

BUILDING SOLIDS WITH MOLECULAR LEGO

INAUGURAL ADDRESS: PROF LEN BARBOUR MAY 2006



ABOUT THE AUTHOR



Len Barbour was born in Pretoria on 9 January 1965. He lived there until 1974 and then followed his parents when they relocated to Cape Town. Despite an uneventful period of schooling to which he was mostly indifferent, he was surprised to find that he had actually liked school enough to want to stay there forever. He therefore attended UCT to obtain a BSc degree with a view to becoming a high-school science teacher. He then discovered that he could avoid two years in the military by signing up for more degrees. After completing a BSc Honours degree in Chemistry (Physics was too difficult), he obtained his MSc in 1989 under the joint guidance of Professor Allen Rodgers and Bruno Pognet. The title of his MSc thesis was “Urinary trace elements in relation to urolithiasis”. By then military service had been reduced to one year, but it still seemed like a long time. Realising that the analysis of urine isn’t for everybody, Len changed direction and joined the research group of Professors Luigi Nassimbeni and Mino Caira as a PhD student. There he was introduced to the marvels of solid-state Supramolecular Chemistry and finally became fascinated by something academic. His PhD research involved the structural, kinetic and thermodynamic aspects of solvate formation and decomposition.

After he started writing his thesis in January 1994, Len met Professor Jerry Atwood, who was then attending a small conference at UCT. At that time Jerry was based at the University of Alabama and was already one of the most well-known and respected personalities in the field of Supramolecular Chemistry. When he offered Len a position as a postdoctoral fellow, it wasn’t very difficult to accept. Len’s patience had been rewarded because by then military service was no longer compulsory and he had also decided that university life seemed far more attractive than high school. He moved to the USA in June, 1994, which is when Jerry relocated his group to the University of Missouri in Columbia (UMC). Len proceeded to spend nine happy years in Columbia, first as a postdoctoral fellow (6/1994 – 5/1997), and then as a Research Assistant Professor. The UMC period was characterised by Len’s development of his own research interests and the ability to occasionally trick the editors of *Nature* and *Science* into publishing his work.

During these years Len maintained contact with Luigi and his group at UCT by visiting almost annually. Luigi was kind enough to finance these trips, which allowed Len to spend some time at UCT and to see his parents frequently (even though they had snuck off to Port Shepstone while he was away). During one of these visits, Len was invited to present a seminar at Stellenbosch University. Once again his timing was impeccable, because a position in the Department of Chemistry and Polymer Science had just become available and he was encouraged to apply. Although he had not anticipated finding an academic position in South Africa, the lure of Stellenbosch (and what seemed like a real job) proved too attractive to pass up. In July 2003 Len was appointed as an Associate Professor in the Inorganic division of the Department. On the basis of his first application he was awarded an A-rating by the NRF owing, no doubt, to a clerical error. Nevertheless, he has been treated very nicely by SU (as evidenced by his recent promotion to Professor) and is continuing his work on the design and assembly of novel porous materials.

Building solids with molecular Lego

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BUILDING SOLIDS WITH MOLECULAR LEGO

INTRODUCTION

For over a century synthetic chemists have been working towards understanding the rules that govern the stepwise formation and cleavage of covalent bonds for the placement of functional groups on molecules. This has culminated in the development of target-oriented synthesis,¹ an enormous achievement encompassing a systematic approach to molecular construction. Covalent bonds are relatively strong interactions between atoms (bond energy = 100 - 350 kJ mol⁻¹), being comparable in strength to ion-ion interactions. However, covalent chemistry is only part of the story of Chemistry. The relatively young field of Supramolecular Chemistry² has been defined as “chemistry beyond the molecule” and is primarily concerned with interactions *between* molecules rather than *within* molecules. Examples of intermolecular interactions include ion-dipole (50 - 200 kJ mol⁻¹), dipole-dipole (5 - 50 kJ mol⁻¹), hydrogen bonding (4 - 120 kJ mol⁻¹), cation- π (5 - 80 kJ mol⁻¹), π - π stacking (0 - 50 kJ mol⁻¹) and van der Waals interactions (< 5 kJ mol⁻¹).² Nature has mastered the use of these forces in order to assemble functional systems (i.e. living organisms) of staggering complexity. Inspired by Nature, the synthetic self-assembly of complex noncovalent systems in both solution and the solid state is becoming increasingly feasible. Indeed, supramolecular chemists have at their disposal a vast Lego® set consisting of millions of different types of molecules, but no instruction manual outlining how the pieces fit together. Therefore we are currently engaged in the laborious but necessary process of unravelling the rules that govern the formation of noncovalent assemblies. Ultimately, mastery of these principles promises to deliver new tailor-made materials with unprecedented functionality and performance.

