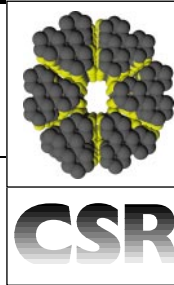


Nanoporous and mesoporous organic structures: new openings for materials research



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Organic solid state and molecular architectures providing nano- or mesoporous space for the inclusion of guest species open up new opportunities for the synthesis of materials showing designed chemical and physical properties. Porous materials are reviewed by taking into account recent progress in inorganic zeolites, metalloorganic and organic networks including carbon nanotubes and condensed cyclodextrins. Various properties requiring a parallel alignment of close-packed guests are addressed. As a particular example of physical property design, spontaneous polarity formation in channel-type inclusion compounds is discussed.

1 Introduction

In the strictest sense of the term, *porous materials* may be regarded as crystalline or amorphous solids which permit the reversible passage of molecules (gas, liquid, solid) through their structures *via* holes in their surface. These pores are generally

† For the rest of this review, we will use the term nanoporous to encompass general discussion on both nano- and mesoporous structures. Readers are, however, encouraged to keep a close inspection on the size ranges being discussed at various points throughout the paper.

regarded as being approximately ≤ 1.5 nm in diameter for nanoporous materials and in the range 1.5–100 nm for mesoporous structures.† From the viewpoint of materials science,¹ the scope for the exploitation of nanoporous materials is enormous: from traditional applications as simple desiccants, to size/shape-selective reaction chambers for effecting purification (including optical resolution of enantiomers) or heterogeneous catalysis, or symmetric/asymmetric syntheses, to more advanced technological applications as chemical sensors, electrodes, data imaging and storage materials, and even lasers.

The classical examples of nanoporous materials are the various natural and synthetic inorganic zeolites.^{1a-c} These microcrystalline materials consist of open aluminosilicate frameworks derived from $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra linked to form cages, channels or cavities of various sizes. The negatively charged frameworks are balanced by positively charged cations of appropriate size located at various positions in the lattice. Neutral and charged *guest* molecules enter and leave the rigid but porous *host* structures by the process of diffusion. Zeolites have been employed for a diverse range of applications, including many of those already outlined above. Contemporary studies have focused on synthetic strategies to obtain the regular, highly ordered pore and channel structures of zeolites to effect orientational and/or conformational properties in included guest molecules which may not be attainable in solution or in the pure solid state.^{1a-c} These properties may

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require specific intermolecular interactions between guest molecules to bring them about, for example, magnetic or charge transport properties. Alternatively, they may belong to single guest molecules, but depend on the relative orientations of the included guests within the zeolite host framework, for example, laser action and the electro-optic effect. As we will outline below, the properties are often at an optimum level when the channels are parallel with respect to one another.

Whilst the enormous research field of inorganic zeolites is a fascinating one, we will not be concerned with specifics here. Readers are referred to review articles^{1a-c} for further informa-

tion, especially with regard to existing and possible materials applications. The key idea, however, of incorporating guest molecules within porous, parallel-aligned, channel-type host architectures^{1d} to achieve properties which may be unique to these materials, forms the central theme of this review (see Fig. 1).

We are primarily concerned here with a relatively new area of nanoporous materials, namely those based on organic materials, or those in which organic units figure largely in the pore-forming structures, specifically, organometallic species. We will not, however, be concerned with the use of organic

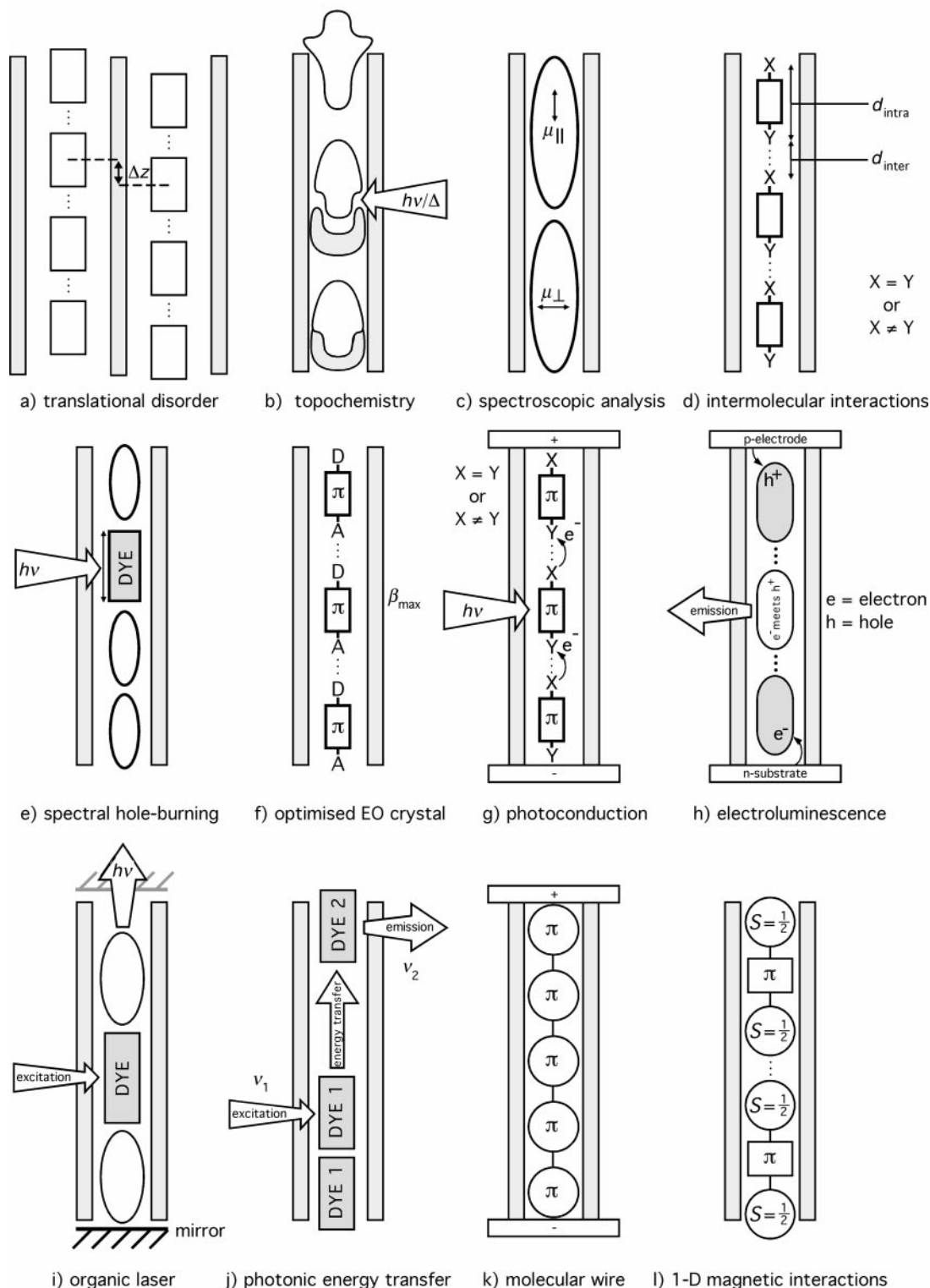


Fig. 1 Schematic drawings of some important physical and chemical properties which may arise when confining guest molecules with certain properties within parallel channels of a porous host structure. Many properties require specific, intra-channel interactions between the guests (e.g., 1f–h, 1j–l); other properties arise from single entities alone, but may depend upon their relative orientation within the channels (e.g., 1f). For details, see main text Chap. 4.

materials as templates or reaction vessels in the construction of porous biomimetic materials — beautiful and diverse inorganic skeletal structures, akin to those produced in nature by the processes of biomineralisation. Readers are referred to key reviews on this subject.² The idea of employing organic molecules to form porous nanoscopic/mesoscopic architectures is an attractive one for many reasons, not least the following:

- Molecular chemistry permits great scope for structural diversification, both at the molecular level and at the *supramolecular* level, *i.e.* the level where we can control the assembly of pre-organised building blocks either in solution or in the solid-state.³
- The inclusion and release of guest molecules in organic hosts is often a much more facile process than the corresponding one in zeolites, since the former structures are generally assembled by a co-crystallisation of the host and guest species, and disassembled by solvation in an appropriate solvent. On the contrary, loaded zeolites rely on the processes of diffusion, which often require the application of heat or pressure to accept/reject guest molecules.

In addition to the above, the use of channel-type porous architectures is an attractive way of probing complex properties of included molecules, since the properties may be reduced to only one dimension. In this account we will give a flavour of what particular properties can be achieved from the crystallisation of organic nanoporous materials, by reviewing key results from the literature in recent years, as well as proposing some possible applications which have not yet been demonstrated. We will show that these concepts require a multi-disciplinary approach and we hope that they stimulate others to enter this developing area of research. First, however, we will give an overview of the supramolecular architectures which have already been studied, and the problems inherent in creating porous organic materials.

