

Emissive Molecular Crystals with Ordered Packing Arrangements

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Keywords: Gold complex; Phase transitions; Single crystal; Photoluminescence.

Recently, various stimuli-responsive molecular crystals exhibiting their property changes or mechanical movements under temperature change/photoirradiation have been attracted significant attentions. In general, properties of molecular crystals are different from those of the corresponding individual molecules. This is because the properties of these molecular crystals depend not only on a molecular structure but also on a molecular arrangement and the pattern of intermolecular interactions in the crystalline lattice. Therefore, when molecular arrangement changes, i.e., phase transitions, take place under some external stimulation, the molecular crystals often display their property changes, for example chromic luminescence and mechanical movements. Our group has intensively developed stimuli-responsive molecular crystals prepared based on a series of gold complexes. So far, we have reported unique responses of the crystals which are initiated by mechanical stimulation, photoirradiation, and temperature changes. Herein, we report our gold complexes that exhibit i) luminescent mechanochromism, ii) salient effect, and iii) ferroelastic properties in which their single crystallinities are retained even after applying external stimulation.

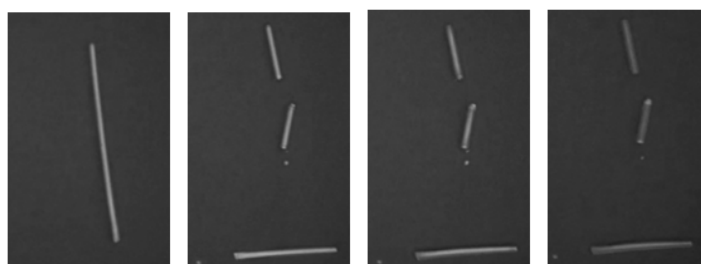
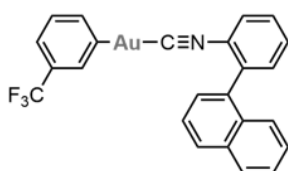
Studies of single-crystal-to-single-crystal phase transitions are attractive because their precise structure analyses are possible by means of X-ray diffraction techniques. Typically, single-crystal-to-single-crystal phase transitions are induced by solvent vapor or temperature change. Contrary, mechanical stimulation is rarely utilized to initiate single-crystal-to-single-crystal phase transitions. Our group have reported mechano-induced single-crystal-to-single-crystal phase transitions of several gold complexes with luminescent mechanochromic properties.^[1-4] We revealed their precise molecular packing even after the phase transitions to clarify the mechanism of their luminescent mechanochromism.

Salient effect is a rapid movement and jumping phenomenon of molecular crystals typically initiated by phase transitions in response to external stimuli. Typically, characterization of the relationship between microscopic strain accumulated during phase transitions and macroscopic mechanical motions is difficult to identify. Our group reported salient effect of a gold complex triggered by photoexcitation.^[5,6] Very recently, we also reported another gold complex showing salient effect by cooling.^[7] DSC analyses indicate the thermal phase transition of the crystals to initiate salient effect. Temperature-dependent single-crystal XRD analyses exhibit anisotropic changes of the molecular arrangement occur in this crystal. The crystallographic *a* axis contracts upon cooling while the *b* axis expands. In addition, a detailed observation of macroscopic changes of the crystal morphology bridges the gap between macroscopic mechanical responses and microscopic changes of the crystal structure.

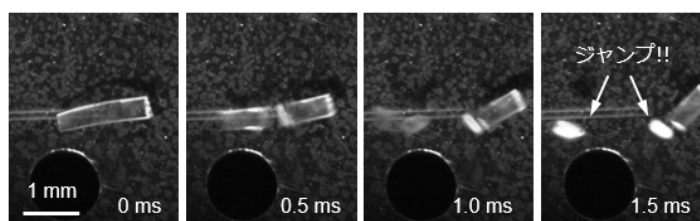
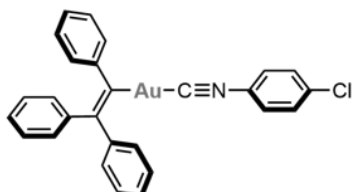
Ferroelasticity is the phenomenon in which molecular crystals plastically bent with a spontaneous strain under mechanical pushing through a twinning deformation. Ferroelasticity

has been typically reported only in alloys. Organic-based ferroelastic molecular crystals have been rarely reported so far. Recently, we found that a gold complex can show a ferroelastic behavior as well as blue photoluminescence.^[8] By applying mechanical pushing to the crystal, it bent plastically with a bending angle of 45°. This bent crystal retains its blue emission, indicating that its photoluminescence property is stable against bending deformation. Single-crystal XRD analyses of the bent crystal reveal that a crystal twinning takes place, i.e., the relative orientation of the packing arrangement is altered in the bending moiety. The single crystal of this gold complex exhibited the stress-strain hysteresis curve which is typical for ferroelastic materials.

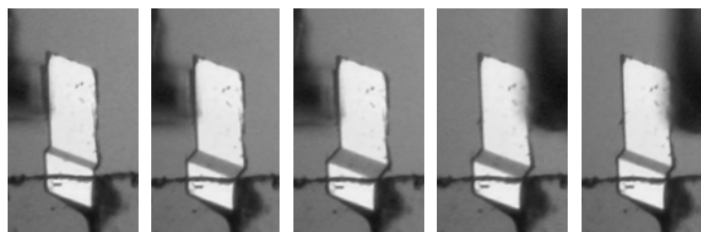
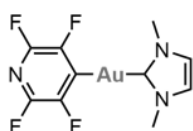
Mechanochromism



Salient effect



Ferroelastic property



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