

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,  $\sim 1.5$  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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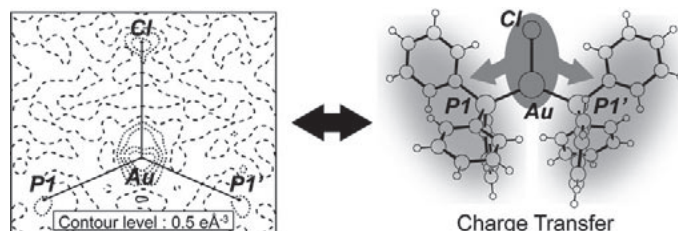
#### Different emission colors and photoexcited structures of [AuCl(PPh<sub>3</sub>)<sub>2</sub>] in two polymorphic crystals

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[AuCl(PPh<sub>3</sub>)<sub>2</sub>] 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  $\pi^*$  orbitals in PPh<sub>3</sub> ligands. In summary, it has been revealed that the photoexcited structure of [AuCl(PPh<sub>3</sub>)<sub>2</sub>] 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 [Cu<sub>2</sub>X<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(L)]<sub>∞</sub> (L = 4,4'-bpy or pyz, X = I or Br) consist of {Cu<sub>2</sub>X<sub>2</sub>} 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 [Cu<sub>2</sub>I<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(L')<sub>2</sub>] (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 {Cu<sub>2</sub>I<sub>2</sub>} plane. Results of the least-square refinements of I and Cu