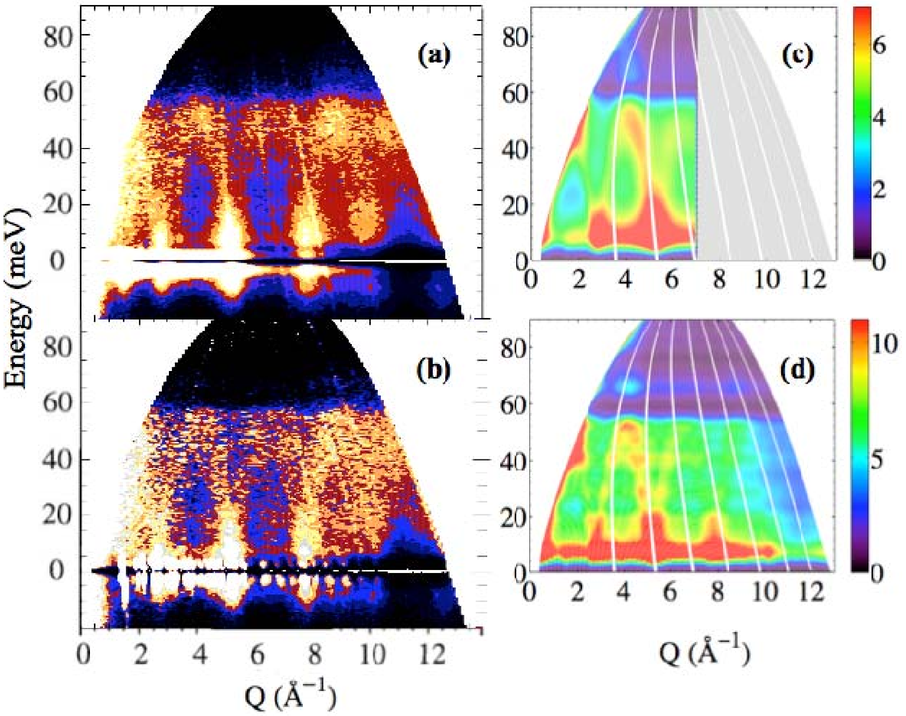
PhD projects in the Condensed Matter Physics group at QMUL (2011)

Project 1
Title: **Fast vibrational dynamics of liquids and glasses: probing the similarities with crystals**
Supervisors: **Martin Dove and Kostya Trachenko**

One fact that we learn at an early stage in our science lessons is that crystals, liquids and glasses are completely different objects: crystals are solids in which atoms are arranged in periodic order, liquids flow and have no long-range order in the arrangement of atoms, and glasses have the same lack of order as liquids but do not show flow. But a remarkable series of experiments obtained from new generation instruments at neutron and x-ray scattering facilities, coupled with new simulation tools, are beginning to show that as far as the fast dynamics of the atoms are concerned, the differences between these three types of materials are rather smaller than you might imagine, particularly when the comparison is made with polycrystalline samples. For example, recent work on amorphous and polycrystalline silica, SiO_2, has shown that the existence of vibrations whose frequency varies with wave vector in a periodic manner, reflecting the dispersion curves in the single-crystal state, identically in both cases (see figure). The same appears also be true for the common ice phase of H_2O. Older measurements have shown an apparent dispersion curve for liquid potassium [] that appears to be nearly identical to that of crystalline potassium for wave vectors propagating along the diagonal direction of the Brillouin zone.

Some of the interesting features observed in the scattering of radiation from liquids and glasses have been interpreted in terms of various different theories, including the existence of new dynamics such as fast sound and rotons, but what has been missing is the comparison with crystalline materials. Our suspicion is that as far as the fast dynamics of materials are concerned, the critical length scales are shorter than the unit cell distances in the crystalline phase, and provided that the local structure in the liquid or glass is similar to that of the crystalline phase, similarities in the dynamical behaviour may not be surprising. However, the main features of dispersion curves of crystalline materials are exactly determined by the crystal periodicity, so there is a lot of new understanding of the links between the dynamics of crystalline, liquid and amorphous materials that we need to develop. The good news is that we now have a new generation of instruments at synchrotron and neutron radiation sources together with new simulation tools, enabling us to begin to tackle these issues.



Neutron scattering data (left, a and b) and corresponding simulation (right, c and d) for amorphous silica (top, a and c) and its corresponding crystalline phase cristobalite (bottom, b and d). Note the close similarities between the amorphous and crystal phases, including the apparent dispersion curves. Data are from Arai et al, Physica B ***263–264****, 268, 1999; calculations are our own unpublished results.*

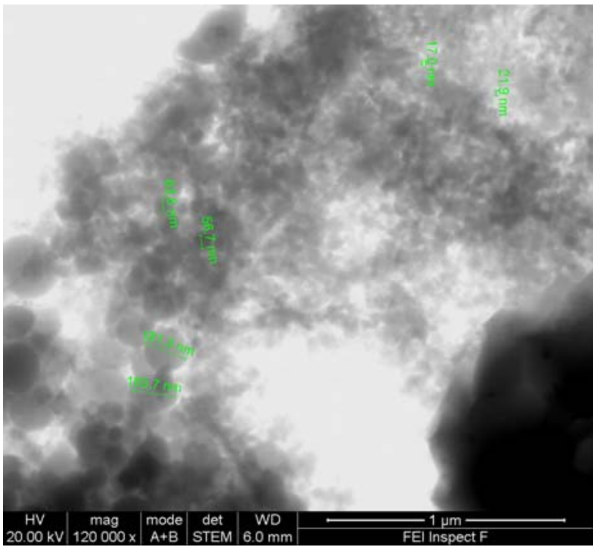
This project involves combining neutron and synchrotron spectroscopy techniques with atomistic simulations. The experimental methods will involve measurements of the intensity of neutron or x-ray scattering as a function of changes in energy and momentum of the scattered beam of radiation, corresponding, respectively, to the frequency and wave vector of the vibration within the sample. Modern spectrometers enable us to map out the frequency and wave vector distributions of the vibrations across a broad range of values. New simulation methods can compute the same maps, and in the few cases tackled so far show good agreement. The link between these two then enable us to identify and visualise the types of atomic motions associated with interesting features in the experimental data. In the case of fluids, the simulations will involve fast-freezing atomic configurations generated by molecular dynamics methods, and computing the excitation spectra for the specific configuration using force constant models. Whilst this exclude us studying the slow long-wavelength convection motions, it will capture the dynamics of interest in this project.

The simulation techniques involve both quantum mechanical and empirical methods. For a material such as fluid potassium, the atomic configurations will need to be generated using quantum mechanical motions, and the force constant models can be obtained relatively easily from the calculated crystal dynamics.

The initial work of the project will involve running simulations for various examples of binary materials, including the simulation of the scattering maps for both liquid and crystal phases. These will be used to propose experiments to be performed at the ISIS neutron source, which will probably take place in the second year. At an early stage we will also carry out the experimental and simulation work on liquid potassium in parallel. The later stages of the project will both extend this work and also use the body of data to develop a general understanding of the link between the dynamics of crystals and liquids/glasses, which is the overall objective of this project.

Project 2
Title: **Probing the atomic structure of nano-scale materials**
Supervisors: **Martin Dove, Mark Baxendale, Andrei Sapelkin**

There is a huge current interest in nano-scale materials. These may include very small particles of well-known bulk materials (such as element materials such as gold or silicon), or new forms of matter (such as carbon nanotubes with encapsulated nanoparticles), or even materials that can only crystallise as nano-scale particulates. There are a number of probes of the atomic structure over the distance of first and second atomic neighbours, or else other probes that can give information about particle sizes, but little work has been done that leads to models of the atomic structure of nanoparticles that includes both within the particle and near the surface.

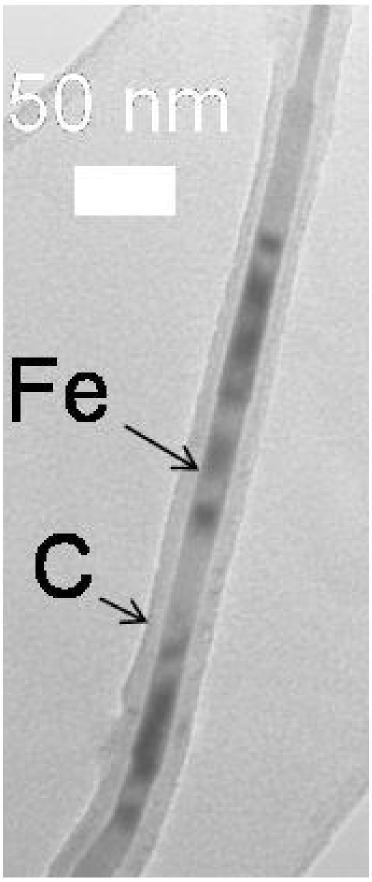


Electron microscope image of nanocrystalline germanium prepared by laser ablation

One technique that is primed to lead to new breakthroughs in understanding the structures of nanoscale materials is an approach called 'total scattering' (Dove et al, European Journal of Mineralogy 14, 331, 2002). This involves measuring the scattering of beams of x-rays or neutrons to high scattering vector, capturing both the Bragg scattering (which will be broadened for nanoparticles) and the diffuse scattering that lies between Bragg peaks. The Fourier transform of the total scattering yields the pair distribution function (PDF), which is essentially a histogram of all the interatomic distances. By measuring the total scattering to high scattering vector (and requiring specialised instruments to do so) we are able to obtain high resolution in the PDF, and we are also able to measure the PDF out to distances than will span the whole length scale of the nanoparticles.

Our approach is to use these data — which can be combined with data and information from other sources, such as EXAFS, NMR and spectroscopy — to build and refine atomic models using a Monte Carlo algorithm (Tucker et al, Journal of Physics: Condensed Matter 19, 335218, 2007). These models will then form the basis for subsequent analysis. This approach has been used successfully for a wide range of different studies, including magnetic systems, amorphous materials, phase transitions, dynamically disordered crystals, and nanoscale ordering in ferroelectrics. However, it has not been used at all for the study of nanoparticles, and this forms the substance of this project.

The main focus of this project will be to develop the Monte Carlo method specifically to tackle issues of nanoscale particles. The project will start by running experiments at neutron and synchrotron radiation sources, followed by extensive development work on the



Electron microscope image of nanocrystals of iron within a carbon nanotube method. This will involve both design of algorithms and programming, together with testing against data. This is completely new territory, and it is highly likely that some considerable ingenuity may be required in this.

The scientific problems we will tackle with this approach include nanoparticles of silicon and germanium (including mixed materials), and carbon nanostructures within which new phases of iron are found to grow. In studying the nanoparticles one central question is to identify how the structure near the surface of the nanoparticle differs from the bulk. In the case of the carbon nanostructures, the scientific challenge is to identify the structure of the new phases found within the nanotubes and to explore the interface between the two.

Project 3
Title: **Negative thermal expansion**
Supervisor: **Martin Dove**

Over the past decade it has been recognised that a large number of materials show properties that are counter-intuitive, such as negative thermal expansion (Miller et al, Journal of Materials Science 44, 5441, 2009). These can be quite significant properties that occur over very wide ranges of temperature. It turns out that many of these materials can be described in terms of three-dimensional networks of corner-linked polyhedral groups of atoms, such as SiO_4 tetrahedra in phases of silica. Typically these polyhedral groups of atoms have strong bonds, and when the polyhedra rotate they can only do so by pulling neighbouring polyhedra towards them rather than by stretching the internal bonds. Typically the forces involved in rotating two polyhedra about a common linkage are much weaker than the forces associated with stretching the bonds, so that flexing the structure at shared linkages typically has quite large amplitude that increases with temperature, so that the inward pull also increases on heating. This simple model to explain negative thermal expansion has much appeal, but it has not been developed much beyond this starting point (Heine et al, Journal of the American Ceramic Society, 82, 1793, 1999). Furthermore, from the standard theory of thermal expansion based on lattice dynamics, there is a connection between thermal expansion and elastic compressibility, and there is emerging evidence that some materials that show negative thermal expansion may also show the similarly counter-intuitive property of becoming softer under compression (Walker et al, Journal of Physics: Condensed Matter 19, 275210, 2007). This property is not understood at all, although in the case of amorphous silica we have shown that there is a clear link to the flexibility of the network as seen in the lattice dynamics (previous reference).

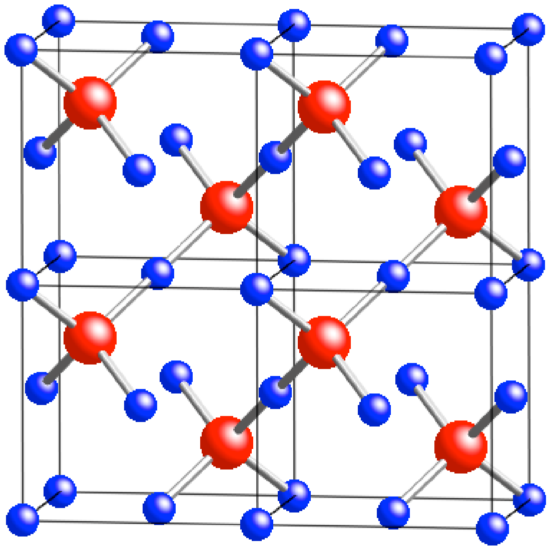


Figure 1. Example of a simple material showing negative thermal expansion, Cu_2O, where the oxygen atoms are shown as the large spheres at the centres of Cu_4O tetrahedral groups of atoms.

The objective of this project is to develop a firmer theoretical understanding of negative thermal expansion materials based on combining lattice dynamics models, elasticity models, and atomistic simulations, anticipating that this work will also lead to a better understanding of compression-induced elastic softening.

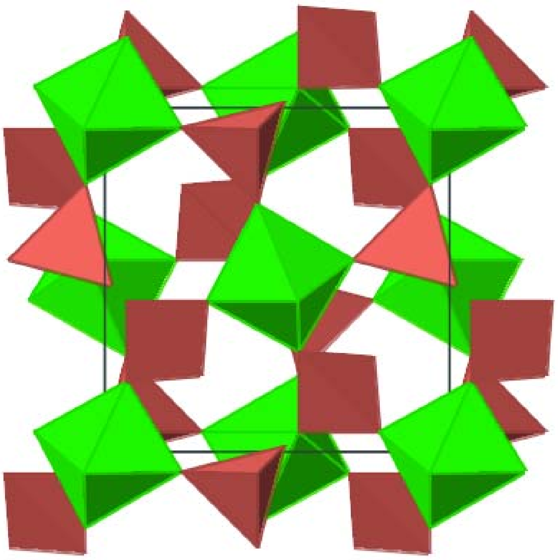


Figure 2. ZrW_2O_8, probably the most strategic example of a material showing negative thermal expansion. The image displays the corner-linked ZrO_6 and WO_4 polyhedra as solid units.