CRYSTAL ENGINEERING

Solid-state Supramolecular Chemistry (generally termed “Crystal Engineering”) has been defined as the understanding of intermolecular interactions in the context of crystal packing, and in the utilisation of such understanding in the design of new solids with desired physical and chemical properties.³ This encompasses the non-covalent bottom-up “synthesis” as well as the modification of structure at the nanometre scale as a direct parallel to the well-established principles of synthetic covalent chemistry. However, the major obstacle to

routine application of the principles of crystal engineering was succinctly summarised by John Maddox: “one of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition.”⁴

With regard to the development of functional materials, targeted applications include (i) molecular sequestration,⁵ (ii) solid-state “green” chemistry,⁶ (iii) stereospecific synthesis,⁷ and (iv) the development of materials with useful optical⁸ and magnetic⁹ properties. We are interested in all of the above-mentioned aspects of functionality. However, our work is primarily focussed on both the fundamental and practical facets associated with the development of novel porous crystalline materials, with a view to mimicking and even surpassing the important properties of the naturally-occurring zeolites.¹⁰ Particular emphasis is placed upon important technological applications related to the “Hydrogen Economy”,¹¹ such as gas storage and purification.

THE HYDROGEN ECONOMY

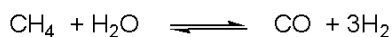
It is widely predicted that oil and gas shortages will occur within the foreseeable future. Therefore, the continued utilisation of fossil fuels to supply the world's energy requirements is becoming an increasingly pressing problem on a global scale. Furthermore, the environmental damage caused by greenhouse gases and chemical or particulate pollution produced during the combustion of fossil fuels is of great concern. However, replacing fossil fuels requires a substantial commitment of effort in terms of research and development. To be viable, an alternative energy source needs to be produced cost-effectively and in sufficient quantities to meet society's demands. In this regard, the implementation of hydrogen fuel cell technology is widely considered to be the most promising alternative to the use of fossil fuels. In a typical fuel cell, hydrogen gas reacts with oxygen to produce liberal amounts of energy, with water as the only by-product. Hydrogen is abundant and widely distributed globally, and the only obstacle is the technology required to harness the gas as an energy carrier. Thus, in order for the hydrogen economy to become a reality, several technological challenges still need to be overcome. Indeed, research aimed at solving these problems has been identified internationally¹² as a research priority. In South Africa the hydrogen economy has recently become a technology mission of the National R&D Strategy.

HYDROGEN STORAGE

Hydrogen storage has been identified as one of the key enabling technologies for the future widespread use of hydrogen fuel cells in stationary, portable and mobile applications.¹³ Factors that contribute to the difficulties involved in efficient hydrogen storage include low molecular weight, high volatility and low energies of interaction - hydrogen gas is difficult to concentrate and thus has a low energy density. Many different solutions to this problem, based on either chemical or physical sequestration, have been proposed. Each method has its own set of seemingly insurmountable technical challenges and no ideal solution has emerged thus far. In this context, physical absorption onto nanoporous substrates has recently become the focus of intense research activity.¹⁴ However, studies to date have focussed mainly on carbon nanotubes or metal-organic frameworks, while molecular crystals composed of purely organic molecules or discrete metal complexes have received comparatively little attention. Furthermore, most sorption studies have been conducted at impractically low temperatures or high pressures, and important issues such as absorption of hydrogen at room temperature and relatively low pressures need to be addressed.

GAS PURIFICATION

In the short term, escalated production of hydrogen will most likely continue to rely on conventional technologies such as steam reforming of natural gas:



followed by the water gas shift reaction:



The final step in the production process involves the purification of H_2 by the removal of impurities such as CH_4 , CO , H_2O and, primarily, CO_2 .

Separation technology is critical to the deployment of hydrogen as a source of energy since the purity of hydrogen supplied to fuel cells affects their performance and longevity, and therefore their economic viability. To fulfil its promise, the hydrogen economy will require compact, durable and inexpensive purification devices. New hydrogen plants are generally based on the use of pressure swing adsorption (PSA) for final hydrogen purification. PSA utilises the difference in adsorption properties of various molecules: components of a gas mixture are selectively adsorbed onto a solid matrix at

high pressure, and subsequently desorbed by lowering the pressure. In recent years, both design and operation of PSA processes have developed to the extent that any notable further improvement in gas separation necessitates the discovery of a novel adsorbent material. Although zeolites and activated carbons are currently employed to good economic effect, there is a continued demand for novel designer materials that can be utilised for gas storage and separation. While carbon nanotubes and metal-organic frameworks have undergone substantial scrutiny in this regard, molecular crystals have received little consideration, since their constituent molecules generally pack with an efficiency deemed to preclude porosity.

