

importance in understanding the polymorphic behaviour of APIs and so employs polymorph screening techniques in an attempt to sample a variety of different crystallization conditions. The large diversity of crystallization conditions provides the pharmaceutical industry with the confidence that all possible polymorphs of an API have been isolated. High-pressure techniques can provide a complementary method for exploring polymorphism and solvate formation in molecular solids. They are particularly useful for the identification and characterization of new forms that do not appear through standard crystallisation techniques such as those employed in conventional polymorph screens performed under ambient conditions. High-pressure methodologies are well-suited for obtaining so-called “disappearing” or elusive polymorphs in a reproducible manner. This presentation will highlight a number of different examples of polymorphism exhibited by pharmaceutical materials when subjected to high pressures.

Keywords: high-pressure crystallography, pharmaceuticals, polymorphism

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Kinetics and mechanisms of pressure-induced phase transitions of ternary model biomembrane systems

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Lipid bilayers, which provide valuable model systems for biomembranes, display a variety of polymorphic phases, depending on their molecular structure and environmental conditions, such as pH, ionic strength, temperature and pressure. By using calorimetric, spectroscopic and diffraction techniques, the temperature and pressure dependent structure and phase behavior of one- and two-component lipid systems, differing in chain configuration and headgroup structure, have been studied in recent years [1-3]. Very little is known about the phase behavior of the biologically more relevant heterogeneous three-component lipid systems, in particular about their kinetic and non-equilibrium behavior. We present data on structural and kinetic aspects of lamellar-to-lamellar lipid bilayer phase transitions of a three-component lipid mixture DOPC:DPPC:cholesterol, which serves as a canonical model raft mixture taking into account the heterogeneity of natural membranes. Applying static synchrotron small-angle x-ray scattering measurements and the pressure-jump relaxation technique in combination with time-resolved measurements (TRSAXS), the various temperature and pressure dependent phases and the kinetics of the lipid phase transformations have been investigated over a temperature range from 10 to 80 °C at pressures from ambient up to 3 kbar (300 MPa). Transitions in both the forward and reverse directions have been measured. The results are discussed in the light of possible kinetic mechanisms and are compared with the results of other lipid mesophase transitions.

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Keywords: lipid phase transitions, TRSAXS, pressure perturbation

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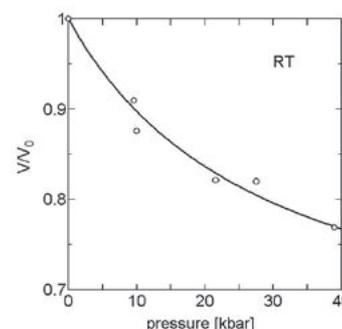
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Equation of state for the low-pressure crystalline phase of tin tetraiodide

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A series of experimental studies on determination of the melting curve of the low-pressure crystalline phase (CP-I) of a molecular crystal tin tetraiodide and its polyamorphism (presented in this congress) has been performed since 2001 onward, utilizing the beam line BL14B1 of SPring-8 in Japan. A multi-anvil press consisted of 6 tungsten carbide anvils with a center flat of 10mm or 6mm was employed to cover a pressure range up to about 6GPa. In situ energy-dispersive synchrotron x-ray diffraction measurements were carried out (refer to Fuchizaki et al., 2004, for details as to the experimental setup). During this period of research sufficient diffraction data for the CP-I structure have been accumulated to construct the equation of state (EOS). In fact, the compression data obtained at room temperature were fitted to corrected second-order Murnaghan's EOS (Fuchizaki, 2006) as depicted in the figure. The bulk modulus and its pressure derivative at ambient conditions turned out to be 7.31GPa and 3.91, respectively. Contribution from the thermal pressure to the EOS will be discussed, together with the results obtained through molecular dynamics simulations.



Keywords: equations of state, high pressure, molecular crystals

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Molecular dynamics simulation study on liquid tin tetraiodide

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Recently, a pressure-induced liquid-to-liquid phase transition has been found in tin tetraiodide (Fuchizaki, presented in this congress). The polyamorphism in this substance, including two solid amorphous states found previously, can be understood in a unified way based on the pseudo-binary regular solution model. The high-pressure amorphous state, which forms beyond ~15GPa on compression at room temperature, was shown to be attained by molecular dissociation, whereas the low-pressure amorphous state consists of randomly oriented molecules. In this context, the high-pressure liquid phase may be attained by polymerization of molecules from the low-pressure molecular liquid state. In order to understand the mechanism of the transition, molecular dynamics simulations were carried out. The molecule was regarded as a rigid tetrahedron. The intermolecular interaction was modeled by van der Waals interactions between

iodine atoms at vertex sites plus octupole-octupole interactions between the central tin sites. The simulations were performed under constant pressure and temperature conditions. Starting from the crystalline state in which the nearest molecules are in face-to-face configuration (type-I), the system was melted by heating. When melted, about the half of the molecular pairs is in vertex-to-face configuration (type-II), whose population increases with increasing pressure. Since the distance between the nearest intermolecular iodines is shorter in type-II than in type-I, polymerization is easier to occur on further compression in the liquid than in the solid in which all the molecules are in type-I. This is why the transition occurs at much lower pressure, ~ 1.5 GPa, in the liquid state than in the solid state.