The approach will be to considered in depth a few important examples, some being relatively simple (like Cu_2O, Figure 1), some more complex but of strategic significance (such as ZrW_2O_8, Figure 2, and $Zn(CN)_2$, which looks like Cu_2O shown in Figure 1 but replacing the link atom by a cyanide molecule), and other examples that have characteristic network structures clearly (such as some zeolites and hybrid metal-organic framework materials). Essential physical quantities will be extracted and analysed using a variety of simulation methods, including molecular dynamics techniques and ab initio lattice dynamics methods.

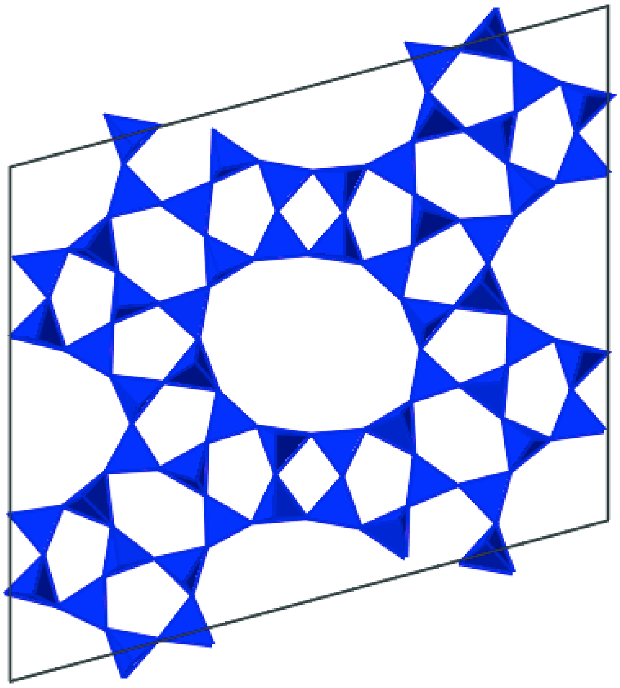
The main theories for normal thermal expansion show how each lattice vibration has a particular contribution to the thermal expansion, and for each example we will identify which modes contribute most to the overall negative thermal expansion, aiming to understand why they have a negative contribution to the thermal expansion and why they have the necessary large amplitude. The role of some particular theories, including our own 'Rigid Unit Mode' theory (Pryde et al, Journal of Physics: Condensed Matter, 8, 10973, 1996), will be critically assessed as part of this process.

Following this critical analysis for a range of examples, we will be in a position to develop a rigorous theoretical understanding of negative thermal expansion. This will be tested by systematically working through some detailed case studies and comparing with experimental data.

Project 4
Title: **Vibrational properties of low-density network glasses and crystals**
Supervisors: **Martin Dove and Kostya Trachenko**

Network glasses are composed of groups of tightly bound atoms, such as SiO_4 tetrahedra in amorphous silica, linked at their corners to form an infinite network. Similar networks are also found in crystalline materials. Frequently these network materials can be produced with different densities, which can be achieved if pores are formed within the network (see figure). The crystalline equivalent phases for silica are zeolite structures, there the pores can enable the network to play the role of molecular-scale sieves. It is to be remarked that there are many aspects of the atomic vibrations of network glasses that are still not properly understood, even though we are getting closer to a complete picture, but the way that the dynamics are affected by the existence of pores in the network is certainly far from being understood. This is the topic of this project.

The main objective of this project is to study the way that density, and effectively the porosity of the structure, affects the dynamics of network glasses, but it is probably that considerable knowledge will also be obtained by investigating corresponding crystalline network materials. The main approach will be to use computer simulations with realistic interatomic potentials.


Example of a porous network – a crystalline zeolite – showing SiO_4 groups of atoms represented by tetrahedral units linked at corners (oxygen atoms). The large pores are connected to form channels in the material.

The main type of network we will explore will be of porous tetrahedral networks. The classic tetrahedral network is the diamond structure, where each carbon atom has found neighbours. It is possible to 'decorate' the diamond structure to generate other know network crystalline materials. For example, by replacing the carbon atom by silicon and placing oxygen atoms half way along each Si–Si nearest-neighbour vector, we can generate a crystalline phase of silica, SiO_2 (albeit after relaxing the structure to give the correct Si–O bond lengths, and allowing rotations

One phase of silica can be described as the diamond structure where the carbon atom is replaced by silicon and oxygen atoms are placed half way along each Si–Si nearest-neighbour vector. There is probably an infinite number of tetrahedral networks that can be generated. For example, amorphous carbon and silicon are known to be described as random tetrahedral networks. There exist algorithms to generate random tetrahedral networks (Barkema & Mousseau, Physical Review B 62, 4985, 2000). The examples generated to correspond to amorphous silicon appear to have atomic structures that have the same short-range order as found experimentally, and when we convert these networks to amorphous silica by addition of oxygens and relax via a molecular dynamics simulation, the derived structure is also in excellent agreement with experimental data (Tucker et al, Journal of Physics: Condensed Matter 17, S67, 2005).

Unfortunately the algorithms for generating network structures do not work well for the case of low-density. The reason for this comes from the form of the interatomic potentials that are required to allow the structure to be relaxed. These potentials are designed specifically for the case of amorphous silicon, which assume that bond angles should be distributed around the ideal tetrahedral angle. However, an empirical observation is that many low-density network materials have 4-membered rings, which are specifically excluded by forcing bond angles to this ideal value. It is proposed that the algorithms could be reformulated in terms of second-neighbour correlations, which is expected to produce some new challenges that will require some thought; in particular is the challenge of avoiding formation of 3-member rings. However, we have previously explored some ideas that might help (Cliffe et al, Physical Review Letters 104, 125501, 2010), and these can be developed and adapted for this particular application. This work on a new algorithm will form the first part of the project.

Armed with a new algorithm, the idea will be to decorate the network with the actual atoms of interest to construct the important test cases. The first example will be SiO_2, and subsequent examples will include hybrid metal-organic framework materials. The dynamics will be explored using both lattice dynamics and molecular dynamics methods, and the objective will be to understand how the dynamics are affected by the density as one general variable, and also by the nature of the structural porosity (for example, the homogeneity of the pore structure). In the case of silica, we will be able to make connections to experiments on the dynamics of porous amorphous materials (silica aerogels).

As an important aside to this work, it will be possible to better understand the role of particular structural motifs (such as the aforementioned 4-member rings) in generating low-density networks. Properly characterising this will be one of the key outputs of this work.

Project 5

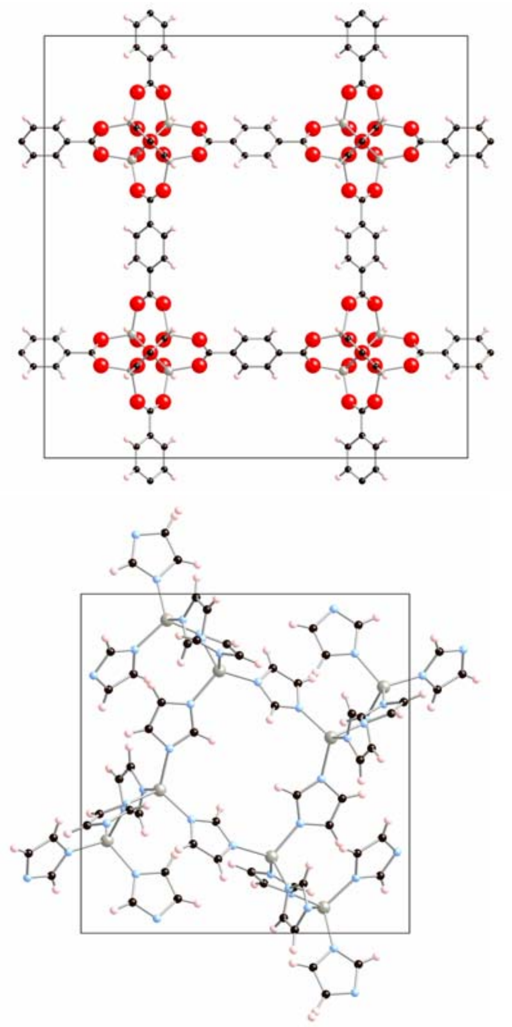
Title: **Metal-organic framework materials for applications in carbon capture and hydrogen storage**
Supervisors: **Martin Dove**

Two issues that are high on the political and environmental agendas are CO_2 in the atmosphere and post-petroleum energy usage. Recently a new class of materials has been created that has generated a lot of excitement because they have potential to have a significant impact in both these areas, namely the class of metal-organic frameworks (abbreviated as MOFs). Their crystal structures contain organic molecules that are linked to each other through metal cations to form stable semi-rigid three-dimensional network structures, as illustrated in the Figure (Rao et al, Journal of Physics: Condensed Matter 20, 083202, 2008).

One potential application for these materials is in CO_2 capture from industrial plants. The approach under current consideration is to bubble effluent gas streams through amine solutions. The CO_2 molecules react chemically with the amine molecules, and the products can easily be separated. The reaction is reversible, and CO_2 can be recovered for storage through a subsequent heating process. Unfortunately this approach is very expensive, and there is a search for economical alternatives to amine solutions; MOFs have emerged as significant candidate materials.

One important group of MOFs for this is based on the imidazolate molecular ligand, ($C_3N_2H_2$), the zeolitic imidazolate frameworks, ZIFs (Wang et al, Nature 453, 207, 2008). This ligand creates a replica of the Si–O–Si bond of ~145° and facilitates the formation of tetrahedral coordination around the metal cation, which enables the formation of structures that share similar features with the polymorphs of silica and related materials, including zeolites.

The crystal structures of zeolites have large pores and channels, and thus large internal surface areas, which gives them widespread applications (e.g. as molecular sieves, catalysts, detergents, soil remediation). MOFs, including ZIFs, can be tailored to have much larger pores and internal surface areas (there are already 1000s of reported MOFs), and industrial-scale production methods can be formulated (already some MOFs are commercially available). A number of papers have reported promising results from experimental studies of the absorption of CO_2 and H_2 in a number of MOFs, including ZIFs, with a range of both chemisorption and physisorption processes. What is now needed is a concerted theoretical/modelling effort to expand this activity. For example, atomistic simulations should be able to identify CO_2 and H_2 adsorption sites within the MOF structure, and provide information on the chemical processes involved. Furthermore, atomistic



Examples of metal-organic framework crystal structures, showing pores and channels. Top shows MOF-5, containing ZnO_4 tetrahedra joined by benzene dicarboxylate ligands. Bottom shows ZIF-1 containing ZnN_4 tetrahedra joined by imidazolate ligands.

simulations will also provide a means for rapid screening of a range of candidate materials for specific applications.

This project will develop the role of atomistic simulation of MOFs for applications in CO_2 capture and hydrogen storage. Atomistic simulations have an excellent record in providing scientific insights and quantitative information across a range of sciences, including work on zeolites for chemistry applications, semiconductors for electronic applications, and silicates for earth and environmental sciences applications.

The first objective of this project is to develop a simulation methodology for the study of MOFs, including interactions involving CO_2 and H_2, that will capture an appropriate level of accuracy, but which will also be general and robust enough to be immediately usable for any desired MOF. Given the complexity of these systems, and the need to simulate for long periods of time (relative to typical atomic time scales, ie of order of 100 ps), the models will be tailored for use with classical molecular dynamics simulation tools. The second objective is to run production-scale simulations using these models.

The plan is to build upon successful but independent approaches in modelling inorganic materials and organic molecules. For the organic part, established and well-tested force-field models will be used. These have been tuned to accurately reproduce the energies of stretching and bending of bonds, and deformations of molecular conformations. Implicit in these models is the need to develop a per-system model of the charge distribution, and this is the first challenge to face. The approach that will be explored is to use the Distributed Multipole Analysis (DMA; Stone, Journal of Chemical Theory and Computation 1, 1128, 2005) method to compute a realistic charge model from the wave functions obtained using quantum mechanical calculations on small charge-neutral clusters. This approach has a number of potential advantages over other charge allocation schemes, including the fact that the projection of the charge and multiple distribution is exact, and that it will identify important higher-order multipole moments. The interactions between the metal cation and the ligand will be parameterised by tuning against a combination of experimental data and quantum mechanical calculations using codes developed for crystalline materials. Interactions between the organic molecules will be based on models developed for the study of organic crystals and polymers, but fine-tuned against the structures of properties of some relevant crystal structures (eg pure imidazole, $C_3H_4N_2$, terephthalic acid, $C_6H_4(COOH)_2$, and related materials). Finally quantum chemistry methods with small clusters will be used to develop models for the interactions involving the MOFs and CO_2 and H_2 molecules.

The second stage of the project will be to perform the main simulations. These will focus on some representative and comparative materials that are based on both the imidazolate ligands, and will be designed to probe a) the structural stability and flexibility of the pure framework structures; b) behaviour of CO_2 and H_2 molecules within the channels and pores and the simulation of adsorption processes. Simulations will be performed for a wide range of temperatures, gas pressure and types of materials. The objective of this stage is to gain sufficient understanding of the processes involved in the capture of molecules within these structures in order to gain a critical assessment of these materials as potential hosts for CO_2 and H_2.

Project 6
Title: **Theory and modelling of disordered condensed matter phases**
Supervisors: **Kostya Trachenko**

http://www.mmp.ph.qmul.ac.uk/~kostya

Some disordered condensed matter phases are common and widely used, including liquids and glasses, whereas others such as crystals amorphized by radiation damage are employed in more specific applications. Compared to crystalline state, physics of disordered phases is much less understood and involves new interesting effects not seen in crystals. In this project, we will use theory and modelling tools to study important effects in disordered condensed matter. Modelling tools will involve classical molecular dynamics simulations, including massive parallel simulations on the UK high-performance parallel computers with many thousands of parallel processors. In addition, ab initio simulations will be employed where relevant.
Examples of systems and physical phenomena to be addressed include but are not limited to:
Structure and dynamics of liquids and glasses (modelling and theory);

Relaxation effects in glass transition (modelling and theory);

Thermodynamic theory of liquids, including classical and quantum liquids (theory);

Structure and dynamics of nano-particles and effects related to surface relaxation (modelling);

Radiation damage effects in materials relevant for encapsulation of nuclear waste and for future fusion reactors, including radiation-induced defects and amorphisation, the effect of radiation damage on materials performance (modelling).

Project 7
Title: **Relaxation and dynamic effects in spin glass systems**
Supervisors: **Kostya Trachenko and Alan Drew**

Since its discovery, spin glass has been considered as a third distinct type of low-temperature magnetic arrangement in solids, in addition to ferromagnetic and anti-ferromagnetic. Great effort went into understanding the nature of the spin glass transition. The collection of new ideas and theories has formed a new large research field in condensed matter physics, with connections proposed to other disciplines such as economics and biology. The continuing interest in this area is due to the presence of fundamental problems that are not understood. In addition, there is current interest in new systems such as magnetic nanoparticles, ferrofluids and so on, where spin glass behaviour is observed.