2 Structural aspects of organic nanoporous materials

The crystallisation of supramolecular structures with pre-defined geometries and properties is a difficult task; the construction of porous architectures based on molecular building-blocks is even more arduous. In the late 1960s, Kitaigorodsky⁴ predicted that molecules will pack together in the most efficient, energy-saving manner possible, similar to close-packed spheres. Using simple geometrical models, he correctly predicted the structures of many simple organic molecules. Porous molecular structures held together by some directional (*e.g.* hydrogen bonding) and weak, non-directional van der Waals (vdW) interactions are therefore intrinsically unstable, and many efforts are currently being made to circumvent this difficulty by an appropriate choice of host and guest components.

2.1 Inclusion compounds

Early examples of nanoporous molecular structures are inclusion compounds. Such systems consist of guest species (typically solvent molecules) spatially confined within a host structure, in channels, layers or cavities.⁵ Such two component crystals aggregate spontaneously if $\Delta G_f < 0$ (free energy of crystal formation), with specific guest or solvent molecules acting as *templating* agents for the construction of the porous geometry. Many beautiful architectures containing separate or interconnected channels or isolated cages are to be found in the literature.⁵ Representative examples of channel-forming inclusion hosts which are the focus of contemporary studies include perhydrotriphenylene (PHTP) (Figs. 2, 3)⁶ urea and thiourea,⁷

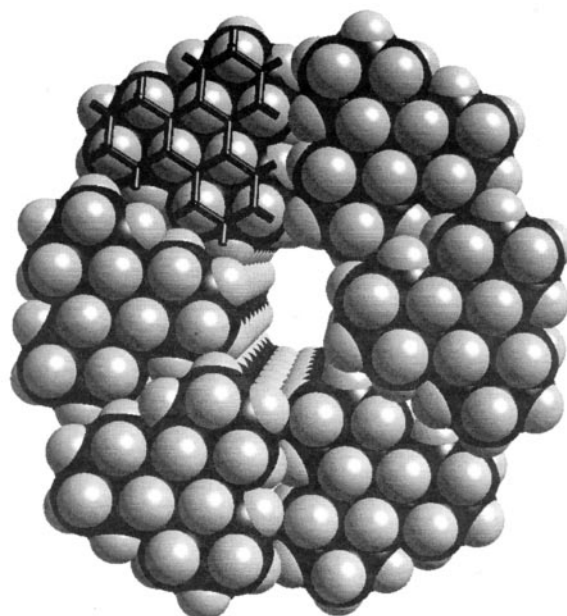


Fig. 2 Corey–Pauling–Koltan (CPK) model of the honeycomb, channel-type architecture of a perhydrotriphenylene (PHTP) inclusion compound.^{6a,9} The guest molecules have been omitted for the sake of clarity. Hexagonal, orthorhombic or monoclinic symmetries of the channels are observed, depending on the shape of the included guest molecules. A large number of different guest molecules can be included into the PHTP inclusion architecture.

and the α -, β - and γ -cyclodextrins — cyclic, toroid-shaped oligomers of glucose containing six, seven and eight glucoside

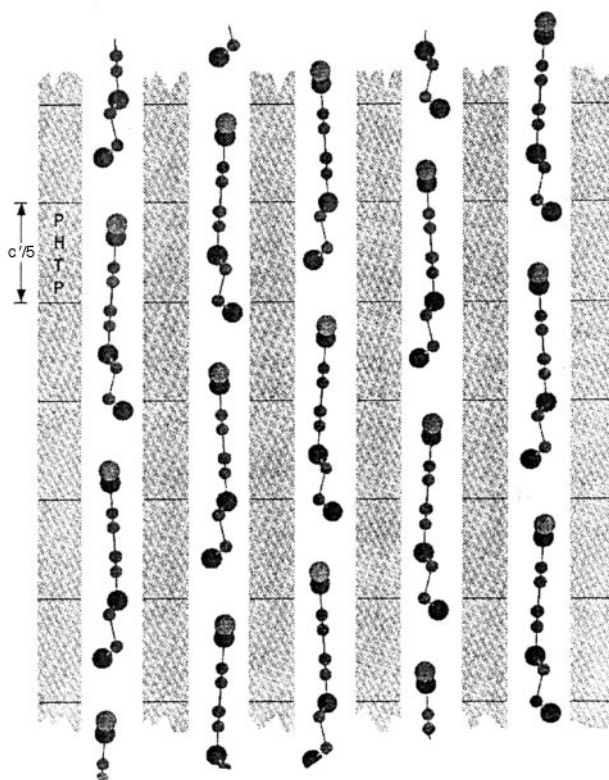


Fig. 3 Model view of the translational disorder prevalent in channel-type inclusion (see also Fig. 1a) compounds. The one-dimensional order along the *c*-axis (*i.e.*, along the channels) gives rise to characteristic X-ray diffraction consisting of diffuse lines superimposed on Bragg reflections which result from long-range ordering of host molecules. For the particular case shown, each guest molecule (in this case, 1-(4-nitrophenyl)piperazine) along the channels is associated with 2.5 PHTP host molecules, and is co-crystallising as a commensurate host–guest lattice (*i.e.*, one in which the ratio of 1-D ordering to the period of the stacking of host molecules, is an integer). For further details, see König *et al.*⁹

units, respectively.⁸ Most of these frameworks, however, can not survive without the presence of the templating guests, and undergo structural deformation or collapse when any attempt is made to remove or exchange guest components.⁷

Although such materials are not truly porous in the sense outlined in our opening statement, they nevertheless feature structural facets of porous materials. For example, in many cases the included guest molecules within a rigid, well-defined host structure have a certain degree of *intra*-channel translational as well as rotational freedom; additionally, there is often significant positional disorder with respect to guests located within different channels. Thus, providing a complete X-ray structural description of the crystal, including the disordered guest sub-lattice, is rare (Figs. 1a, 3).⁹ Materials applications of organic inclusion compounds are as diverse as those of their inorganic counterparts, and we will address some of these below.

2.2 Crystal engineering of porous molecular organic materials

Until recent times, the discovery of inclusion-forming properties for a molecular crystal was a hit-and-miss affair. Clearly, if materials chemists are to exercise proper control over the synthesis of molecular-based materials with tailor-made properties, then it is essential that they have at least a grasp of the

processes and rules of self-assembly at the molecular level.³ In this respect, great effort has been exerted over the last two decades in an attempt to address this fundamental problem. From these efforts has sprung a relatively new sub-branch of solid-state structural chemistry termed ‘Crystal Engineering’¹⁰ or ‘Molecular Tectonics’.¹¹ Crystal engineers attempt to predict and control the solid-state structures of molecular organic and organometallic materials by analysing the shapes and functionalities present in the component molecules (‘molecular building-blocks’ or ‘tectons’ and ‘coordination centres’) (Fig. 4). By recognising certain key intermolecular interactions (‘supramolecular synthons’),¹² whose strengths and geometrical arrangements remain fairly constant throughout a large number of published crystal structures, then it has been possible to predict at least the main topological features of the crystal packing of many simple building blocks. This is especially true for coordination compounds and molecules which are capable of classical hydrogen bonding — a relatively strong, highly directional intermolecular interaction which has been the subject of intensive investigations.^{10,11,13}

One of the first attempts at deliberately engineering a porous organic architecture comes from Ermer.¹⁴ 2,6-Dimethylideneadamantane-1,3,5,7-tetracarboxylic acid forms a hollow, superdiamond network structure, held together by pairs of hydrogen bonds. The voids in the structure, however, are filled by four other identical, interpenetrating networks, to give a fivefold-diamond architecture. Such interpenetration of two or more sub-

