

on building units (Bus) consisting in oxo-centered O(BiM)₄ tetrahedra sharing edges and surrounded by isolated phosphate groups. These 2D Bus are able to self-organize in versatile 3D regular intergrowths. A large number of intergrowths, with long Bus have been evidenced, rationalized and enabling the establishment of a method being able to predict hypothetical new materials [3].

In this work the prediction, formulation and synthesis of new phases with ribbons n = 5, 8 has been completed. The dielectric properties and SHG measurements of these non centrosymmetric compounds will be presented. The mega-series corresponding to the intergrowths has been rationalized as a function of n and fully applied to the synthesis of new materials. The figure 1 shows the design of a predicted structure with n = 8 and the structural verification by HREM.

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Keywords: predictive approach, non centrosymetry, bismuth phosphates

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Changing solid-state reaction stereochemistry: Heavy-atom – co-crystal method

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Solid-state reactions exhibit high stereoselectivity compared with conventional solution reactions, but that cannot be generally altered as the origin of the selectivity is generally dictated by the molecular and crystal structures themselves[1], although in some cases they proceed in stages to give different products with time [2]. We have found that intramolecular photocyclization reaction of 2-(*o*-substituted-arylthio)-3-methyl-2-cyclohexenones (**1-3**, (R= CH₃ (**1**), Cl (**2**) and Br (**3**)) in crystals highly depends on the substituent at the ortho position. Compounds **1-3** are crystallized in the space group of *P*-1, *Pbca* and *Pbca*, respectively. Crystals **X(2)** and **X(3)** (**X** signifies crystal) are isomorphous to each other. Compound **3** in **X(3)** gave only the *cis* product, whereas **2** in **X(2)** gave both the *trans* and the *cis* isomers. **1** in **X(1)** gave only the *trans* product. Time course experiments have revealed that there are two reaction pathways; Path A and Path B. Path A is initiated by the photoexcited ³(π - π^*) state via an intersystem crossing from the ¹(n - π^*) state, which is the typical reaction path of photoreaction of cyclohexenones in solution. The reaction first produces the *trans* product which is converted to the *cis*-isomer slowly by proton abstraction by the carbonyl oxygen followed by keto-enol tautomerism. On the other hand, Path B is a newly found path in the solid state which produces the *cis* product directly, initiated most likely by the photoexcited ³(n - π^*) state. Formation of *cis* products **2c** and **3c** from the beginning of the reaction cannot be explained by the *trans*-to-*cis* isomerisation, an intrinsically slow reaction.

X(1) adopts Path A, **X(3)** Path B, whereas **X(2)** both Path A and Path B. Solution reactions of **1**, **2** and **3** all gave similar reaction products. Thus, the choice of reaction pathway is determined by the external heavy atom (H-A) effect in the crystal through spin-orbit coupling. This means that by placing molecules concerned under the different degree of influence of heavy atoms, we can switch the reaction pathways and hence product distribution. We could achieve this by making co-crystals of heavy-atom containing and non-containing analogues in various ratios (1:1, 9:1 and 1:9), and then carrying out photoreaction on them. Indeed, the reaction products have dramatically

changed depending on the co-crystals of different stoichiometry. As being solid-state reactions, they are fast and free from by-products.

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Keywords: solid-state reactions, Heavy-Atom effect, spin-orbit coupling

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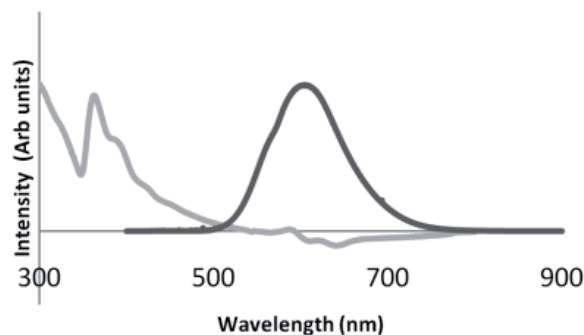
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Structure and optical properties of natural low dimensional semiconductors

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Inorganic-organic nanocomposite materials have been studied extensively in recent years because of the variety of interesting and useful properties associated with this family of compounds. The layered hybrids specifically the 2D (RNH₃)₂MX₄ and (NH₃RNH₃)₂MX₄ series, have shown good semiconduction, photoconductivity, photoluminescent and electroluminescent behaviour due to their inherent quantum well nature [1]. In essence, by taking an inorganic semiconductor material, and effectively intercalating organic amine cations into it, the materials' dimensionality is changed, and in so doing, so too optical properties of the material. The features most greatly affected by a change in dimensionality is, firstly, the band structure i.e., the tuning of the band gap, secondly, the electron mobility of the compound, and thirdly and most importantly, the ability to confine the electron and hole orbit's (excitons), which drastically alters the materials recombination luminescence (Fig.1). A practical advantage of inorganic organic hybrids is that they self assemble and are easily solution processed into thin films, this has positive implications regarding cost and the ease of processability for further technological applications such as LCD's displays [1]. Previously published results show the binding energy of the excitons increase as the dimensionality is decreased i.e. from 3D to 2D and from 2D to 1D. However there is a much larger increase in the binding energy from 2D to 1D systems as seen in Fig.1. Here we report the structure and optical properties of 1D hybrids with the general formula (RN⁺)PbI₃, in which we further investigate the tunability of the band structure, the large binding energy associated with the excitonic behavior, and charge transfer effects between wires and spacers [3-5].

