

What is the most likely outcome when a homogeneous solution containing different molecular solutes is allowed to evaporate to dryness? Unless a chemical reaction driven by the formation of covalent bonds takes place between the two solutes, one would, as a rule, expect the appearance of two separate molecular solids – the equivalent of a recrystallization. In the supramolecular laboratory, however, the very same process provides an opportunity to move in a completely different direction – a co-crystallization is a deliberate attempt at bringing together different molecular species within one periodic crystalline lattice without making or breaking covalent bonds. The goal of the former is a homomeric product, whereas the latter procedure strives for a heteromeric product and, in general, the odds are stacked firmly in favor of a homomeric product, so how do we go about developing reliable, effective, and versatile synthetic methods for the directed assembly of heteromeric co-crystals? This presentation will (a) outline practical strategies for modular and directed assembly of co-crystals [1], [2], [3] and (b) demonstrate how different physical properties of an active ingredient (such as a pharmaceutically relevant compound) can be altered through co-crystal synthesis [4]. Several co-crystals of a family of anti-cancer compound have been synthesized using a precise and well-defined hydrogen-bond based supramolecular approach which has produced structural consistency in the resulting solids. The melting points of the co-crystals correlate very well with the melting points of the individual acids, and the aqueous solubility can be changed in a predictable way compared to that of the individual drug. Consequently, co-crystals can offer new solid forms from which to choose an active ingredient where a particular physical property can be dialed-in, provided that the co-crystals show structural consistency and that systematic changes are made to the participating co-crystallizing agents.

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Probing mechanical anisotropy in molecular crystals using nanoindentation methods

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The control of mechanical properties of molecular solids is a particularly challenging aspect of crystal engineering and this is true especially in the case of pharmaceutically relevant substances. Since many organic compounds that are used in the pharmaceutical industry have to be crushed and ground during tableting, a correlative understanding of their hardness and toughness is important. With the recent advent of the nanoindentation technique, wherein loads and displacements can be measured with resolutions of 1 nN and 0.2 nm respectively, it is possible to evaluate the mechanical behavior of extremely small-scale systems such as thin films and small single crystals. We have employed the nanoindentation technique to relate the mechanical properties of saccharin single crystals with the underlying structure.¹ Indentations were performed on (100) and (011) faces to assess the mechanical anisotropy. The load-displacement

(*P-h*) curves indicate significant differences in the nature of plastic deformation. The *P-h* curves obtained on the (011) plane are smooth reflecting homogeneous plasticity. However discrete displacement bursts (pop-ins) are observed in the *P-h* curves obtained on the (100) plane suggesting a discrete deformation mechanism. The crystals of monoclinic form of sodium saccharinate (Na(sac).1.875 H₂O) was also studied using nanoindentation technique. The *P-h* curves obtained on two different facets of the crystals that the mechanical behavior of the crystals is indeed anisotropic. The structural origins of these fundamentally different deformation mechanisms have been analyzed in terms of the dimensionality of the hydrogen bonding networks. The study quantifies the relation between interaction anisotropy and mechanical properties such as plastic deformation and lack of continuous response to mechanical deformation. Notably, such a correlation between micro and macro level properties has the promise of designing organic crystals with pre-targeted properties. Further, nanoindentation of molecular crystals offers the scope to quantify the strengths of intermolecular interactions experimentally and to compare different types of interactions in a direct way.

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Removal of hydrocarbons from water by using organophilic zeolites

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Chlorinated volatile organic compounds (VOCs), such as 1,1-dichloroethylene (DCE) and aromatic hydrocarbons, BTX (benzene, toluene, and xylene) constitute a significant fraction of the hazardous air and water pollution [1]. Human beings are exposed to elevated levels of a wide spectrum of volatile organic carbons many of which have been found to be potentially carcinogenic. Research on hydrocarbon removal has been mainly focussed on single components from air matrix, whereas the studies involving aqueous dilute solutions are few. However, in most environmental applications, these pollutants are present in the form of mixtures in very dilute aqueous solution. Removal of organic contaminants from water and wastewater has been achieved using several treatment technologies, such as advanced oxidation processes, air stripping, reverse osmosis, ultrafiltration, and adsorption [2]. Recently, high-silica zeolites were shown to be more effective in removing certain organics from water than activated carbon [3]. In this work the efficiency of zeolite adsorbent materials for the removal of organic contaminant was tested in order to get a better understanding of the host-guest interactions occurring during adsorption processes.

In particular, evidences of 1,2-dichloroethane (DCE), methyl tert-butyl-ether (MTBE) and toluene (TOL) adsorption from dilute solutions into organophilic zeolites will be presented. A combined diffractometric, thermogravimetric and gas chromatographic study was used to: 1) investigate the adsorptive properties of hydrophobic synthetic zeolites; 2) characterise their structure after the adsorption of DCE, MTBE and TOL; 3) localise the organic species in the zeolite channel systems; 4) probe the interactions between organic molecules, water molecules and framework oxygen atoms.