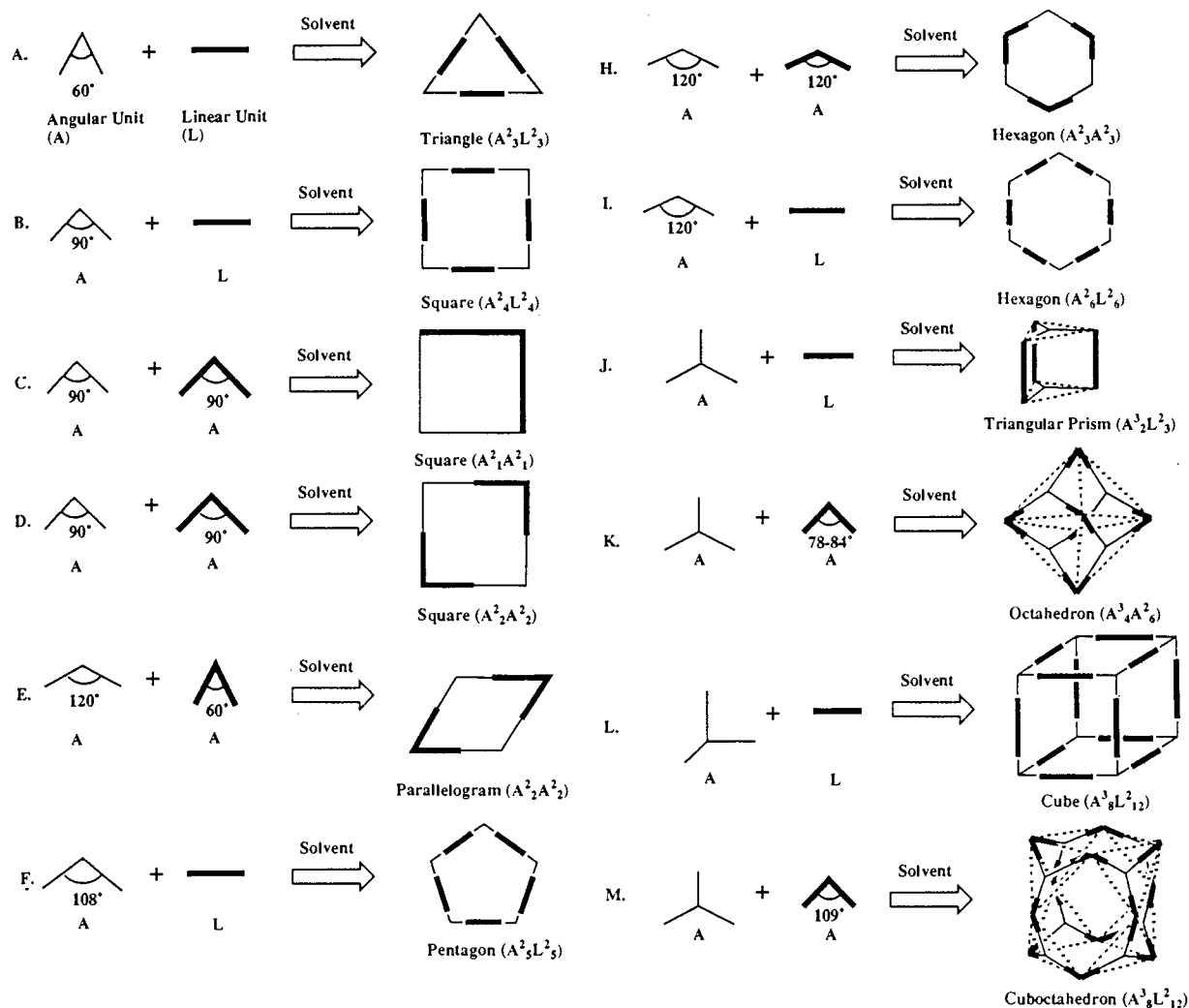


Fig. 4 An outlay of the supramolecular ‘meccano’, i.e. construction elements used in the design of metal–ligand based supramolecular architectures: ‘With these simple governing principles and the large diverse number of potential multidentate ligands and transition metals it is possible to assemble all manner of polygons and polyhedra with tremendous variations in geometric features’ (from Stang *et al.*¹⁷). Similar structures can also be constructed by using organic molecules which form construction motifs by the specific interactions of various non-covalent bonds (e.g., hydrogen bonding).^{11,12} Reprinted with permission from P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502. Copyright 1997 American Chemical Society.

lattices, driven by the close-packing requirements alluded to above, is a frequently encountered problem in the design of porous materials. By modulating the periphery of the adamantane building-block by introducing two oxo-moieties, Ermer and Lindenberg reduced interpenetration to only two networks, giving a superstructure with a propensity for including a variety of solvent molecules in the various cavities.

One of the most striking, recent examples of a tailor-made, all-organic porous structure emanates from the group of Ward *et al.*¹⁵ The Minnesota group took advantage of the two-dimensional, network-forming ability of guanidinium ions hydrogen-bonded to organic sulfonate anions, in which every cation is bonded *via* three pairs of hydrogen bonds to three anions and *vice versa*. Replacing the monosulfonate by disulfonate ions leads to pillared, nanoporous galleries (Fig. 5)

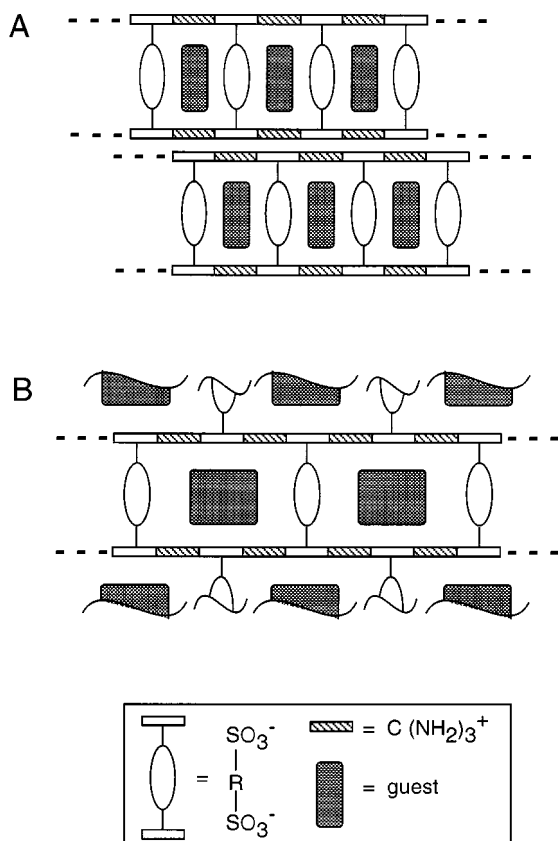


Fig. 5 Schematic representation of the molecular scaffolding formed by guanidinium organodisulfates (from Ward *et al.*)¹⁵ Dashed lines represent hydrogen-bonded sheets. A: bilayer structure; B: brick-like motif of a continuous, single-layer structure. Reproduced with permission from *Science*, 1997, **276**, 575. Copyright 1997 American Association for the Advancement of Science.

whose height can be varied by changing the length of the spacer-group of the disulfonate anions; increasing their widths leads to continuous layer stacking. The 1-D channels formed by these galleries are filled with solvent molecules, and because of the remarkable flexibility and strength of the hydrogen-bonded network, they can adapt in size to accommodate different guest molecules.

2.3 Coordination compounds

Other approaches to the production of robust, nanoporous materials have taken advantage of the spatially well-defined and pre-organised geometries of organometallic compounds. The advantages of employing the coordinative metal–ligand bond to construct porous supramolecular architectures are several fold: (i) it pre-organises in space ligands which may contain further functionalities capable of intermolecular bonding; (ii) both the

coordination stereogeometry around the metal centre and the extramolecular bonding capacity may be tuned by varying the metal and/or its oxidation state. These crystal engineering aspects of organometallic architectures have been reviewed recently.¹⁶ The mainly organic periphery around the metal centres, however, means that these metal-containing molecules generally pack in a manner similar to purely organic compounds. The predictable nature and geometric versatility of coordination chemistry helps greatly in the design of open-framework supramolecular structures, since large, metallocyclic polygons and polyhedra can in theory be constructed by simple consideration of the shape and symmetry required in the desired supramolecular structure (Fig. 4).¹⁷ The structure can then be broken down into its simpler components which consist of varying ratios of metal centres and ligands which vary in their chelating power (bidentate, tridentate, *etc.*) and shape (linear, bent).

With these approaches, it has been possible to design several nanoporous organometallic materials with significantly large pore volumes. Elegant examples come from the groups of Stang¹⁷ and Yaghi.¹⁸ The latter reports the hydrothermal synthesis of $\text{Cu}(4,4'\text{-bpy})_{1.5}\cdot\text{NO}_3(\text{H}_2\text{O})_{1.25}$ (where bpy = 4,4'-bipyridyl) which consists of an extended cationic framework of trigonal planar Cu(I) centres linked together by rod-like 4,4'-bpy ligands to form six porous and identical interpenetrated networks (Fig. 6). In this case, the extent of interpenetration is

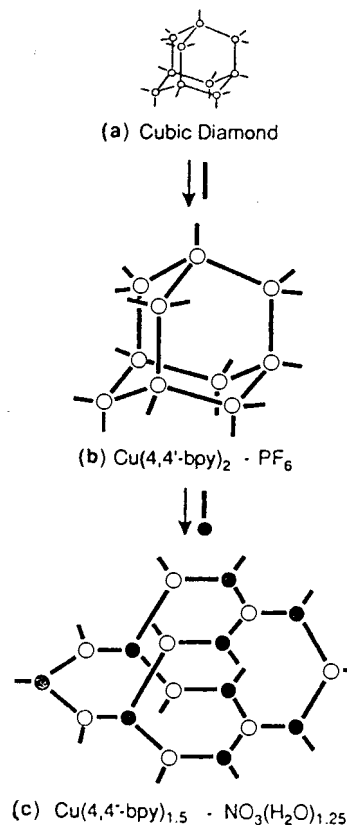


Fig. 6 An illustration of the structural analogy between the structure of diamond and two $\text{Cu}(4,4'\text{-bpy})$ solids forming a six fold interpenetrating diamond-like network leaving behind channels of about $6 \times 6 \text{ \AA}$ (from Yaghi *et al.*¹⁸). Reprinted with permission from O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1995, **117**, 10401. Copyright 1995 American Chemical Society.

low, and therefore extended, rectangular channels pervade the structure. The nitrate ions necessarily present within the channels (along with water molecules) can even be exchanged with other simple ions. This example shows that whilst it is possible to exert significant control over the supramolecular architecture, it is still very difficult to regulate how the individual supermolecules pack in the solid state, depending as they do on the packing efficiency and weaker vdW inter-

molecular interactions of the ligands. Stang and co-workers combined 4,4'-bpy ligands with Pt- or Pd-bisphosphane complexes to promote the self-assembly of planar molecular squares.¹⁷ Here, the cationic molecular squares stack in register in a non-interpenetrated manner to form long channel-like cavities (Fig. 7). However, it is difficult to remove the solvent of crystallisation from the channels. Despite the various shortcomings of these pioneering attempts, the significant advantages of the organometallic approach to self-assembling nanoporous architectures will ensure that it remains at the forefront of future efforts.

