devices and sensors, etc. In order to effectively control the processing, structure and performance of these nano-materials, there is a priority on the development of robust non-destructive techniques for imaging nano-particles. The destructive and generally two-dimensional nature of electron microscopy often limits the nano-particle imaging to qualitative or semi-quantitative analysis. X-ray small-angle scattering can estimate the average scale of nano-particles over a large area/volume without destroying the specimen, however it does not resolve the shape of the particles. Here we show that x-ray diffraction intensity collected as a multi-dimensional function of scattering angle can be treated to reconstruct the three-dimensional (3D) shape of an average nano-particle with a spatial resolution of a few nanometres.

Our results demonstrate that this approach to x-ray diffraction data analysis provides the potential for 3D non-destructive analysis [1]. The methodology is based on the measurement of a high angular resolution x-ray Fraunhofer diffraction patterns with further application of a phase-retrieval formalism. The advantage of experimental data collection in momentum transfer (angular) space is that the diffraction pattern of the object is not susceptible to any of its linear translation and, consequently, the intensity distribution measured as a function of the angular direction in reciprocal space does not require coherent radiation and/or extraordinary stability of the radiation source and/or sample. The non-destructive nature of the technique renders it perfect for *in-situ* studies of nucleation and growth of nanoparticles in engineered nanocomposites [2]. The possibility of using incoherent x-ray sources allows the method to be implemented in any laboratory [1]. The only principal restriction on achievable resolution is the physical limit of the order of sub-nanometer.

We present results relative to ~50 nm diameter nano-particles dispersed in a polymer matrix with a spatial resolution of 2 nm, 50-350 nm intermetallic nanoparticles in ultra-strong Al-Cu alloys with a spatial resolution of 5-8 nm, and ~10 nm diameter carbon nanotubes with spatial resolution of 1 nm. Unlike a microscopy technique, the method to be presented does not allow one to distinguish the shape and size of individual nanoparticles within a distribution. This limits the application of the method to studies of structures with mono-dispersed nanoparticles. However, this very same limitation is a significant advantage of the method for materials science as it does allow non-destructive, *in-situ* analysis over large volumes (several mm^3) of material, with determination of the modal shape-size of the dispersed particles and a close evaluation of the distribution of particle sizes [3].

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Keywords: nanocrystal, diffraction, phasing

MS24.P07

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Can heats of sublimation and melting points of organic crystals be predicted?

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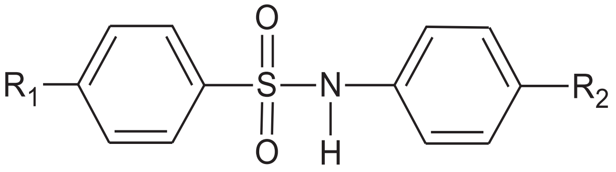
The accurate calculation of the lattice energies of small organic molecules has only recently become possible as a result of developments in Density Functional Theory (DFT), including the introduction of several methods for the incorporation of non-local dispersive interactions. Much has been done to verify these developments using very accurate molecular calculations, but few publications address the validity of these methodologies for organic molecular crystals [1]. The experimental heats of sublimation of 33 compounds will be compared with the lattice energy predictions of some of the latest solid state DFT methods. In particular, methods incorporating a dispersive correction through a damped molecular mechanics type interaction [2] (DFT(D)), will be compared with new approaches incorporating dispersive interactions as part of the functional [3]. A method incorporating dispersion as part of the functional will be shown to perform slightly better than the best DFT(D) method.

The possible prediction of melting point from knowledge of molecular structure alone has intriguing possibilities and many quantitative structure property relationships (QSPRs) [4] have been developed to allow the prediction of melting point with varying degrees of success. There is a rule of thumb that relates trends in melting points to lattice energies and, using one of the solid state DFT methods used in the study of heats of sublimation, accurate lattice energy calculations are performed on a series of 4,4'-disubstituted benzenesulfonamidobenzenes. Experimental crystal structures and melting points are available for 100 compounds with the generic molecular structure shown in the Figure.[5]. The substituents considered include Br, CF_3, Me, Cl, CN, F, H, I, NO_2 and MeO. Solid state DFT calculations are used to optimise the geometry and unit cell of all the observed crystal structures. A comparison of the deviations between the experimental and calculated geometries allows the accuracy of the geometrical predictions of the method to be assessed. The minimised lattice energies are then used to establish correlations with the observed melting points. Preliminary results indicate that there is a significant correlation for an isostructural subset of the molecules.



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Keywords: lattice energy, melting point, density functional theory

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An entire class of new compounds forming polar crystals

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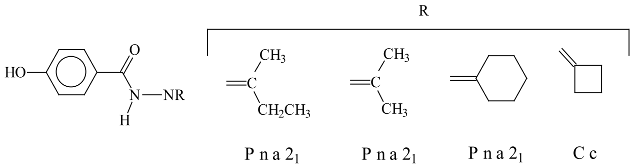
In a polar crystal there is a direction which is not transformed in the opposite direction by any symmetry operation of the crystal class; that direction is the polar axis of the crystal. Centrosymmetric crystals are not polar, because the center of symmetry transforms any direction in the opposite one. However, only 10, out of the 21 crystal classes lacking the center of symmetry, are polar. In spite of their rarity, polar structures are very interesting. In fact, several functional properties requested in materials for advanced applications (piezoelectricity, pyroelectricity, ferroelectricity, second harmonic generation, electrooptic response) are only allowed or they are enhanced in polar structures.