Most experimental and theoretical studies have concentrated on the effects near spin glass transition temperature T_g. On the other hand, recent theories of structural glass transition attribute most importance to relaxation effects above T_g. One such theory predicts universal dynamic crossovers taking place in both liquids and spin glass systems above T_g. In this project, we will explore the dynamics of spin glass systems above T_g using muon relaxation experiments that measure system relaxation properties. Muon experiments will be performed at ISIS, the world-leading centre for research in the physical and life sciences at the Rutherford Appleton Laboratory near Oxford in the UK.

Using the obtained data, we will study the predicted dynamic crossovers at high temperature, crossover from exponential to stretched-exponential relaxation at high temperature and from Vogel-Fulcher-Tammann to Arrhenius relaxation at low temperature. We will also perform a systematic study of the dependence of T_g on system size. The results will provide new important insights into dynamic behaviour of disordered magnetic systems.

Project 8
Title: Superresolution spectroscopy and imaging for physics-life sciences interface
Supervisors: Andrei Sapelkin

Our aim is to establish optical supperresolution spectroscopy capability within the School of Physics. This capability is required to further extend our research into the interaction between objects that exhibit quantum effects (e.g. quantum dots) and living neuron cells – an activity initiated by recent EPSRC grants. The ultimate objective is to use quantum effects for the purpose of detecting cell communications and to study cell life cycles. This will be achieved by constructing a superresolution microscope in the School of Physics and conducting research on nanoparticle uptake by neuron cells and on sensitivity of light emission to cell-related processes. The superresolution method will be based on recent advances [1] in 3D localisation of nanometer sized objects using laser interferometery that enable to bypass a diffraction limit imposed by commonly used fluorescence and confocal imaging methods. We will also take advantage of blinking effects [2] observed in nanoparticles and relatively low toxicity of the nanoparticles available to us (e.g. Si and Ge). We aim to combine the superresolution techniques with existing microscopy and spectroscopy imaging capability to provide complimentary information set for visual, life cycle and cell signalling characterisation. By the end of the project we will demonstrate the capability to detect single quantum dot location within a neuron cell to within 100 nm using visible light microscopy. We will be able to answer a question of whether light emission due to quantum effects in nanoparticles is sufficiently sensitive to be used for observations of cell lifecycle. Questions of relative toxicity of variety of nanoparticles will also be addressed. This methodology would also enable us to study the details of nanoparticle uptake by, and migration within, neuron cells. Our objectives will be:
Construct and test a superresolution system based on interference-based photon assisted laser microscopy (iPALM)
Test the system using off-the-shelf quantum dots
Carry out spectroscopic and imaging studies on in-house produced Si and Ge nanoparticles
Conduct investigations of uptake of nanoparticles by neuron cell lines (in-house) and primary cultures (UCL)
Assess the possibility of using light emission in nanoparticles for long terms cell imaging and spectroscopy
This lab space, equipment and supplies for sample preparation, standard characterisation and optical spectroscopy are available at QMUL. It will draw from extensive expertise in laser-based spectroscopy available in the Condensed Matter Group. Some of the work will be conducted in collaboration with the University of Toulouse, France who will lend their expertise in interference-based imaging techniques. Our work with primary neuron cultures will be conducted in collaboration with Institute of Neuroscience, University College London.

References:

G. Shtengel et al, PNAS 2009, vol. 106 no. 9, pp 3125-3130
A. L. Efros, Nature Materials, 2008, vol. 7, pp 612-613

Project 9
Title: **Optically-Detected X-ray absorption in nanoparticles**
Supervisors: **Andrei Sapelkin**

The technique of X-ray absorption spectroscopy (XAS) has proved to be very powerful tool for structural investigations of materials over last 40 years. There are several specialized modes of data collection despite straightforward transmission measurements. One of such modes is optically-detected (OD) data collection which utilizes the link between x-ray absorption events and light emission from a material in question. A variation of integral photoluminescence intensity can be identical to an x-ray absorption signal as the incident x-ray energy is scanned across an absorption edge. Thus it can be a very powerful technique indeed for identification of local structures responsible for light emission in a multi component system. Moreover, various regions of a light emission spectrum can be examined to reveal contributions of the atomic-scale structures involved in a de-excitation process accompanied by the light emission. Therefore, this method is invaluable if not unique for identification of nano and subnano regions responsible for light emission in nanostructures and for testing quantum confinement models. However, successful application of the method crucially depends on the excitation decay pathways available in a material. In some instances incorrect or even no meaningful structural information can be obtained. Also, the spatial sensitivity of the method is still a subject of debates. With this project we plan to address these outstanding problems by using synchrotron radiation and a range of materials specifically tailored for OD-XAS measurements. These materials include of nanocrystalline Ge, alternating layers of nanocrystalline SiGe and ZnO nanowires. We also intend to develop a methodology based on OD-XAS measurements that would allow identification of various light emitting and non-emitting pathways and their structural and optical interrogation. The work will be carried out in close collaboration with Diamond Light Source – the UK's national synchrotron. Our objectives will be:
Establishing a data analysis methodology for data reduction and analysis
Test methodology on standard samples (nano-Ge, quantum dots)
Identify structures on nano and sub-nano scale responsible for light emission in nano-Ge and ZnO nanowires
Determine spatial sensitivity of method using nanometer-sized layers of SiGe and data collection in OD and standard transmission modes
The objectives will also include improving the team's exploitation of latest XANES simulation software and establishing a streamlined methodology for data analysis. The project will also develop tools for particle size calculations based on Raman and PL data and quantum confinement models. This project will be based on extensive expertise of the team in the use of these methods for materials characterization and their recent experimental results. Materials will be sourced from SEMS, QMUL (Steve Dunn); GPI, Moscow and prepared in-house using a range of laser-based techniques such as ablation.
This lab space, equipment and supplies for sample preparation, standard characterisation and optical spectroscopy are available at QMUL. Beamtime and associated support will be applied for at synchrotrons in the UK (DIAMOND) and Europe (ESRF, MAXLAB). Materials will also be obtained via existing collaborations with institutions external to QMUL (GPI, Moscow; UCL).

Project 10
Title: **Local atomic dynamics in liquids**
Supervisors: **Andrei Sapelkin, Kostya Trachenko**

Unlike solids and gases that are fairly well understood, a consistent theory of liquids remains one of the main challenges in physics. In liquids, phonons have a very short lifetime and the total potential energy does not depend linearly on temperature. Thus it may appear that atomic vibrations in liquids cannot be described by the harmonic oscillator model and that the equipartition theorem for the potential energy is not upheld. Furthermore, the potential energy of liquids generally does not depend linearly on temperature. A major reason for this difficulty is that the structure of a liquid is temperature dependent and a part of the temperature dependence of the total potential energy originates from the temperature-dependent configurational energy. Then it may be possible that the vibrational part of the energy can be described in terms of the harmonic excitation models while the temperature dependence of the configurational energy could be expressed separately. Some early theoretical calculations and modelling has been made for the short-range modified Johnson pair potential developed for iron, the Lennard-Jones potential, the modified Johnson potential [1]. However, there is currently very little experimental evidence to support these theoretical results. With this project we will address the gap in experimental information and test current theoretical approaches by conducting temperature-dependent x-ray absorption measurements in a wide temperature range (10 K - 1000K) in Ga. Gallium is a particularly convenient object for such tests due to the relatively low melting temperature (T = 303 K) and it's K absorption edge located within region easily accessible at variety of experimental station at Diamond Light Source. Our aim will be to test weather indeed the structures of liquid are determined by repulsive part of the potential and to what extent the unharmonicity of a potential affects the local atomic configuration. XAS measurements will provide information on local symmetry and level of unharmonicity in local interactions. Moreover, we plan to conduct similar studies on Galinstan (melting T = 254 K) – an alloy of Ga, In and Sn. These would be the first study of local atomic dynamics and ordering in a wide temperature range in liquid and solid state. Again K edges of all three elements in the alloy are accessible at Diamond and measurements will provide pair distribution information, site symmetry and local dynamics for each of elements. Thus we will be able to test whether proposed theoretical approaches can be extended to multicomponent systems. Our objectives will be:
Conduct series of XAS experiments at Ga K-edge in Gallium and obtain information about temperature dependence of local symmetry, level of unharmonisty of local potential (via cumulant expansion) , numbers of nearest neighbours. Solid state of Gallium will be used as a reference point.
Conduct series of XAS experiments at Ga, In and Sn K-edge in Galinstan and optain information on temperature dependence of local symmetry, level of unharmonisty of local potential, numbers of nearest neighbours for each of the elements.
Based on our experimental results verify the validity of current theoretical models.
This project will be based on extensive expertise of the team at QMUL in XAS spectroscopy and theoretical calculations of liquid state.

References

1. V. A. Levashov et al, PRB 78, 064205 (2008)

Project 11
Title: **Length distribution of Carbon Nanotubes.**
Supervisors: **Kevin Donovan**

Outline of project.

By applying a transient (square pulsed) electric field across a suspension of carbon nanotubes, SWNTs, in a viscous medium a dipole is induced on the SWNT and the SWNT will then rotate in the applied electric field in an attempt to minimise its potential energy. This rotation and consequent ordering of the nanotube suspension into an anisotropic suspension from what was an isotropic suspension (in zero field) may be followed in real time using observation of transient optical changes of the suspension as an experimental probe of the order. For example figure 1a shows how the difference in transmission through the suspension of laser light polarised parallel and perpendicular to the applied electric field evolves with time after the application of the square pulse electric field of ≈ 40 ms duration. Such studies have allowed us to deduce a great deal concerning the electronic properties of nanotubes. For example we have succeeded in demonstrating, from the steady state values of figure 1a (and similar data), that the metallic nanotubes are excellent models of rigid metallic cylinders with a polarisability as predicted by theory. From the rise time of data such as that in figure 1a it has been shown that the SWNTs “feel” a local viscosity identical to the macroscopic viscosity of the suspending medium they are in, unaffected by the nanoscopic size of the particle.

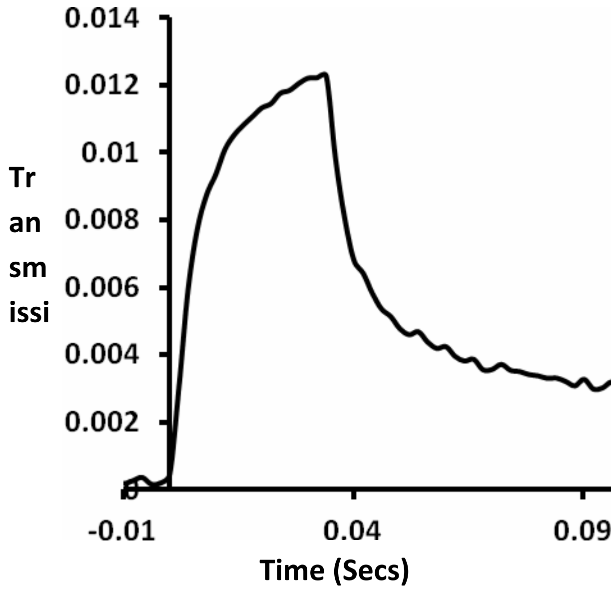


Figure 1a

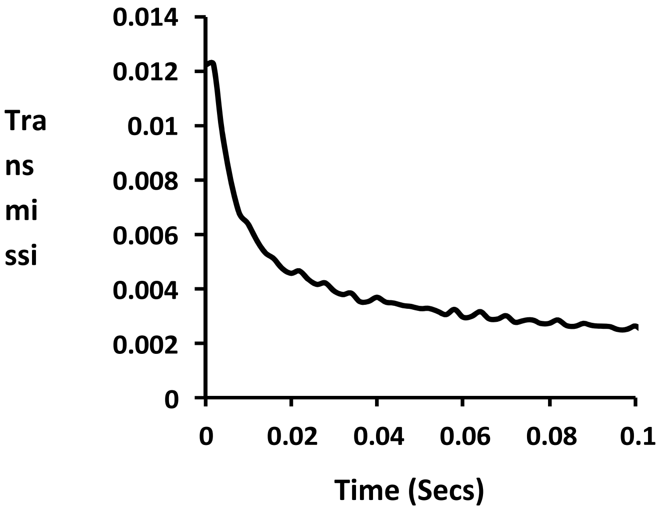


Figure 1b

It is now proposed that the techniques that have been developed for this purpose are turned to the task of determining the distribution of nanotube lengths in a given sample g(L) with g(L)dL being the fraction of nanotubes with length between L and L + dL The samples that have been used (and all commercially available samples) have an ill defined length distribution where the length is claimed by the manufacturers to lie typically between 0.5μm and 2μm for SWNTs produced by Chemical Vapour Deposition with no further information given. A well defined length distribution is notoriously difficult to establish and to date efforts to this end have been confined to direct imaging techniques with AFM followed by counting.

A method for finding the length distribution is suggested by considering the data of figure 1 and in particular the decay seen in figure 1b. While the data from figure 1a may be extremely well fitted to a single exponential risetime the decay of the optical transmission is clearly not exponential in

character as seen in figure 1b. It is because there is a distribution of SWNT lengths that the decay of figure 1b is more complex than a single exponential decay.
We can consider a monodisperse sample where the randomisation of the nanotube orientation due to Brownian forces would follow a monoexponential decay with

$$\Delta n(t) = A_L \, exp\left(-\frac{t}{\tau_L} \right) \quad (1)$$

The decay time, τ_L , is related to the rotational diffusion coefficient, D_R , with

$$\tau_L^{-1} = \alpha = 6D_R \quad (2)$$

and D_R being related to the rotational friction coefficient and nanotube length through the Einstein relation

$$D_R = \frac{k_B T}{\zeta_R} = \frac{3k_B T\left(ln\left(\frac{L}{b}\right) - \kappa \right)}{\pi \eta_S L^3} \quad (3)$$

With the decay rate $\alpha_L = \tau_L^{-1} \propto L^{-3}$ depending on length..
With this in mind we may consider the decay of order in a polydisperse sample of nanotubes by considering it as a superposition of effects due to different lengths present and writing the birefringence (or linear dichroism) as a sum of effects due to different lengths/decay rates, α.

$$\Delta n = C_1 \mathbf{exp}(-\alpha_1 t) + C_2 \mathbf{exp}(-\alpha_2 t) + C_3 \mathbf{exp}(-\alpha_3 t) + C_4 \mathbf{exp}(-\alpha_4 t) + \mathbf{.......} C_m \mathbf{exp}(-\alpha_m t) \quad (4).$$

Aims and Objectives
The length distribution of a sample is one of the more useful pieces of information that manufacturers of nanotubes, researchers and consumers would all wish to know. The length distribution would be of significance, for example, for the many applications involving the use of SWNTs in composites where their extraordinary mechanical or electronic properties are intended to improve the composite material.
It is the goal of the project to discover the values of the pre-factors C_m in equation (4) and from these find the length distribution of the SWNTs in the suspension.
There are a number of ways in which this may be done including;

The peeling technique

Discrete inverse z transfom of the data of figure 2.