2.4 Carbon and molecular nanotubes

One class of porous materials which stands somewhat apart from the preceding classifications is that of *carbon nanotubes*. Whilst these structures are hardly engineered in the sense outlined above, they are probably closer to achieving real-world utilisation than most of the foregoing organic materials; as such, they merit a discussion in their own right. Carbon nanotubes are quite unusual but fascinating structures — a structural sub-class of the third allotrope of carbon, namely the fullerenes — first discovered as a by-product of fullerene research by Iijima¹⁹ in 1991. Since then, they have generated a surge of intensive research because of their diverse properties and considerable potential in a variety of possible applications.²⁰ Carbon nanotubes were originally formed on the carbon electrode of an arc-discharge apparatus used in the mass production of C₆₀ and C₇₀. These discrete particles are structurally stable, hollow entities composed of sheets of graphite (individual layers are commonly termed *graphene* sheets), rolled up in a helical fashion, and can be closed at both ends with capping domes of mainly fused pentagonal rings (Fig. 8). The tubes may be single- or multi-walled, scroll-like structures; inner diameters range from *ca.* 2 nm for the inner tubes of multi-walled species, to *ca.* 30 nm for the larger species, and they are typically 1 μm or even longer in length, giving them an extremely high aspect ratio.²⁰

The high structural anisotropy of carbon nanotubes, coupled with their very good stiffness-to-weight ratio and relatively low number of defects, make them probably the strongest fibre known to date. Additionally, their highly conductive structure is being exploited in the production of probe tips for scanning microscopy techniques. Huge advances in the bulk production and purification of the various nanotubes, especially of the highly desirable uniform, single-walled variety is considered

important because of the possibility of assembling carbon nanotubes as more complex structures.²¹ Whilst we have already stated that the hollow tubes are generally closed at either end in the as-obtained state, the more reactive nature of the pentagonal rings which make up the majority of the capping domes permits them to be opened up under oxidative conditions and filled with various guests, either by diffusion or by a strong capillary action. For example, by oxidising the tips in the presence of lead, Iijima was able to partly fill nanotubes with lead, opening up the possibility of synthesising conducting nanowires.¹⁹

Closely related to the carbon nanotubes are *molecular nanotubular species*. The difference between a molecular nanotube and a simple channel-type inclusion compound is somewhat subjective. For the present discussion we define a molecular nanotube as a macromolecular entity made up of one (*e.g.* a polymer) or more (strongly-interacting stacked sub-units) constituent molecules, capable in principle of existing as a discrete monotubular particle showing a high aspect ratio, *i.e.* its walls are not shared with other tubes. The individual tubes may exist either alone or in aggregates in the solid-state, analogous to the multi- and single-walled carbon nanotubes, respectively. This rules out the extended, 3-D network structures and many of the inclusion compounds referred to earlier. Again, the advantages of a molecular approach to such a tubular structure stem from 'tailorability' — in principle, the diameter of the tube, and the chemical nature of its inner and outer peripheries, can be adapted according to specific needs (for example, one may wish to make one surface hydrophilic, and the other one hydrophobic).

Ghadiri²² has pointed out that there are actually only a few ways in which one can construct a molecular nanotube. One method is to apply the same approach used for carbon nanotubes, namely to take a macromolecular, sheet-like structure which self-assembles under certain conditions into a tube-like structure *via* some sort of intramolecular coupling process (this could be either be the formation of covalent bonds, or by supramolecular interactions). To the best of our knowledge, no such approach has yet been described in practice. The most versatile and feasible approach to date, however, has been to construct the tube from the self-assembled stacking of hollow, disk-like or toroidal sub-units which maintain the tube structure *via* strong, intermolecular (intra-tube) non-covalent interactions, or by being subsequently cross-linked in a polymerisation reaction.

Representative sub-units which have been employed successfully in these strategies are cyclic oligopeptide structures and

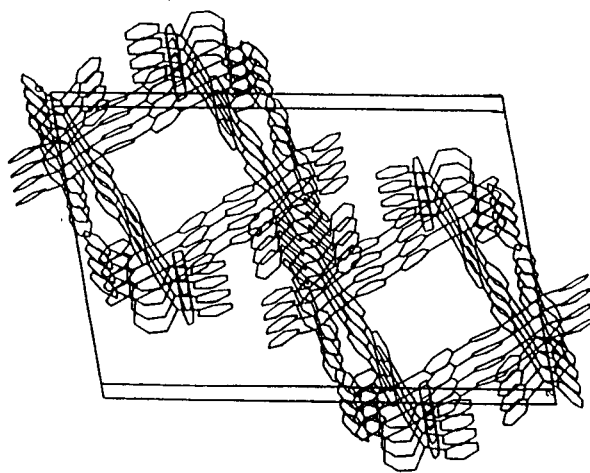
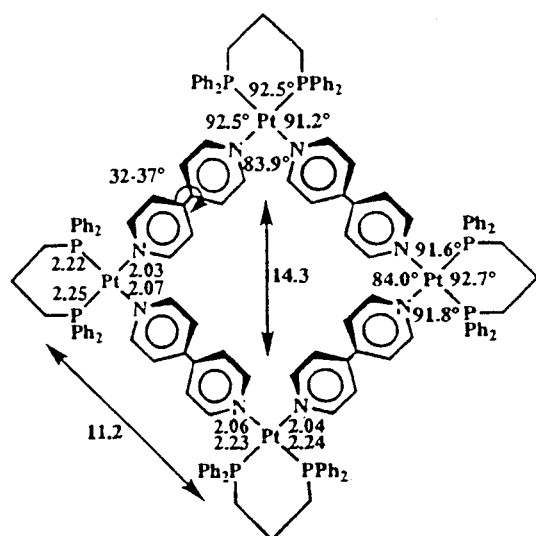


Fig. 7 One of many examples of solid-state packing representing a square (see also Fig. 4). Channels are filled with solvent molecules (from Stang *et al.*¹⁷). Reprinted with permission from P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502. Copyright 1997 American Chemical Society.

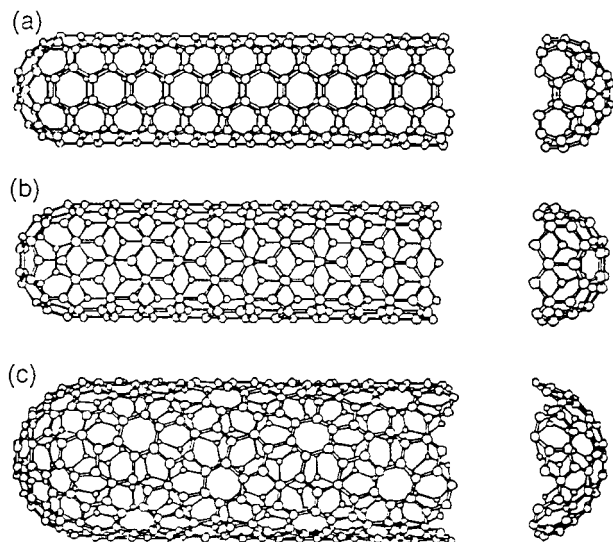


Fig. 8 A representation of different types of single-walled carbon nanotubes: (a) arm-chair configuration; (b) zig-zig configuration; (c) chiral configuration. Reprinted from *Carbon*, 33, M. S. Dresselhaus, G. Dresselhaus and R. Saito, page 883, Copyright 1995, with permission from Elsevier Science.

the various cyclodextrins, respectively. In the former case, for example, cyclic peptides of alternating D- and L-amino acids were predicted as long ago as 1974 by De Santis *et al.*²³ to self-assemble into tubular structures. These speculations fuelled more recent successful efforts by the groups of Ghadiri²² and Lorenzi²⁴ to produce such structures in the laboratory. It was found that certain alternating oligopeptides undergo self-assembly into discrete, extended stacks of conformationally flat peptide rings, *via* backbone–backbone hydrogen-bonding interactions reminiscent of the β -sheet-like arrangement found in many proteins (Fig. 9).^{22,24} Pore sizes range from *ca.* 7 Å for one octapeptide to *ca.* 13 Å for the dodecapeptide cyclo[-(L-Gln-D-Ala-L-Glu-D-Ala)₃]. These structures have already proven to be potentially useful as artificial transmembrane channels, permitting the efficient transport of ions such as K⁺ and Na⁺, and also hydrophilic molecules such as glucose, across the hydrophobic bulk of the lipid bilayers.^{22a} Some of the structures can be repeatedly dehydrated and rehydrated without any significant losses in structural integrity. It should be possible in principle to independently tune the chemical composition of the inner and outer walls of a molecular tube, as well as its pore size.

