

than optimal" [1]. Nevertheless, it is important to appreciate the preferred arrangement of functional groups within a non-covalent interaction if a crystal is to be engineered. An understanding of the relative energetics of different interaction motifs as well as the effect of changes in the geometry on the interaction energy is also crucial when designing or analysing crystal structures. Towards this goal a number of intermolecular interaction types have been investigated based on energy and geometry, including cyano...cyano contacts and hydrogen bonds to C=S acceptors. A combination of approaches has been used in this study to investigate the changes in the non-covalent interactions. Firstly, a study of structures available in the Cambridge Structural Database [2] has been performed to determine the relative directionalities of the interactions and their preferred geometries in the solid state. Intermolecular interaction energy calculations have then been carried out using intermolecular perturbation theory as implemented in the CADPAC 6.5 program package [3].

[1] Dunitz, J. D., Schweizer, W. B. (2007). *CrystEngComm*, 9, 266-269.

[2] Allen, F. H. (2002). *Acta Crystallographica*, Section B58, 380-388.

[3] Amos, R. D. et al. (1998). CADPAC 6.5, The Cambridge Analytic Derivatives Package.

Keywords: intermolecular interactions, energy calculations, cambridge structural database

## P09.07.47

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### Controlling the formation of co-crystal polymorphs

Craig R Martin, Adam Jibson, Craig Wales, Andrew Parkin  
University of Glasgow, Chemistry, A5-22a Joseph Black Building,  
Glasgow, West Lanarkshire, G12 8QQ, UK, E-mail : craima@chem.gla.ac.uk

Crystal engineering as a concept is approaching its 20th birthday, since first defined by Desiraju<sup>1</sup> in 1989. This area of chemistry has been of increasing importance, as our knowledge of the solid-state has developed. Crystal engineers have tended to focus solely on the single crystal products of their co-crystallisation experiments, although increasingly polymorphism is being observed in these products grown under different conditions<sup>2</sup>. It seems, therefore, that as with traditional chemical synthesis and the crystallization of single-component systems, the method of synthesis can greatly affect the observed product. Polymorphism adds a new level to the challenge facing crystal engineers; not only is it necessary to understand the co-crystal (we use the term here in its broadest sense, encompassing all "multi-component" crystals) in terms of the supramolecular synthon, but to successfully predict and synthesise new co-crystal complexes it is also necessary to investigate the method of co-crystal formation. Our aim has been to prepare, characterise and control new co-crystal complexes by varying the physical conditions under which they are grown. This poster will present some results of our investigations into the control of polymorphism in co-crystals by using a range of solvents, and will illustrate how the combined use of a number of analytical techniques – including single crystal diffraction, powder diffraction, Differential Scanning Calorimetry and Infra-Red Spectroscopy – is necessary to fully investigate the compounds observed.

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2. Sreekanth, B.R., Vishweshwar, P and Vyas, K. (2007). *Chem. Comm.* 2375-2377.

Keywords: polymorphs, solvent effects, crystal engineering

## P09.07.48

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### Comparing entire crystal structures: Structural genetic fingerprinting

Andrew Parkin<sup>1</sup>, Gordon Barr<sup>1</sup>, Wei Dong<sup>1</sup>, Christopher J Gilmore<sup>1</sup>, Dylan Jayatilaka<sup>2</sup>, Joshua J McKinnon<sup>2</sup>, Mark A Spackman<sup>2</sup>, Chick C Wilson<sup>1</sup>

<sup>1</sup>University of Glasgow, Department of Chemistry, University Avenue, Glasgow, Lanarkshire, G12 8QQ, UK, <sup>2</sup>Chemistry M313, School of Biomedical, Biomolecular & Chemical Sciences, University of Western Australia, Crawley, WA 6009, Australia., E-mail : a.parkin@chem.gla.ac.uk

A method is described that is both robust and generally applicable, which allows the calculation of a similarity index between whole molecular crystal structures [1]. It is based on the use of fingerprint plots derived from Hirshfeld surfaces coupled with cluster analysis and associated multivariate statistics. Using this formalism, it is possible to show quantitatively that naphthalene is more similar to anthracene than to benzene, and moreover that benzodicyclopentene is more similar to anthracene than naphthalene is to anthracene. Whereas the correlation coefficients themselves obtained say nothing about the ways in which the patterns of intermolecular interactions are similar or different for two different structures, the fingerprint plots do contain such information. For the first time structural analysts have a robust method for quantifying structural similarities of whole molecular crystal structures; this has been termed 'Structural Genetic Fingerprinting'. Developments of this method, including the use of partial fingerprints, will be presented. A number of examples will be used to illustrate the broad applicability of the method, including a comparison of predicted crystal structures and a comparison of intermolecular interactions in apparently dissimilar structures. The method will be shown to be suitable for large datasets of hundreds or even thousands of structures.

