

by detecting the fluorescence X-ray signals just after and just before the laser pulse using gated integrators synchronized with the laser pulse (945 Hz). [7] Obtained results clearly demonstrate the success in probing both structural and electronic state changes induced by 267nm femtosecond laser pulse excitation with 100ps resolution.

[1] L.X. Chen, W.J.H. Jäger, G. Jennings, D.J. Gosztola, A. Munkholm, J.P. Hessler *Science* **2001**, 292, 262–264. [2] H. Ihee, M. Lorenc, T.K. Kim, Q.Y. Kong, M. Cammarata, J.H. Lee, S. Bratos, M. Wulff *Science* **2005**, 309, 1223–1227. [3] W.Gawelda, M. Johnson, F.M. de Groot, R. Abelda, C. Bressler, M. Chergui *J. Am. Chem. Soc.* **2006**, 128, 5001–5009. [4] W. Gawelda, V.T. Pham, M. Benfatto, Y. Zaushitsyn, M. Kaiser, D. Grolimund, S. L. Johnson, R. Abela, A. Hauser, C. Bressler and Majed Chergui *Phys. Rev. Lett.* **2007**, 98, 057401–(4) [5] J.K. McCusker, K.N. Walda, D. Madge and D.N. Hendrickson *Inorg. Chem.*, **1993**, 32, 394–399. [6] S. Nozawa, S. Adachi, J. Takahashi, R. Tazaki, L. Gerin, M. Daimon, A. Tomita, T. Sato, M. Chollet, E. Collet, H. Cailleau, S. Yamamoto, K. Tsuchiya, T. Shioya, H. Sasaki, T. Mori, K. Ichianagi, H. Sawa, H. Kawata, S. Koshihara, *J. Synchrotron. Rad.* **2007**, 14, 313–319. [7] T. Sato, S. Nozawa, K. Ichianagi, A. Tomita, M. Chollet, H. Ichikawa, H. Fujii, S. Adachi, S. Koshihara, *J. Synchrotron. Rad.* **2009**, 16, 110–115.

**Keywords:** XAFS, dynamics, photochemistry

## MS45.P06

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### Development for X-ray Crystal Structure Analysis of a Surface-Shallow Layer

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Chemical and physical phenomena that happen in a shallow layer of a crystalline material such as photo-induced chemical reaction and transport of small molecules on crystal surface should be elucidated more clearly if three-dimensional structure of the crystal surface layer up to 1  $\mu\text{m}$  in depth could be determined by a depth-resolved X-ray diffraction technique. This new diffraction method could be achieved by measuring diffraction intensities on the condition of exactly controlling the X-ray penetration depth.

Epitaxial crystals of the halogen-bridged mixed-valence platinum(II,IV) complexes should be suitable to evaluate whether the structure analysis of a surface shallow layer can be achieved. The surface film crystal of the chloro-bridged platinum(II,IV) complex (1) was successfully crystallized on the (001) plane of the bromo-bridged platinum(II,IV) base crystals (2) which was isomorphous to (1) with slightly different cell dimensions. The X-ray diffraction experiments were performed using the multi-axis diffractometer at SPring-8 BL13XU. The epitaxial crystals of (1) that grows up on the substrate of (2) with dimensions of 1.25x0.5 mm by thickness of about 0.3  $\mu\text{m}$  was investigated.

Out-of-plane reflections were measured using 8 keV X-ray beam focused on 3x4  $\mu\text{m}$  with 2D lens for a grazing incident angle of 0.1°–0.7°. The diffraction image measured for a grazing incidence of 0.3° is shown in Figure 1. Reflections from the surface film crystal of (1) and those from the substrate of (2) are observed as sharp Bragg spots without powder lines. The reflection pairs with the same indexes are located at neighboring positions. This indicates that the epitaxial film crystal is just a single crystal with its orientation being almost the same as the substrate crystal. Integrated intensities of both the film and substrate crystals were obtained. Although the measured intensity ratios of the film crystal to the substrate become smaller as incident

angle increase, its decreasing ratio is smaller than the value calculated for the thickness of the film crystal. This suggests that it is necessary to improve smoothness on the crystal surface.