In a similar manner, Harada *et al.*²⁵ have exploited the ability of α -cyclodextrin molecules⁸ to be threaded onto a polyethylene glycol (PEG) chain, where they stack in a close-packed fashion. The cyclodextrin (CD) rings of these ‘polyrotaxanes’ may then be coupled with epichlorohydrin to form a polymeric tube along the PEG chain. Removal of ‘stopper’ groups from the PEG chain permits its removal from the core of the CD polymer, yielding porous polymer tubes *ca.* 0.5–0.9 nm in diameter and with average molecular masses of *ca.* 17 000 (approx. 14 stacked, polymerised α -CD units) (Fig. 10).²⁵ Other approaches to molecular nanotubes, such as polymerisation of labile, non-lamellar lipid assemblies, columnar-stacking of disc-shaped, liquid crystalline molecules (discotic mesophases) and helical-coiling of hydrocarbon oligomers, have also been described in the literature.²⁶

3 Applications of channel-type nanoporous architectures

It can be seen from the above survey that there is a very diverse range of organic and organometallic architectures which can

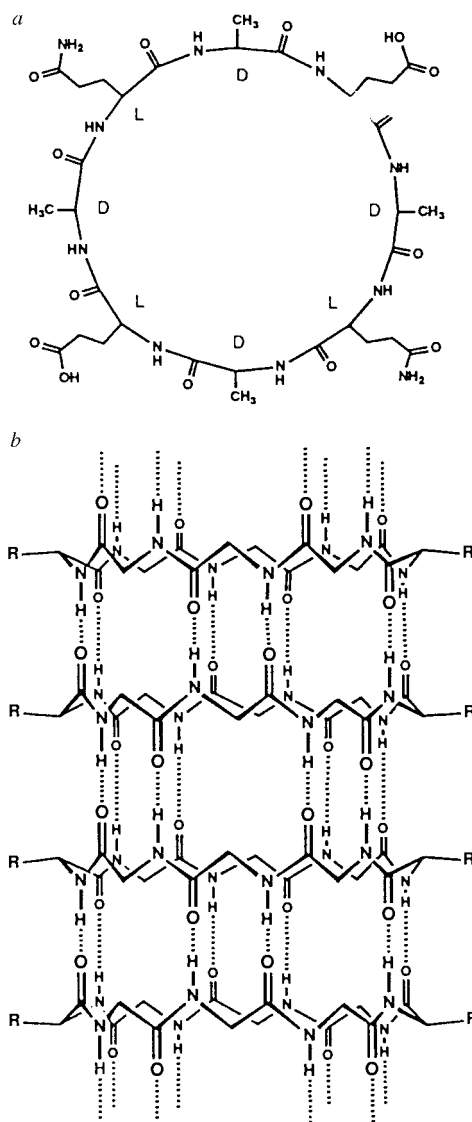


Fig. 9 An illustration of the self-assembled peptide subunit cyclo[-(D-Ala-Glu-D-Ala-Gln)₂] stacking into a tubular configuration (from Ghadiri *et al.*^{22b}). (a) Molecular brick; (b) side view showing the strong hydrogen-bonding responsible for the tubular architecture. Reproduced with permission from *Nature*, 1993, 366, 324. <http://www.nature.com/>. Copyright 1999 MacMillan.

many ways be described as nanoporous, or at least have many of the structural features of channel-type nanoporous materials. We have already touched briefly on some of the interesting *physical properties*^{1d} and potential applications (Fig. 1) which one may expect from the interaction of various guest molecules or ions within channel-type cavities. In the following section we will delve deeper into this aspect of nanoporous organic materials. In particular we will put an emphasis on cases where one can take advantage of a *parallel alignment* of functional molecules which form laterally well-separated chains. Following the schematic views of Fig. 1, we address these properties below.

3.1 Isomer separation and topochemical reactions

Probably the most widespread and long-lived practical use of porous organic frameworks has been the separation of mixtures of different molecules. Inclusion compounds can form when there is a reasonably tight fit between host and guest, and there is also topological compatibility between components (the so-called ‘lock and key’ principle, introduced by E. Fischer in

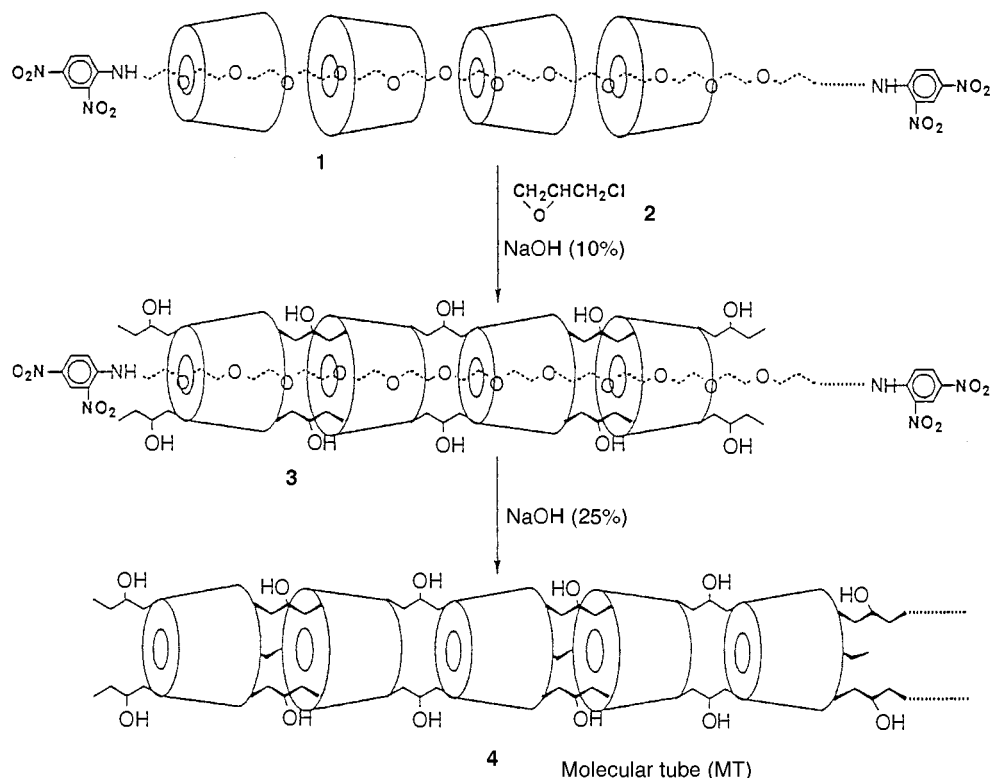


Fig. 10 Synthesis of a molecular tube based on α -cyclodextrin from polyrotaxane (after Harada *et al.*²⁵). Reproduced by permission from *Nature*, 1993, **364**, 510. [Http://www.nature.com/](http://www.nature.com/). Copyright 1999 MacMillan.

1894). Consequently, an element of discrimination can be introduced in a system containing a suitable host and a mixture of potential guests of varying shapes and sizes, providing the host lattice is of a certain flexibility — too hard a lattice will reduce its generality of application; too soft a lattice will lead to significantly reduced discrimination, as the host will adapt itself to accommodate all and sundry. Urea⁵ has been employed successfully in this respect by industrial and research chemists; the narrow (*ca.* 4–5 Å) diameter of the channels formed by this compound lead to the selective inclusion of straight chain hydrocarbons over their small-branched analogues.⁷ This discrimination on the basis of shape and size offers a means of separating compounds which differ very little in electronic functionality and are not likely to be separated by more classical laboratory techniques (*e.g.* distillation or chromatography).

