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We report here the *ab initio* crystal structure solution of three  $\text{MgCl}_2 \cdot n\text{C}_2\text{H}_5\text{OH}$  adducts, precisely  $2\text{MgCl}_2 \cdot 3\text{EtOH}$  ( $n=1.5$ ),  $5\text{MgCl}_2 \cdot 14\text{EtOH}$  ( $n=2.8$ ) and  $3\text{MgCl}_2 \cdot 10\text{EtOH}$  ( $n=3.3$ ), obtained from high-resolution X-ray powder diffraction data collected using synchrotron radiation (ID31 at ESRF, Grenoble).

The above-mentioned complexes are fundamental precursors of the latest generation Ziegler-Natta catalysts, which consist of  $\text{TiCl}_4$  supported on  $\text{MgCl}_2$ , used to produce polyolefins on a global scale. The catalytic yield and isotacticity degree of the derived polymers strongly depend on the Lewis base-to- $\text{MgCl}_2$  ratio of the  $\text{MgCl}_2 \cdot n\text{EtOH}$  adducts [1]. It has been suggested that the formation of  $\text{MgCl}_2/\text{TiCl}_4$ , produced with  $\text{MgCl}_2/\text{Lewis base}$  complexes, retains the memory of the ligand distribution in the precursor [2]. The catalyst models developed to date are based on the insertion of  $\text{TiCl}_4$  species and donors on selected cut surfaces of  $\alpha\text{-MgCl}_2$  [3]; whereas the effects of the precursor properties on the catalytic activity are invariably neglected due to the lack of knowledge of the precursor atomic structures.

Our direct structural analysis confirmed that the structures of  $\text{MgCl}_2 \cdot n\text{EtOH}$  adducts with  $n=1.5$  and  $n=2.8$  are based on ribbons of metal-centered octahedra similar to  $\text{MnCl}_2 \cdot n\text{EtOH}$  complexes, as previously suggested [4, 2]. However the bonding scheme in  $\text{MgCl}_2 \cdot n\text{EtOH}$  with  $n=1.5$  is different when compared to the  $\text{MnCl}_2 \cdot n\text{EtOH}$  complex with the same stoichiometry. With  $n=3.3$  the chain-like structure of the  $\text{MgCl}_2 \cdot n\text{EtOH}$  complex breaks in a thread-like structure of isolated octahedra linked by hydrogen bonds. The different bonding network and packing model of the chain-like and thread-like isomers will be the starting point to model the formation of different condensed blocks upon de-alcoholation.

Therefore, we predict that the structural description at atomic scale of  $\text{MgCl}_2 \cdot n\text{EtOH}$  supports will offer new possibilities to model and to improve the performances of Ziegler-Natta catalysts at the industrial level.

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## MS24.P15

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### Influence of a robust supramolecular synthon on structure-property relationships in ammonium carboxylates

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One of the aims of crystal engineering is to produce crystalline materials with predictable and reproducible supramolecular interactions. Although a number of other interactions are possible, the most common supramolecular "glue" used in crystal engineering is the hydrogen bond.

We have recently undertaken a systematic survey of the charge-assisted supramolecular heterosynths that occur in ammonium carboxylate salts [1-4]. Most structures reported previously incorporate

either regularly repeating hydrogen-bonded rings propagated by a 2-fold screw axis or alternating hydrogen bonded rings propagated by a centre of inversion. We set out to examine how robust these supramolecular synths would be under the influence of various molecular interferences. Compounds have been characterised by single crystal and powder X-ray diffraction. Their thermal stability and decomposition behaviour have been studied using Differential Scanning Calorimetry, Thermogravimetry and Hot Stage Microscopy.

Active pharmaceutical ingredients (API) suffer from some disadvantages in the solid state, particularly poor solubility or bioavailability and polymorphism. By making use of crystal engineering concepts to make pharmaceutical co-crystals and pharmaceutical salts, which are hydrogen bonded assemblies between the API and a GRAS (generally-regarded-as-safe) substance, it is possible to increase the water solubility, or to reduce the likelihood of polymorphic behaviour of the API itself. The same supramolecular synths are observed in amine salts of carboxylic acid containing APIs such as (S)-Ibuprofen, Diclofenac and Fenofibrate [5]. We have found that these supramolecular synths are extremely robust but can be switched off under the influence of various molecular interferences. We have also established some principles involving the physical properties (such as melting points and solubilities) of materials containing these supramolecular synths.

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**Keywords:** crystal engineering, supramolecular synthon, ammonium carboxylates

## MS24.P16

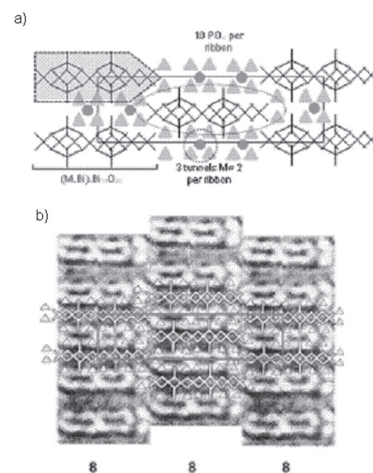
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### Predictive approach of new bismuth oxo-phosphates

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One important challenge in today's solid state chemistry is to be able to conceive materials with particular physico-chemical properties. The possibility of predicting new structures according to a wished property and the faculty to formulate it, is surely a main advantage in the design of new materials.

In the  $\text{Bi}_2\text{O}_3\text{-M}_x\text{O}_y\text{-P}_2\text{O}_5$  ternary systems, on the basis of previous compounds based on 2D-ribbon like units [1] [2], we have prepared numerous compounds with an original predictive approach, based



**Figure 1:** a) Design of a predicted structure  $n=8$ , b) HREM image showing the evidence of a new intergrowth (Structural verification).

on building units (Bus) consisting in oxo-centered O(BiM)<sub>4</sub> 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

### MS24.P17

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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= CH<sub>3</sub> (**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 <sup>3</sup>( $\pi$ - $\pi^*$ ) state via an intersystem crossing from the <sup>1</sup>( $n$ - $\pi^*$ ) 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 <sup>3</sup>( $n$ - $\pi^*$ ) 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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### MS24.P18

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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 (RNH<sub>3</sub>)<sub>2</sub>MX<sub>4</sub> and (NH<sub>3</sub>RNH<sub>3</sub>)<sub>2</sub>MX<sub>4</sub> 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<sup>+</sup>)PbI<sub>3</sub>, 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)PbI<sub>3</sub> wires where we see the 1s exciton absorption peak at 365nm and the resultant 600nm photoluminescence emission both at 77K.

