

examine whether fabrication of SRG on the organic "single crystal" is possible or not by irradiation with two coherent laser beams. If possible, the study of photoinduced SRG formation using single crystals may provide information about not only the mechanism of the SRG formation but also the molecular motion near the surface of the organic crystal. In the present study, photoinduced SRG formation on an organic single crystal has been demonstrated by using 4-(dimethylamino)azobenzene. It was found that the SRG formation was greatly depending upon both the orientation of the crystal and the polarization of the writing beams. The dependence of the polarization of the writing beams on the SRG formation using the single crystal was found to be quite different from that reported for amorphous polymers and photochromic amorphous molecular materials.

Keywords: photochromism, surface morphology, materials science

**P08.04.15**

*Acta Cryst.* (2008). A64, C423

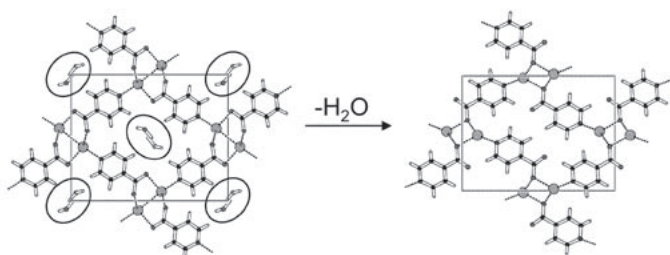
**From crystal to crystal: Dehydration of (4-carboxylato)-silver(I) monohydrate**

Ulli Englert, Irmgard Kalf, Patrick Mathieu

RWTH Aachen University, Institute of Inorganic Chemistry, Landoltweg 1, Aachen, NRW, 52074, Germany, E-mail : ullrich.englert@ac.rwth-aachen.de

(4-carboxylato)silver(I) monohydrate was obtained via reaction of isonicotinic acid and silver carbonate. The resulting three-dimensional coordination polymer was described recently. [1] The left part of the figure shows a projection of the unit cell in which the water-containing voids have been highlighted. The solvent molecules do not strongly interact with the framework. Under vacuum the topotactic dehydration of this monohydrate to its unsolvated form (Figure, right) occurs. The reaction proceeds as single-crystal-to-single-crystal transformation and is irreversible. During the topotactic desolvation, the 3D framework transforms into a two-dimensional layer structure.

[1] W.-G. Lu, J.-Z. Gu, L. Jiang, C.-Y. Su, T.-B. Lu, *Chin. J. Inorg. Chem.*, 22, 1977 (2006).



Keywords: topochemistry, coordination polymer, single-crystal-to-single-crystal transformation

**P08.04.16**

*Acta Cryst.* (2008). A64, C423

**Synthesis and characterization of  $TAgM_3X_6$  (T = Mn, Fe; M = Sb, Bi; X = Se)**

Chi-Shen Lee, Nei-Lun Cheng

National Chiao Tung University, Applied Chemistry, 1001 University Road, Hsinchu, Taiwan, 30010, Taiwan, E-mail : chishen@mail.nctu.edu.

tw

Three new quaternary selenides  $TAgM_3X_6$  (T = Mn, Fe; M = Sb, Bi; X = Se) has been prepared by heating stoichiometric amounts of the constituent metals and selenium in evacuated silica tubes at 1023K. The crystal structures were determined by single-crystal X-ray diffraction and the compound crystallizes in  $Ag_3Bi_7S_{12}$  structure type with monoclinic space group  $C2/m$  (No. 12, Z = 4). This structure features two NaCl (311)-type slabs, which stack along *c*-axis. The transition metals Mn and Fe are essential element to synthesize these compounds. Theoretical studies performed on  $MnAgBi_3Se_6$  show that the material is a semiconductor, which has been confirmed by the electric conductivity measurements. Magnetic susceptibility measurements show that the  $MnAgBi_3Se_6$  materials exhibit temperature dependent paramagnetism and obey the Curie-Weiss law with high-spin state of  $Mn^{2+}$ , whereas  $FeAgBi_3Se_6$  does not. The optical band gaps are  $\sim 0.75$  eV that are estimated by diffuse reflectance measurements.