Selective introduction of guests into a porous lattice is not the end of the story concerning the exploitation of the size- and shape-selectiveness of the cavity: it is also possible to do chemistry within the cavities. In particular, the novel environment of the host cavities permits: (i) the stable isolation of reactive species formed *in situ*; (ii) the possibility of performing intra-cavity stereoselective reactions. An elegant example of the former is the generation by Cram and Maverick²⁷ of cyclobutadiene within the porous cavity of a hemicarcerand — a closed-surface, spherical but hollow organic host with rigid walls which enforces the incarceration of included guests, but also contains portals connecting the inner cavity with the outer environment. Thus, photoirradiation of solutions of α -pyrone and hemicarcerand led to the generation of single molecules of cyclobutadiene within each cavity (thereby stabilising the diene by preventing dimerisation), with selective ejection of CO₂ byproduct from the cavity *via* the portals.²⁷

An illustration of stereoselective reactions within porous architectures comes from a series of publications by Aoyama *et al.*²⁸ Anthracene-bis(resorcinol) derivatives form porous, hydrogen-bonded networks. The large cavities formed by these materials are capable of selective crystalline-phase guest addition, removal and exchange. The solid-state reaction of a catalytic amount of this host with cyclohexadiene and acrolein

leads to the corresponding Diels–Alder adduct with high (95%) *endo* selectivity and with a considerable enhancement in the reaction rate (*cf.* the liquid-phase reaction). The reactions are all the more remarkable because they are performed completely in the solid-state, and involve pre-formed, porous, guest-free organic hosts which in some cases have catalytic activity. (The topic of organic solid-state chemistry has been reviewed recently).^{29,30} With these porous solid-state systems, one must investigate carefully whether the catalytic activity derives from deep within the bulk itself or results merely from a surface phenomenon. The effect of pulverised and non-pulverised host samples on the reaction rate may provide a simple check, since the former would not be expected to increase the catalytic activity of the system if the activity is a bulk phenomenon.²⁸

3.2 Enantioselective separations and reactions

If a porous structure is capable of forming chiral cavities, then there exists the possibility of discriminating between the enantiomers of a racemic mixture, leading to enantiomer enrichment or even resolution. To form a chiral cavity, the host molecule must either be chiral itself or must crystallise in a chiral space group. The most well-studied examples of the former include the cyclodextrins, tri-*o*-thymotide and various bile acids;³¹ the urea molecule is the best example of the latter.^{7,31} In addition to chiral cavities, the requirements for enantiomer discrimination once again include a sufficiently rigid host-lattice, and topological compatibility of guest and host. Both temperature and the chemical functionality of the guest can play significant roles. For the chiral hosts described above, enantiomer resolution experiments have led in general to low to moderate levels of enrichment, with a few exceptions.³¹

Of considerable interest to synthetic chemists is the use of porous crystals to effect asymmetric syntheses. Many examples involve the pre-formation of the crystalline ‘inclusion complex’ of the prochiral substrate, followed by exposure to an attacking

reagent in gaseous or liquid form. However, several completely solid-state enantioselective additions, oxidations and substitutions have been described in the literature.²⁹ Once reacted, the inclusion complex is simply dissolved in aqueous solution and the products extracted with organic solvent and purified using standard techniques. The various cyclodextrins have provided perhaps the biggest playground for such enantioselective heterogeneous and homogeneous reactions; the topic is comprehensively covered in the recent review by Takahashi (in ref. 7, p. 2013) and briefly elsewhere.³¹ In this respect, the work by Tanaka and Sakuraba merits special attention.³² These workers have performed a variety of halogenations and hydrohalogenation of prochiral unfunctionalised olefins and α,β -unsaturated acids in cyclodextrins, to produce optically active products with a broad range of optical purity. The most spectacular reaction thus far is the 100% enantioselective chlorination of methacrylic acid in α -CD. Hydrogen bonding between the primary or secondary hydroxy groups of the CD and the various substrates appears to play an important role in anchoring the substrates within the CD cavity in a precise manner which enhances enantiofacial-selective attack by the incoming reagent (Cl_2 or HBr).^{8,32} A wide range of enantioselective oxidations and reductions in CD cavities have also been reported.⁸

4 Properties requiring a parallel alignment of close-packed guests

Confining close-packed, functionalised molecules within parallel-aligned porous channels permits the possibility of addressing a number of interesting solid-state properties, especially when the guests themselves are aligned co-parallel within the cavities. Several of the most important applications are summarised schematically in Fig. 1. The properties may be grouped into four different areas: (i) optical effects; (ii) non-linear optical (NLO) effects; (iii) transport of charge carriers along the channels; and (iv) magnetic phenomena.

4.1 Single molecule spectroscopy and hole-burning

The electronic spectra of organic compounds in solution or in the solid-state are characterised by poorly resolved, inhomogeneously broadened bands. Alignment of such materials within parallel porous channels can provide spectroscopists with an environment for studying the electronic transition moments of the included guests by narrow-band laser spectroscopy, since: (i) the chromophores are held in a strict uniaxial orientation, thus permitting precise measurement of their transition dipole moments in specific directions (Fig. 1c); and (ii) if the chromophores are greatly diluted in the channel with non-chromophoric co-guests, then there exists the possibility of performing single molecule spectroscopy (SMS)³³ — the study of the fluorescence excitation line of a single chromophore in a low temperature solid. Since inhomogeneous contributions and ensemble averaging are reduced or absent, the technique is a high resolution optical probe of the local nano-environment and information on the dynamic processes taking place on a time-scale from picoseconds to days can be obtained. The related technique of hole-burning (Fig. 1e)³³ involves the irradiation of the material with an intense laser source, to excite selectively a small sub-set of molecules in a unique nano-environment, thus ‘burning a hole’ in the inhomogeneously-broadened band. Photochromic dye molecules (*e.g.* *cis*-retinal, azobenzenes, and other aromatic systems) which can be site-selectively ‘switched’ between slightly different spectroscopic states using this technique have been applied in the field of optical data storage.

4.2 Photonic energy transfer

In addition to mediating the transfer of molecules and ions through cavities, porous structures can also facilitate the transfer of photonic energy between close-packed, spatially confined guest species. One prominent exploitation of this phenomenon is in the development of *artificial antennae*, which mimic the light-harvesting and utilisation apparatus found in natural photosynthesis and involve the extremely fast migration of energy from source to the reaction centre. Calzaferri and co-workers³⁴ have demonstrated this energy migration between dye molecules loaded in channel-type inorganic zeolites (Fig. 11). Light is absorbed by a strongly luminescent chromophore

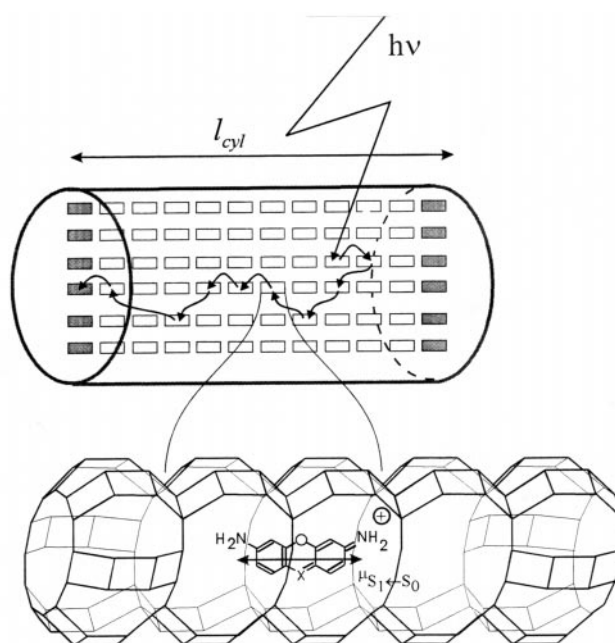


Fig. 11 Schematic view of an artificial antenna mimicking part of the process of light harvesting. Here, molecules are included in the channels of an inorganic zeolite (from Calzaferri *et al.*³⁴). Reprinted with permission from N. Gfeller, S. Megelski and G. Calzaferri, *J. Phys. Chem. B*, 1999, **103**, 1250. Copyright 1999 American Chemical Society.

which can then relax, re-irradiating the energy which migrates to a neighbouring acceptor dye molecule which itself absorbs and re-emits the energy and so forth. The role of the porous, channel-type zeolite is several-fold: (i) it prevents dimerisation of the dye molecules which tend to form aggregates which inhibit energy transfer; (ii) it imposes a well-defined anisotropic, close-packed organisation of the guest molecules whose electronic transition dipole moments lie parallel to and along the channel axes. This optimised geometrical/electronic arrangement permits extremely fast intra-cavity photonic energy transfer (based on the so-called Förster mechanism) between dye molecules (Fig. 1j).