Multi Variate Linear Regression Analysis, MVLA, may also be used.

Work plan
To achieve accurate results for the length distribution, data such as that of figure 1b must be obtained extending over many decades in time and therefore involving a large dynamic range of the sample transmission. Refining the data acquisition technique is thus a key first step.

Having obtained sufficiently good data the techniques of analysis listed above may be tried and a length distribution obtained.

Having obtained a length distribution the result will need to be tested in a number of ways in order to confirm that it behaves sensibly;

Obtain the decay data at low, medium and high fields, ie. at low medium and high initial order and demonstrate that the length distribution g(L) obtained is independent of electric field.
Obtain the decay data with suspending media of low, medium and high viscosity and demonstrate that the length distribution g(L) obtained is independent of suspending medium and therefore a property of the SWNTs.
Obtain the decay data at low, medium and high SWNT concentration and demonstrate that the length distribution g(L) obtained is independent of concentration and therefore a property of single SWNTs.
Obtain the decay data on commercial SWNT samples from different manufacturers and synthesised by different methods in order to find out if g(L) is determined by synthetic method.
Obtain the decay data on SWNTs that have been reduced in length by means described in the literature and verify that the g(L) is shifted to shorter lengths.
Use AFM of SWNTs to check the length distribution by an alternative method.

Project 12
Title: **Isomer-Pure Bis-PCBM-based Organic Solar-Cells**
Supervisors: **John Dennis**

Introduction

Bis-PCBM is easy to synthesise and highly soluble, and solar cells based on this material are relatively simple to fabricate and have one of the highest known certified power conversion efficiencies amongst organic photo-volvaics. However, Bis-PCBM's potential in this area is certainly considerably higher. This is because bis-PCBM comes as a mixture of a larger number of structural isomers; a mixture of the good, the bad, and the ugly, with an overall good performance. The proposed research plan is to purify each and every isomer and determine their molecular structures, test the photo-voltaic performance of each isomer to determine which isomer are excellent, good, fair, poor, and electron traps and to answer the academically useful question, why that is so.

Background

Concerns about climate change and rising fuel costs, etc., driving a search for cheap, widely available photovoltaics to harness solar energy. Traditional silicon-based solar cells have a disadvantage in that to operate properly they require very high purity raw materials and ultra-clean manufacturing environments; which implies high costs. Organic photovoltaics on the other hand offer the potential to greatly decrease the cost and availability of photovoltaic energy due to lower materials costs and lower manufacturing costs, but currently this comes at the cost of decreased efficiency. The certified power conversion efficiencies ("PCE") of state-of-the-art plastic solar cells are 4 – 5%. While adequate for the first commercial applications, developers are aggressively seeking to increase the PCE to allow for a broader market (e.g., powering so-called cheap electronics). The best-performing organic photovoltaic device architectures use the bulk heterojunction configuration; which consists of a polymer electron donor (p-type) and fullerene-derivative electron acceptor (n-type) mixture in the active layer. Thus, improving the properties of the p-type and/or n-type materials are key areas of research and development for increasing the PCE. With optimal materials the performance of plastic solar devices could theoretically approach the best silicon devices.

Most of the focus in developing new materials has centred on improving the electronic properties of the p-type polymer. While several new generations of p-type polymer have provided advances over the last 10 years, the n-type used in state-of-the-art systems over the last 12 years has almost exclusively been fullerene-based. Although C_{60} is an excellent electron acceptor, it suffers from very low solubility, and thereby low processability. A substantial increase in solubility (processability) came with the development of the methanofullerene Phenyl-C_{61}-Butyric-acid-Methyl-ester, ("PCBM") as the n-type. Indeed, PCBM is now almost universally used at the acceptor in plastic solar-cells. Similarly to the p-type polymer, various strategies have been tried to improve performance of the n-type fullerene derivative, with varying degrees of success. These include improving optical absorption; solubility; miscibility with the p-type polymer; and/or increasing the energy level of the lowest unoccupied molecular orbital.

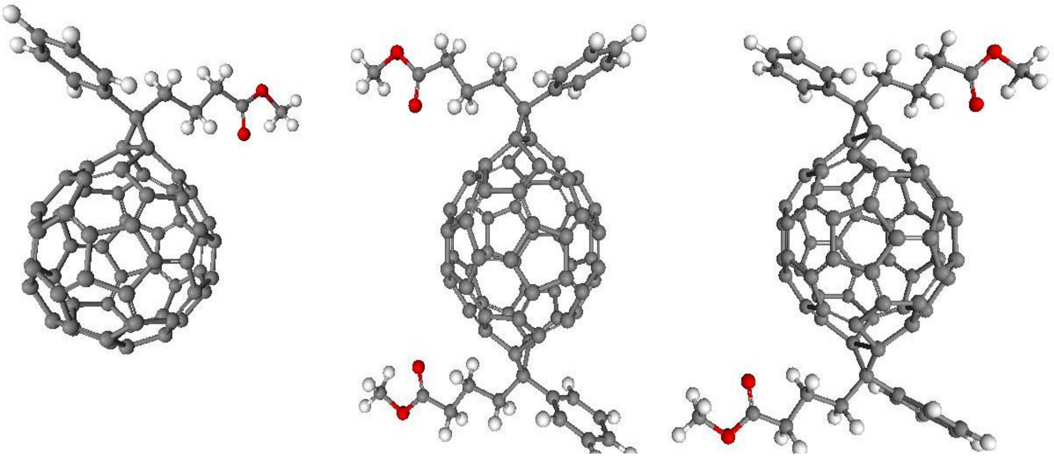
It is well known that the open circuit voltage (V_{OC}) of solar cells is a function of the energy difference between the highest occupied molecular orbital ("HOMO") of the donor and the lowest unoccupied molecular orbital ("LUMO") of the acceptor. Although, using electron-donating groups to influence the electronic properties of the fullerene cage has confirmed that a raised acceptor LUMO improves V_{OC}, the changes in the LUMO are quite small and fabrication problems arise owing to poor solubility.

A much more effective approach, and the one to be adopted here, is to raise the LUMO by altering the fullerene cage by adding multiple constituents directly to it. A very promising molecule of this type is bis-PCBM; where two constituents are attached to the C_{60} cage. The LUMO of Bis-PCBM is

110 meV higher than that of PCBM, a very significant increase. Furthermore, the solubility (processability) of bis-PCBM is more than 10 times greater than that for PCBM; making it considerably more convenient for fabrication of solar cell devices.

Our collaborator, Prof J.C. Hummelen of the University of Groningen (who pioneered the abovementioned research into PCBM), has already substituted bis-PCBM for PCBM in devices based on the well-known P3HT acceptor configuration. Optimal conditions for bis-PCBM were obtained by using slightly more n-type in the blend at slightly thinner film thickness than for PCBM. The resulting optimized devices gave a certified PCE of 4.5%, which is among the highest public certified efficiencies recorded for a P3HT organic solar device.

Unfortunately (and unlike PCBM), bis-PCBM can exist in hundreds of different structural isomeric forms; each with a unique LUMO energy. However, previous work on PCBM suggests that the modified fullerene is a methanofullerene involving only an inter-pentagonal (double) bond. If this remains the case for bis-PCBM (which is chemically reasonable) there would be a 32 possible isomers; resulting from 16 distinguishable double-bonds across which the two constituents can attach in either a trans or cis arrangement. The LUMOs of these isomers vary considerably, which implies that so will the PCEs of solar-cells fabricated with isomer-pure samples. Those with a low LUMO will act as electron traps, whereas those with high LUMOs will act as excellent solar cell active materials. Being able to make devices only with isomers with high LUMOs would represent considerable progress over research carried out on the isomer mixture.



PCBM and two of the isomers of bis-PCBM. Both bis-PCBM isomers shown above are both based on fullerene carbons 1,9 (at the top) and 52,60 (at the bottom) but the two constituents are in cis and trans arrangements. Substituting across each of the remaining 15 distinguishable fullerene double bonds in both cis and trans configurations gives another 30 possible structural isomers (32 in total).

Dr Dennis' laboratory has the best preparative recycling high pressure liquid chromatography ("HPLC") purification facilities in Europe dedicated to fullerene-based research. These include two fully preparative Japan Analytical Industries LC-980 HPLC machines, each with peak-recycling capabilities. Peak recycling is crucial to this proposal is it effectively gives a many-fold increase in column length. These are coupled to a range on complimentary Cosmosil preparative (20 mm diameter) HPLC columns (including Buckyprep-M, 5-PYE and 5-PBB) and a dedicated Bruker Autoflex mass spectrometer for routine monitoring of fullerene purification.

It is proposed to combine those purification facilities and expertise with the photovoltaic-device characterisation fabrication expertise and facilities of the World's leading researcher on PCBM-based solar-cells (Prof Hummelen - University of Groningen) to produce and systematically study solar cells based on pure bis-PCBM isomers with the aim of producing high-efficiency organic solar cells.

The Proposed Research Plan

Objectives

The objectives of the project are to have:

Purified all as-produced isomers of bisPCBM from each other, and to have structurally characterise each and every isomer by multinuclear NMR spectroscopy (together with the associated quantum-chemical simulations). Other characterisation methods including IR/Raman spectroscopy, UV-Vis absorption spectroscopy and cyclic voltammetry, will also be employed.

Synthesised, characterised, optimised production for photovoltaic devices of the above type for each and every individual isomer.

Determine which isomers produce efficient/inefficient devices (ranked them in order), and hypothesised reasons why some isomers are more efficient than others.

Purification

BisPCBM will be synthesised by standard techniques, which can potentially produce a mixture of 32 methanofullerene isomers. Although not all of these isomers are expected for form owing steric effects, etc., our preliminary analysis suggests that there are at least 24 isomers in the as-produced mixture. All of these isomers will be separated from each other by recycling preparative HPLC. This is the most important stage as it is the stage that separates the proposed research from that being undertaken elsewhere. No other group working on these or similar materials possesses the recycling HPLC facilities, which is the reason why no isomer pure samples have been previously studied.

Characterisation

Structure identification: Once purified each isomer-pure bisPCBM sample will be characterised by ^{13}C NMR spectroscopy in order to determine its molecular structure. To aid in the analysis of the spectra, quantum chemistry calculations employing HF/DFT hybrid methods will be used to simulate the spectra of each isomer, which will be compare to the experimental spectra. For additional confirmation of structure simulated IR/Raman spectra for each isomer will be compared with experimental IR and Raman vibrational spectra. LUMO levels, etc., will be obtained by cyclic voltammetry aided by UV-Vis absorption spectroscopy.

Device Fabrication

Essentially the solar cells will consist of a transparent glass or polymer base coated with a cell in which an 'active layer' is sandwiched between a transparent indium tin oxide (“ITO”) anode and a reflective aluminium electrode. Light enters the cell through the base and travels through the ITO anode and enters the active layer where photo-induced charge separation occurs. Any light leaving the cell is reflected back by the aluminium cathode to enhance operation. In the active layer the separated charges are transported to the anode/cathode (as appropriate) and the electrons travel from the cathode to the anode via an external circuit.

The project is concerned with improving the performance of the active layer by increasing the LUMO of the acceptor. To this end, electron accepting (n-type) isomer-pure bis-PCBM samples will be mixed with a suitable electron-donating (p-type) polymer: e.g., P3HT. The p-type:n-type ratio and active later thickness will be optimised for each isomer during the project. Our collaborators at the University of Groningen pioneered similar research into PCBM and carried out the preliminary work on the bis-PCBM isomer mixture; and the student will work alongside these researchers, gaining their expertise, during this stage of the project.

The main driving force behind this project is that the open-circuit voltage scales with the difference between the HOMO of the donor and the LUMO of the acceptor. However, it is unlikely to be the only factor affecting device performance. For example, side different chain positions may lead to differences in the microstructure of the P3HT:bisPCBM active layer, and electron transport through the fullerene phase may be affected by side chain-related steric factors. With the availability to the project of data from more than 20 different isomers the student in the final stage of the project will involve deriving hypotheses on why some isomers are better/worse than others.

Training

The students will gain training, experience and expertise in (1) chromatographic molecular purification techniques, (2) molecular structure determination by spectroscopic (e.g., ^{13}C NMR, and IR/Raman) together with associated molecular modelling through quantum chemical calculations, (3) solar-cell fabrication techniques, and (4) methods of characterising the electronic properties and efficiencies of solar cells.

Work Plan

Months 1 – 4: Synthesise enough bis-PBCM for the entire project and carrying out a rough HPLC separations into 4 sub-fractions each containing ca. 6 isomers of bis-PCBM.

This will be followed by 4 seven-month cycles working on each of the 4 sub-fractions from above, as follows:

Months 5 – 6: Purifying all (ca. 6) isomers by recycling preparative HPLC from the sub-fraction.

Month 7 – 8: Measuring and analysing the^{13}C NMR spectra of each isomer in association with quantum chemical molecular modelling and spectroscopic simulations. Cyclic voltammetry and IR/Raman spectra of the purified isomers will also be measured and analysed during this period

Months 9 – 11: Optimising device fabrication the electronic characterisation of each optimised device.

[the work-plan for months 5 – 11 is repeated during months, 12 – 18, 19 – 25, and 26 – 32 on the other three sub-fractions]

The final 4 months will be spent analysing the results from all (ca.) 24 isomers as a whole, drawing and over-arching conclusions, and hypothesising from them why some isomers are better than others as solar cells.

Project 13
Title: **Synthesis of Novel Thermodynamically Stable C_{70} Derivatives**
Supervisors: **John Dennis**

Introduction

Ever since their discovery in 1985, fullerenes have attracted wide interest owing to their novel structure and potential applications in electronics, magnetics, spintronics, photophysics, biology and medicine. Although a large range of fullerenes from C_{60} to C_{98} (including several isomers in many cases) may be solvent extracted from arc-processed graphite, their abundances are about 70 % C_{60} (I_h isomer), 30% C_{70} (D_{5d} isomer) with all other fullerenes combined contributing less than 1% of the total. Hence, C_{60} and C_{70} are the only fullerenes where large scale production is feasible at reasonable cost.

The major fullerene C_{60} is shaped like a football (soccer) in which all carbon atom environments are identical. C_{70} on the other hand is shaped like a rugby ball and possesses 5 different carbon atom environments, which give rise to 8 different types of bonds. Additionally, being rugby-ball shaped the curvature of the surface of C_{70} varies as one goes from one pole to the other (curvature is constant for C_{60}). That curvature is greatest at the poles and at a minimum (flattest) at the equator. The five different types of carbon atom have different chemistry that in turn depends on which of the 8 different types of bond is involved. Additionally, the varying curvature contributes a further dimension to that chemistry. Hence, the synthetic chemistry of C_{70} is potentially much richer than that of C_{60} in that is involves both chemo- and regio-selectivity.

