties. As in the case of polymer films, the molecules are physically trapped in the lattice or covalently attached to the network. Electric field poling techniques may be

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employed when the matrix is in the gel state, to achieve specific orientation of the molecular dipoles.

Concluding Remarks

In this article we have reviewed the subject of molecular solids in a historic context. We have analysed the variety of novel interactions that characterise this class of solids and the logic of design of molecular materials which involves the 'two-level synthesis' of first the molecule and subsequently the material. Throughout, we have focussed on the general attributes of molecular materials. In the subsequent articles in this series we analyse the close link between material design and its functionality by considering several examples from liquid crystals, conducting molecular materials, molecule-based magnetic systems and molecular non-linear optical materials. The ultimate target of current research efforts in molecular materials is the development of molecular devices. We dwell briefly on the progress in this direction, in the concluding article.

Suggested Reading

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- ◆ G R Desiraju. *Crystal Engineering, The Design of Organic Solids*. Elsevier. Amsterdam, 1989.
- ◆ P Day, D C Bradley and D Bloor (Eds). Molecular Chemistry for Electronics. *Proceedings of the Royal Society Discussion Meeting*. Royal Society. London, 1990.
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Trust is less than truth until it is made known.

John A Wheeler