

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

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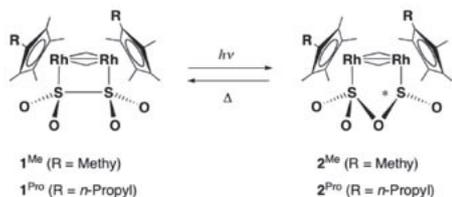
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Crystalline-state photochromism of a dithionite complex in chiral crystal

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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 (O_2SSO_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

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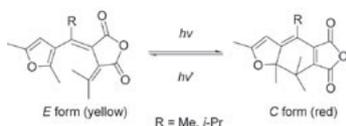
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Photochromism of fulgides: Crystalline state reactions induced by one- and two-photon excitation

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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

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

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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

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

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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

molecular packing structure of the guest amines was dependent on the structure of the guest amines. Next, we investigated the intercalation behavior of azobenzene derivatives, which were designed based on the intercalation characteristic of several guest amines previously reported. In the present study, azobenzene derivatives containing amino and diamino groups were synthesized and used as the guest for the intercalation. The intercalation of azobenzene derivatives into the interlayer space of poly(muconic acid) crystals was successfully carried out by the dispersion method. We investigated the intercalation and photoisomerization behaviors depending on the structure of the used azobenzene derivatives.

Keywords: intercalation materials, organic crystals, photochemistry

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Fabrication of thin-film organic crystals by vapor deposition and their solid-state polymerization

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The solid-state polymerization of unsaturated monomers is one of the useful methods for the synthesis of polymers with a highly controlled structure. In particular, topochemical polymerization has unique features, such as complete tacticity control and the in-situ fabrication of polymer crystals. We previously reported the topochemical polymerization of some derivatives of muconic and sorbic acids as the 1,3-diene monomers in the solid state under photoirradiation, which produced stereoregular polymers in the form of polymer crystals. The polymerization reactivity and the structure of the resulting polymers are strictly determined by the monomer crystal structure, that is, the fashion of the molecular arrangement in the monomer crystals. However, the polymorphism often prevents us designing the organic solid materials and controlling their physical properties. In the present study, we have fabricated the organic thin films of bis(3,4-methylenedioxybenzyl) (E,E)-muconate by the vapor deposition method in order to control crystal growth and crystal structures using interaction between the surface of a substrate and the monomer molecules. We have investigated the structure of the obtained thin films of the monomer crystals by AFM observation, IR spectroscopy, and powder X-ray diffraction measurements. The polymerization was carried out in the solid state under UV or gamma-ray radiation. The epitaxial crystal growth on various substrates, the polymerization reactivity of the obtained thin films, and the control of polymer structures are discussed.

Keywords: topochemistry, epitaxial growth, polymer synthesis

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Photocyclization of isopropylbenzophenone derivatives in crystals and the shape changes

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Crystalline state photocyclizations and the morphological changes of isopropylbenzophenone derivatives were investigated. We found diastereospecific photocyclization via single-crystal-to-single-crystal transformation. Absolute asymmetric photocyclization was also achieved. The surface morphological changes of the crystals were traced by atomic force microscopy on photoirradiation.

Keywords: photocyclization, isopropylbenzophenone derivatives, morphology change

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Solvent inclusion induces helical molecular assembly in crystals of halobenzoates of *myo*-inositol

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Reactions in crystals often proceed with high facility, regio- and stereo-selectivity due to topochemical control as compared to those in solution. Earlier, we reported clean solid-state benzoyl transfer reactions in crystals of racemic 2,6-di-O-benzoyl *myo*-inositol 1,3,5-orthoesters [1]. Structure correlation studies [2] suggest that pre-organization of the electrophile (E1) and nucleophile (Nu) close to tetrahedral angle 110 °C at a distance of about 3 Å is essential for reaction to occur. Structures of reactive orthoesters revealed helical self-assembly of the molecules via O-H...O hydrogen bonds bringing electrophile (-C=O) and nucleophile (-OH) in favourable proximity with weak interactions supporting the migrating group. To investigate molecular organization and solid-state reactivity further, racemic 2,6-di-O-(4-halobenzoyl)-*myo*-inositol 1,3,5-orthoformate (halo = fluoro, chloro, bromo) were synthesized. Solvent free crystals obtained from methanol and ethyl acetate [3] did not possess the right organization for acyl transfer; however, inclusion crystals from almost all common organic solvents revealed a helical self-assembly of host molecules linked via O-H...O hydrogen bonding with E1...Nu geometry close to that observed for reactive orthoesters [1]. One of the inclusion crystals with favorable geometry exhibited neat acyl transfer reaction.

[1] C. Murali, M. S. Shashidhar, R. G. Gonnade, M. M. Bhadbhade, *Eur.J.Org Chem.* **2007**, 7, 1153 and references cited therein. [2] H. B. Bürgi, J. D. Dunitz, In *Structure Correlation*, VCH:Weinheim, **1994**, 2,767. [3] R. G. Gonnade, M. S. Shashidhar, M. M. Bhadbhade, *CrystEngComm* **2008**, 10, 288.

Keywords: solid-state reactions, inositols, inclusion crystals

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Oxide and metal silicide precipitation on structural defects in mc silicon studied by TEM

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