Bond-strain and Reactivity

Fullerenes are made from sp^2-hybrisides carbon atoms. Like benzene or a graphene sheet, sp^2 carbon atoms prefer to be flat, but to close to form a fullerene they must be curved. Curvature increases the energy of the carbon atoms (which want to be at an energy minimum). A flat C_{70} graphene sheet is also unstable despite being flat owing to the presence of so-called dangling bonds at the edge of the sheet. The dangling bonds can be pacified by the C_{70} sheet curving to give a ball in which the dangling bonds terminate with each other. Hence, the relatively highly curved poles of C_{70} have the least thermodynamically stable carbon atoms; equator; and those at the relatively flat equator are the most stable atoms in the molecule. A corollary of this is that owing to the consequent lower activations barriers for reactions at the poles compared to those at the stable equator the carbon atoms at the poles are more chemically reactive that those at the equator. Hence, the chemistry of C_{70} is kinetically rather than thermodynamically controlled (i.e., one gets the compounds that form the most readily, rather than those that are the most stable). For this reason all previous chemistry of C_{70} has centred near the poles (never at the equator).

The Supervisor's Contribution

Recently, collaborative research between researchers at China's Key Laboratory for Molecular Nanostructures and Nanotechnology (which is within the Institute of Chemistry, CAS, Beijing) and the Supervisor led to the development of two high-temperature synthesis methods that enabled us to overcome these barriers and obtain the first thermodynamically stable adduct of C_{70} (i.e., one where the addend adds to the equator). Such adducts cannot be formed by normal synthetic chemistry techniques owing to the abovementioned very high activation barriers that need to be overcome (which we have calculated to be higher than 10 kcal mol^{-1} than it on any other area of C_{70}). Our work, published in Angewandte Chemie International Edition during 2010, has opened the way to the formation of exciting new fullerene compounds that were previously impossible to obtain. Importantly, and in terms of potential applications of such species, as addition to the equator of C_{70} cannot be achieved by 'wet chemistry', the addend cannot be removed by normal chemical methods. Hence, the addend is a thermodynamically stable 'anchor' that will remain in place should the adduct as a whole be subjected to further synthetic chemistry (e.g., to make it water soluble via multiple –OH additions to the cage). This stability points towards potential applications where functional groups can be wedded to the anchor of a water soluble fullerene – examples might include targeted drug delivery systems there the drug and the specific tissue-targeting group are attached to thermodynamically stable anchor (or anchors should multiple additions to the equator be achieved).

Program and Methodology

High-Temperature Synthesis

Our UK/China research collaboration has led to the development two distinct high-temperature synthesis methods for the preparation of the most thermodynamically stable C_{70}-CH_2 isomer. The first is a modification of the 'standard' Krätschmer–Huffman contact-arc fullerene synthesis method, in which a trace of a reactant gas is introduced to the arc chamber together with the helium buffer gas. The second is a 'CVD'–based method in which a reactant gas is passed over pre-purified C_{70} at low pressure and high temperature. The former method makes fullerenes within a generator where an electric arc produces a high temperature under an inert atmosphere, while the latter method provide a direct reaction of fullerene (C_{70} gas for instance) with the reactant gas at high temperature.

Objectives

The objectives of the proposed research are to have:

(1) optimized the experiment parameters for the production of the thermodynamically stable isomers of C_{70}-based adducts (C_{2V}-$C_{70}CH_2$ for instance);

(2) synthesized and spectroscopically characterized several new thermodynamically stable derivatives of C_{70} by our high-temperature synthesis methods with various reactive gas (NH_3, CO, NO, etc.).

(3) compared properties (electrochemical property for instance) of thermodynamically stable isomer with other isomers.

Optimization: We have shown that both methods successfully produce the most thermodynamically stable isomer of a carbene derivative of C_{70}. Additionally, we have produced enough material by both methods for lab-scale spectroscopic characterization. Although the relative yield is species are very high (relative in the sense that little of something is many times more than practically none of something), the absolute yields were quite low (ca. 5 mg). Clearly, this is not enough for commercially viable applications. The major contribution to the low yield is that the productions conditions resulted from an educated guess [which worked]. However, the production conditions have not been yet been optimized in any way. Thus, there exists within the parameter-space considerable scope to optimize yields, and is proposed to this optimization will be thoroughly carried out during the 1st year.

Synthesis: As addition to the waist of C_{70} cannot be achieved under normal synthetic chemistry conditions, once formed (by our pyrogenetic methods) the addend cannot be removed chemically. Hence, as mentioned above in the Background Section, the addend is a thermodynamically stable anchor that will remain in place should the adduct be subjected to further synthetic chemistry. It would be desirable to add some kind of 'useful' unit, e.g., a drug and/or a specific tissue-targeting group (in relation to potential bio-medical applications at least) to the anchor of C_{70}, which can then be waters-solublized. However, to this end, carbene is not an ideal anchor for further derivitization of that site. Adding an amino group or a carbonyl group as a thermodynamically stable anchor instead of carbene would make the addend more amenable to further synthetic chemistry at the anchor. Hence, once the conditions are optimized, other gases such as NH_3, CO, NO, will be employed in place of the CH_4 used in the carbene addition. With the aim of producing such novel thermodynamically stable C_{70} addends.

The Host Environment (Host Researcher, Laboratory and Institution)

The Host Researcher's laboratory has contact-arc and tube-furnace fullerene production equipment coupled to world-leading HPLC facilities for fullerene purification. These include four Japan Analytical Industries LC-980 fully preparative peak-recycling HPLC machines. Peak recycling is crucial to this proposal is it effectively gives a many-fold increase in column length, which facilitates the separation of species with nearly identical HPLC retention times. The QMUL group has a range on complimentary Cosmosil preparative (20 mm diameter) HPLC columns (including Buckyprep-M, 5-PYE and 5-PBB) and a dedicated Bruker Autoflex mass spectrometer for routine monitoring of fullerene purification. These facilities are housed with a laboratory that was refurbished by a Wolfson Award from the Royal Society. Within the host institution, we have access to a range of spectrometers for fullerene characterization including FTIR/Raman, UV-Vis absorption, 600 MHz multinuclear NMR.

Work-Plan

Task 1 [optimisation] is to be completed during the first 6 months.

Task 2 [synthesis, purification and characterisation] will consist of three 9-month cycles where (a) a nitro group, (b) a carbonyl group and (c) and an amino group will each be added to the C_{70} cage and the resulting the products purified and then spectrscopically characterised by a range ot techniques.

Task 3 [property comparisons and conclusions] is to be completed during the final three months of the studentship.

Project 14
Title: Sensitized up- and down- conversion in Yb^{3+} and Tb^{3+} containing perfluoro-organolanthanides.
Supervisors: Ignacio Hernandez, William Gillin

Energy conversion via up- and down-conversion has been suggested as a means to increase the efficiency of solar cells and light emitting devices. The idea is to harvest the light at selected wavelength and re-emit it a region of the spectrum more suited to the performance of the device. We have proved the occurrence of up-conversion and down-conversion, through quantum-cutting, in a number of organolanthanide containing coordination polymers.

The project will be devoted to the study of new sensitized energy converting perfluorinated organic systems based on energy transfer from the organic chromophore to Yb^{3+} and Tb^{3+}. This will be done by the combination of organolanthanides with moieties presenting high broad absorptions in the UV (for quantum-cutting: Tb^{3+} sensitization →Yb^{3+} emission) and in the IR (for up-conversion: Yb^{3+} sensitization → Tb^{3+} emission). A number of ligands with absorption bands in the range 200 - 500 nm are already available for Tb^{3+} sensitization. Sensitization of the Yb^{3+} will be explored through a range of perfluorinated IR absorbing bands in the range 700-1000 nm.

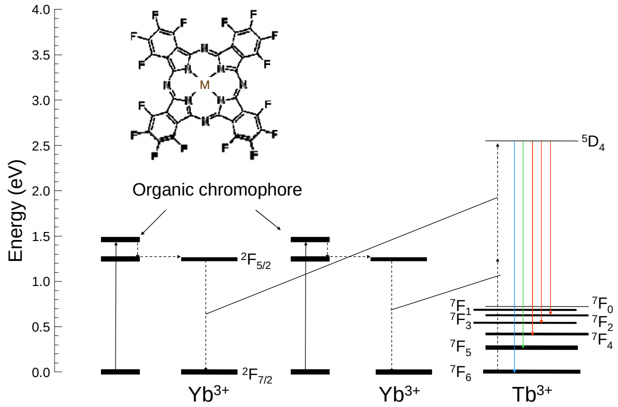


Figure 1. Sensitized Yb^{3+} upconversion process. Two IR photons are absorbed and a visible photon emitted via energy transfer from Yb^{3+} to Tb^{3+}.

These materials will be produced and characterized through a full spectroscopic study in order to analyze their performance.

The research will extended to other rare-earths, such as Er^{3+}, Ho^{3+}and Tm^{3+} studying the processes in detail. This includes the characterization of energy transfer routes and possible non-radiative mechanisms limiting the efficiency of the systems. After acquiring an understanding of the involved processes the aim will be to increase the energy-conversion properties in new materials. This could be done by combination with species controlling the distance between the different sensitizers and activators or in multi-layered systems obtained by spin-coating or evaporation of the different components. The electronic properties of the thus obtained products will be thoroughly characterized at this point.

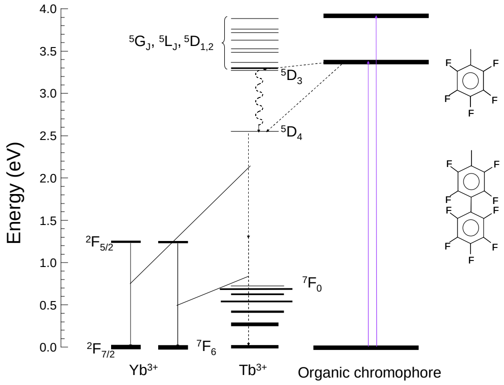


Figure 2. Sensitized quantum-cutting downconversion: A photon in the visible produces two IR photons via energy transfer from Tb^{3+} to Yb^{3+}

As a final step, implementation in the corresponding solar cell or light emitting units will be done on selected materials.

REF: I. Hernandez et al. Advanced Materials (2010) in press DOI : 10.1002/adma.201002674

Project 15

Title: **Transition metal-ion complexes as light harvesting materials for rare-earth based infra-red emitters**

Supervisors: **Ignacio Hernandez, William Gillin**

At present, most of commercially available optical amplifiers for optical telecommunications are based on lanthanide-doped silica optical fibres. However, the limited erbium concentration that can be achieved in these systems, together with the low absorption coefficient of the erbium ions means that relatively long lengths of fibre are required along with high-power pump-lasers for amplification. These factors mean that the technology cannot be integrated into planar waveguides for integrated amplifying devices in short distances.

Highly absorbing organics in combination with erbium provide a potential means of improving on the properties of this ion (or indeed other lanthanides, for different wavelength regions) as a gain medium. A number of organo-metallic complexes based on lanthanides exist, showing energy transfer from the organic parts to the central ion allowing an increase of the effective excitation cross-section at the required wavelengths by orders of magnitude. However the presence of hydrogen-containing groups in the organics produces a decrease in the luminescence lifetime and overall emission efficiency due to their high vibrational energy. Hence, the most interesting organic ligands must be fully halogenated in order to keep the vibrational frequencies low and thus preserve the emission capabilities of the central ion. Available perfluorinated ligands usually provide absorption at short wavelengths.

Some transition metal ions provide extremely coloured organic complexes meaning strong absorption of light in the visible range. We will try to produce systems in which the energy absorbed by these moieties is transferred to infra-red emitters by means of inter-molecular energy transfer.

The student will obtain fully halogenated organolanthanides materials on the basis of established synthesis routes (or through collaboration with chemistry groups) as well as highly coloured perhalogenated transition metal complexes (some of which are commercially available). He or she will study the spectroscopic and excited state dynamical processes in the isolated organolanthanides and in the transition-metal containing dyes. Mixed transition metal-organolanthanide compounds with different species concentrations will be produced though physical or chemical methods and will be subsequently studied spectroscopically in order to characterize the intermolecular processes. From the thus obtained information, new materials will be produced aiming at optimizing the sensitization of the lanthanides.

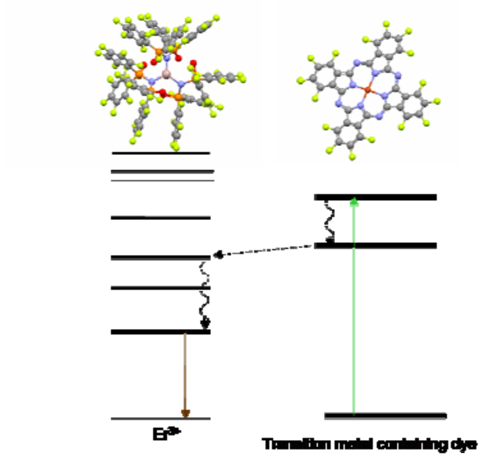


Figure 1. Sensitized Er^{3+} emission. Visible photons are absorbed in the transition metal-containing dye and the energy is subsequently transferred to the Er^{3+} ion, which emits in the IR range (of interest for telecommunications).

Project 16
Title: **Carbon Nanotubes as Langmuir Blodgett Multilayers.**
Supervisors: **Kevin Donovan**

Outline of Project

The physics of single walled carbon nanotubes, SWNTs, as suspensions has been studied in the QMUL group where both transient photoconduction and transient electro-optic effects (Kerr effect, Linear Dichroism) have been of major interest.
It is possible, with appropriate functionalisation of the exterior surface of an SWNT, to allow them to float on water as a monolayer (cf an oil film). By doing this on a Langmuir Blodgett, LB, trough it is possible to compress the floating SWNTs thus changing the monolayer from a dilute two dimensional, 2D "gas" phase of non-interacting SWNTs, figure 1a, to an increased density (per unit area) film causing the onset of SWNT-SWNT interaction and a pseudo 2D, solid, figure 1b. This phase change can be monitored by measuring variation of the surface pressure of the film as it is compressed.