POROSITY IN CRYSTALS

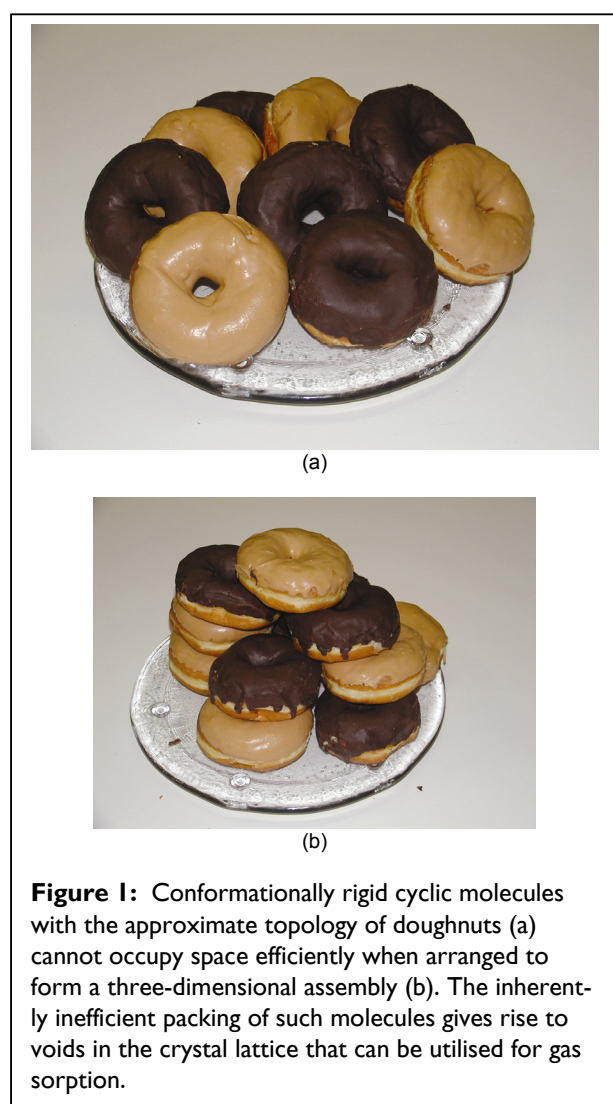
Conventional porosity functions at the molecular scale and thus requires the presence of infinite channels with a minimum diameter of about 3 Å (typically 3 to 10 Å) in the skeletal host framework. It is widely understood that molecules in crystals tend to pack as close to one another as possible in order to maximise attractive intermolecular contacts. Therefore it is quite rare to encounter molecular crystals with open channels, or with discrete lattice voids larger than about 25 Å.⁵ For this reason, molecular crystals have generally not received much attention from researchers aiming to produce porous materials as functional analogues of zeolites. However, coordination polymers (metal-organic frameworks, or MOFs) are far more attractive in this regard because, like zeolites, they consist of effectively infinite frameworks of interconnected structural units.¹⁴ These frameworks are based on the well-defined coordination geometries around metal centres, so the structural permutations accessible by combining a vast array of metal ions with various anions and bridging ligands are practically limitless. In many cases, solvent molecules fill the gaps formed by the metal-ligand networks and a growing number of these systems are being shown to possess the rigidity necessary to survive evacuation to yield robust porous structures. Although some success has been achieved using these types of coordination polymeric materials, the ultimate goals of 6 and 35 percent by weight (wt%) for hydrogen and methane storage, respectively, are still far from realisation.¹⁵

The most widely applied method of producing porous crystals is to assemble a coordination polymeric MOF with solvent molecules trapped in its lattice, and subsequently to extract the solvent without disrupting the host framework. The utilisation of robust exo-

bidentate metal-ligand-metal bridges is crucial for the success of this approach because weakly coordinating complexes generally rearrange upon desolvation to form a different, yet also efficiently packed phase.^{14,16} Indeed, with only a few known exceptions,¹⁷ rearrangement to achieve close-packing upon solvent removal is almost always observed for organic molecular crystals,¹⁸ as well as for metal-organic complexes.¹⁹

