

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

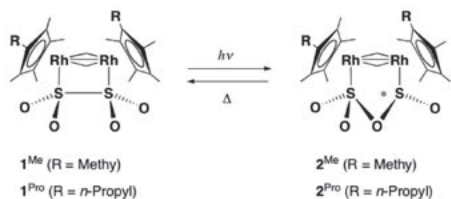
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**Crystalline-state photochromism of a dithionite complex in chiral crystal**

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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 ( $\text{O}_2\text{SSO}_2$ ) 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

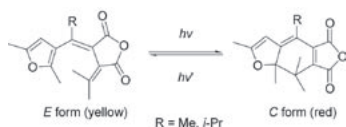
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**Photochromism of fulgides: Crystalline state reactions induced by one- and two-photon excitation**

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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