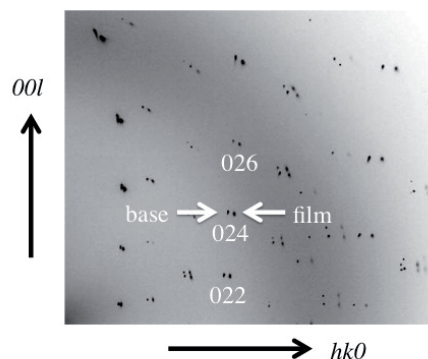


Fig. 1. Diffraction images measured for a grazing angle of 0.3°.

**Keywords:** surface, structure, epitaxial

## MS45.P07

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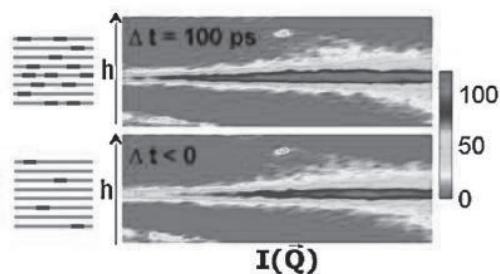
### Evidence of one-dimensional precursors in the photoinduced transformation in TTF-CA

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The photoinduced phase transition in TTF-CA was intensively studied the last ten years both experimentally and theoretically [1–4]. It is the archetype organic system where cooperativity [1] and coherence [5] play a major role in the transformation. Here we investigate the precursors of the photoinduced phase transition in the highly cooperative charge-transfer molecular crystal TTF-CA and provide key insights. The photogeneration of one-dimensional nanoscale clusters was detected by time-resolved diffuse x-ray scattering with 50-ps time resolution at NW14 beamline, KEK, Japan.

The mapping of the diffuse plane shows a time dependence after excitation and is the direct signature of the formation of 1D clusters induced by light occurring at the first step of the photoinduced phase transition. [6]

Such clustering of structurally relaxed electronic excitations is expected to be a common process in many materials presenting photoinduced transformations.



[1] S. Koshihara *et al.*, *J. Phys. Chem. B* **1999**, 103, 2592–2600 [2] E. Collet *et al.*, *Science* **2003**, 300, 612–615. [3] L. Guérin *et al.*, *Chem. Phys.* **2004**, 299,

163-170. [4] Photoinduced Phase Transitions, K. Nasu ed., *World Scientific*, 2004. [5] S. Iwai et al., *Phys. Rev. Lett.* **2006**, *96*, 057403. [6] L. Guérin et al., *Phys. Rev. Lett* 2010, *105*,246101.

**Keywords:** Diffuse scattering, Photoinduced Phase Transition, precursor phenomena

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### Structural and electrochemical study of copper complexes derived from dehydroacetic acid

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Dehydroacetic acid or [DHA = 3-acetyl-6-methyl-2H-pyran-2,4(3H)-dione], Is an industrially product used as a fungicide, a bactericide and also as an important intermediate in organic synthesis. usually obtained through the auto-condensation of ethyl acetoacetate [1]. However, little is known on its metal complexes. The Cu and Zn complexes have been reported to be, respectively, a fungicide [2]. and a heat stabilizer for vinyl chloride resins[3]. There are some other reports in the patent literature [3] and also the stability constantes of some complexes have been measured [4].

This has motivated our study of the structural characterization of complexes of dehydroacetic acid. We present here the crystal structures determination of the complexes, [Cu(DHA)<sub>2</sub>·2DMF], [Cu(DHA)<sub>2</sub>·2DMSO].

[Cu(DHA)<sub>2</sub>·2DMF], has the following structural properties : triclinic, P-1, a = 7.689(5), b = 8.541(5), c = 9.386(5) Å, α = 84.870(5)°, β = 86.964(5)°, γ = 78.852(5)°, V = 601.9(6) Å<sup>3</sup> and Z = 1; for [Cu(DHA)<sub>2</sub>·2DMSO] : Monoclinic P2<sub>1</sub>/n a = 11.580(5) b = 6.320 (5) c = 16.4024 (5) Å; β = 92.269(5); V = 1201.1(11) Å<sup>3</sup> and Z = 2.