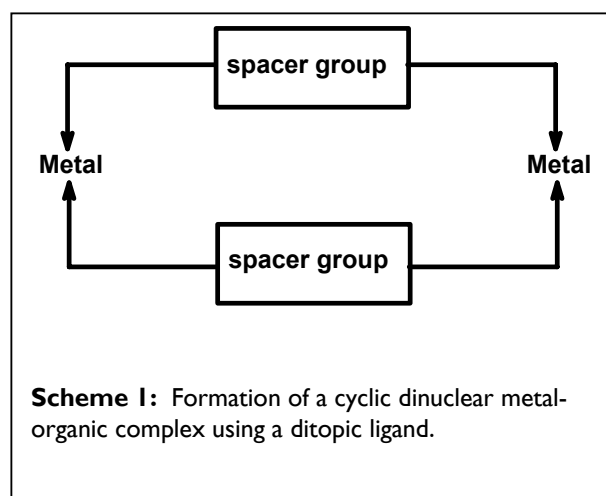
MOLECULAR DOUGHNUTS

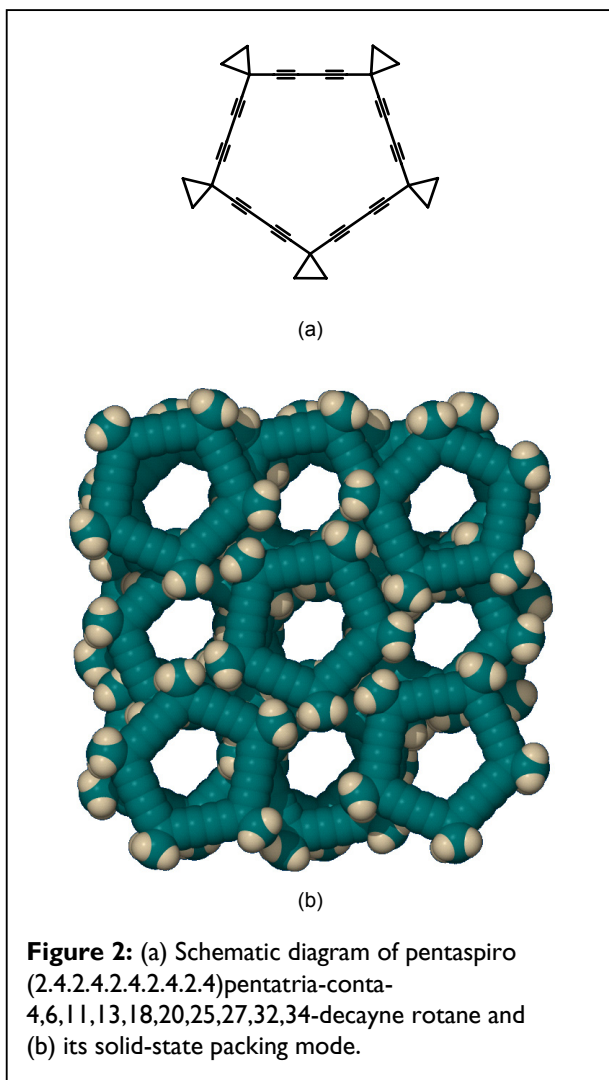
One of our approaches to producing porous crystals involves the use of discrete “doughnut-shaped” organic molecules or metal-organic complexes. Owing to their lack of topological self-complementarity, such



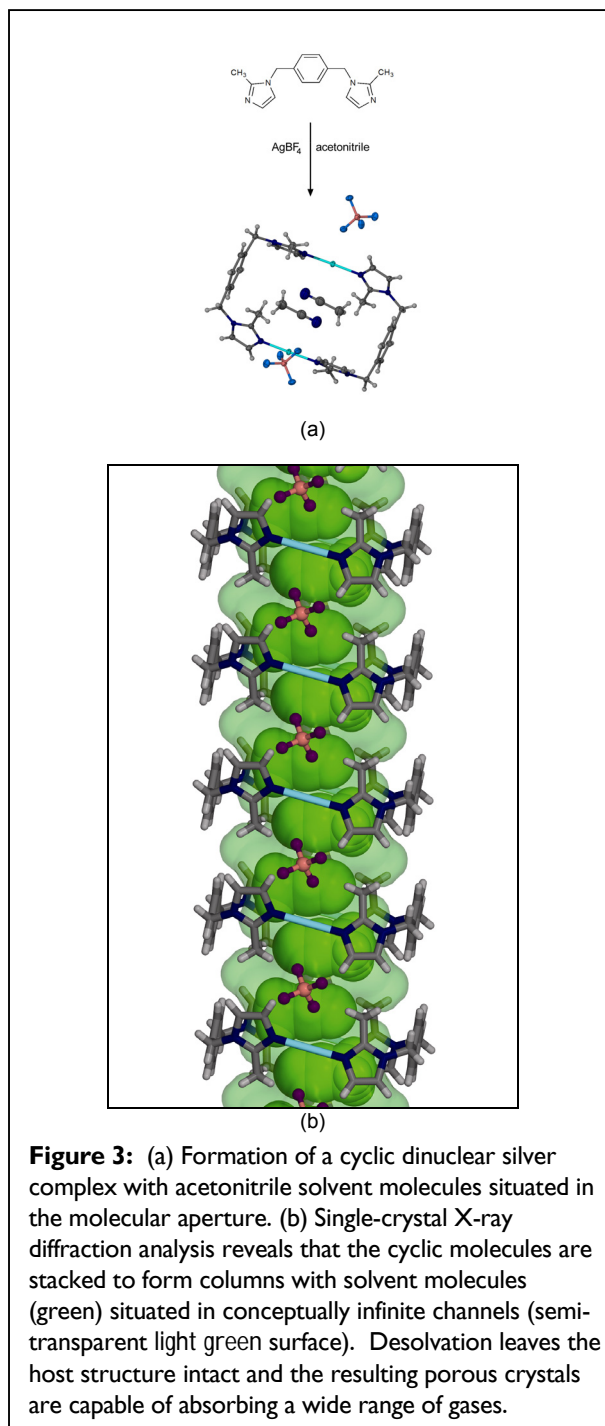
species cannot pack efficiently (Figure 1) and, when crystallised from a suitable solvent, they usually appropriate solvent molecules into their approximately circular apertures. Desolvation ultimately results in the formation of voids or channels, if the host molecules can retain their shape instead of collapsing. This concept can readily be exploited using purely organic molecules as building blocks (see Figure 2). However, such molecules are often difficult to synthesise in appreciable yields.