4.3 Laser crystals

All-organic, solid-state lasers have not yet reached real-world applications, although stimulated emission has been observed in polymer thin films and in some organic crystals.³⁵ The requirements for laser action in the latter are severe: (i) the active component molecules aligned parallel should be strongly fluorescent at an appropriate live time; (ii) crystals must have suitable dimensions to act as optical resonators, be of optical quality and have parallel, smooth end-faces; (iii) thermal stability is necessary to withstand the high input pump energy necessary to stimulate laser action.³⁵ Given these requirements, then the use of porous, channel-type materials containing

elongated organic dye molecules seems a possible approach to the demonstration of an all-organic solid-state laser, since several of the demands are necessarily already met (Fig. 1i). Encouragement in this area comes once again from dye-loaded inorganic zeolites.¹ Schüth *et al.*³⁶ have aligned an elongated, highly-polarisable pyridinium perchlorate derivative within the parallel channels of the molecular sieve AlPO₄-5. When excited with a frequency-doubled Nd:YAG pulse laser (532 nm), the needle-like crystals (up to 500 μm in length) demonstrated laser action (observed by narrow spikes in the fluorescence band above a pump intensity of 0.5 MW cm⁻²).

4.4 Optimized electro-optic crystals

Non-linear optical (NLO) phenomena result from the interaction of the electric field of a high-intensity light source with polarisable electrons in a dielectric material, bringing about a redistribution of electrons.³⁰ At the molecular level, the *extent* of redistribution (the electrical polarisation) is measured by the dipole moment (ground state) and the ease of redistribution by the molecular polarizability α , the first- and higher-order hyperpolarizabilities β , γ , respectively. Depending on the particular NLO effect to be used, an effective coefficient must be maximised in crystals to produce a large NLO response. Third rank tensorial properties such as second harmonic generation (SHG) — the doubling of the frequency of an incident laser beam — and the linear electro-optic (EO) effect — the electric-field-induced change of the refractive index of a material — are among some of the most widely studied and technologically useful NLO phenomena. An essential condition for both processes is that the molecular hyperpolarizability β_{\max} and the bulk second-order hyperpolarizability and electro-optic coefficients (geometrically related to β_{\max}) have finite values, and this is satisfied when the molecules pack in a non-centrosymmetric manner. Thus highly polarisable, rod-like dipolar molecules which crystallise in a polar fashion are widely exploited. One problem with such molecules is their tendency to pack head-to-tail to minimise electrostatic repulsions, giving rise to a *centrosymmetric* material. The use of porous host materials with non-centrosymmetric structures is one method of aligning the NLO-active guest molecules in a polar fashion in the bulk state (Figs. 1f, 12). Zeolites such as AlPO₄-5 have been employed successfully with small dipolar organic molecules which pack centrosymmetrically in their native crystal structure.^{1b,c} Inclusion formation with channel-type organic host molecules³⁷ such as PHTP^{1d,6,9} and thiourea⁷ has proved to be a highly successful approach in generating polar materials. Whilst such channel-forming hosts are not effective for SHG (an angle of *ca.* 55° between the molecular dipolar axis and the polar crystal axis is necessary for an optimum phase matched SHG response), they are suitable for the optimisation of the *linear EO effect*, which requires perfect co-parallel alignment of the individual molecular hyperpolarizability β_{\max} components with the charge transfer directions within the molecules, which themselves must pack in a parallel non-centrosymmetric fashion.³⁸

4.5 1-D Photoconduction, photorefraction and rectification

Polarisable molecules which are close-packed and aligned parallel within channel-type porous materials are suitable systems to study the phenomenon of 1-D photoconduction (Fig. 1g). Moreover, if the molecules have large β_{\max} values and are aligned in a polar fashion (thus permitting the possibility of electronic interaction between the chromophores along the channels) then the materials may exhibit the phenomenon of photorefraction — an alteration of the refractive index of a material when exposed to a spatially inhomogeneous light

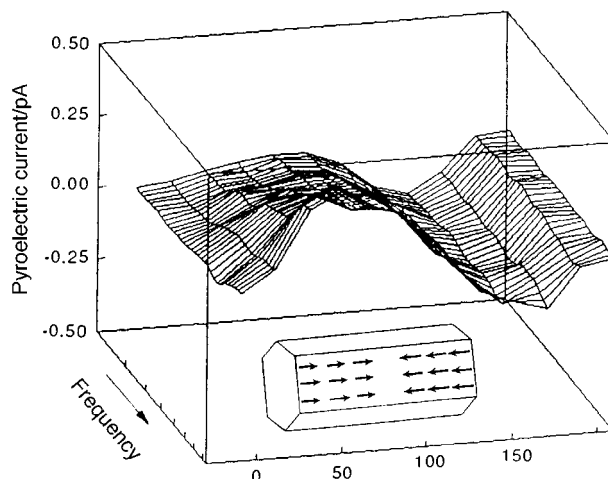


Fig. 12 Three-dimensional graph showing that the orientations of dipolar guests (*p*-nitroaniline) diffused into the zeolite AlPO₄-5 vary as a function of their position along the long axis of the crystal.⁴⁶ The orientations are determined by the pyroelectric response of the crystal to an incident laser beam, a response which results from a change in the density of the compensating charges at the surface due to the localised heating effect of the laser beam. The intensity of the incident beam may be modulated in order to probe the crystal at different depths. The technique, termed *scanning pyroelectric microscopy* (SPEM), reveals the overall bipolar nature of the crystal. For further details, see Caro *et al.*⁴⁶ Reprinted with permission from J. Caro, F. Marlow and M. Wübbenhorst, *Adv. Mater.*, 1994, **6**, 413. Copyright 1994 Wiley-VCH.

source.^{39a} Crystalline organic photorefractive materials were discovered only as recently as 1990 by Sutter *et al.*⁴⁰ and have potential applications in the fields of high-density optical storage and image-processing techniques.³⁹

Because of the polar alignment of molecules within the porous architecture, there is another interesting property which can be exploited here, namely electrical rectification. When a photocurrent is generated by illumination of a suitable material, a difference in the current should occur with respect to the polarity of the applied electrical potential for measuring the current. Such rectification properties have so far only been observed for Langmuir–Blodgett and other films. Recent experiments on PHTP inclusion compounds have provided a first example of rectification in a bulk organic crystal.^{39b}

4.6 Electroluminescent nanotube crystals

Electroluminescence — the emission of light when generated by the flow of an electric current — is a phenomenon exploited in the increasingly rapid development of polymeric light-emitting devices (LEDs).⁴¹ The principle operating mechanism in an LED is as follows: a highly fluorescent material is sandwiched between two plate electrodes and a voltage applied. Holes (p) and electrons (n) are introduced into the emitting material in the vicinity of the anode and cathode (Fig. 1h), respectively. These may then undergo migration through the active material under the influence of the applied electric field. If an electron and hole meet, they may combine to form a triplet or a singlet excited state, and it is the latter which may relax back to the ground state with the emission of light. Clearly in a polymer film such occurrences are likely to be random and fairly infrequent, given the typically large conduction pathways envisaged for such polymer devices. By utilising porous, channel-type materials containing light-emitting and electronically interacting guests, it may be possible to confer a greater degree of order on such events since the pathways open for n/p migration–recombination are limited essentially to only one dimension. Our group is presently exploring the possibility of engineering such a device by growing thin films of channel-type inclusion compounds containing fluorescent guest molecules.

4.7 Supramolecular nanowires

We have already referred earlier to Iijima's experiments on filling carbon nanotubes with lead.¹⁹ There is also the possibility of encapsulating highly conjugated, electrically conducting polymers within porous channels. Typical examples of such polymers include polyacetylene, polythiophene, polypyrrole and polyaniline. However, most polymers exhibit significant levels of electrical conduction only in the presence of suitable dopants. This may cause crystal packing problems when trying to encapsulate both the polymer chain and the dopant, although a number of successful experiments on such polymers have been performed within zeolite cavities.^{1a-c} One polymer which is intrinsically electrically conducting is poly(sulfur nitride), more commonly known as (SN)_x.⁴² This polymer can be prepared by the topochemical ring-opening polymerisation of the highly reactive molecule S₂N₂ in its crystalline state (an interesting solid-state reaction). Attempts by our group to include (SN)_x within the channels of PHTP have so far met with no success (Fig. 1k). However, the possibility of assembling a conducting polymer chain within a non-polarisable porous channel such as PHTP is a fascinating one, not only because it would yield a true molecular nanowire (albeit encapsulated), but also because it would allow us to study selectively the charge transport mechanisms operating *along* the polymer chains, as opposed to known interchain (charge-hopping) modes of carriers which appear to be the main mechanism attributable to the transport of electrical charge in bulk polymeric materials.

4.8 1-D Magnetic interactions

The development of stable organic radicals, including bis-radicals, in the search for new organic *ferromagnets* with high ordering temperatures T_c is a prominent area of contemporary materials research. One problem in designing such ferromagnets is determining the exchange pathways in existing bulk materials (Fig. 1l). Only by understanding how bulk magnetic properties are mediated by the molecular and supramolecular architecture can we aim to engineer new structures with improved properties. Limiting magnetic exchange interactions to only one dimension is one way of facilitating such characterisations. Recently, we examined such exchange interactions through the inclusion of a stable organic radical (dithiadiazolyl) aligned into polar chains within PHTP channels.⁴³ The polar alignment is very similar to that found for the pure radical but in this case interactions between the parallel chains are magnetically decoupled by the diamagnetic PHTP host lattice and by the large distance separating the channels. By confining magnetic interactions to just one dimension, *i.e.* along the channels, we were able to demonstrate that in the solid-state of the radical itself, coupling along the chains is not as efficient as inter-chain magnetic interactions.