Many strategies used for increasing the probability of getting a polar crystal are based on overriding dipole-dipole interactions and include ionic chromophores, or the lowering of the rod-like symmetric shape of the molecule by introducing lateral substituents. Other approaches are based on crystal engineering strategies exploiting directional intermolecular interactions (e.g. H-bonding, halogen bonding), or supramolecular approaches as inclusion compounds and co-crystals [1].

However, all these approaches are highly empirical and fundamentally trial-and-error based. To get a polar crystal is still a challenging task.

Here, we report some preliminary results on the discovery of a class of nonchiral compounds forming polar crystal structures, with favourable orientation of the molecule with respect to the polar axis. Chemical diagrams of the compounds prepared up to now are given in the Scheme below, together with their space groups.

The angle between the polar axis and the long molecular axis joining phenolic oxygen to imino carbon is, respectively, 60°, 41°, 60° and 28° in the four compounds of the Scheme. The functionality resulting from the polar order of the first compound in the scheme has been confirmed by the powder second harmonic generation measurements by the method of Kurtz and Perry, where the efficiency is 120 % that of urea standard at the non-resonant fundamental wavelength of 1907 nm.



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Keywords: polar crystals, second harmonic generation, H-bonding synthons.

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New coordination polymers with embedded molecular recognition functionality

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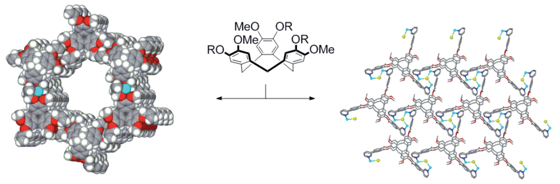
The use of molecular hosts as tectons for the self-assembly of coordination polymers promises crystalline materials with embedded molecular recognition sites, as well as the more common lattice-type guest sites [1], [2], [3], [4], [5]. We have developed a range of host molecules based on the cyclotriveratrylene (CTV) framework with additional metal-binding groups at their upper rims.

Tripodal CTV-analogues have a distinctive open pyramidal shape which creates the specific guest-binding site. The rigid "corner-piece" shape also means that coordination polymers resulting from these ligands may have unusual structural and topological aspects to them. For example, 2D networks of linked metallo-cages; [1] rare (3,4)-connected network topologies such as $(4^2.6^2)(4.6^2)_2$; and highly complex and unprecedented 3D topologies [2].

As these tectons are molecular hosts, host-guest interactions may play an important role in both the assembly of the coordination polymers and in their potential applications. Host-guest associations may be structure-directing, and generally, binding large guests in the molecular cavity of the ligand promotes formation of a coordination polymer instead of a discrete species [3], [4]. For example, binding of a large *o*-carborane guests dictates whether a discrete [Cd$_3$(OAc)$_6$L] complex or 2D 4.8^2 coordination polymer is formed when L = tris(4-pyridyl)aminocyclotriguaiacylene [3] Self-inclusion motifs also play an important role. Crystalline clathrates of CTV-analogues are known to form a hand-shake dimer where an upper-rim R group of one host is the guest for another host and vice versa, and the same motif is found within coordination chains [5]. Host-guest interactions may also result in associations between networks, including within polycatenation motifs.

Here, different coordination polymers from ligands with N-donor, carboxylate, N-oxide or allyl metal-binding groups will be presented, and the importance of host-guest interactions of these ligands in terms of coordination polymer construction and functionality highlighted.



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Keywords: supramolecular, crystal engineering, coordination polymers

MS24.P10

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Kinetic assembly of porous coordination networks and ab initio powder structure determination

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The chemistry of porous coordination networks has undergone explosive growth in the last decade because of fascinating features. Porous coordination networks can be used for gas sorption/separation/storage, molecular recognition, drug delivery, catalysis, and so on. Especially porous materials have been paid much attention as potential hydrogen storage materials for fuel cells. Thanks to the high flexibility in design, a number of porous coordination networks were prepared and were analyzed by single crystal X-ray crystallography. Here we would like to report new aspects in porous coordination network chemistry. A pore of porous materials can be used as crystalline molecular flask in order to not only make a reaction but also directly observe the reaction by X-rays [1-5]. In this talk, especially we will focus on selective kinetic assembly of porous coordination networks, the usage, and the *ab initio* powder structure determination [6-10]. The kinetic study of porous coordination networks compared with zeolite is a totally unexplored field, because of difficulties in powder structure determination. We succeeded in solving powder crystal structures having unit cells larger than 15000 Å^3.

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