

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.

[1] M. Huvé, M. Colmont, O. Mentré, *Inorganic Chemistry* **2006**, *17*, 6604-6611 (Part 1). [2] M. Huvé, M. Colmont, O. Mentré, *Inorganic Chemistry* **2006**, *17*, 6612-6619 (Part 2). [3] M. Huvé, M. Colmont, J. Lejay, P. Aschehoug, O. Mentré, *Chemistry of Materials* **2009**, *21*, 4019-4029.

Keywords: predictive approach, non centrosymmetry, bismuth phosphates

MS24.P17

Acta Cryst. (2011) **A67**, C362

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

Reiko Kuroda, Ryo Sekiya, *Department of Life Sciences, Graduate School of Arts and Sciences, The University of Tokyo (Japan)*. E-mail: ckuroda@mail.ecc.u-tokyo.ac.jp

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.

[1] G.M. Schmidt, *Pure Appl. Chem.* **1971**, *27*, 647-678. [2] (a) H.E. Zimmerman, E.E. Nesterov, *J. Am. Chem. Soc.* **2002**, *124*, 2818-2830. (b) H.E. Zimmerman, E.E. Nesterov, *Org. Lett.* **2000**, *2*, 1169-1171. [3] R. Sekiya, R. Kuroda, *submitted*.

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

MS24.P18

Acta Cryst. (2011) **A67**, C362-C363

Structure and optical properties of natural low dimensional semiconductors

David G Billing,^a Robert S Black,^a Rudolph Erasmus,^b ^a*Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, (South Africa)*. ^b*School of Physics, University of the Witwatersrand, Johannesburg, (South Africa)*. E-mail: dave.billing@wits.ac.za

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.