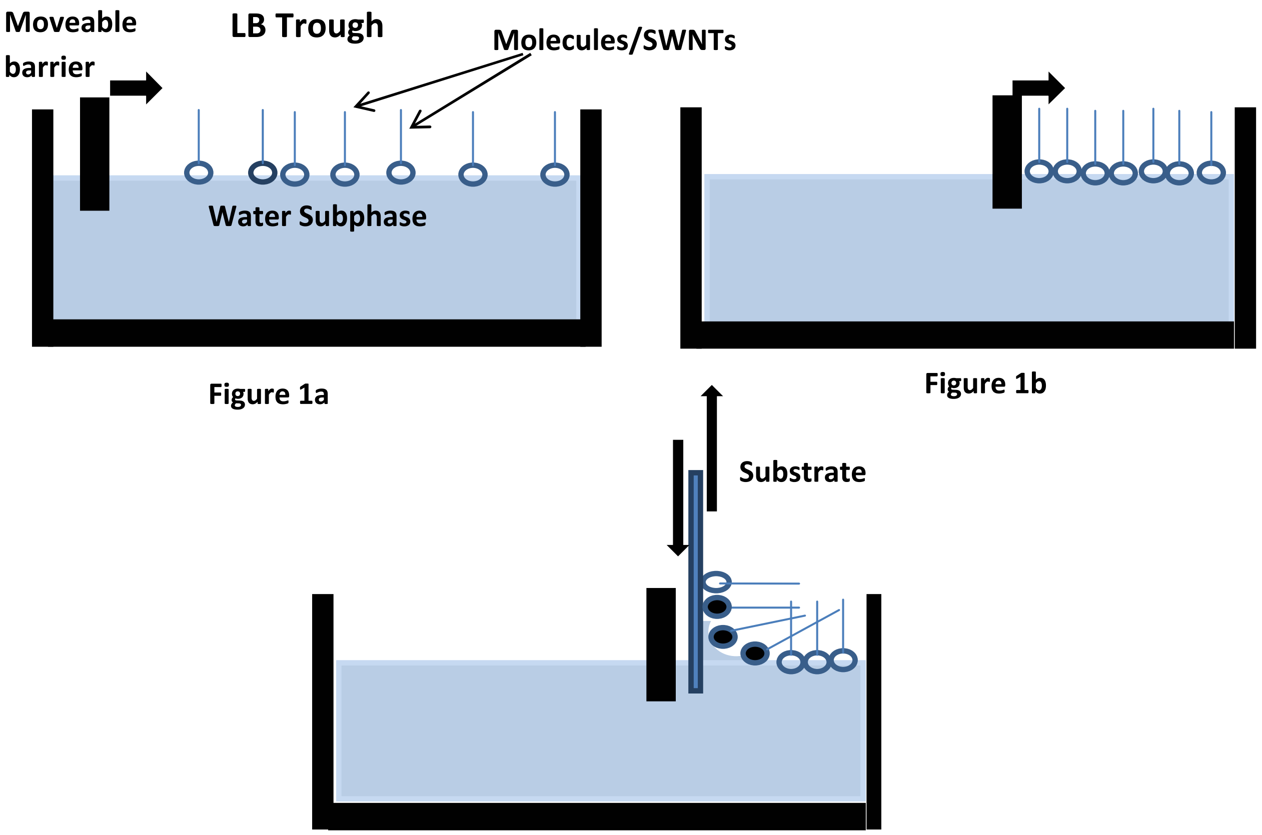


Figure 1a

Figure 1b

Figure 1c

Once the LB film has been spread and compressed on the LB trough it is possible to pass a prepared solid substrate through the air/water interface and to then deposit SWNTs onto the substrate layer by layer, figure 1c.

Aims and Objectives

Having obtained a multilayer with known number of layers (equal to the number of passes that the substrate makes through the interface) it is now possible to;
i) Carry out optical experiments.
by pre-treating the substrate to have electrodes on it, it will also be possible to ,

ii) Carry out conduction and photoconduction experiments.
iii) Carry out electro-optic experiments.

Work plan
SWNTs functionalised with OctaDecylAmine, ODA, may be bought commercially and these tubes will float at the air water interface as a monolayer on an LB trough.
The class 100 cleanroom is equipped with two LB troughs one of which is able to form alternating layer systems. These LB troughs and the student would begin by gaining expertise in the technique of producing LB multilayers using commercially available amphiphilic (molecules with a hydrophilic head group and a hydrophobic tail group) molecules such as ω-tricosenoic acid.

This project would then seek to;
i) Establish the correct conditions for good layer deposition.
ii) Examining the orientation of SWNTs on substrate with respect to the dipping direction using Atomic Force Microscopy, AFM.
iii) Measure how the optical properties (transmission/absorption) vary as the polarisation of the light is altered between a polarisation parallel to the dipping direction and a polarisation perpendicular to the dipping direction.
iv) Measure how the conductivity varies with the electric field applied parallel and perpendicular to the dipping direction.

These measurements can be carried out while varying the number of multilayers and the dipping conditions (surface pressure) under which the multilayer was created.

The electronic profile of the layer may be studied using the Kelvin probe technique to map the surface potential. This will be able to distinguish metallic and semiconducting nanotubes on the substrate.

Having gained an understanding of the behaviour of SWNT multilayers it will then be possible to create more complex structures by mixing the SWNTs with amphiphilic molecules such as ω-tricosenoic acid which readily form layers on the LB trough.

1. Create a mixed phase SWNT/ω-tricosenoic acid (amphiphilic) film and multilayers in order to try and enhance conduction/photoconduction of the mixed multilayers when compared to the SWNT multilayers.
2. Create an alternating SWNT/ω-tricosenoic acid /SWNT/…structure and sandwich this between two electrodes in order to study electron tunnelling between layers of differing electron affinity.

Project 17
Title: **Magnetic Carbon Nanotubes for Cancer Treatment**
Supervisors: **Mark Baxendale, John Dennis**

Background

The heating of cancerous tissue by hysteresis losses in magnetic nanoparticles in alternating magnetic fields has great potential as a new approach to cancer therapy. Research has focused on nanoparticles of the iron oxides Fe_3O_4 and γ-Fe_2O_3 [1,2]. Metallic Fe offers advantages over its oxides owing to a higher saturation magnetisation but usage is hindered by oxidation when handling in the atmosphere and in a biological environment. Multi-wall carbon nanotubes (MWCNTs) can be filled with Fe by a self-organised process in which the graphitic MWCNT cylinder and the Fe filling grow simultaneously [3], Fig.1. The advantages of these structures relative to conventional approaches to the cancer treatment application are: i) the MWCNT serves to chemically passivate the Fe core (against oxidation), ii) the MWCNT wall provides a surface for binding functional chemical groups, iii)the ferromagnetic response of the core can be engineered through the anisotropy ratio (diameter~10s nm, length$\leq$100 μm), and iv) rotational translation of the structure can be achieved with a constant magnetic field. In addition to the ferromagnetic core, a material with temperature-dependent nuclear magnetic resonance (NMR) parameters must be introduced into the core so that temperatures in the range 20-60 °C can be monitored by NMR with an accuracy of < 0.1 °C.

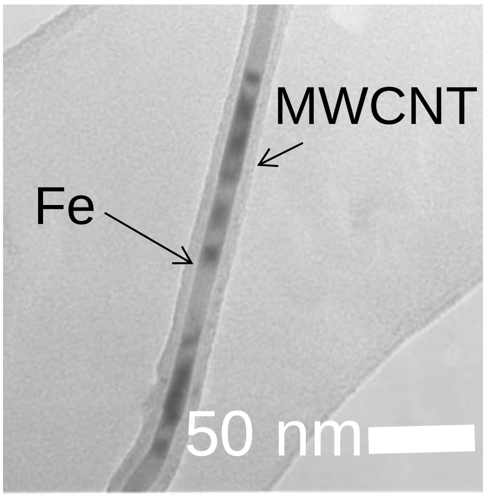


Fig.1. A TEM image of a Fe-filled multi-wall carbon nanotube. The length of the structure is typically 1 μm but the structures can be grown with length ~ 100 μm.

Aims and Objectives

Optimise the core material for use in the cancer treatment application by measuring the magnetic response variation with synthesis conditions.

Introduce the incar fullerene molecule $iGdC_{82}$, or other, into an opened Fe-filled MWCNT for temperature sensing and magnetic resonance imaging contrast agent functions. The integration of the ferromagnet, NMR temperature sensor, and MRI contrast agent would be a world-first.

Demonstrate superior temperature sensing capabilities relative to the conventional temperature sensing materials: CuI, CuBr, $CuCl_2$, AgCl.

Achieve heating (as measured by the specific absorption rate) and temperature sensing capability that is superior to conventional iron oxide nanoparticles.

Demonstrate surface functionalisation with an antibody.

Work plan

Task 1. Fe-filled MWCNT synthesis by pyrolysis of ferrocene (MB)
Task 2. Measurement of specific absorption rate for Fe-filled MWCNTs (MB)
Task 3. Demonstrate iGdC_{82} filling and MWCNT closure, Fig.2 (JD)
Task 4. Measure variation of NMR parameter vs. temperature (JD)
Task 5. Surface functionalisation with an antibody (JD)

Tasks approximately distributed in time as in Table 1 below.

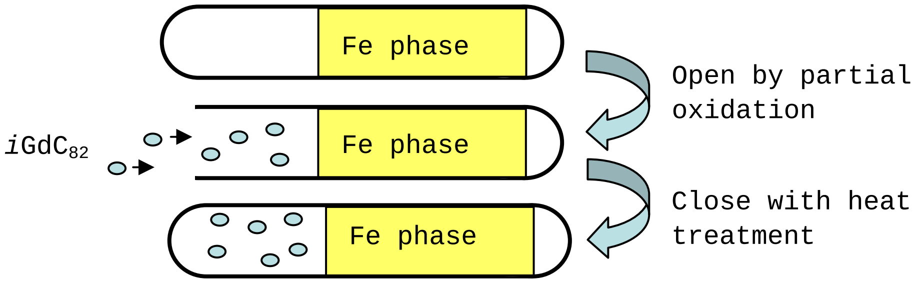


Fig.2 The cancer treatment nanoparticle synthesis steps. MWCNTs partially filled with the Fe phase(s)- that are optimised against specific absorption rate - will be opened by partial oxidation (all MB). (Both partial filling and opening by oxidation have been previously demonstrated). iGdC_{82} - synthesised and purified by JD - will be introduced by a liquid phase route and close achieved by heat treatment (all JD).

	Year I	Year II	Year III
Task 1	▨		
Task 2	▨		
Task 3		▨	
Task 4		▨	▨
Task 5		▨	▨

Table 1.

Refs.

[1]R.Hergt et al, J. Phys. Condens. Matter 18, S2919 (2006)
[2]R.Hergt et al, J. Magn. Magn. Matter 270, 345 (2004)
[3]H. Terrones et al, Solid State Sciences 8, 303 (2006)

Project 18
Title: Optically tuneable organic dielectrics
Supervisors: Theo Kreouzis, Rob Donnan (SEECS)

Organic semiconductors are easy to process at room temperature using solution based methods. They are flexible, can cover large areas and can be readily chemically modified to alter their optical and electronic characteristics. They have been successfully used in light emitting diode (LED) applications for displays and in photovoltaic (PV) applications, as well as being used in xerography and field effect transistors (FET).

It is possible to generate mobile charges (holes, electrons) in semiconducting polymers using light (this is exactly what happens in PV devices). The photogeneration of mobile charge carriers has an effect which hitherto has been ignored. Mobile photogenerated charges alter the dielectric properties of the organic material. This is an entirely new application for these materials where they are not used as current carrying elements in electronic devices, but as optically tuneable dielectrics in microwave devices (commonly used in telecommunications and imaging, for example transmission lines, antennas and filters).

Controlling the performance of simple devices is of increasing interest. Current methods of altering (tuning) device performance can be mechanical (moving a dielectric slab relative to the conductor) or electronic and involve large numbers of active or passive lumped elements. These elements require large numbers of connections, for bias and control, leading to complications in the structure design and reliability issues.

In the first ever application of organic semiconductors to microwave structures we have fabricated stripline transmission lines using the organic semiconductor poly-3-hexyl-thiophene (P3HT) as the dielectric. We showed that their microwave propagation properties could be modified, reversibly and controllably, by illumination [1]. This result is both exciting and surprising. It opens up a broad range of novel optically tunable applications for organic (mainly polymer) semiconductors where we take advantage of their availability and processing ease.

Initial calculations in [1] were based on a small change in the real part of the dielectric constant, of the order of 10^{-1}, consistent with device modelling. The calculations used literature values for the charge carrier mobility, photogeneration quantum efficiency and recombination constant in P3HT. Unphysically large steady state carrier densities were obtained which pointed out the need to elucidate the fundamental physics behind photoinduced dielectric changes in the microwave regime.

The project is based on reconciling fundamental physical properties, relating to charge generation and charge transport in polymer semiconductors, with optically induced dielectric changes in the microwave regime.

In order to do this, transient and steady state (photo)conduction experiments will be used to measure the carrier mobility, photogeneration quantum efficiency and recombination coefficients. The successful candidate will measure carrier mobility by the Time of Flight (TOF) and Dark Injection (DI) techniques, parametric in electric field and temperature, over a range of sample thicknesses for both electrons and holes.

Steady state and transient photoconduction measurements in the dilute charge regime (low illumintation), will provide the quantum efficiency. The recombination coefficients will be obtained by taking the low illumination (linear) photoconduction and comparing it to the high carrier density, high illumination (sub-linear), bimolecular recombination regimes.

The transport, generation and recombination data thus obtained will be used to predict the dielectric change under given illumination conditions.

The dielectric changes themselves can be measured at low frequencies using impedance spectroscopy (on capacitative structures built using the organic semiconductor) and at actual microwave frequencies by measuring the complex transmittance (amplitude and phase) of an actual thin organic layer (the latter using existing facilities in the School of Electronic Engineering and Computing at QMUL).

The use of organic semiconductors as optically actuated dielectrics is entirely new and the aim of the project is to reconcile the molecular electronic (microscopic) properties of polymer semiconductors with optically induced dielectric changes. This will provide a robust, fundamental theoretical framework on which future applications can be based.

[1] H. Tang, R.S.Donnan and T.Kreouzis, Applied Physics Letters, 91, 202101 (2007)

Project 19

Title: **Influence of excited states and molecular structure on hopping transport in organic semiconductors**

Supervisors: **Theo Kreouzis, William Gillin**

The performance of organic optoelectronic devices is often limited by low charge carrier mobilities. Measured mobilities are influenced by the intrinsic disorder resulting from the molecular nature of the materials and also by measurements conditions. In particular the presence of excited states has been shown to reduce measured mobility values, suggesting strong interaction between charged and neutral states [1,2]. This project will explore the influence of charge-exciton and charge-charge interactions on measured mobility using a joint experimental and modelling approach.
Dark injection and other techniques will be used to study the effect of neutral and charged excited states on mobility in test devices, as a function of electric field, exciton concentration and temperature. A Monte Carlo model will be developed to simulate the effects using different models of the process. The studies will be repeated for similar materials of different molecular structure. The study will then be extended to complementary mobility measurement techniques and to materials with different excitonic properties. The effect on working optoelectronic devices will also be studied. The initial model will then be developed for the mechanism by which excited states influence transport to incorporate more advanced simulation of realistic systems.

