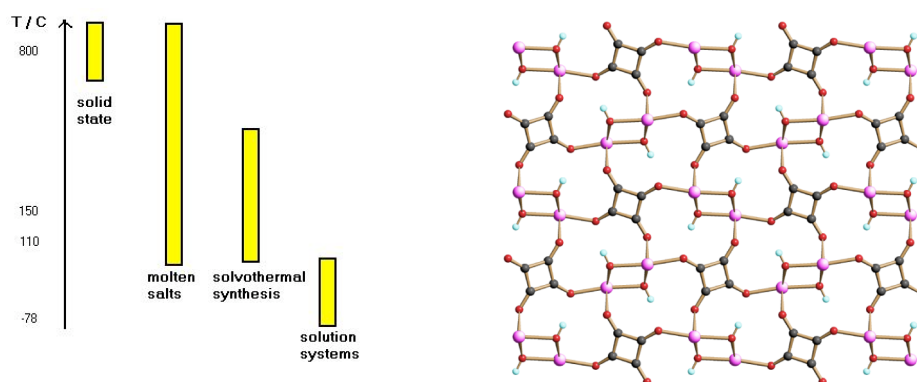


Novel routes to new materials

The drive for materials displaying novel functionalities, of potential use in new devices, has led to a host of synthetic routes being employed. Classical *wet* chemistry has given us everyday chemicals ranging from pharmaceuticals to agrochemicals, cosmetics to detergents and materials such as nylon and kevlar. Another widely used approach, that of solid state chemistry, or *shake and bake*, has been the dominant synthetic route to the host of materials finding current use in storage devices, the so called *colossal magneto-restrictive* materials such as manganites, or those that continue to promise significant future applications such as the series of superconducting cuprates.

The solvothermal route to synthesising materials is a relative newcomer to toolkit of chemists and materials scientists. This makes use of pressure vessels to heat reagents to temperatures above the ambient boiling points of the solvents. In this subcritical regime, intrinsic solvent properties such as viscosity and the solubility of reactants are greatly modified, resulting in reaction pathways unobtainable under more traditional wet chemical methods. In addition, the relatively low temperatures employed (typically below 200°C) allow one to make use of organic ligands which would not survive the high temperatures used in *shake and bake* methods (typically >500°C). This results in a whole new area of chemistry and potentially new materials.



Left: how solvothermal methods complement other synthetic routes; **Right:** the nuclear structure of one 3D network, incorporating M(II) ions and oxalate ([C₂O₄]²⁻) ions.

Solvothermal methods were largely developed for use in aqueous media, predominantly as a means of studying geo-thermal processes in the laboratory. The extension of this to the wide range of organic solvents readily available in the laboratory has led to hundreds of new materials being synthesised. Our current interest is in producing extended networks of transition metal ions in which organic ligands are used as the links between the metal ions; these materials often display novel magnetic interactions and many have even been found to exhibit guest:host interactions, potentially opening the way for use in devices such as sensors or even as trapping media with environmental applications. The interplay between the geometric constraints imposed by the ligands, the nature of the solvent and the coordination shell of the transition metals, provides a huge phase-space to investigate.

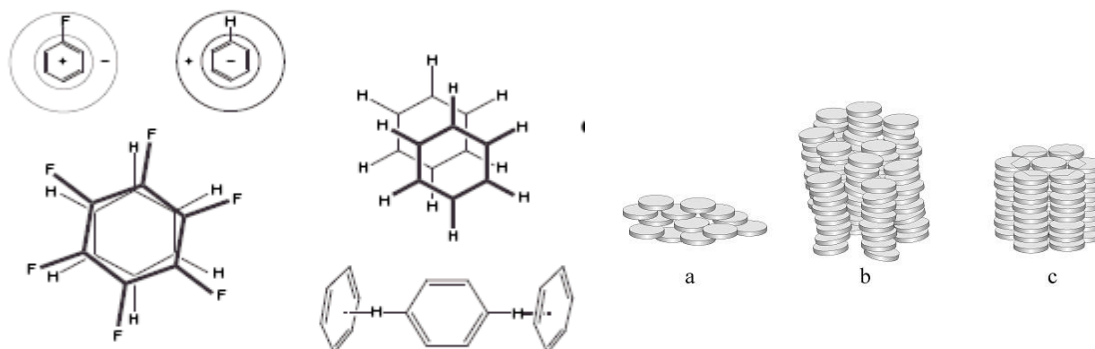
Whilst increasingly used around the world, solvothermal synthetic methods have not been employed at UNSW to date. We are keen to develop a laboratory to do exactly this and to extend the boundaries of traditional chemistry to develop new materials. These materials will need to be carefully characterised, making use of traditional

