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Control of photochromic reactivity in hybrid type cobaloxime complex

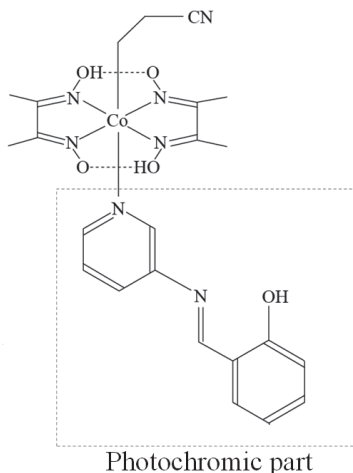
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Photochromic materials have attracted attention in recent years. One of our challenges in this field is to control the Photochromic reactivities of those materials. In order to create new materials that have dynamically controllable photochromic property, we designed new hybrid type cobaloxime complexes with photochromic compounds. In such crystals, photochromism is expected to change dynamically associating with crystalline-state photo-isomerization of cobaloxime complexes. In this study, (1) salicylideneaminopyridine (SAP) and (2) aminoazobenzene (AAB) derivatives are used as photochromic compounds, and the relationships between the structure dependent photochromic reactivity and isomerization reaction of cobaloxime complex in the crystalline state were investigated.

(β -cyanoethyl)(*N*-(3,5-di-*tert*-butylsalicylidene)-3-aminopyridine)cobaloxime, (Co-SAP), and (β -cyanoethyl)(4-aminoazobenzene)cobaloxime, (Co-AAB), for (1) and (2), respectively, were successfully synthesized. Single crystal of Co-SAP was obtained from diethylether solution and the structure was characterized by single crystal X-ray diffraction analyses. The dihedral angle of phenyl rings of SAP is 45.28° and it has non-planer conformation, which means solid-state photochromic reaction is expected in SAP moiety. In the photoreactivity measurement of Co-SAP, the SAP moiety displayed the photochromism in the solid-state upon UV irradiation. After the photoisomerization of the cobaloxime moiety upon visible light irradiation, the photochromic property was examined to show the lifetime of colored species became significantly shorter than before reaction. It would be explained that the reaction cavity around the SAP moiety was modified by solid-state photoisomerization reaction of alkyl group of the cobaloxime complex, which successfully enabled the control of the photochromism.

The azobenzene derivative (AAB) shows no photochromic reaction in its crystalline-state as the trans-cis conformational change would not be allowed in confined crystalline environment. However, such photoreaction can be expected if the photo-isomerization of cobaloxime moiety loosens the reaction cavity around AAB moiety in Co-AAB. Actually, only after the photoisomerization reaction upon visible light irradiation on powdery crystals, the trans-cis type photochromism of AAB in solid-state was successfully observed for the first time, showing the hybrid cobaloxime complex strategy is so effective.

Keywords: photochromism, photoisomerization, solid state reaction



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Photo-induced metastable low spin state in a iron(II) high spin complex

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Six-coordinated Fe(II) spin crossover compounds are commonly observed to undergo a light-induced low spin (LS) to metastable high spin (HS) transition through the LIESST phenomenon (Light-Induced Excited Spin-State Trapping). The generated metastable HS state is possible to transfer back to the LS ground state in the light irradiation of different wavelength through the reverse-LIESST procedure. Polymorph A of complex [Fe^{II}(abpt)₂(NCS)₂] is known to undergo a temperature dependent spin transition with a LS ground state, and the observed LIESST phenomenon confirms the existence of low-lying metastable HS state. Polymorph B is reported to be a high spin complex in the studied temperature range 2-300 K, considering the same mononuclear molecule constitution but different packing crystal structure, a low-lying metastable LS state is expected and was studied by photocystallographic, photomagnetic and light-induced FTIR experiments.

For thiocyanate-coordinating spin crossover complexes, the Fe-N bond length difference associated with HS and LS states makes the thiocyanate C≡N stretching frequency shifts significantly. The CN stretching frequency in the range of 1900-2200 cm⁻¹ is thus used to monitor the spin state change at various conditions. The light-induced FTIR experiment was accomplished with an 808 nm laser light source. By comparing the spectra before and after the laser treatment, the emerging absorption band at 2122 cm⁻¹ indicates the partial formation of metastable LS state. The photomagnetic measurement was also used to verify the metastable LS state. At 10 K, there is an abrupt drop in magnetic moment after 808 nm laser irradiation, which corresponds to a partial spin transition from HS (S=2) to metastable LS (S=0) state. When the sample is subsequently warmed up slowly in the dark, the magnetic moment raises gradually and meets the original cooling curve at temperature higher than 50 K (T_{LIESST} (LS->HS) = 45 K). The metastable LS species induced by 808 nm laser below 45 K can also be excited to HS state via consecutive 532 nm laser treatment.

The photocystallographic experiment was carried out at beamline BLB02B1 in SPring8, single crystal diffraction data sets were collected first in the dark and then on the continuous 808 nm laser irradiation at 25 K. With the space group remains unchanged and only minor difference observed in cell parameters, the intensity of some reflection did varied significantly after irradiation of 808 nm laser. The molecular structure for metastable LS was successfully extracted by introducing the fixed HS ground state one (in the dark) and refined using a disordered model. The site occupancy factor indicates 20 % of metastable LS component is formed, that is consistent with the photomagnetic experiment result. The Fe-N bond distances 2.060, 2.003, 1.972 Å for metastable LS is in agreement with the expected LS state configuration, while that of the HS ground state are 2.214, 2.160, 2.127 Å, respectively.

Keywords: photocystallography, spin transition, metastable