Keywords: solid-state chemistry, solid-state compounds, selenides

**P08.04.17**

*Acta Cryst.* (2008). A64, C423-424

**Availability of solid-state polymerization of amino acid NCAs as compared with solution reactions**

Hitoshi Kanazawa, Aya Inada, Arai Takayuki

Fukushima University, Faculty of Symbiotic Systems Science, Kanayagawa 1, Fukushima-shi, Fukushima Prefecture, 960-1296, Japan, E-mail : kana@sss.fukushima-u.ac.jp

In general, *N*-carboxy amino acid anhydrides (amino acid NCAs) have been polymerized in solutions to obtain high-molecular-weight polypeptides. As the solution polymerization of  $\gamma$ -benzyl-L-glutamate NCA (BLG NCA) has been extensively investigated, the reaction in dioxane, dichloromethane, etc. was compared with the solid-state polymerization. The solid-state polymerization was carried out by putting the NCA crystals into hexane which cannot dissolve the NCA and the polymer. Butyl amine was added as initiator. We found that the solid-state reaction was more reactive than the solution reaction, avoiding a moisture contamination (see Fig.1). The reactivity of NCA was affected by the purity of the NCAs. The polypeptides with monodisperse high-molecular-weight, which had not been prepared so far were obtained. Crystal structures of BLG, L-leucine and L-phenylalanine NCAs were found to be preferable for the polymerization in the solid state (see Fig.2). Polypeptides of alanine, valine, leucine, etc. which are not soluble in usual solvents can be prepared by the solid-state polymerization of the NCA. It is necessary to correct the misunderstanding concerning the reactivity of the NCAs.

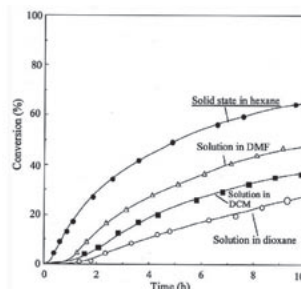


Fig.1 Time conversion curves of the polymerization of BLG NCA in the solid state in hexane and solutions at 30° C; M/I=200 and Cl content of NCA=0.0512 wt%.

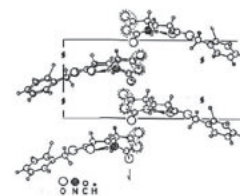


Fig.2 BLG NCA crystal (P212121)

Keywords: amino acid NCA, solid-state polymerization, polypeptides with monodisperse molecular weight

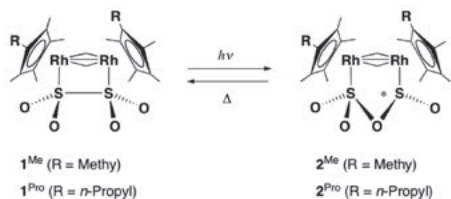
**P08.04.18**

*Acta Cryst.* (2008). **A64**, C424

**Crystalline-state photochromism of a dithionite complex in chiral crystal**

Hidetaka Nakai, Mayu Hatake, Kiyoshi Isobe  
Kanazawa University, Chemistry, Kakuma-machi, Kanazawa, Ishikawa, 920-1192, Japan, E-mail: nakai@cacheibm.s.kanazawa-u.ac.jp

Stereospecific solid-state chemical reactions of chiral crystals formed from achiral molecules are defined as absolute asymmetric reactions. We have recently found that a new class of transition-metal based photochromic compounds, a rhodium dithionite complex  $[(\text{RhCp}^*)_2(\mu\text{-CH}_2)(\mu\text{-O}_2\text{SSO}_2)]$  ( $\mathbf{1}^{\text{Me}}$ ) with a photo-responsive dithionite group ( $\text{O}_2\text{SSO}_2$ ) and two pentamethylcyclopentadienyl ligands ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ), shows the reversible crystalline-state photochromic reaction with essentially 100% inter conversion ratio. The photochemical atom rearrangement reaction of the dithionite unit can possibly generate enantiomers with *R* and *S* absolute configurations originating from an asymmetric sulfur atom in the photoisomerization product. Herein, we present an absolute asymmetric photoisomerization of a new achiral photochromic dithionite complex having *n*-propyl moieties  $[(\text{RhCp}^{\text{Pro}})_2(\mu\text{-CH}_2)(\mu\text{-O}_2\text{SSO}_2)]$  ( $\text{Cp}^{\text{Pro}} = \eta^5\text{-C}_5\text{Me}_4\text{n-Propyl}$ ) ( $\mathbf{1}^{\text{Pro}}$ ) in chiral crystals.