1. A. Parkin, G. Barr, W. Dong, C. J. Gilmore, D. Jayatilaka, J. J. McKinnon, M. A. Spackman and C. C. Wilson, *CrystEngComm.*, 2007, pp 648-652.

Keywords: structure comparison, hirshfeld surface, structural genetic fingerprinting

## P09.06.49

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### Mixed crystal of bidentate and tridentate perfluoro-phenylmercury Lewis acids with organic molecules

Mikhail Yu. Antipin<sup>1,2</sup>, Fedor M. Dolgushin<sup>2</sup>, Andrey A. Yakovenko<sup>2</sup>, Jose H. Gallegos<sup>1</sup>, Tatiana V. Timofeeva<sup>1</sup>

<sup>1</sup>New Mexico Highlands University, Department of Natural Sciences, Diamond Ave., Las Vegas, NM, 87701, USA, <sup>2</sup>Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 119991, Russia, E-mail : m\_antipin@yahoo.com

At present a number of studied organic/organic mixed crystals (co-crystals) is quite significant, however not many mixed organic/organometallic crystals have been synthesised and described till now. Our group collected a large array of experimental data that have shown affinity of Lewis acids, such as cyclic tridentate perfluoro-o-phenylmercury, o-C<sub>6</sub>F<sub>4</sub>(Hg)<sub>3</sub> (I) and bidentate 1,2-bis(chloromercurio) tetrafluorobenzene o-(C<sub>6</sub>F<sub>4</sub>)(HgCl)<sub>2</sub> (II), to formation of mixed crystals with numerous neutral and ionic organic molecules. Formation of mixed crystals can influence catalytic activity, solid state polymerization, prevent decomposition of unstable guest-molecules, transform spectral behaviour of guest,

etc. We are looking in particular for supramolecular organization in mixed crystals that can modify centrosymmetric structure of pure material into acentric structure of host-guest compound. Such approach can help to alter organization of strongly polarized donor-acceptor molecules in crystals and make them useful for applications as optoelectronic materials. In the mixed crystals of I and II organic components are benzene derivatives such as isomers of nitrotoluene, low-melting or liquid at room temperature. Crystal growth of these materials has been done using zone melting technique and molecular structure of these materials in pure compounds was compared with their structures in mixed crystals. It was found that number of acentric crystals in the series mixed crystals of I with nitrobenzene derivatives is higher than statistical expectation. Explanation of this phenomenon can be found in specific intermolecular interactions forming supramolecular associates in these materials.

Keywords: co-crystals, organometallic, Lewis acids

### P09.07.50

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#### Crucible rotation dependence of oxygen concentration during solidification of multicrystalline Si

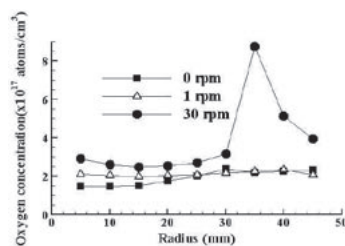
Hitoshi Matsuo<sup>1</sup>, R. Bairava Ganesh<sup>1,2</sup>, Satoshi Nakano<sup>3</sup>, Liu Lijun<sup>3,4</sup>, Yoshihiro Kangawa<sup>1,3</sup>, Koji Arafune<sup>5</sup>, Yoshio Ohshita<sup>5</sup>, Masafumi Yamaguchi<sup>5</sup>, Koichi Kakimoto<sup>1,3</sup>

<sup>1</sup>Kyushu University, Graduate School of Engineering, Research Institute for Applied Mechanics, 6-1 Kasuga-koen, Kasuga, Fukuoka, 816-8580, Japan, <sup>2</sup>Crystal Growth Centre, Anna University, Chennai 600025 India, <sup>3</sup>Research Institute for Applied Mechanics, Kyushu University, 6-1 Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan, <sup>4</sup>Xi'an Jiaotong University, Xi'an 710049, China, <sup>5</sup>Toyota Technological Institute, 2-12-1 Hisakata, Tempaku-ku, Nagoya 468-8511, Japan, E-mail : matsuo@riam.kyushu-u.ac.jp