The organophilic zeolites (FAU, MFI and MOR-type framework topology, respectively) were purchased in their protonated form by Tosoh Corporation (200 SiO₂/Al₂O₃ ratio). Kinetics and adsorption isotherm batch data were obtained via Headspace Solid Phase Microextraction -

Gas Chromatography. XRD powder patterns were collected on zeolites before and after adsorption on a Bruker D8 Advance diffractometer. Thermal analyses (TG and DTA) were performed in air up to 900°C at 10°C/min.

The experimental results prove that the kinetic of adsorption of all components is fast and indicates that competition exists between the organic compounds at low cosolute concentrations.

Rietveld refinements indicate that the relevant incorporation of DCE, MTBE and TOL in the organophilic zeolites causes significant increase of all unit cell parameters in comparison to those of the untreated material as well as strong distortions of the channel systems where the contaminants are hosted. The very favorable adsorption kinetics along with the effective and highly irreversible adsorption of DCE, MTBE and TOL molecules into zeolite pores make this cheap and environmental friendly material a tool with interesting applications for the removal of hydrocarbons from wastewater.

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Keywords: organophilic zeolites, X-ray diffraction, adsorption

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Synthesis and structures of new layered and framework anion exchangeable hydroxides

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New anion exchangeable intercalation compounds with either lanthanide hydroxide layers or lanthanide oxyhydroxide cationic inorganic frameworks have been synthesised. The layered materials have the general composition $\text{Ln}_2(\text{OH})_2\text{X}\cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Y, Gd} - \text{Lu}$; $\text{X} = \text{NO}_3, \text{Cl, Br}$) and have been shown to be flexible intercalation hosts undergoing anion exchange reactions with a wide range of organic carboxylates and sulfonates. [1], [2] Structural characterisation of the halide intercalates has shown them to comprise 8 and 9 coordinate lanthanide cations within the $[\text{Ln}_2(\text{OH})_2]^+$ layers with bridging hydroxide anions and coordinated water molecules making up the coordination sphere.

Time resolved in situ X-ray diffraction studies of the synthesis of these materials have shown that their mechanism of formation is complex with four distinct phases being identified and isolated.[3] Three of these phases are layered intercalation hosts with the layer composition $[\text{Yb}_2(\text{OH})_5]^+$ with differing interlayer separations controlled by the level of hydration. The fourth phase is $\text{Yb}_4\text{O}(\text{OH})_9\text{NO}_3$ which has a 3D structure with 1D channels which contain the nitrate anions and as such this system represents a rare case where a 2D material has been observed to transform to a 3D structure. For the halide materials a different framework material, $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$ which has much larger channels is formed.[4] In this material the chloride anions can be exchanged for a range of small organic and inorganic anions and is therefore the first anion exchangeable hydroxide framework material. Additionally the framework is stable up to 200 °C and can be reversibly dehydrated.

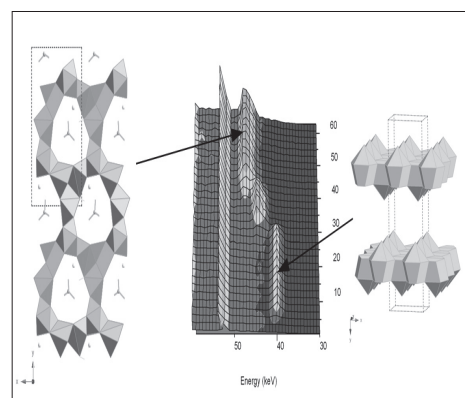


Figure 1 In situ diffraction pattern of the synthesis of $\text{Yb}_4\text{O}(\text{OH})_9\text{NO}_3$ showing the intermediate layered phases $\text{Yb}_2(\text{OH})_5\text{NO}_3\cdot n\text{H}_2\text{O}$.

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Keywords: framework, hydroxide, exchange

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LHT-9: layered nano-material with reductive adsorption and exchange properties

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Layered hydrazinium titanate, LHT-9 for short, is a layered material with a lepidocrocite structure and $\approx 9\text{\AA}$ interlayer distance. It has been prepared by a simple one-pot synthesis at near ambient conditions. Its idealized chemical formula is $(\text{N}_2\text{H}_5)_{0.5}\text{Ti}_{1.87}\text{O}_4$, space group Immm, $a \approx 3.8\text{\AA}$, $b \approx 18.46\text{\AA}$, $c \approx 2.98\text{\AA}$. Under the correct conditions it forms as nano-crystalline material which, however, displays important non-periodic structural characteristics. It has been characterized by various methods, notably high resolution transmission electron microscopy, x-ray diffraction, IR spectroscopy with analysis of gas evolution upon heating, XANES and EXAFS. From the analysis it is clear that LHT-9 consists of bent and deformed nano-flakes with only a few layers thickness, a high concentration of titanyl-groups and Brønsted-sites at the surface, and chemically bound hydrazinium $(\text{N}_2\text{H}_5)^+$ in the interlayers. The reductive properties of the hydrazinium and the structural characteristics add to the remarkable properties of LHT-9 and make it a valuable tool kit for many applications. More than 50 elements of the periodic table have been shown to be reduced, adsorbed and/or ion exchanged by LHT-9. Several of these reactions have possible or even proved ecological or economical value, such as removal of toxic or radioactive species from industrial waste waters or combustion gases, or extraction of noble metals from solutions [1].