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学 位 論 文 審 査 の 要 旨

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Crystal Structures and Mechanical Properties of Luminescent Gold(I) Complexes
(発光性有機金錯体の結晶構造と力学特性)

Mechanical flexibility of solid materials is often described by elasticity and plasticity. These concepts have been mainly used for inorganic or polymer materials. However, organic ferroelastic and superelastic crystals were recently discovered as new classes of flexible solid materials. The research for such molecular crystals is at an early stage, and only a few examples of superelastic and ferroelastic crystals were reported. The known superelastic and ferroelastic crystals were discovered coincidentally or by an experimental random screening of solid crystalline compounds because the molecular structure features for such molecular crystals are not well understood. In addition, mechanistic studies for the ferroelastic and superelastic crystals are still in their infancy, and essential questions are still not understood. Researchers lack a critical understanding of what crystal structure a given molecule takes and why it may or may not change crystal structures in response to mechanical stimuli. On the other hand, molecular compounds have the advantage that a wide variety of molecular structures can be constructed or that luminescent properties and other functions can be easily imparted. This advantage could be exploited to design flexible molecular crystals with high functionality and flexibility, but such studies have not been conducted.

To develop ferroelastic and superelastic molecular crystals that exhibit photoluminescence properties, I focused on the gold (I) complexes. Gold (I) complexes have prominent solid-state phosphorescent properties. It is also known that gold complexes exhibit luminescence changes or mechanical behavior in response to external stimuli such as temperature changes, mechanical stress, or light. In this thesis, I have attempted to design luminescent gold complexes with reference to the structures of molecular ferroelastic and superelastic crystals that have been reported previously. I have prepared various structurally simple N-heterocyclic (NHC) gold complexes and achieved luminescent ferroelasticity and superelasticity in the gold (I) complexes.

This thesis comprises four chapters, with the research background in Chapter 1, the research results in Chapters 2 to 3, and the thesis summary in Chapter 4.

In Chapter 2, I described the first photoluminescent ferroelastic molecular crystals. Ferroelasticity is the phenomenon in which a crystal sample exhibits plastic bending with spontaneous strain and changes in orientation of molecular arrangement when mechanical stress is applied. There are no examples of luminescent organic ferroelastic molecular crystals. In this work, I prepared various structurally simple NHC gold complexes and discovered an NHC gold(I) complex that exhibits ferroelastic behavior as well as photoluminescence for the first time. Moreover, I found that the ferroelastic crystals undergo a ferroelastic to superelastic transition at low temperatures. Based on single-crystal X-ray diffraction (XRD) measurements, a comparison with the single-crystal structures of related NHC gold(I) complexes without ferroelasticity elucidates the structural origin of the ferroelastic behavior.

In Chapter 3, I described a reversible multi-stage shape-changing effect after mechanical deformation in a molecular crystal. The shape memory effect is referred to as the phenomenon that mechanically deformed materials (i.e., alloys or polymers) can reverse the deformation upon changing the temperature. Shape memory alloys or polymers are attracting attention for their scientific and technical significance. Recently, the first example of an organic molecular crystal with a shape memory effect was reported. The interesting mechanical properties of gold (I) complexes described in Chapter 1 suggested that the further screening of gold (I) complexes can give an opportunity for the development shape memory effect of gold(I) complexes by combining the ferro- and super elasticity and thermal phase changes. In this work, I discovered an NHC gold(I) complex with a reversible multi-stage shape-changing effect after mechanical deformation with luminescent color changes. Based on XRD, spectroscopic and thermal analyses, and mechanical property measurements, the origin of this unique stimulus-responsivity was discussed.

In this thesis, I developed photoluminescent ferroelastic and shape-changing organic materials in gold(I) complexes. As demonstrated in the thesis, crystals composed of gold complexes tend to exhibit pronounced phosphorescent properties, which allow for changes in the luminescent color associated with shape-changing phenomena. This study also revealed the structural origin of the ferroelastic behavior and the multi-stage shape-changing effect. The development of luminescent ferroelastic and shape-changing materials and insight into their mechanisms will facilitate the further development of new flexible organic materials.

The author is therefore found eligible to be awarded the degree of Doctor of Engineering, Hokkaido University.