5 Polarity: a first example of a tunable solid-state property

Throughout this review we have been reporting on various types of properties resulting from the incorporation of guest molecules into porous matrices. Although there is in most cases a certain degree of tunability of such physical properties, finally, experiments will have to confirm the existence and extent of such properties. Recently, we have introduced a general principle⁴⁴ which can be used in the design of *polar molecular crystals self-assembled from dipolar compounds*. When applied to inclusion compounds of PHTP, polarity originates from an intrinsic mechanism typical of the co-crystallization of PHTP and dipolar guest molecules. Channel formation essentially

precludes any strong lateral interactions between guest molecules and, therefore, molecules entering channels are mainly subjected to selective interactions between terminal functional groups (Figs. 1d, 13). Polarity within two adjacent macro-

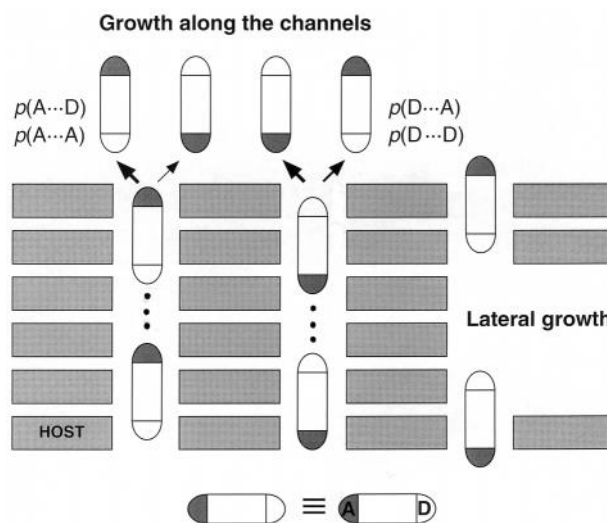


Fig. 13 Schematic representation of the growth mechanism operating during the evolution of a typical channel-type inclusion compound containing dipolar guests (shown as simple capsules).³⁸ The probabilities $p(X\cdots Y)$ of the various possible longitudinal attachments between donor (D) and acceptor (A) groups are indicated, and the relative magnitudes of the probabilities expressed qualitatively by arrows. The probability of guest attachment in the lateral directions is 0.5 for both possible orientations (up or down). The combination of both mechanisms acting during each new growth step q (corresponding in this example to the deposition of a layer being three host molecules thick) influences the final polarity state of the macroscopic crystal. In terms of a mathematical model, the evolution can be described by a homogeneous Markov chain.

domains results from a Markov-type process,^{9,38} which provides selectivity by a non-vanishing energy difference $E_{AA} - E_{DD} \neq 0$, *i.e.* different probabilities $p(A\cdots D)$, $p(A\cdots A)$ and $p(D\cdots A)$, $p(D\cdots D)$ for the attachment of dipoles to corresponding acceptor (A) or donor (D) sites at the growing interface (Fig. 13). This means that the synthesis of polar inclusion compounds can be seen as being driven by two mechanistically different processes: (i) crystal formation, and (ii) evolution of polarity into two adjacent macro-domains. Both processes resemble the nature of *reactions*, and therefore we have here the first example of a physical property being directly 'produced' (Fig. 14) by a

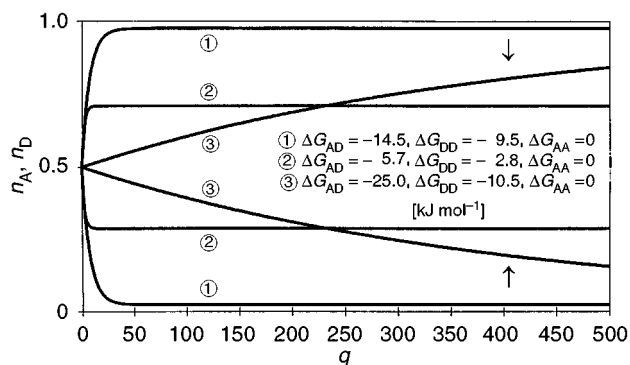


Fig. 14 Calculated evolution of polarity (vertical axis) in a channel-type inclusion compound as a function of the number of attachments q (horizontal axis) of guest molecules along the channel axis ($T = 300$ K). Depending on the intermolecular interaction energies E_{AD} , E_{DD} and E_{AA} polarity can evolve as long as $E_{AA} - E_{DD}$ differs from zero. $n_A = \downarrow$, $n_D = \uparrow$ are the number of dipole orientations with respect to the channel/growth direction.³⁸

process which depends on key energetic parameters available from a numerical calculation of the collinear intermolecular

interaction energies of the guest molecules. A stochastically generated real-structure showing the 'as grown' polarity distribution in two dimensions features two macro-domains yielding stationary values of polarity after a certain number of growth steps (Fig. 15). That this type of a real structure is spontaneously adapted in real crystallisation experiments, has been demonstrated by scanning pyroelectric microscopy (see Fig. 12⁴⁶).

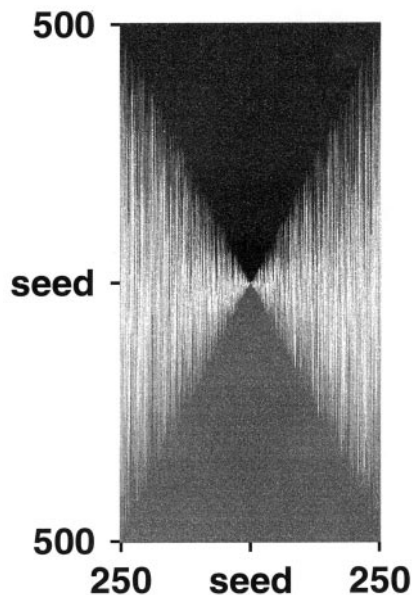


Fig. 15 Stochastic simulation of the polarity evolution (vertical axis: growth of twice $q = 500$ steps along the channel axis; horizontal axis: 200 (twice) channels growing in the lateral direction) of a channel-type inclusion compound shown in two dimensions. Note the cone-structure featuring a stationary polarisation in the upper and the lower macro-domain. Black pixels correspond to \downarrow dipoles and grey pixels represent \uparrow dipoles, white corresponds to areas where dipoles add to give zero polarity. The simulation started in the center of the figure, assuming a stochastically determined state of a seed crystal, e.g. a non-polar state $\uparrow\downarrow$ ($E_{AD} = -3$, $E_{AA} = 8$, $E_{DD} = -1$ [kJ mol^{-1}]; $T = 300$ K). Ratio of the growth speeds: 5:1 (along the channels vs. perpendicular to them). The polarity has been averaged over 10 by 10 pixels in order to show a resolution which is close to what would be observed by e.g. scanning nearfield optical microscopy (SNOM).

6 Summary and conclusions

In this review we have tried to highlight several interesting aspects of a broad class of organic materials that may be termed nanoporous or mesoporous. We have shown that most contemporary studies have focused on overcoming the difficulties inherent in the design of open-framed supramolecular structures. Rational approaches to this problem have been developed, and utilise the philosophy of 'Crystal Engineering' to build up such porous frameworks in a predictable and reliable manner.

Given that most efforts to date have concentrated on developing and understanding rules for the self-assembly of such architectures, most of the physical properties envisaged for organic nanoporous materials have yet to be fully realised. Many of these properties, however, have precedents in the field of inorganic zeolites. One particularly fascinating exception is the study and exploitation of carbon⁴⁵ and molecular²⁵ nanotubes. These discrete structures may self-assemble in bundles or other aggregates and may contain a variety of guest atoms/molecules capable of producing physical properties, as well as acting as material storage and transport vessels at the nanoscopic or mesoscopic level.

Concerning the truly rational design of porous materials with specific pre-determined properties, then one-dimensional (channel-type) inclusion compounds represent at present the

only example of a class of materials where we can influence or control a property such as *polarity* of the final macroscopic solid by first understanding: (i) the mechanisms of self-assembly and (ii) the energetic parameters important to these mechanisms. Extending this understanding to the three-dimensional level of organic crystals has just recently been achieved. With respect to the synthesis of a non-interpenetrating open porous and purely organic zeolites, most recent results by Sozzani *et al.*⁴⁷ seem to provide a first example of spirocyclotriphosphazene host material, where the channel structure is stable after the release of guest entities. In spite of this, or rather *because* of this fact, we envisage that the progress and perspectives described in this review — both from a structural and property-directed point of view — will stimulate further efforts from researchers all across the materials community.

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