Keywords: crystalline state reactions, photochromic compounds, chirality

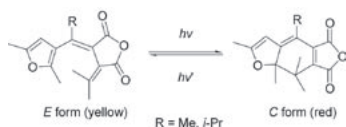
**P08.04.19**

*Acta Cryst.* (2008). **A64**, C424

**Photochromism of fulgides: Crystalline state reactions induced by one- and two-photon excitation**

Jun Harada, Ryo Nakajima, Keiichiro Ogawa  
The University of Tokyo, Department of Basic Science, Graduate School of Arts and Sciences, 3-8-1 Komaba, Meguro-ku, Tokyo, Tokyo, 153-8902, Japan, E-mail: harada@ramie.c.u-tokyo.ac.jp

Photochromism of fulgides has been studied in various fields of chemistry and discussed in many papers and books. Although most fulgides show their photochromism in the solid state, crystal structure changes accompanying the photochromism have not been previously observed. The photochromic reactions have been so far considered to take place on surfaces or at defects of the crystals, or to proceed with destruction of the crystals. In this study we have succeeded in observing crystal structure changes accompanying the photochromism of fulgides using X-ray diffraction analysis. Detection of the photoproducts in the crystal structures was not possible when the single crystals of the fulgides were irradiated with steady UV light. Two-photon excitation by pulsed laser light was essential to produce a sufficient amount of photoproducts without



significant deterioration in quality of the crystals.  
Harada, J.; Nakajima, R.; Ogawa, K. *J. Am. Chem. Soc.* **2008**, in press.

Keywords: photochromism, solid-state photochemistry, crystalline state reactions

**P08.04.20**

*Acta Cryst.* (2008). **A64**, C424

**Observation of aminyl radical during photoinduced Orton rearrangement in single crystalline state**

Pance Naumov<sup>1,2</sup>, Kenji Sakurai<sup>3</sup>, Masahiko Tanaka<sup>4</sup>, Hideyuki Hara<sup>5</sup>  
<sup>1</sup>Osaka University, Graduate School of Engineering, 2-1 Yamadaoka, Osaka, Suita, 565-0871, Japan, <sup>2</sup>Sts. Cyril and Methodius University (POB 162, MK-1000 Skopje, Macedonia), <sup>3</sup>National Institute for Materials Science (1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan), <sup>4</sup>National Institute for Materials Science and SPring-8 (1-1-1 Kouto, Mikazuki, Sayo, Hyogo 679-5198, Japan), <sup>5</sup>Bruker Biospin K.K. (3-21-5 Ninomiya, Tsukuba, Ibaraki 305-0051, Japan), E-mail: npance@wakate.frc.eng.osaka-u.ac.jp

A photoinduced analogue of the thermal Orton rearrangement reaction by which an N-chlorine atom from a side amino group is transferred to a phenyl ring, was studied in the solid state. Contrary to the mixture of products obtained in solution, in the N-chloro-N-acetylaminobenzene crystals the photoreaction proceeds with complete preservation of crystallinity, affording selectively and quantitatively the para isomer of chloroacetanilide. Study of the reaction mechanism by in situ steady-state photodiffraction, a combination of photoexcitation by UV light and single crystal X-ray diffraction analysis, provided evidence for creation of N-acetyl-N-phenylaminyl (AcPhN) radical as a metastable reaction intermediate. The structure of the aminyl radical produced in 9.2% yield from the major disordered component in the statically 85.6:14.4 disordered crystal was directly observed for the first time.

Keywords: single-crystal structure analysis, reaction pathways, reactivity of solids

**P08.04.21**

*Acta Cryst.* (2008). **A64**, C424-425

**Intercalation of bifunctional guest molecules into poly(muconic acid) as the host**

Tomoyo Shimogaki, Shinya Oshita, Akikazu Matsumoto  
Osaka City University, Department of Applied Chemistry and Bioengineering, Graduate School of Engineering, 3-3-138, Sugimoto, Sumiyoshi-ku, Osaka, Osaka, 558-8585, Japan, E-mail: a04tc011@ex.media.osaka-cu.ac.jp

We have reported that poly(muconic acid)s, stereoregular polymer crystals obtained by topochemical polymerization using supermolecular control, function as the layered host solids for organic intercalation. During the intercalation, various alkylamines as the guest species are reversibly inserted into the polymer crystals through an acid-base interaction. In this work, we investigated the organic intercalation using poly(muconic acid) as the host and various alkanediamines as the guests under various reaction conditions, and compared intercalation behavior with the results of intercalation using alkylamines. As a result, it was revealed that alkanediamines are intercalated when they are used under the limited conditions, for example, at a higher concentration and for a longer reaction time. The