spectroscopic tools and finally X-ray and neutron crystallography to determine nuclear and magnetic structures. Other techniques such as magnetisation and adsorption measurements may also be employed, depending upon the nature of the materials produced.

π -interactions

Intermolecular interactions often act as templating mechanisms in solid structures - molecules display an inherent rationality when condensing into the solid state. It is the attempt to understand these interactions that has been dubbed supra-molecular chemistry and is a research area that has seen rapid growth over the past 10-15 years. Intermolecular forces come in different flavours, the strongest, Coulombic interactions, tend not to display great affinity for directionality, simple ionic structures such as table salt (NaCl) are governed more by size effects and packing density than directionality. In the solid state, the classical hydrogen-bond is a highly directional intermolecular interaction, which is intermediate in strength and responsible for the fact that ice is less dense than water - we all know that ice floats due to the relatively open tetrahedral ordering of water molecules. This latter facet has been central to the preservation of life on earth. Another notable and well-known example is the dimerisation of acids such as benzoic acid in the solid state. However, most molecules have neither ionic nor highly polar functionalities and yet display distinct packing effects in the solid state. For example benzene adopts a herringbone zig-zag when crystallised, a motif found in many other aromatic systems as well. In this case, a weak π -H interaction drives the intermolecular packing such that neighbouring molecules adopt perpendicular orientations. However, other aromatic systems adopt stack-like columnar, or layered structures; for example, replace each hydrogen on benzene with a methyl group and hexamethylbenzene has a highly layered structure with no sign of herringbones. Clearly as the intermolecular potentials become increasingly soft, then the interplay between the enthalpy and entropy of the system can lead to dramatically differing structures. If one considers co-crystallised systems then the scope for the interplay between interaction types increases; for example, at room temperature, the two liquids benzene and hexafluoro-benzene spontaneously form a solid upon mixing, which displays a columnar structure and is due to an increased affinity for π - π stacking. Some π -stacked co-crystallites display charge transfer effects (often they are intensely coloured) and may even lead to complete ionisation, leading to the possibility of molecular magnetism. Discotic liquid crystals which have potential applications in molecular electronics, field effect transistors or photovoltaics due to their highly anisotropic electron transport properties, are held in a columnar arrangement via π - π interactions of the aromatic cores.

Left: π -H interactions in solid benzene:hexafluorobenzene and benzene; Right: π - π



interactions between aromatic cores of discotic liquid crystals dominate their temperature dependence - in order of decreasing temperature (a) nematic discotic phase, (b) nematic columnar phase and (c) columnar hexagonal phase.

We are interested in understanding these very important interactions at the fundamental level and propose to investigate aromatic materials of increasing complexity, making use of standard spectroscopic tools, to study the nature of the intermolecular interactions and the modulation of such, with ring substituents.

Group XIV materials

Much research effort has gone into the production of porous open-framework materials for use in catalysis and selective-uptake of adsorbants. Perhaps the most widely studied series of materials are the aluminosilicate zeolites (both synthetic and natural) that have found widespread use in catalysis. More recently, efforts have moved toward increasingly detailed functionality of the porous media such that the materials themselves may be magnetic, highly adsorbant specific and even of some biological relevance. The dramatic increase in the diversity of porous media has seen various network-templates being used. One potential area that has not been widely investigated is that of molecule-based Group XIV materials - C, Si, Ge, Sn and Pb. The structural motif of this group is tetrahedral and provides an ideal opportunity to investigate the variation in both central atom size (X) and coordinating chemical units. For example, the tetraphenyls of Group XIV elements are isostructural, despite the very large size differences in the central atom. Functionalisation of the phenyls, to tolyls for example, breaks this symmetry due to the increasingly complex intermolecular interactions. Other than a few crystal structures, this field has received little attention and so we plan to arrive at a more complete understanding between X and the solid-state structures, whilst making use of phenyl group functionality to modify and hopefully engineer, the resulting materials. Of course, the final goal of the project is to arrive at a method of bringing together the isolated molecular tetrahedra into extended open 3D diamond-like structures, the porosity of which may be tunable by the size of the central atom. As such, the proposed project includes aspects of both careful synthetic procedures and sample characterisation, making use of IR, NMR and crystallographic methods, for example, with the aim of obtaining a potentially highly versatile series of tunable materials, having electron-rich cavities.