An analogous approach involves the use of simple dinuclear metal-organic complexes as outlined in Scheme 1. The ditopic ligand consists of a molecular spacer which is symmetrically functionalised with two coordinating groups. In this context we recently reported the formation of a crystalline solvate by a discrete cyclic dinuclear silver complex as shown in Figure 3.²⁰ The rectangular host complexes stack to form channels that entrap acetonitrile guest molecules. Upon removal of the guest by gentle heating, the packing arrangement of the host is preserved, thus yielding a porous lattice capable of absorbing various gases. The sample was crushed and gas sorption isotherms were recorded for CO₂, N₂, CH₄ and H₂ at 30°C. At low pressure (< 10 bar) the bulky gases are absorbed more readily, presumably as a result of their more favourable binding affinities with the pore surface. However, at higher pressures (> 48 bar) the smaller gases are absorbed in larger molar quantities, as might be expected based on space-filling criteria. To date, most studies of H₂ sorption by MOFs have been conducted at 77K, while relatively few reports of room temperature experiments have been published. The hydrogen sorption capacity of our material (i.e. ca 1 weight percentage at 78 bar and 30°C) compares favourably with the best of these previously reported results.





Notably, the formation of porous materials by means of single-crystal transformations is of significant value because this phenomenon allows one to study the structural features of a gas sorption substrate at the atomic scale in the hope of ultimately understanding the underlying principles that govern gas-solid interactions. Since structure cannot be predicted in general, it should also be mentioned that the coordination of ditopic ligands by transition metals, as described above, is expected to yield a wide variety of infinite framework structures and not only the targeted discrete complexes. Although many of these systems will most likely not be porous, this is an accepted part of the rich panoply of crystal engineering and highlights the fact that this area is still more reliant on discovery than design.

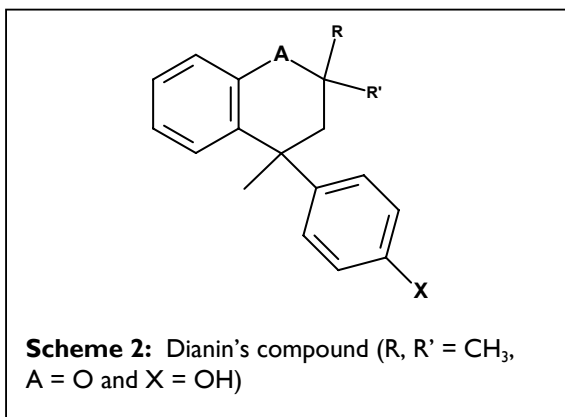


PORE-SIZE ENGINEERING

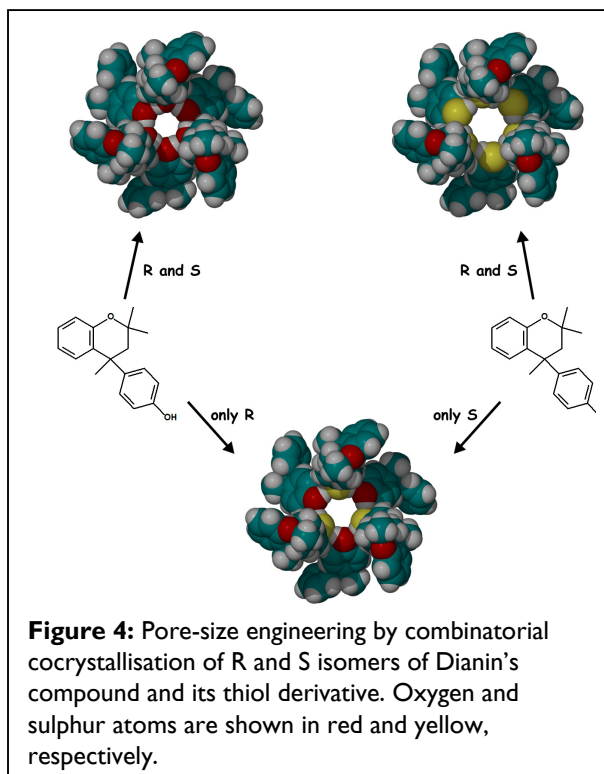
Research on porosity has focused mainly on new synthetic strategies for producing open framework structures and much emphasis is placed on their gas storage

capacities. While the tendency has been towards developing larger pores/cavities (i.e. more vacant interstitial space) in order to enhance gas storage capacities, relatively little effort has been devoted to pore-size engineering for applications such as gas separation by size exclusion. Selective sorption of gases by porous crystalline substrates such as zeolites, coordination polymers and organic materials has mostly been based on the interaction potentials between the solid matrix and the targeted gas molecules.

