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Mingoo Jin

# Novel Luminescent Crystalline Materials of Gold(I) Complexes with Stimuli-Responsive Properties

Doctoral Thesis accepted by  
the Hokkaido University, Sapporo, Japan

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# Supervisor's Foreword

Near a decade, research on solid-state luminescent molecular materials exhibiting alterations of photo-physical properties by external stimuli, such as heat, vapor, and mechanical stress, has attracted many interests because of its high potential not only to generate new functional sensor or security materials but also to have fundamental scientific insight on solid-state physical chemistry. Generally, solid-state luminescence has many differences to luminescence properties in solution phase. For example, excited state of luminophore will experience large steric effect in solid state comparing to those in solution, resulting in different luminescence pathways. Furthermore, luminophores are densely packed in solid state, which can form intermolecular interactions, such as  $\pi$ - $\pi$  stacking, generating different electronic environments comparing to those in solution phase. In other words, photoluminescent properties in solid state are strongly affected by intermolecular packing mode and/or molecular conformation, as well known as "crystal structure." Thus, exploring a rational design to control the crystal structure of luminescent materials correlating the external stimulation would highly contribute to develop novel stimuli-responsive luminescent properties. For development of the stimulus-responsive solid-state materials, generating multiple phases and inter-conversion between the phases via stimulations should be designed. In the case of molecular crystals, molecular structure is highly correlated with physical properties of the crystals, as well as molecular arrangement and electronic environment.

The Ph.D. thesis of Mingoo Jin explores several molecular designs of luminophores which can form luminescent crystals exhibiting mechanical, vapor, or thermal stimuli-responsive properties. The main strategy is hybrid of luminescent properties of gold(I) complex and structural factors of biaryl moiety or dumbbell-shaped molecule which could afford high chance to control molecular arrangement and/or conformation in solid state.

In general, luminescence properties of gold(I) complexes originate from ligands, especially their geometry around the gold atom, or from the presence of metal-metal interaction, so-called *auriphilic* interaction. According to these features, the electronic environment of gold(I) complex can easily be influenced by internal or external changes, molecular conformations, the dipole moment of neighboring

systems, and alternative molecular arrangements, resulting that the luminescence properties can be altered by such a change of external or internal environment of the gold(I) complex.

Biaryl group possessing two aryl plans connected by C–C bonding can form various geometries via rotatable aryl plan. Such a structure feature may enable to realize structural variation of molecule in a crystalline phase. Furthermore, biaryl structure can exhibit “axial chirality.” For instance, 2,2'-disubstituted binaphthyl compounds can exhibit stable axial chirality as (*R*) and (*S*) conformations. And, 2-mono-substituted biphenyl compounds can adopt (*M*) or (*P*) conformations based on their helical chirality. In solution phase, these conformers rapidly interconvert between each other, but in the solid state, the conformers should be trapped in some conformation by the intermolecular packed environment, resulting in molecular or crystalline chirality. This chirality in the solid state should guide to design concept for controlling molecular arrangement and/or conformations in solid phase.

Generally, molecular crystals are assembled into close packing arrangements that minimize the amount of empty space; consequently, molecules are forced to decrease their individual degrees of freedom in the crystals. On the other hand, it has been revealed that dumbbell-shaped molecules designed for having gyroscope properties could form many types of crystalline phase having both highly ordered molecular packing mode and fast molecular rotation dynamics, known as amphidynamic crystal.

This Ph.D. thesis describes several succeed examples of external stimuli-responsive luminescent solid-state materials via hybrid luminescent gold(I) complex and structural engineering approach based on chirality and/or molecular rotation in solid state. These results afford frontier concepts to understand and engineer the photo-physical properties in molecular crystals and those external stimuli-responsive properties.

Sapporo, Hokkaido, Japan  
February 2020

Prof. Hajime Ito

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