The metal atoms are, located on an inversion centre, are surrounded by two DHA ligands occupying the equatorial plane. The two axial positions are occupied by O atoms of two solvent molecules. The structures is stabilized by intermolecular C-H...O hydrogen bonds.

An electrochemical study (cyclic voltammetry) indicates that the reduction of the two complexes, two steps are indicated out : the first as attributed to the reduction of the metal and the seconde to the reduction of the coordinated ligands.

[1] M.E.Smith, R.A.J.Andersen, *Am. Chem. Soc.* **1996**, *118*, 11119–11128. [2] D.S. Rao, M.C. Ganorkar, D.L.S. Rao, V.T. John, *Natl. Acad.Sci. Lett.* **1978**, *1*, 402.. [3] F. Arndt, B. Eistert, H. Scholz, E. Aron, *Berichte Teil B*, **1936**, *69*, 2373-2380. [4] J. Casabo, J. Marquet, M. Moreno-manas, M. Prior, Teixidor, *Polyhedron*, **1987**, 1235–1238.

**Keywords:** structural study-1, complexe-2, dha-3.

## MS45.P09

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### Humidity-induced phase transition of xylose isomerase

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We have been examining humidity-induced phase transitions of nucleotide and protein crystals. The dehydration accompanies not only shrinkage of the unit cell volume but also transformation of crystal symmetry and/or conformational changes of biomolecules. Such a phenomenon helps our understanding of the role of hydration which influences the biological function. The role of hydration water is also argued on electronic properties of hydrates of molecular conductors and ferroelectrics.

Xylose isomerase is one of the protein crystals, where the humidity-induced phase transition occurs. An as-grown crystal (the space group *I*222) changes to the dry form (the space group *P*2<sub>1</sub>2<sub>1</sub>2) at approximately 84 % relative humidity [1,2]. The intermediate stage was determined crystallographically, and the scheme of the phase transition will be discussed paying attention to the hydration networks.

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[1] M. Ootaki et al., *Joint Conference of AsCA '06 and CrSJ*, Tsukuba, Japan, **2006**, P21-217. [2] C. Besnard et al., *Acta Cryst. A*, **2008**, *64*, C372.

**Keywords:** phase transition, protein, hydration

## MS46.P01

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### X-ray diffraction study of some natural resins

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Most copal incense in Mesoamerica is traceable to several species in the family Burseraceae, usually of the genus *Bursera*. Additionally the genus *Hymenaea* of the family Leguminosae has been said to be represented among the bearers of incense resin. In the Maya region of southern Mexico and Central Mexico, resin from *Bursera bipinnata* is among the most frequently employed of the copal incenses today and apparently also in former times.

*Bursera* species were used in diverse medical practices among mesoamericans. Leaves frequently spray a mist of volatile oils when broken. These gums and oils were applied directly to induced wounds before the ceremony so that a direct connection with the circulatory system of the blood might be established. In contemporary Mexico some species of *Bursera* (especially *B. penicillata*) are used to allay pain in instances of toothache.

The important uses attributed to resin from this particular species are concerned to its adhesive and medicinal properties. It was used as a paint binder in Mesoamerican murals that have long been wrongly called frescoes; and also for dental incrustations of precious stones in dental apatite from the X to VI centuries B.C. [1-3]. In a previous work [4] we have reported the presence of a crystalline phase in a copal resin from a Texcoco market which now, we have identified as α-amyrin. This crystalline phase was also identified to be present in a sample of copal from the archaeological site of Templo Mayor located in Mexico City and also in the species *B. laxiflora* and *B. excelsa*.

[1] S. Fastlicht. *Revista de la Asociación Dental Mexicana y del Colegio de Cirujanos Dentistas*, Mexico City, **1971**, 39-59. [2] J.A. Pompa y Padilla. *Arqueología Mexicana*, **1995**, *3*, 62-65. [3] F. Martínez Cortes, *SEP-Setentas Mexico City* **1974**, *124*, 134-136. [4] L. Bucio, I.A. Belío-Reyes, J.A. Rodríguez, M.N. Orta, J. Arenas-Alatorre, C. Magaña, R. Velázquez, *Zeit. Krist. Suppl.* **2006**, *23*, 569-574.

**Keywords:** triterpenoid, X-ray, powder