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**Keywords:** hydrogen bonding, supramolecular synthons, coordination networks

## MS.17.4

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### Cocrystallization of amino acids

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Cocrystals are multi-component systems where intermolecular interactions are used to form supramolecular networks containing more than one molecular entity. Cocrystals offer potential benefits in manufacturing of Active Pharmaceutical Ingredients in solid state with improved pharmaceutical properties like solubility, stability, manufacturability and bioavailability.

A series of hydrophobic amino acids L- Leucine, L- Isoleucine and L- Valine were selected to develop cocrystals by employing different crystallization strategies under various conditions of temperature and pressure. Crystals suitable for single crystal X-Ray diffraction were grown and the structures of these novel forms were resolved. Raman spectroscopy was also used to aid in the identification of these new forms. The final structures were compared to the pure forms of the amino acids so that structural similarities could be drawn.

**Keywords:** amino acids, cocrystallization, X-ray diffraction

## MS.17.5

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### The XPac dissimilarity index as a quantitative descriptor of isostructurality

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We investigate the crystal structures formed by closely related organic molecules. In this way, it should be possible to examine the effects of incremental changes in molecular shape, van der Waals interactions and other, more directed intermolecular forces on the crystal packing. A  $9 \times 8$  matrix of 4,4'-benzenesulfonamido-2-pyridines was obtained by the systematic variation of the substituents  $R^1$  at the benzene and  $R^2$  at the pyridine ring.  $R^1$  and  $R^2$  can be CN,  $CF_3$ , I, Br, Cl, F, Me or H (and  $R^1$  additionally OMe). 103 crystal structures were determined in total, at least one for each of the 72 compounds investigated. The computer program XPac [1] was used to establish the packing relationships between individual crystal structures.

One particular 1D stack of N-H...N bonded dimers was identified as the common building block of 37 crystals. These in turn belong to eight distinct 3D packing types. The most frequent of these fundamental structure types comprises all compounds with  $R^1 = CF_3$ , I, Br, Cl, F,

Me, H and  $R^2 = CF_3$  or I. Thus, this fundamental 3D crystal packing arrangement is maintained even if  $R^1 = H$  is exchanged against  $R^1 = I$ , which leads to an approximate doubling of the effective distance at  $R^1$  and increases the molecular volume by 11 %.

A detailed picture of the incremental changes in geometry that occur within this series of 14 isostructures was obtained from matrix maps. These are collections of XPac dissimilarity indices  $x$  which have been calculated for individual crystal structure pairs. An inspection of XPac  $\delta$ -plots provides additional information. It was found that the structural change in this series is predominantly translational and occurs in the direction of the crystallographic  $c$ -axes, which lies approximately parallel to the C- $R^1$  bond. Within the common 1D stack of N-H...N bonded dimers, the relative orientation of the molecules varies with the volume of  $R^1$ .

The analogous geometrical analysis of another series from the same compound class showed that in this case a common basic 3D packing arrangement is maintained only approximately and with substantial geometrical alterations. Therefore, the relationship between these crystals is homeostructural rather than isostructural.

This systematic investigation of 4,4'-benzenesulfonamido-2-pyridines provides a set of universal reference values for the study of packing similarity in molecular crystals.

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**Keywords:** packing, isostructurality, polymorphism

## MS.18.1

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### Structure of nanosized crystals by total x-ray diffraction

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Nanosized crystals show diffraction patterns with a few, if any, Bragg-like peaks and a pronounced diffuse component that are difficult to be analyzed in the traditional way. The problem has a solution based on an approach involving high-energy x-ray diffraction coupled to atomic pair distribution functions analysis [1]. In the talk, the foundations of the approach will be introduced and its great potential in characterizing the atomic scale structure, size and shape of nanosized crystals illustrated with examples from several recent studies [2-6].

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**Keywords:** nano, WAXS, structure

## MS.18.2

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### Contrasting $p$ and $T$ -induced amorphization using $ZrW_2O_8$ and ZIF-4 as case studies

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Solid-state amorphization transitions, induced via heating or the application of pressure, significantly increase the range of materials that might yield amorphous phases. The debate about the materials that result from such transitions is whether they are 'typical' (i.e. similar to those produced via melt-quenching), whether they form a new amorphous class or indeed whether they should be classed as amorphous at all.