In considering the amount of effort being devoted to studies of gas-solid diffusion processes, it is rather surprising that the issue of pore size in relation to the presumed dimensions of the gas molecules has received little attention to date. In the few reported examples of pore metrics being used to rationalise selectivity, the kinetic diameters of the gas molecules are considered rather than their van der Waals dimensions. In this context the most commonly cited reference for kinetic diameters of various gases is the comprehensive book on zeolite molecular sieves by Breck. We have embarked on a study in which we have identified several well-known porous systems that possess apertures close to the van der Waals radii of commonly studied gases.



The inclusion behaviour of Dianin's compound²¹ (Scheme 2) is arguably the most recognised archetype of solid-state supramolecular chemistry. The original ground-breaking studies of this system were conducted many decades before the availability of today's state-of-the-art equipment. Nevertheless, Dianin's compound has been largely ignored in recent years simply because there is a general perception that it no longer offers any new surprises. We have recently proven this notion to be incorrect by unlocking hitherto unexplored inclusion behaviour exhibited by Dianin's compound.²²



Our primary interest in Dianin's compound is that crystals grown by sublimation possess vacant lattice voids of approximately 240\AA^3 in volume. Access to these voids is restricted by a hexagonal arrangement of hydrogen bonds between hydroxyl moieties and the crystals can be considered to be porous with regard to a spherical probe of radius 1.2\AA . Synthetic modification of Dianin's compound (mainly by modification of R, R', A and X) is well-established.²³ For example, when $X = \text{SH}$, a packing arrangement isostructural to that of Dianin's compound is obtained.²⁴ However, Figure 4 shows that substitution of X influences the diameter of the pore leading to the interstitial void. This observation has important implications for fine control over pore dimensions – a key feature with significant relevance to the separation of gases by size exclusion.

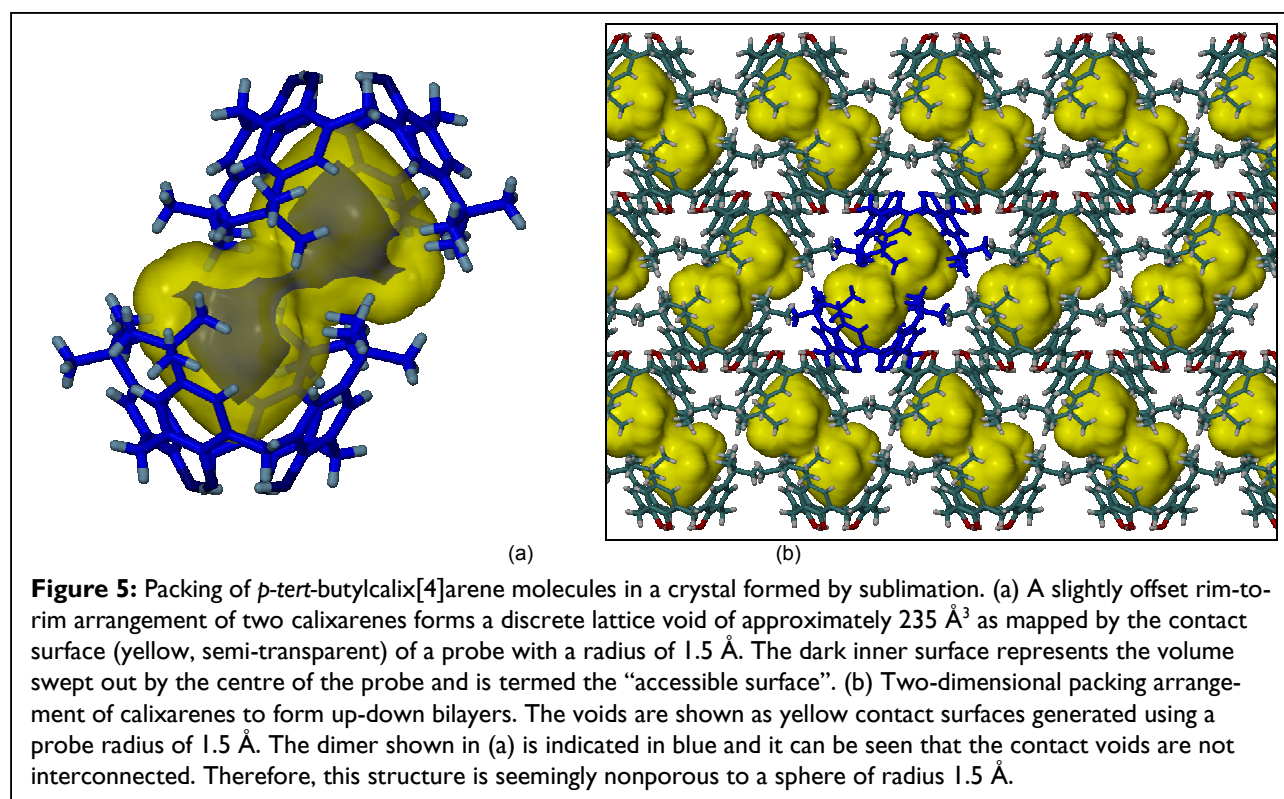
To date, all of the known inclusion chemistry of Dianin's compound has involved racemic mixtures of structural isomers. Indeed, both stereoisomers are required in order to form the characteristic lattice void with its circular windows, since each void is bounded by six molecules in a cyclic $(R\cdots S\cdots)_3$ arrangement of enantiomers. To the best of our knowledge, the cocrystal structures of different derivatives of Dianin's compound with opposite chirality have not been reported to date. Figure 4 shows that combination of the R isomer of

