

Poster Sessions

Kawamichi, T. Kodama, M. Kawano, M. Fujita, *Angew. Chem. Int. Ed.* **2008**, *47*, 8030-8032. [5] T. Kawamichi, T. Haneda, M. Kawano, M. Fujita, *Nature* **2009**, *461*, 633-635. [6] M. Kawano, T. Haneda, D. Hashizume, F. Izumi, M. Fujita, *Angew. Chem. Int. Ed.* **2008**, *47*, 1269-1271. [7] K. Ohara, J. Marti-Rujas, T. Haneda, M. Kawano, D. Hashizume, F. Izumi, M. Fujita, *J. Am. Chem. Soc.* **2009**, *131*, 3860-3861. [8] J. Marti-Rujas, Y. Matsushita, F. Izumi, M. Fujita, and M. Kawano, *Chem. Commun.* **2010**, *46*, 6515-6517. [9] J. Marti-Rujas, N. Islam, D. Hashizume, F. Izumi, M. Fujita, M. Kawano, *J. Am. Chem. Soc.*, in press. [10] J. Marti-Rujas, N. Islam, D. Hashizume, F. Izumi, M. Fujita, H. J. Song, H. C. Choi, M. Kawano, *Angew. Chem. Int. Ed.*, in press.

Keywords: MOF, kinetic assembly, powder structure determination

MS24.P11

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Structure and gas adsorption study on metal organic frameworks

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Recent work in the field of hydrogen storage and CO₂ sequestration has been overwhelmingly dominated by the use of a narrow range of materials, specifically high surface area carbons (including carbon nanotubes) zeolites and metal hydrides. Activated carbons have the attraction that they are very cheap, their capacities on a weight % basis are very good due to their very low densities, and the adsorption process is readily reversible under mild conditions. Their shortcomings stem from the fact that the fundamental interactions between carbons and hydrogen are non-bonding in nature (i.e. they involve physisorption) and are therefore rather weak. Metal hydrides, adsorb hydrogen by a chemisorption process that is accompanied by dissociation of the dihydrogen molecules. The interaction is much stronger, but facile reversibility is a problem in many cases and such systems are often prone to irreversible poisoning by oxygen. There is clearly an urgent need to develop new classes of materials that have the potential to provide superior performance for hydrogen storage and CO₂ sequestration. Some of the more recent developments in this area include the use of Metal Organic Frameworks (MOFs). Our strategy is aimed at the development of new materials systems where the host-guest interactions are intermediate between those found in the carbons and the metal hydrides.

[1] C. Dey, P. Pachfule, R. Das, P. Poddar, R. Banerjee, *Cryst. Growth Des.* **2011**, *11*, 139-146. [2] T. Panda, P. Pachfule, Y. Chen, J. Jiang, R. Banerjee, *Chem. Commun.* **2011**, *47*(7), 2011-2013.

Keywords: porous, zeolytic, adsorption

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Photo-responsive Pores of Porous Coordination Polymers

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Porous coordination polymers (PCPs) or metal-organic frameworks (MOFs), which are constructed from metal ions and organic ligands, have been extensively investigated to provide the nanometer-sized space that is potentially applicable in separation, heterogeneous catalysis, and gas separation/storage. Recently, we reported porous crystalline materials that can be activated by photostimulation [1] and demonstrated that photochemical modification is a powerful method for the control of physical properties of PCPs or MOFs.

In this report, synthesis and properties of new PCPs containing *trans*-1,2-bis(4-pyridyl)ethene (bpe) as a photoreactive module will be presented. The photoreactive PCPs adsorb gaseous molecules such as carbon dioxide. The bpe molecules quantitatively take place topochemical [2+2] cycloaddition reactions and the PCPs show single-crystal to single-crystal (SCSC) transformations upon UV irradiation (> 300 nm). We will discuss not only the SCSC transformations but also the impact on the photochemical transformations on the sorption properties.

[1] H. Sato, R. Matsuda, K. Sugimoto, M. Takata, S. Kitagawa, *Nature Materials* **2010**, *9*, 661-666.

Keywords: microporous, photoreaction, adsorption

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Pressure-induced magnetic switching in molecular framework materials

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The design and characterization of molecular materials with targeted functionalities, such as magnetism and/or nanoporosity, is part of a major international push aimed at developing systems with technologically important applications (e.g., molecular sensing and storage). As such, the accurate elucidation of their often complex structure-function relationships presents a crucial step in their advancement. For molecular magnetism, these approaches are commonly focused on variations of temperature and/or magnetic field, while comparatively little attention has been given to how these materials behave as a function of pressure. Here, we report magneto-structural investigations of magnetic molecular materials using synchrotron-based structural studies (powder diffraction and pair distribution function) and magnetic susceptibility measurements at high pressures. These studies have revealed a range of interesting phenomena such as orbital reorientations, spin crossover, phase transitions, and extreme compressibility [1].

[1] G.J. Halder, K.W. Chapman, J.A. Schlueter, J.L. Manson, *Angew. Chem. Int. Ed.* **2011**, *50*, 419-421.

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The crystal structure of Ziegler-Natta catalyst supports

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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 TiCl_4 supported on 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- 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 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.

[1] R. Huang, F. Malizia, G. Pennini, C.E. Koning, J.C. Chadwick, *Macromol. Rapid Commun.* **2008**, *29*, 1732-1738. [2] P. Sozzani, S. Bracco, A. Comotti, R. Simonutti, I. Camurati, *J. Am. Chem. Soc.* **2003**, *125*, 12881-12893. [3] K. Vanka, G. Singh, D. Iyer, V. Gupta, *J. Phys. Chem. C* **2010**, *114*, 15771-15781. [4] a) P.L'Haridon, M.T. LeBihan, Y. Laurent, *Acta Cryst.* **1972**, *B28*, 2743-2748, b) P.L'Haridon, M.T. LeBihan, *Acta Cryst* **1973**, *B29*, 2195-2203.

Keywords: crystal structure determination, ziegler-zatta catalyst, $\text{MgCl}_2\text{-EtOH}$ adducts

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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.

[1] A. Lemmerer, S.A. Bourne, M.A. Fernandes. *Crystal Growth & Design*, **2008**, *8*, 1106-1109. [2] A. Lemmerer, S.A. Bourne, M.A. Fernandes. *CrystEngComm*. **2008**, *10*, 1605-1612. [3] A. Lemmerer, S.A. Bourne, M.A. Fernandes. *CrystEngComm*, **2008**, *10*, 1750-1757. [4] A. Lemmerer, N.B. Báthori, S.A. Bourne. *Acta Cryst.* **2008**, *B64*, 780-790. [5] A. Lemmerer, S.A. Bourne, M.R. Caira, J. Cotton, U. Hendricks, L.C. Peinke, L. Trollope. *CrystEngComm*, **2010**, *12*, 3634-3641.

Keywords: crystal engineering, supramolecular synthon, ammonium carboxylates

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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

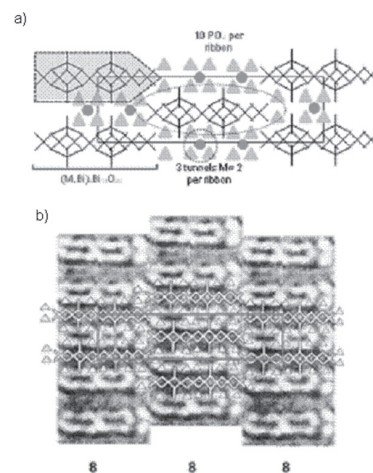


Figure 1: a) Design of a predicted structure $n=8$, b) HREM image showing the evidence of a new intergrowth (Structural verification).