[1] Reduced hole mobility due to the presence of excited states in poly-(3-hexylthiophene)
Song, JY; Stingelin, N; Gillin, WP and Kreouzis,T
APPLIED PHYSICS LETTERS, 93, 23, Article Number: 233306 (2008)

[2] Effect of excited states and applied magnetic fields on the measured hole mobility in an organic semiconductor
Song JY, Stingelin N, Drew AJ, Kreouzis T, Gillin WP
PHYS REV B 82(8): Article number 085205 20 Aug 2010

Project 20

Title: **An “atomic composite” approach to develop new multiferroic materials**
Supervisors: **Alan. Drew, Martin Dove**

Background

Multiferroic materials that exhibit both ferroelectric (ordering of electric dipole moments) and (anti)ferromagnetic (ordering of magnetic dipole moments) properties are of great technological importance offering the potential for the design of novel multifunctional devices such as transducers, actuators, sensors and memories [1,2]. The synthesis of single-phase multiferroic materials represents a significant challenge since the two different forms of order (electric and magnetic) tend to be mutually exclusive. Work in this area has primarily centred on crystals based on the perovskite structure, such as $BiFeO_3$ and $BiMnO_3$ due to their simplicity and relative ease of synthesis. The tetragonal tungsten bronze (TTB) structure, $A1_2A2_4C_4B1_2B2_8O_{30}$, is closely related to perovskite and offers similar compositional flexibility [3,4]. The TTB structure (shown in Figure 1), however, offers extra degrees of freedom for compositional tuning of properties by vacant C-sites, up to 1/6 A-site vacancies and also the presence of crystallographically distinct sites on both A- and B- cation sublattices. The latter is of particular interest as it offers the opportunity to order magnetically and ferroelectrically active ions on different A- and B-sites by co-operative doping. This essentially allows an “atomic composite” approach to develop novel multiferroic materials.

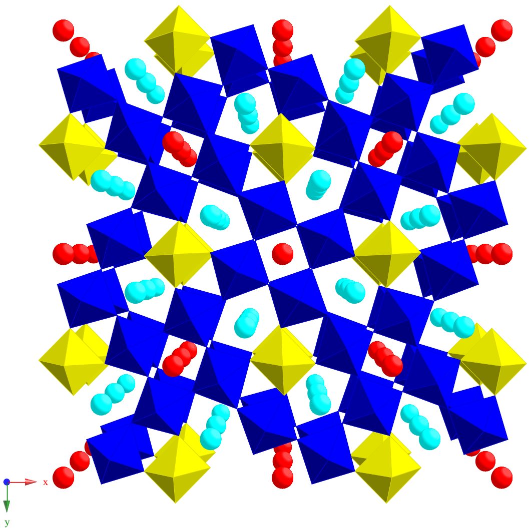


Figure 1: The TTB $A1_2A2_4C_4B1_2B2_8O_{30}$ structure, which allows considerable flexibility.

This methodology has led us to develop a class of materials that is based on BaNbO doped with magnetically active Dy^{3+} ($4f^9$) on the A-cation sublattice and ferroelectrically active Nb^{5+} ($3d^0$) and Ga^{3+} ($3d^{10}$) on the B-sites [3]. The phase diagram of different material compositions is shown in Figure 2. In these materials, 1/6 A-site vacancies are critical in driving the electric dipole ordering. Fully occupied compositions contain disordered electric dipole moments, known as a ‘dipole glass’, whose crystallographic unit cell size changes as electric fields are applied. We have recently performed measurements of the magnetism in $Ba_3Dy_2GaNb_3O_3$ (bottom-right corner of the phase diagram in Figure 2), where there is a relatively complex mix of static magnetism and magnetic fluctuations, with signatures of a spin glass at high temperatures. Interestingly, the control and coupling of the magnetic and electric dipole glasses is as yet uninvestigated in any material; this is clearly one of the goals of this project. Indeed, magnetism tends to be rather complex in general in multiferroics, related to the antagonistic nature of the two (magnetic and electric) orders. Spatial disorder such as phase separation or domain formation, as well as temporal disorder present in spin glasses, is common. In this respect, the use of local probes such as muon spin spectroscopy and neutron or x-ray total scattering has significant advantages over working with other more ‘standard’ techniques, such as traditional diffraction or magnetization measurements, which provide information about the average structure and magnetisation over the whole sample. In contrast, we are easily able to measure how the magnetism contained within the unit cell evolves with temperature, material composition and electric field. The two techniques we intend to use are complementary; muon spectroscopy gives the time dependence on a local scale, and total scattering gives spatial fluctuations on a local scale.

Project description

The project is to investigate the magnetic and electric properties of TTB materials, and their coupling, using local probes situated at central facilities (for example, ISIS in the UK, PSI in Switzerland, ILL in France, and international synchrotron sources).

The main experimental techniques utilized in the proposed research are:

Muon spin rotation/relaxation to understand the local magnetic properties and spin fluctuation timescales. The application of in-situ electric fields will allow unrivalled information on the coupling of magnetism/spins to electric dipoles to be gathered.

Total scattering to probe fluctations in local structure. The experiments give the histogram of interatomic distances – the pair distribution function – and subsequent analysis is focussed on using simulation techniques to develop atomistic configurations that are fully consistent with the experimentally-derived data. These configuration then reveal local structure and magnetic fluctuations, including short-range domains.

Extensive characterization of the materials, including vibrating sample magnetometry, AC-susceptibility, AC and DC electric polarizability and X-ray diffraction .

We intend on investigating

The four corners of the dipole glass region of the phase diagram in Figure 2. Here we wish to map out how the change in chemical structure alters the magnetic and electrical properties of the material, and more importantly, their coupling. The physics contained within this region of the phase diagram (dipole glass coupling to a spin glass) has not been investigated before in any material. Subsequent experiments are anticipated to fill in interesting regions identified by the first study.

The ferroelectric region in the phase diagram of Figure 2. Similar to the above, we wish to map out the magnetic and electrical properties of the materials as a function of chemical constituent, and again, how their coupling changes. The magnetic properties of new class of materials, and the coupling to the electric properties, has not been investigated before.

Add more accurate phase boundaries to the phase diagram in Figure 2 and create a magnetic equivalent. Use this information to identify key regions with interesting properties e.g compositions close to phase boundaries that could exhibit metastability that enhances the coupling of the magnetic and electric dipole moments.

Understand the fundamental mechanisms driving the different forms of order. There are many questions that need to be answered, such as: Why you do you get a dipole glass? What does it look like locally? How is local magnetisation coupled to local structural fluctuations? Is it a magnetostrictive/electrostrictive coupling or something more direct?

This project is designed for two PhD students, working closely together on the same materials. One will focus on muon spectroscopy and the other on total scattering, with both students performing the laboratory based characterization in parallel. Considerable international and national travel will be involved, with regular visits to institutes in England, Scotland, Switzerland, France and the USA, as well as less regular trips elsewhere.

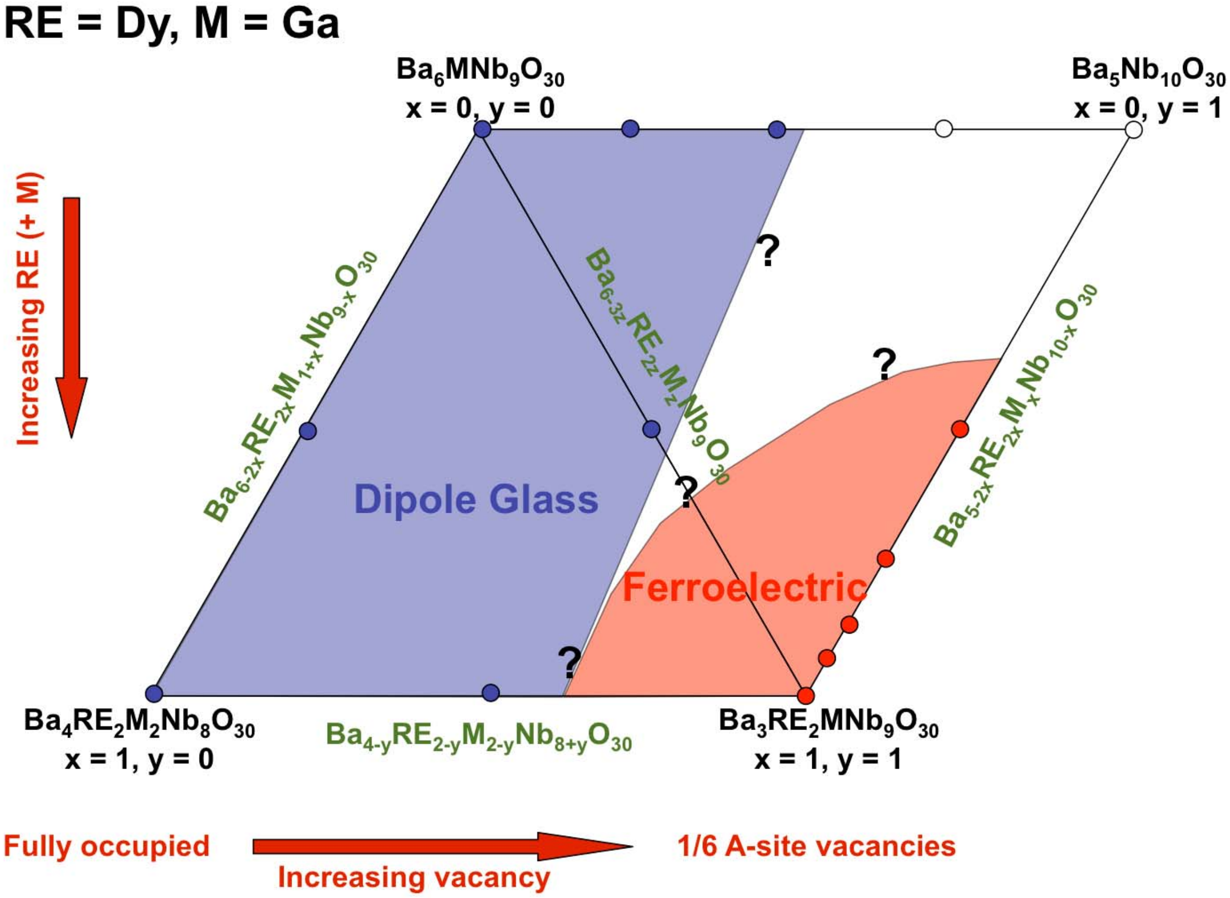


Figure 2: the electrical phase diagram of the TTB system, based on BaNbO doped with magnetically active Dy^{3+} ($4f^9$) ferroelectrically active Nb^{5+} ($3d^0$) and Ga^{3+} ($3d^{10}$). The points represent materials we have already synthesized.

[1] N. A. Spaldin, M. Fiebig, Science, 2005, 309, 391
[2] W. Eerenstein, N. D. Mathur, J. F. Scott, Nature, 2006, 442, 759
[3] D. C. Arnold, F. D. Morrison, J. Mater. Chem., 2009, 19, 6485
[4] P. G.Dickens and M. S. Whittingham, Q. Rev. Chem. Soc., 22 (1968) 30

Project 21
Title: Organic spintronic devices with multifunctional interfaces
Supervisors: Alan Drew, William Gillin

Background
Adding the spin degree of freedom to semiconductor based electronics can substantially increase the performance of devices. Examples of emerging “spintronic” devices are spin-FET (field effect transistor), spin-LED (light emitting diode), spin-RTD (resonant tunnelling diode), THz optical switches and quantum bits for quantum computation. Recently, the use of organic semiconductors (OSC) in spintronics has become of significant interest [1-3], primarily due to their small cost, ease of processing and their electronic and structural flexibility. Another key property of OSC is their intrinsically long spin coherence times and this, combined with the flexibility of OSC, has lead to considerable recent activity in the area of organic spintronics.

To offer insight into many of these areas, we have recently developed a low energy muon spin rotation (LE-mSR), which can image the depth profile of current injected spin polarisation in organic semiconductors (OSC), propagating from buried ferromagnetic/OSC interfaces [4]. Calculations suggest that Polarised Neutron Reflectivity (PNR) is also an ideal and complimentary technique for performing these measurements, where we have already imaged novel magnetic states in thin film heterostructures using this technique [5]. Perhaps more importantly, we have recently used these techniques to understand the role of polar materials at the injection interfaces. It was shown that the presence of electric dipole moments, brought about by the ionic material LiF, can reverse the spin polarisation of extracted charge carriers [6]. This has some important technological implications; for example, with the inclusion of a ferroelectric, one would be able to electrically switch resistance of the organic spin valve. Interestingly, this phenomena has never been observed in conventional spintronic devices, potentially opening up a new technology area for OSC, although novel interface states have been the focus of recent attention [3]. Furthermore, rather than using a thin ferroelectric interface layer, another route to electrically switchable spintronic devices is to use multiferroic materials in the devices. This could either take the form of two-phase materials, such as ferroelectric-piezoelectric juxtaposed with ferromagnetic-magneostrictive multilayers [7] or composites of such materials, or single phase multiferroic such as $BiFeO_3$.

Project description
The main objective of this proposal is to focus on developing the materials for conceptually new devices and applications. Novel materials will be developed and engineered into hybrid organic-inorganic interfaces with conceptually new electric and magnetic behaviour, then formed into device concepts for test and demonstration purposes. The three goals are:
Increase the spintronic device efficiency by using new OSC
It is well known that organic molecules have both structural and electronic flexibility, but these traits have not been extensively used in the organic spintronics community, with the majority of publications using the archetypical Alq_3. We will grow devices from organic molecules with optimised electronic energy levels of the OSC, such that electron and hole injection/extraction efficiency is increased for the magnetic electrodes. We will focus on molecules with the highest transport properties and flourinated molecules, which are known to shift the HOMO/LUMO levels relative to the vacuum level and could therefore optimise extraction/injection from the magnetic electrodes.
Introduce multifunctionality into OSC spintronic devices by the use of interface layers
Thin layers of organic ferroeletrics, suitable for growing on top of OSC layers, could allow electrical switching of the spin polarisation of injected charge carriers from the top electrode. Example materials are phenazine-chloranilic acid, tanane and croconic acid, as well as the more well-known polymer ferroelectrics (for an extensive review, please consult [1]). It is worth noting

that the fluorinated molecules developed above may exhibit ferroelectric properties, which will be investigated prior to usage in a device. We will develop and synthesise organic ferroelectrics suitable for inclusion into thin film spintronic devices.

We will also attempt to include conventional ferroelectrics, such as (Na,K)NbO_3 and Pb(Zr,Ti)O_3, although it is unlikely that we will be able to grow these on top of the organic devices. Finally, we will attempt to include multiferroic materials into the functionality of the electrodes, opening up the possibility of the polarisation from both of the electrodes being electrically switchable.