Fig. 1. The binding energy effect as displayed in (piperdium)PbI₃ wires where we see the 1s exciton absorption peak at 365nm and the resultant 600nm photoluminescence emission both at 77K.



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Structural diversity in layered organic materials through templating Co-crystallisation

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Layered materials are desirable targets in designing crystalline architectures, due to their many distinct, favourable physical properties. For example, in the pharmaceutical manufacturing industry, layered materials are more compactable into tablets, especially where the interactions between layers are much weaker than those within the layers, while in the design of porous materials, layered materials are much more likely to lead to channel structures and therefore provide an easy route to solvent or gas exchange. Crystal engineering is a well-developed approach for generating supramolecular constructs, mainly using hydrogen bonding as its structure-directing tool. However, it is often the presence of weaker interactions which lead to the formation of a truly layered structure - this is inevitably more difficult to control and can also often lead to the presence of significant structural defects, some of them beneficial to function.

We have developed a wide range of approaches for generating layered materials from multi-component crystallisations. This has not only involved conventional co-crystallisation of more than one molecule into the crystalline lattice, but also utilising co-molecules in a templating role, guiding the assembly of molecules towards a layered crystalline form. Amongst the significant findings in engineering and controlling the assembly of materials whose functionality is based on a layered architecture, the following will be discussed:

- a simple and reliable route to the formation of paracetamol Form II, a layered metastable polymorph with favourable compaction properties, produced through templating multi-component crystallisation [1];
- the porous, layered molecular material 4-phenoxyphenol, which is based on a dominant hexagonal hydrogen bonded motif, with *breathable* channels that are robust when both solvent-filled and empty;
- layered, channel-containing molecular complexes of nucleic acid bases, that show promise for the possibility of solvent or gas exchange, where C-H...F hydrogen bonds are integral to the formation of channels;
- multi-component systems including hydrates of both phloroglucinol and gallic acid in which solvent molecules play a crucial role in constructing and connecting the layers, and whose disposition can be elucidated by a combination of diffraction and quantum chemical calculations. The significant functional features of these structures are both layered and porous channel architectures, and the locally ordered defect structure is also vital to their function.

These functional molecular materials have as a common theme, a strongly hydrogen bonded motif, assembled into layers by weaker or stronger interlayer interactions, together with the possibility of local ordering, all of which can be vital in lending these materials their particular potential functional capabilities.

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Ionic co-crystals of active pharmaceutical ingredients and their applications in the pharmaceutical industry

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The use of electrostatic interactions such as those present in ionic co-crystals (ICCs) containing alkali metals and alkaline earth metals compounds has never been systematically explored in the field of molecular Crystal Engineering. In this type of structures the interaction between inorganic ions and organic molecules must be seen as a special case of solvation, with the organic molecules acting as a solvent molecules (in competition with water if present) towards metal ions [1]. In the case of primary and secondary amides, N-H and C=O dipoles act respectively as donor and acceptor for hydrogen bonds, thus with the possibility of "solvating" inorganic salts.

We present here our results, from the serendipitous co-crystallization of barbituric acid with alkali halides, to the exploitation of the phenomenon and its application to crystal engineering issues. In particular we have investigated: the thermal behaviour of barbituric acid ICCs with alkali bromide and the associated dehydration processes; the "solvating properties" of a number of molecules, some of which are active pharmaceutical ingredients (APIs): diacetamide, malonamide, oxamide, urea, cyanuric acid, uric acid, carbamazepine, nicotinamide and piracetam. As for the inorganic counterpart, the CaCl₂ salt was chosen because of its non-toxicity and potential applications in the Pharmaceutical field. Synthetic methods for this study vary from classical crystallization from solution, to slurry and mechanochemical solid state techniques (grinding and kneading).

ICCs were obtained for most of the organic molecules. Crystal structures were solved from single crystal data, or by powder diffraction using simulated annealing (SA) procedures when no single crystal was available. Due to the high number of degrees of freedom in the SA algorithm, an alternative approach was adopted: Ca...O_{water} fragments extracted from the Cambridge Structural Database were inserted as rigid bodies in the algorithm to minimize calculation time and bias solutions towards chemically reasonable coordination patterns. All crystalline compounds were analyzed with DSC, TGA and variable temperature XRD. Dissolution rate measurements were performed on ICCs of APIs. The new phases differ from the starting components for physical properties such as melting point and solubility rate.

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