Multicrystalline silicon (mc-Si) has a market share of more than 50 % in all photovoltaic materials. Oxygen in mc-Si forms defects, which decrease conversion efficiency of solar cells. Therefore, control of oxygen concentration in a silicon ingot is an important issue to improve conversion efficiency. A crucible is rotated during solidification process to control and/or homogenize oxygen concentration. Since oxygen concentration is affected by a melt flow. The radial flow velocity is suppressed by the crucible rotation because centrifugal force acts in the opposite direction [1]. From view of this point, we optimized crucible rotation during solidification process in order to minimize oxygen concentration in the growth direction and homogenize that in the radial direction. Fig. 1 shows oxygen concentration as a function of radius in the ingot measured by FTIR at 50 mm from bottom of the ingot. Oxygen concentration at crucible rotation rates of 0 and 1 rpm is homogenized in the radial direction. Therefore, we concluded that crucible rotation rate from 0 to 1 rpm is optimal rotation rate.

References

[1] K. Kakimoto, et al., *Int. J. Heat Mass Transfer*, 35 (1992) 2551.



Keywords: multicrystalline silicon, crystal growth, FTIR

### P09.04.51

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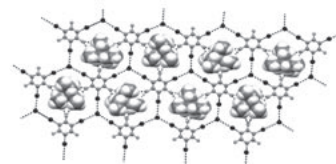
#### Supramolecular anion coordination networks with (6.3) cation-templated topologies

Giuseppe Resnati<sup>1,2</sup>, Pierangelo Metrangolo<sup>1</sup>, Franck Meyer<sup>1</sup>, Tullio Pilati<sup>2</sup>, Giancarlo Terraneo<sup>1</sup>, Calimero Ticozzi<sup>1</sup>

<sup>1</sup>Politecnico di Milano, Department of Chemistry, Materials, and Chemical Engineering, 7, via Mancinelli, Milan, Lombardy, I-20131, Italy, <sup>2</sup>ISTM-CNR, Milan, Italy, E-mail: giuseppe.resnati@polimi.it

In this presentation we show the use of the halogen bonding between various naked iodide anions and 1,3,5-trifluoro-2,4,6-triiodobenzene (TFTIB) for the deliberate construction of anionic honeycomb-like networks with a degree of precision and accuracy that is unusual for crystal engineering. The 3-fold symmetry of TFTIB elicits the three coordinate profile of I<sup>-</sup> thanks to a mutual induced fitting process of the valencies of interacting partners. Anionic networks characterize all the complexes obtained, where cations sit in the hexagonal cavities, filling the potential voids and stabilizing these 2D networks. TFTIB functions as a reliable tridentate and trigonal tecton in halogen bonding-based crystal engineering [1].

[1] Metrangolo P., Meyer F., Pilati T., Resnati G., Terraneo, G., *Chem. Commun.* 2008, 1635-1637.



Keywords: halogen bonding, anion coordination, supramolecular chemistry

### P09.02.52

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#### Co-crystallisation and crystal engineering

Ghazala Sadiq, Roger J Davey, Keith Chadwick  
University of Manchester, School of Chemical Engineering and Analytical Sciences, The Mill, Sackville Street, Manchester, PO Box 88, M60 1QD, UK, E-mail: ghazala.sadiq@manchester.ac.uk

As pharmaceutical interest in co-crystals continues to grow, understanding why and how certain molecular functionalities aid or inhibit the formation of co-crystals has become paramount. In this paper we looked at the use of crystal structure database searching and molecular modeling in order to develop protocols for designing co-crystals of commercial compounds that contain different molecular functionalities. Searching the Cambridge Structural Database for known co-crystals containing the desired intermolecular interactions helped identify the class of compound most likely to form co-crystals with our compounds of interest. Using binary and ternary phase diagram data co-crystallisation of a known compound with various formers were carried out from melt, solution and solid phases. The solid phases obtained were subsequently characterized using single crystal x-ray diffraction and to a lesser extent powder diffraction and DSC. Molecular modeling, using Materials Studio, of all the systems studied was used in order to try and understand the success/failure of specific systems in forming co-crystals. In general it was found that those systems which formed co-crystals, the heterodimer present in the co-crystal structure was more energetically favourable than the two homodimers.

Keywords: co-crystallisation, ternary phase diagrams, crystal engineering