Dianin's compound with the *S* isomer of the thiol derivative (or vice versa) should yield a pore intermediate in size between those obtained for the racemic mixtures of the isomers. Various combinations of resolved and separately derivatised compounds offer exciting possibilities for further engineering of pore size. Modelling of Dianin's compound currently shows that the $\cdots\text{OH}\cdots\text{OH}$ hydrogen bonding plays a major role in the formation of the aperture; consequently the exploitation of, for example, $\text{NH}\cdots\text{Cl}$ hydrogen bonding should allow modification of the aperture and/or pore size. For example, the *R* isomer with $\text{X} = \text{NH}_2$ could be cocrystallised together with the *S* isomer with $\text{X} = \text{Cl}$ to form a structure in which the pore size is determined by a cyclic arrangement of $(\cdots\text{H}-\text{N}-\text{H}\cdots\text{Cl})_3$ hydrogen bonds.

We have conducted an exploratory study which indicates that Dianin's compound is capable of absorbing only hydrogen gas at room temperature (CO_2 , CO , N_2 and O_2 are not absorbed). To the best of our knowledge, this represents the first instance of a porous compound that is selective for hydrogen gas. Although the amount of hydrogen absorbed by weight is insufficient for effective storage, the observed selectivity could be exploited for applications such as sensing and separation.

POROSITY "WITHOUT PORES"

One of the most important considerations with regard to permeable systems concerns the dimensions of the pores. On the other hand, recent studies have uncovered materials that are highly permeable despite their seemingly nonporous solid-state structures. We recently reported that a crystalline polymorph of pure *p*-tert-butylcalix[4]arene (TBC4), prepared by sublimation, forms a bilayer-type structure which contains large lattice voids of approximately 235 \AA^3 (Figure 5).²⁵ Immersing these crystals in liquid vinyl bromide for a period of 15 minutes results in a single-crystal-to-single-crystal phase transition during which the vinyl bromide diffuses through the lattice to fill the vacancies. The phase transition is characterised by a $\sim 6 \text{ \AA}$ lateral shift of the bilayers relative to one another in order to allow guest diffusion, and to achieve a well-packed final structure incorporating one molecule of vinyl bromide per TBC4 cavity. In our continued efforts directed at understanding the dynamics of guest transport through the TBC4 lattice, we noted that addition of sublimed TBC4 to liquid nitrobenzene caused numerous bubbles to emanate from the crystals. This chance observation implies that the crystals initially contain highly volatile molecules which are forced out of



the lattice by incoming nitrobenzene. Since the pure host phase is crystallised under vacuum at 230°C, the possibility of having formed the lattice around small gas molecules can be ruled out. The most plausible explanation is that, upon removal from the sublimation apparatus, the crystals absorb air while left exposed to the atmosphere prior to further handling.

It is expected that further systems with similar properties will be discovered in the near future. These results have important implications for the area because they show that porosity cannot always be rationalised using simple geometric arguments based purely on static atomic coordinates and van der Waals surfaces. To date, the transport of molecular species through a solid, non-porous lattice has defied explanation and there is an urgent need to investigate this unprecedented phenomenon more thoroughly. Important questions that need to be addressed include:

- Can further analogous systems be identified/designed?
- Can these systems be tailored for guest specificity?
- What are the mechanisms involved in guest uptake and release?
- How do these new gas sorption systems perform relative to known systems such as activated carbons and zeolites?
- How do external factors such as temperature and pressure affect sorption behaviour?
- How can these systems be implemented as functional materials?

DESCRIBING POROSITY

In order to be of maximum use, any description of crystal porosity should be as comprehensive as possible. If known, the affinity for different kinds of guest molecules should be revealed. For example, would the host be more likely to include hydrophilic or hydrophobic guests? Are polarisable gases absorbed preferentially? Interrelated factors such as temperature, pressure, concentration, occupancy and uptake/release kinetics are highly relevant and should also be discussed. Most importantly, the size and shape of the pores should be described. To use a macroscopic analogy, the average door is porous to humans but perhaps not to an elephant. Thus use of the word “pore” to describe the door in this context should consider the nature of the guest. In general, a thorough description of a pore opening could conceivably involve a complicated topological treatment and thus pore metrics are often

difficult to represent properly with a simple set of parameters. Usually it is more feasible to simply specify the maximum radius of a spherical probe that will pass through the narrowest region of a pore. This simplified approach is practicable in most cases, since many channels are approximately circular in cross-section and volatile guests are usually associated with a kinetic diameter, implying that they can generally be approximated as spherical entities. Square or rectangular channels are also easily described using one or two parameters, respectively.