*Determination of their structure is the key to resolving this debate.* Here we use atomistic modelling, based on the reverse Monte Carlo method, of x-ray and neutron diffraction to investigate the structures that result from pressure-induced amorphization (PIA) and temperature-induced amorphization (TIA) of  $ZrW_2O_8$  and the zeolitic imidazolate framework material ZIF-4, respectively. In both cases the amorphous phase forms from a low-density crystal phase with a connected framework structure. We show that whereas amorphous  $ZrW_2O_8$  has a structure that can be reconciled with a displacive-like phase transition from the crystal structure [1], [2], the structure of amorphous ZIF is more akin to a continuous random network that would only come from ZIF-4 via a reconstructive phase transition [3], [4]. As well as describing the phase transitions and structures of these two materials, we will discuss the implications of this work on PIA and TIA in general.

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**Keywords: amorphization, PDF, modelling**

## MS.18.3

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### Diffraction and nanoscale molecular electronic

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The Organic semiconductors are key components of photovoltaic cells, light-emitting diodes, and organic thin-film transistors. In these systems, knowledge of the molecular organization in the bulk, in the film, and in the interface region is crucial for any technological development. X-Ray Diffraction techniques have provided a host of information that guided the development of these devices [1].

Often it is impossible to grow crystalline samples of size and quality suitable for complete structural analysis. Less conventional structural powder diffraction methods, from which one can also retrieve otherwise inaccessible structural information, can come to the rescue. Grazing Incidence X-ray Diffraction (GIXD) gives information at nano-scale on the structure of films during the first stages of formation, as well as on their evolution during growth. X-Ray Reflectivity (XRR) measurements contribute to describe growth mechanisms (layer by layer or 3D) and monitor surface morphology.

Perylenes di-imide (PDI), and its derivatives, are considered most promising candidates for high performances organic electronics [2]. In order to establish the relationship between a PDI derivative film structure and its device performance, an assessment of the molecular arrangement was carried out by combining powder and thin film diffraction techniques. Moreover XRR performed *in situ* and in real time, during the high vacuum deposition, allowed us to identify the

structural and orientational transitions, which determine the charge mobility of the device. The role of temperature and the deposition flux on the growth mechanism were elucidated.

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**Keywords: organic semiconductors, grazing incidence diffraction, nanoscale structure**

## MS.18.4

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### Debye-Waller factor and thermal expansion in gold nanoparticles

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High q-space x-ray diffraction measurements are used to determine the Debye-Waller factor and the thermal expansion coefficient of Gold Nanoparticles of 2, 4 and 9 nm sizes. Bulk Gold was also measured for comparison purposes. Given the broad peaks present in nanoparticles, the solution to extract more information from the diffraction experiment lies in using the high q region of the diffraction pattern. In this work we measured the diffraction patterns up to  $20 \text{ \AA}^{-1}$  at 50, 150, 200, 250 and 300 K for each nanoparticle size. The diffraction patterns were then fit using the 15 K data as a 'model', so that only the Debye-Waller factor, the thermal expansion coefficient and a scale factor were optimized in a fitting code developed by the authors. The results show that the thermal expansion coefficient and the Debye-Waller factor depend on the nanoparticle size. The smaller the nanoparticle the smaller are both, the Debye-Waller factor and the thermal expansion coefficient. This surprising result could be explained by the strong surface effects present in the nanoparticles.

**Keywords: gold nanoparticles, thermal expansion, Debye-Waller factor**

## MS.18.5

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### Debye function analysis on disordered metal-organic compounds: the pathfinder $[\text{Ru}(\text{CO})_4]_n$

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Several metal-organic compounds (such as, for instance, polymeric  $[\text{Ru}(\text{CO})_4]_n$  [1]) show a peculiar form of anisotropic paracrystalline disorder where all Bragg peaks are dramatically broadened, except those along some axis – in this case the  $h00$ ,  $0k0$  and  $00l$  peaks – which instead are sharp, as shown in figure. This kind of disorder is of high interest currently as it often occurs in Metal-Organic Framework materials (MOFs), a recent member of the smart materials family, and it relates to the actual display of the properties that make them attractive [2].