Understand the physical principles behind spin injection and transport in OSC

LE-mSR will be used to visualise and quantify spin transfer and propagation from the buried interfaces in the devices. It will used to understand the fundamental physics of both spin polarised charge carriers for the various materials combinations. It is possible to quantify both spin diffusion length as well as the absolute value and sign of injected spin polarisation of each interface independently and track these as a function of experimental parameter (e.g voltage, temperature, magnetic field) and material. PNR will also be used, but it has the advantage that it can simultaneously measure both spin injection and extraction, resulting in quantitative information about lengthscales and absolute values (and sign) of spin polarisation. It is also possible to perform off-specular measurements of spin injection/transport, offering information on lateral as well as vertical lengthscales.

This proposal is for two PhD students, one associated with organic spintronic device preparation and the other with spectroscopic investigation (PNR and LE-mSR) of these devices. It will be further supported by one Postdoctoral Research Fellow. International travel will be involved for both students, with more anticipated for the student performing spectroscopy.

[1] ZH Xoing et al., Nature 427, 821 (2004)
[2] A Dediu et al., Nature Materials 8, 707 (2009)
[3] C Barraud et al., Nature Physics 6, 615 (2010)
[4] AJ Drew et al., Nature Materials 8, 109 (2009)
[5] J Hoppler et al., Nature Materials 8, 315 (2009)
[6] L Schulz et al., Nature Materials, at press (2010)
[7] Q. Jiang et al., Applied Physics Letters, 95(1), 012909 (2009).

Project 22
Title: Foamed Metals for Harsh Environments
Supervisors: Andy Bushby (SEMS), David Dunstan

Background: This PhD programme forms part of an on-going research programme on the strength of materials in restricted volumes [1 – 4]. It is closely related to two other PhD projects also offered.

Our recent work suggests that the size effect (Smaller is Stronger) is in evidence at yield, i.e. the elastic limit is higher for small volumes, due to the critical thickness effect [1] in which dislocations cannot relieve stress unless the volume is great enough.

This model is independent of the material, and it implies that the size effect should operate for any material including pure elements such as nanoporous foamed gold, under severe conditions such as high temperature or severe radiation damage. The purpose of this PhD project is to test this prediction by studying foamed metal specimens at elevated temperatures and after radiation damage.

Programme: Existing equipment for measuring stress-strain relationships in thin wires operates at room temperature. Testing nanoporous foamed gold wires simply for the elastic limit in torsion and tension in this equipment will yield very valuable data on the temperature dependence of the size effect; data which will guide both theoretical work and further experimental work. This will take up to month 24 of the project.

High temperature equipment will be under development and as soon as the experimental equipment is established, some data will be obtained on the temperature and time dependence of creep – that is, continued slow plastic deformation under load. We expect that the size effect will prevent creep in small volumes, and therefore in the foamed materials. By the final year of the PhD programme, testing this prediction will be the major experimental target.

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T.T. Zhu, A.J. Bushby and D.J. Dunstan, Materials Technology 23 (2009) 193
B. Ehrler, X.D. Hou, T.T. Zhu, K.M.Y. P’ng, C.J. Walker, A.J. Bushby and D.J. Dunstan, Phil. Mag. 88 (2008) 3043.
D.J. Dunstan, B. Ehrler, R. Bossis, S. Joly. K.M.Y. P’ng and A.J. Bushby, Phys. Rev. Lett. 103 (2009) 155501.

Project 23
Title: High-temperature micromechanical testing
Supervisors: David Dunstan, Andy Bushby (SEMS)

Background: This PhD programme forms part of an on-going research programme on the strength of materials in restricted volumes [1 – 4]. It is closely related to two other PhD projects also offered.

Our recent work suggests that the size effect (Smaller is Stronger) is in evidence at yield, i.e. the elastic limit is higher for small volumes, due to the critical thickness effect [1] in which dislocations cannot relieve stress unless the volume is great enough.

This model is independent of temperature and that implies that the size effect should operate at all temperatures right up to the melting point. The purpose of this PhD project is to test this prediction by building equipment for micromechanical testing at elevated temperatures and using it to test the elastic limit of thin metal wires in torsion and in tension.

Programme: Existing equipment for measuring stress-strain relationships in thin wires needs development for operation at high temperatures. Building this new equipment will occupy the student for the first 6-12 months of the project. Then testing thin wires simply for the elastic limit in torsion and tension as a function of temperature will yield very valuable data on the temperature dependence of the size effect; data which will guide both theoretical work and further experimental work. This will take up to month 24 of the project.

Also as soon as the experimental equipment is established, some data will be obtained on the temperature and time dependence of creep – that is, continued slow plastic deformation under load. We expect that the size effect will prevent creep in small volumes. By the final year of the PhD programme, testing this prediction will be the major experimental target.

References:

D.J. Dunstan, J. Mater. Sci.: Mater. Electon. 8 (1997) 337.
T.T. Zhu, A.J. Bushby and D.J. Dunstan, Materials Technology 23 (2009) 193
B. Ehrler, X.D. Hou, T.T. Zhu, K.M.Y. P’ng, C.J. Walker, A.J. Bushby and D.J. Dunstan, Phil. Mag. 88 (2008) 3043.
D.J. Dunstan, B. Ehrler, R. Bossis, S. Joly. K.M.Y. P’ng and A.J. Bushby, Phys. Rev. Lett. 103 (2009) 155501.

Project 24
Title: **Exploiting substrate dipoles for controlled molecular growth**
Supervisors: **William Gillin, Steve Dunn**

The project will investigate the influence of functional inorganic substrates on small molecule morphology, orientation and structure. These effects will be exploited to control the alignment of organic molecules on surfaces so as to vastly improve organic device performance.

It is known that for some organic molecules properties such as the carrier mobility are high in single crystal samples (e.g. 10 cm^2/VS) but very low (~10^{-4} cm^2/Vs) when the same materials are deposited by other methods, such as vacuum sublimation. This is in part due to the way that the molecules align on the surface during evaporation to form amorphous layers which result in poor overlap of the molecular orbitals. This introduces “defects” which greatly reduce carrier hopping probabilities.

The aim of the project is to determine if the fringing depolarisation field from a polar (ferroelectric material) can influence the ordering of small functional molecules that have been deposited on the surface. A ferroelectric material is a material that can sustain a surface dipole through anisotropy of charge in the crystal lattice. This is manifested as a surface charge that range from 3μC/cm^2 to 60μC/cm^2 depending on the ferroelectric material, which strongly influences the space charge layer, see Figure 1, and the way the material interacts with mobile species such as electrons, ions or small molecules such as methanol or formaldehyde, see Figure 2. A range or length scales for the patterns will be investigated from nm’s to mm’s to determine the influence of pattern size on molecular

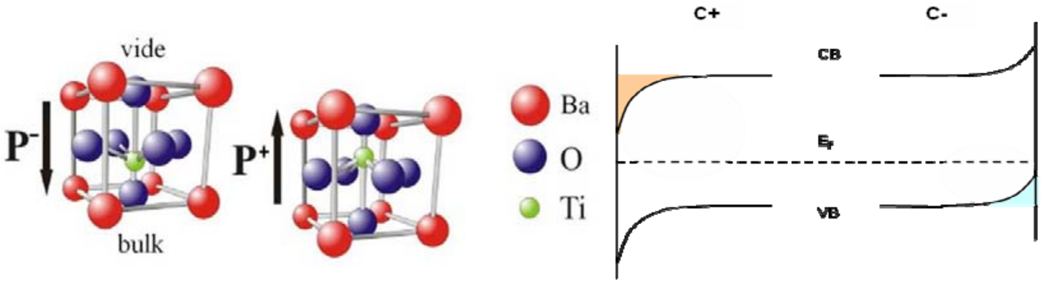

Figure 1, Movement of the ion in BaTiO$_3$ to give a resulting surface dipole (left) and the resulting space charge layer that forms across the thickness of the sample due to interaction with mobile carriers and the internal dipole (right) c+ and c- represent the two surface charge states available.

Devices made from small functional molecules show degradation in performance as they move from crystalline systems to amorphous; this degradation can be many orders of magnitude in reduction of carrier mobility. It is possible to produce ferroelectric materials that are highly structured with thicknesses that are on the order of 1-5nm to many μm. This nanostructured control is important as ferroelectric materials are typically insulators with a band gap of 3.2 to 3.5eV and so thin layer will enable carriers to tunnel over the barrier. The project will focus on deposition of molecules on polar surfaces and the physical characterisation of the interface to get structure-property relationships.

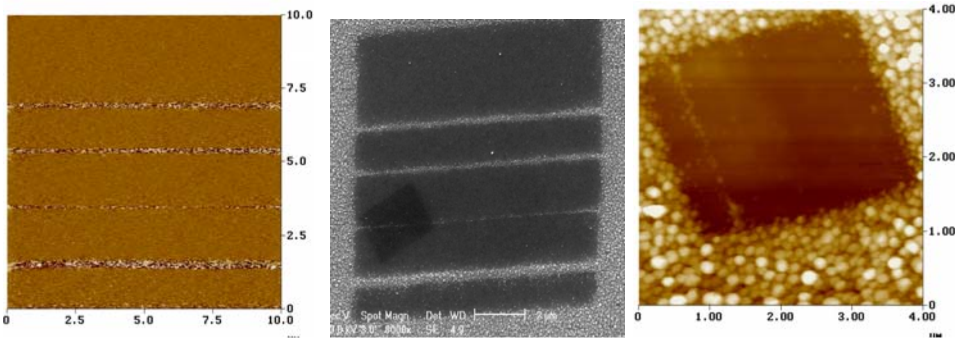

Figure 2, selective photocatalysis of Ag^+ in solution using the resulting depolarisation field of patterned PZT, pattern written into PZT using modified AFM where the light stripes are c+ regions and so bring photoexcited electrons to the ferroelectric interface (left), pattern of photocatalysed Ag nanowires after interaction with Ag^+ due to depolarisation field interaction showing no Ag on the regions of c- (middle) and a single 70nm Ag nanowire showing extent of fidelity (right).

The polarisation of the ferroelectric can be determined to be fully up (positive dipole top) and or fully down (positive dipole down) by the processing of the ferroelectric. We will investigate how the substrate dipole will affect the orientation of the molecules deposited on top of it, investigating parameters such as substrate polarity, molecule electronegativity, ferroelectric pattern size and molecular deposition parameters. The ferroelectric films will be grown by PLD with our collaborators in Australia in addition to those that are grown on single crystal substrates. Organic molecule deposition and device fabrication will be performed in our organic electronics clean room. We will pay particular attention to the orientation of the molecules on the substrate, the molecular crystallinity and film morphology. Mixtures of molecules will be coevaporated and designed for their differential affinity to the substrate dipoles. This will then be exploited to generate a template for phase segregated molecular structures that can ultimately be used to produce novel optimised device architectures. Once the ability to produce good quality aligned films has been demonstrated they will be characterised for their mobility using time-of-flight and organic field effect transistor (OFET) characterisation.

Dr Dunn has just moved into a £250k laboratory refurbishment with £75k of equipment purchased to further develop his activity investigating the influence of polar (ferroelectric) surfaces with the local environment[1]. His background studies have shown that the ferroelectric depolarisation field can influence photochemical REDOX reactions[2], interactions with small species such as viruses[3], the sorption/desorption of molecules and develop patterns with reproducible fidelity ranging from 100nm to 100µm[4]. The current work in this area is focusing on investigating the influence ultra thin epitaxial films (2-5nm) of ferroelectric materials on the behaviour of physic or chemisorbed molecules on the surface through control of the depolarisation field of the ferroelectric[5]. This could have two possible implications for the development of optoelectronic devices. The first it that it may aid charge separation in the active device, the second is that field may cause selective alignment of the molecules on the surface allowing for selective morphologies to be developed.

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Project 25
Title: The dynamics of organic magnetoresistance
Supervisors: William Gillin, Theo Kreouzis

Organic magnetoresistance (OMR) is the term that has been used to describe the effect of a magnetic field on the current transport in organic devices. The effect was first observed by Kalinowski *et al.* in 2003 who showed that for Alq_3 based devices it was possible to increase the light output by 5% and the current through the device by 3% with the application of a modest magnetic field. Following this work there have been a number of papers which have shown that the effect appears to be common to most organic semiconductors but there is still considerable debate as to the cause of the effect. The proposed mechanisms behind OMR fall into two classes: excitonic and non-excitonic. The excitonic models are based around a B-field change in the intersystem crossing between singlets and triplets, at either the pair state or excitonic level. Within the excitonic models there are two subdivisions, one of which suggests that the change in device current is due to increased dissociation of singlets compared to triplets whereas the other, the QMUL model, suggests that polarons can interact with triplets (PTI model) which affect their mobility [1]. As the triplet population is modified by the intersystem crossing this in turn modifies the mobility. The non-exciton model relies on the B-field altering the probability of bipolaron formation and ascribes the effect on current as being due to differences in the mobility of polarons and bipolarons.

We have recently demonstrated that the presence of excited states directly affects the mobility of holes within an organic semiconductors [2,3]. Furthermore we have demonstrated that the mobility of the organic semiconductor is also modified by the presence of a magnetic field but that this is only the case in the presence of excitons [3]. This observation supports our view that the presence of excitons significantly modifies the mobility of carriers in organic semiconductors. We have also shown that the organic magnetoresistance in an OLED can be deconvolved into two processes, simple site blocking by triplets and an interaction between triplets and polarons, these two processes have been shown to scale linearly with exciton concentration over ~six orders of magnitude [4]. These results demonstrate that the application of a magnetic field to organic devices provides an important new tool for understanding the processes that are operating within real devices.

This project aims to build on our understanding of the role of excited states on the transport in organic materials by studying the dynamics of these interactions. At the moment we have generally performed measurements in the steady state regime where the current has been allowed to reach an equilibrium. However, because the triplet lifetime is of the order of microseconds to milliseconds it is possible to measure how the current and light emission in an OLED changes in real time as the triplet population is changing. This approach will provide us with fresh insights in to the dynamics of current transport and light emission in organic light emitting devices and how they are affected by applied magnetic fields.

The work will involve the fabrication of OLED devices using our state-of-the-art Kurt J. Lesker SPECTROS evaporation system. This system has six organic sources and two metal sources in a single vacuum chamber with a load lock to allow quick sample entry. All mask changes can be performed in vacuum. The evaporator is housed in our organic electronics clean room that also has two further organic evaporator systems as well as extensive electrical and optical characterisation facilities which can all be used as a function of applied field. The clean room also contains a new field controlled magnet system that allows for fields of up to 1T to be applied. For higher fields we also have a new superconducting magnet system which will allow measurements at fields up to 7T.

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