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The solution x-ray scattering technique permits studies of biological macromolecules in near physiological conditions, which are not always compatible with high-resolution structural studies. Time-resolved solution scattering studies have been used to examine a number of different conformational changes as a function of time primarily at the tertiary and/or quaternary structure level. There exist a number of macromolecular systems which simply can not be contained within the crystallographic lattice structure. All virus and bacteriophage systems undergo complex assembly and maturation processes. Solution x-ray scattering and their time-resolved studies cover small proteins of several thousands of Da to multimega Da virus/phage particles, allowing structural studies of initial assembly processes as well as the late maturation processes. This talk will highlight the time-resolved study on the scaffolding protein-mediated assembly of P22 bacteriophage capsid and the maturation structural kinetics of HK97 bacteriophage capsid to illustrate how time-resolved solution scattering studies can complement crystallography and cryoelectron microscopy in structural virology. It will be shown that the scaffolding protein monomer-dimer assembly equilibrium controls the entire P22 capsid assembly process. In the case of HK97 maturation, the highly cooperative all-or-nothing structural transitions of 420 capsid proteins preveil in all steps so far been examined.

Keywords: small angle X-ray scattering, viral structure and function, time-resolved x-ray analysis

MS.51.5

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Real-time SAXS observation of assembly and disassembly dynamics of cyanobacterial clock proteins

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Circadian clocks are the endogenous timing systems enabling a variety of living organisms to adapt daily alternation of environments. Cyanobacterium *Synechococcus elongatus* PCC 7942 is known to have an oscillator composed of three clock proteins termed KaiA, KaiB, and KaiC. KaiA promotes the autophosphorylation of KaiC, whereas KaiB promotes the autodephosphorylation of KaiC. Three Kai proteins incubated in the presence of ATP are assembled and disassembled into heteromultimeric Kai complexes to effect a rhythmic change of the phosphorylation state of KaiC. To date, the crystal structure of the individual Kai protein has already been determined independently. However, a relationship between the assembly/disassembly dynamics and the KaiC phosphorylation cycle is still poorly understood because of the difficulty in unraveling the underlying mechanisms solely from the static molecular picture of individual clock components. We thus followed the assembly/disassembly dynamics of a ternary mixture containing KaiA, KaiB, and KaiC in real-time by using small-angle x-ray scattering (SAXS) at beamline BL45XU of SPring-8. The scattering from the ternary mixture robustly oscillated with a period of approximately 24 h, indicating a repeated assembly and disassembly of the Kai complexes. Based on the size and shape of the clock complexes, we will discuss the assembly/disassembly mechanism of the Kai oscillator.

Keywords: small-angle scattering, macromolecular complexes, dynamics thermodynamics of biomacromolecules

MS.52.1

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Novel cyclic salicylide derivatives: Guest inclusion and organo-gellation

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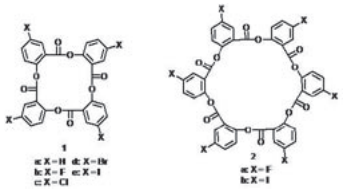
Some novel tetra- and hexasalicylide derivatives (1 and 2) were synthesized. The tetrasalicylide derivatives (1b-1e) having a 5-substituted halogen atom on the aromatic ring form organo-gels with several kinds of organic solvents, whereas the parent compound (1a) does not. In contrast, hexasalicylide derivatives (2a-2b) form stable inclusion crystals with several organic guest molecules.



Keywords: inclusion chemistry, host-guest complexes, crystal structures

MS.52.2

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Porous material behaviour in non-porous crystals: A route to chemical reactions

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In porous crystalline materials an important emphasis is on interactions between the host framework and the guest molecules and upon transport of the guests in and out of the framework pores. Surprisingly, in a small number of examples reported to date, such transport can also occur in non-porous crystals leading to entrapment of small molecules.[1] In this presentation two examples will be discussed in which such transport behaviour in non-porous crystal leads to subsequent chemical reactions within the crystal. These reactions involve changes in hydrogen bonding and changes in coordination bonds. In the first case we explore the reversible uptake/release of gaseous HCl leading to interconversion between square-planar coordination complexes trans-$[CuCl_2(3\text{-}Xpy)_2]$ and salts $(3\text{-}XpyH)_2[CuCl_4]$ (3-Xpy = 3-halopyridine) which has tetrahedral metal coordination geometry.[2,3] In the second, reversible uptake of

alcohol by a coordination polymer involving insertion/de-insertion of the alcohol into a Ag-O(carboxylate) bond will be described.[4] The presentation will further develop the results of recently published work with discussion of ongoing studies of the two systems.
[1] S. J. Delgarno et al., Chem. Soc. Rev. 2007, 36, 236.
[2] G. Minguez Espallargas et al., J. Am. Chem. Soc. 2006, 128, 9584.
[3] G. Minguez Espallargas et al., J. Am. Chem. Soc. 2007, 129, 15606.
[4] S. Libri et al., Angew Chem. Int. Ed. 2008, 47, 1693.