Keywords: liquid state, high pressure, molecular dynamics simulations

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Solid state reactions with photocrystallography

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X-ray crystallography is an important analytical method for the characterisation of molecules and array materials in the solid state, but until recently it has always been viewed as a static ground state technique. However, during the last decade, the methodology has developed so that techniques such as photocrystallography can be used to look at the structures of materials as they change. Photocrystallography is crystallography applied to photo-induced species. It combines spectroscopic and crystallographic techniques to allow the study of light-induced metastable and transient species. The technique can be used in single crystal or powder X-ray diffraction studies. Since the work of Schmidt, who established the principles for [2+2] photoreactions in the solid state, further research has commenced into the design of crystals, which then can readily undergo a reaction in the solid state. MacGillivray and coworkers have described a method for aligning alkenes in crystals with the help of a template. By developing this methodology further we have prepared a series of metal complexes with pyridylethylene derivatives as ligands. We now present an analysis of the solid state reaction of these complexes and of a series of coumarins using single crystal and powder diffraction methods. The research includes kinetic studies of the [2+2] photoreaction in solution and a comparison to that in the solid state. The effect of external changes on the systems, such as high pressure, has also been investigated. The first results that show the tolerance of systematically changing the dynamic equilibrium in these cycloaddition reactions is presented.

Keywords: high pressure crystallography, time-resolved analysis, solid state photochemistry

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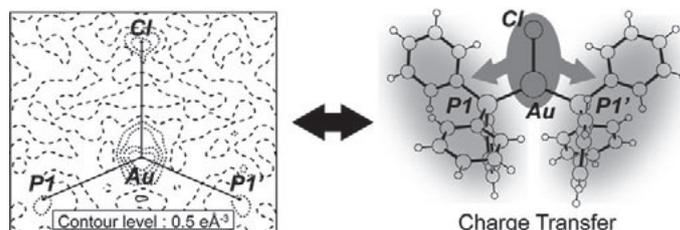
Different emission colors and photoexcited structures of [AuCl(PPh₃)₂] in two polymorphic crystals

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[AuCl(PPh₃)₂] crystal (**1a**) shows green emission ($\lambda = 510$ nm) by UV irradiation, which is related with shrinkage of all metal-ligand bond in photoexcited structure. However, the novel polymorphic crystal (**1b**) shows blue emission ($\lambda = 470$ nm), indicating different photoexcited structure in **1b**. So, the photoexcited structure in **1b** was examined by X-ray structural analysis of the photo-stabled crystal. Diffraction data were collected at SPring-8 BL02B1, using the multiple-exposure IP method on the low-temperature vacuum X-ray camera. The photo-difference ($F_{\text{on}} - F_{\text{off}}$) Fourier synthesis indicated that charges on Au and Cl atoms are decreased and no geometrical change occurred by photoexcitation. By comparison with the results of emission spectrum measurement and DFT calculation, these decreasing of charges around Au and Cl are due to charge transfer from the orbital around the Au-Cl bond to the electron-delocalized π^* orbitals in PPh₃ ligands. In summary, it has been revealed that the photoexcited structure of [AuCl(PPh₃)₂] in **1b** shows no geometrical change and has the charge-transferred nature, which leads blue emission.



Keywords: charge density distribution, photocrystallography, polymorphism

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Single crystal structure analysis of photo-excited state of halogen-bridged dicopper(I) complexes

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Photo-luminescent halogen-bridged dicopper(I) complexes [Cu₂X₂(PPh₃)₂(L)]_∞ (L = 4,4'-bpy or pyz, X = I or Br) consist of {Cu₂X₂} planer units, which are bridged by diimine (L) ligands constructing infinite chain structures. The assignments of intense emission bands of these copper(I) compounds is the copper to ligand charge transfer (MLCT) states. We have tried to observe direct geometrical distortion of the complex by photo excited state crystallographic technique. We also have made the same experiments for discrete dimeric copper(I) complexes [Cu₂I₂(PPh₃)₂(L')₂] (L' = Phpy, pyz) having similar metal-organic frameworks which show less luminescent performance. Single crystal X-ray diffraction experiments were performed by using the low temperature vacuum X-ray camera at SPring-8 BL02B1 beamline. Full intensity data of both under light irradiated by CW laser, and non-irradiated conditions were collected by multiple-exposure IP method. Photo-difference Fourier syntheses for the bipyridine complex show that a small portion of two Iodine atoms shift toward close to each other in the {Cu₂I₂} plane. Results of the least-square refinements of I and Cu