Photo induced isomerization reaction and phase transition of an organo-dirhodium dithionite complex

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An organo-dirhodium dithionite complex [{Rh(η⁵-C₅Me₄Et)}₂-(μ-CH₂)₂(μ-O₂SSO₂)] (1) shows fully reversible photochromism in which one of four terminal oxygen atoms in the side-on type dithionite μ-O₂SSO₂ moiety is converted to a bridged one to produce geometrical isomer form μ-O₂SO₃⁻ by visible light irradiation in crystalline-state [1]. An analogous dirhodium complex [{Rh(η⁵-C₅Me₅)}₂(μ-CH₂)₂(μ-O₂SSO₂)] (2) that contains η⁵-C₅Me₅ instead of η⁵-C₅Me₄Et has similar crystal structure with (1). We have tried to analyze the photo-isomerization process of the dirhodium complex (2) in single crystals by X-ray structure analyses [2]. The photo-irradiation wavelength, intensity and time dependences of the photo-generated isomer ratio were measured for (2). By using Xeon light passing through band pass filters, it was revealed that the light not on absorption peaks but on absorption tail produced photo-generated isomers. This should be owing to that the light on the absorption peak could not pass through the crystal. At the initial stage of the photo-isomerization process, it was revealed that the cell volume becomes half by the light irradiation. Structure analyses were made for the crystals before and after the photo induced phase transition, indicating that η⁵-C₅Me₅ rings are positionally disordered for the original crystals but is ordered for the photo irradiated crystals which is isostructure to (1) with space group P2₁/n. 1) H. Nakai, et al., Angew. Chem. Int. Ed., 2006, 45, 6473-6476. 2) K. Toriumi, et al., AsCA 07, Taipei, Taiwan, 2007/11.

Keywords: solid state reaction, photo chemical reaction, phase transition

A structural study on a nano-porous vapochromic Pt complex

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One-dimensional stacking Pt-dimine complexes have attracted much attention because of their characteristic luminescence based on the Pt-Pt interaction and potential for a chemical sensors [1,2]. Our attention have been focused on the properties of Pt(CN)₂(dcbpy) (dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) which has nano-size pores and exhibits interesting vapochromism [3]. In this paper, we discuss the vapochromism on the basis of powder X-ray diffraction (PXRD). Fig. 1 shows the PXRD patterns in vacuum and DMF vapors. Observed PXRD patterns indicate that the porous structure could be broke down by removal of crystal water in vacuum and then regenerated on exposure to DMF vapor. The emission peak also shifted from 647 nm to 710 nm and retuned to 640 nm. Further exposure to DMF vapor induced the structural phase transition and a new emission peak appeared at 560 nm. These results suggest that the vapochromism of this complex originates from the structural flexibility and nano-sized pore which can absorb various organic vapors.

Keywords: coordination chemistry compounds, luminescence, crystal synthesis and phase transitions

Atomic displacement parameters and specific heat of α-glycine polymorph between 10 and 298 K

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Synchrotron data to 0.5 Å resolution of the α-polymorph of glycine were collected between 10 and 298 K at the two synchrotron sources in Japan, KEK Photon Factory (PF) and SPring-8. Data from KEK-PF and SPring-8 were processed with RAPID AUTO and DENZO/SCALEPACK and refined with SHELXL-97, yielding comparable data quality. Simultaneous analysis of the multi-temperature atomic displacement parameters (ADPs) were performed to obtain the libration and translation frequencies [1]. The six external vibration frequencies from normal mode analysis and the intramolecular vibration frequencies from ab initio calculations were used together with the molecular Einstein, Debye, and Nernst ~ Lindemann models to estimate heat capacities C_v, C_p and found to be in fair agreement with C_v from calorimetric measurements [2]. Figure below shows the results obtained from SPring-8.

Keywords: atomic displacement parameters, specific heat, polymorphs

Keywords: coordination chemistry compounds, luminescence, crystal synthesis and phase transitions