Keywords: reactivity of solids, coordination chemistry, hydrogen bonding

MS.52.3

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Polymorphism, isostructurality and selectivity in inclusion compounds

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Structures of host compounds with mixed guests are useful in understanding the process of molecular recognition in the solid state. We have elucidated the structures of three polymorphs of the host H1 = 2,2'-bis (hydroxydiphenylmethyl-1,1'-binaphthyl) and a series of its inclusion compounds with pyridine, morpholine and benzene in various proportions. A number of these compounds are isostructural and guests are located at fixed sites in the crystal structures. A second host compound H2 = 9-(2-naphthyl)-9H-xanthen-9-ol was studied in terms of the selectivity towards pairs of guests dioxane/cyclohexanone and dioxane/cyclohexanol. Selectivity profiles are evaluated in terms of the structures of the inclusion compounds with mixed guests. The results were studied by means of triangular diagrams which yielded the stoichiometries of the crystalline inclusion compounds resulting from competition experiments. Structural data is correlated to results of Thermo Gravimetry (TG) and Differential Scanning Calorimetry (DSC) and interpreted via Hirschfeld Surface Fingerprint Plots, lattice energy calculations and host-guest interactions.

Keywords: selectivity, isostructurality, polymorphism

MS.52.4

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What are the molecular properties that influence the formation of methanol solvates?

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Despite the considerable scientific interest in solvate crystals, it is generally not possible to predict whether a given molecule will form a solvate when crystallised from a particular solvent. Following a similar account on crystal hydrates [1], the aim of this contribution is the identification of molecular properties that influence the formation of methanol solvates. The Cambridge Structural Database (November 2007 release, [2]) was searched for molecular organic crystal structures that contain methanol or that are known to be crystallised from methanol. The retrieved structures can be grouped into four main categories: unsolvated crystals, methanol solvates, hydrates and methanol solvate hydrates. Molecular descriptors were calculated for the non-solvent molecules in each group, and statistical methods (t-test, Wilcoxon rank-sum test, Kullback-Liebler divergence) were used to identify the descriptors that best discriminate the four groups. The formation of any solvate was found to depend on the hydrogen bonding functionality of the molecules. Polar surface area and the number of heteroatoms are also useful indicators of solvate formation. The formation of a hydrate from a solution in methanol becomes more likely with increasing molecular polarity (as expressed, e.g., by [nr. of N atoms + nr. of O atoms] / nr. of heavy atoms) and less likely for molecules with a globular shape. The molecules that form mixed solvates are, on average, larger than either methanol solvates or hydrates, they have several hydrogen bonding groups and they are more polar than methanol solvates.
[1] Infantes, L.; Fabian, L. & Motherwell, W. D. S. (2007). CrystEngComm, 9, 65-71.
[2] Allen, F. H. (2002). Acta Cryst., B58, 380-388.

Keywords: solvates, molecular properties, databases

MS.52.5

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Framework deformation and guest packing in a microporous vanadium benzenedicarboxylate

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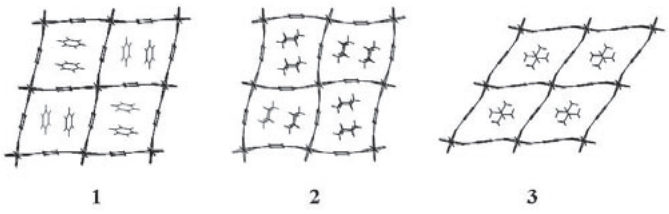
The microporous vanadium benzenedicarboxylate (VObdc, bdc = 1,4-benzenedicarboxylate) belongs to the third-generation hybrid organic-inorganic materials with flexible or dynamic frameworks that respond to changes in guests and external conditions. The cooperative relations between framework deformations and guest structures in VObdc loaded with various guest molecules are studied by single crystal X-ray diffraction. The VObdc framework contains chains of corner-sharing VO_6 octahedra that are cross-linked by bdc ligands. The 1D channels have a diamond shaped section outlined on each side by V-$O_2C(C_6H_4)CO_2$-V walls. The walls are flat when the channels are empty. Slight bending of the walls toward L shape is observed when the channels are loaded with flat guest molecules such as benzene that are packed in a herring bone pattern, 1. Strong bending of the walls to a C shape is observed when the guest benzene is replaced by bulkier molecules such as cyclohexane, 2, which is in contrast to an S shaped bending of the channel walls when the channels are filled by acetone molecules that are packed in an antiparallel mode, 3.



Keywords: microporous, flexible framework, framework deformation