One of the most important parameters associated with porous crystals is the amount of free volume within the material. Several computer programs are available for calculating solvent-contact (e.g. MSROLL²⁶) or solvent-accessible volumes (e.g. PLATON²⁷) which are normally represented as their bounding surfaces. These routines map the volume that a spherical probe of given radius can sweep out within a molecular void or channel and the results of these calculations tend to be highly sensitive to the probe radius chosen, as illustrated in Table I. It is therefore imperative to use a sensible probe radius in order to realistically represent the space available to a particular guest. A smaller probe radius results in a larger estimated free volume, but choosing a probe radius smaller than that of a hydrogen atom (1.17Å) is clearly meaningless (typically, probe radii of 1.4 to 1.7 Å produce meaningful results). Furthermore, the probe radius can dramatically influence whether or not a structure should be considered to be conventionally porous, as illustrated by the packing in sublimed (i.e. guest-free) crystals of Dianin’s compound (Figure 6). While a probe of radius 1.3 Å is too large to pass from one cavity to the next through the hydrogen-bonded ring, a probe of radius 1.2 Å is able to pass through. Therefore, by considering the static atomic coordinates of the host framework of Dianin’s compound, the crystals are conventionally porous to a probe of radius 1.2 Å, but not to a probe of radius 1.3 Å. The purpose of this example is to illustrate that, when describing a structure as being conventionally porous, it is imperative to specify the probe radius. Figure 6 also shows that a continuous contact surface does not imply porosity, since it is possible for contact surfaces of adjacent cavities to merge without allowing the probe to pass from one cavity to the next. Indeed, the true test of conventional porosity in such cases is whether or not the accessible surface is continuous.

Table 1: Calculated cavity volumes (i.e. bounded by contact surfaces) for dimeric *p*-*tert*-butylcalix[4]arene shown in Figure 5a.

Probe radius (Å)	Cavity volume (Å ³)
1.3	270
1.4	254
1.5	237
1.6	226*
1.7	212*

* Probes with radii ≥ 1.6 Å are unable to traverse the constriction at the centroid of the dimer and therefore two cavities of identical size and shape are obtained. In these instances, the combined volume of the two cavities is given.

SUMMARY

While it is still true that Crystal Engineering has yet to evolve to the extent that structure can be designed and “synthesised” at will, it is possible even now to exploit the tenets of Supramolecular Chemistry in order to assemble simple materials with useful properties. Most functional materials are discovered rather than designed. However, by systematic study of the relationships between structure and function, we can hope to ultimately master the principles that govern the process of self-assembly at the nano-scale. Synthetic covalent chemists have been through this process and Nature shows that the possibilities for noncovalent assembly are limitless.

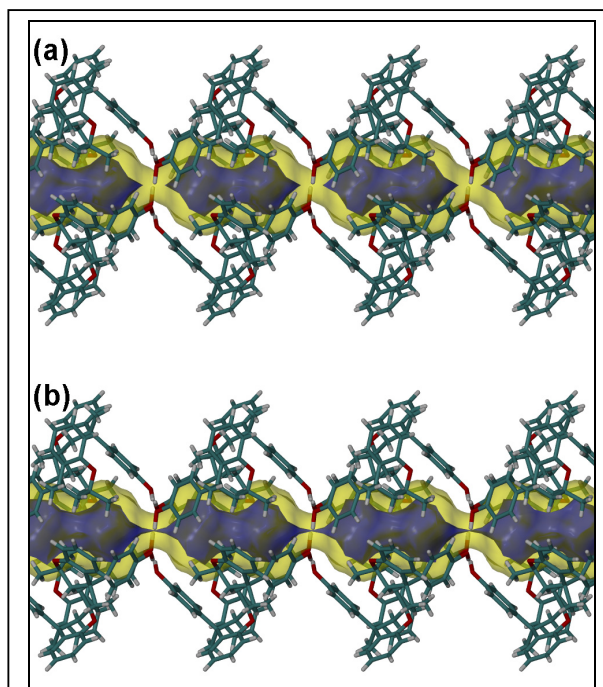


Figure 6: Dianin’s compound forms linear columns of hexamers that enclose cavities. Depending on the probe radius, and considering the structure to be static, the cavities are either isolated from one another, or interconnected via an aperture formed by a cyclic arrangement of six O-H···O hydrogen bonds. (a) Using a probe radius of 1.3 Å, the contact surfaces (yellow, semi-transparent) represent an infinite channel, although the probe sphere cannot pass from one cavity to the next as shown by its accessible surface (blue). (b) A probe of radius 1.2 Å forms a contact surface similar to that shown in (a). However, the accessible surface is continuous, implying that the 1.2 Å probe can just pass through the hexameric hydroxyl aperture from one void to the next. Thus Dianin’s compound is porous to a probe of radius 1.2 Å but not to a probe of radius 1.3 Å.

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