New routes to nanostructures

The use of alternative preparative procedures in chemistry and materials science, such as the so-called solvothermal route, have resulted in the discovery of hundreds of new chemical and nano-structured materials over the past decade. The solvothermal technique is finding an increasing number of applications in nanotechnology and offers a unique means of making highly functionalised materials, having potential applications such as sensors, separation and catalysis, molecular devices and spintronics.

The term solvothermal derives from the better known hydrothermal technique, in which aqueous solutions are used under non-ambient conditions of temperature and pressure¹. Hydrothermal methods have been widely used in earth studies, such as geology, to obtain a better understanding of the processes leading to mineral

formation². The solvothermal method extends this range of reactions to include non-aqueous solutions and usually covers the temperature range of up to ~350 °C and pressures of up to ~100 bar and has seen an exponential growth over the past few years, Figure 1.

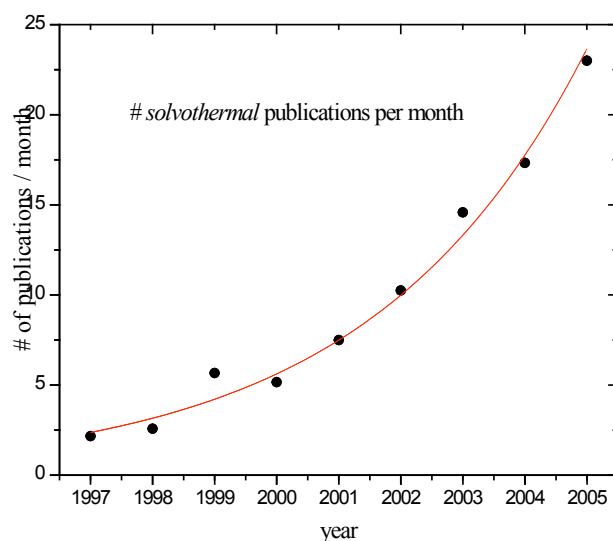


Figure 1: The exponential increase of research papers citing the word *solvothermal* in the title, abstract or keywords. (source: *ISI Web of Science*³).

Much of the work in solvothermal methods has resulted in nanostructures that are unobtainable by more traditional synthetic procedures. For example, the solvothermal route has become a relatively low temperature method of producing carbon nanotubes³, with nanotubes also being fabricated from an expanding range of materials.⁴ Along with tubes, other nanostructures, such as nano-wires, -ribbons, -rods, and -sheets have also been produced in this way. Indeed, the solvothermal method appears to currently be at the central in the use of alternative routes to obtaining pure carbon nanotubes³. Only this route can prevent contamination by the metal ions used as catalysts in the more traditional methods of preparation, such as laser ablation, arc discharge and chemical vapour deposition. By varying the carbon feedstock, solvent and reaction conditions, one should be able increase the current nanotube yield of 20%. To date the mechanism of tube formation by this route is not apparent and only with further investigations of the free parameters, can one hope to arrive at a better understanding of the complex chemistry. For example, the role of silica and sodium chloride have been alluded to³, but what of the nature of the long-chain ethoxylated alcohol and the solvent itself?

Whilst carbon nanotubes continue to attract much research attention, they represent only a fraction of the nano-structured materials now being studied. Solvothermal methods have become central to the production of structures as diverse as ribbons, wires, rods, sheets and particles, from materials ranging from pure and doped carbon, to metal oxides and hydroxides, iron sulfide, zinc cyanide and even vanadates⁴. This diverse research field is ripe for the production and investigation of new nano- materials. The current project aims to draw upon the growing body of published work to move towards new procedures and/or materials and will make use of the range of techniques available at UNSW and ANSTO to characterise the samples.

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