Studies on Self-Assembly of Chromic Materials and Their Physical Properties

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論　文　内　容　の　要　旨

Orders are universally found in materials, for example, packing of atoms and molecules, and alignment of electric and magnetic dipoles. The orders are directly associated with different optical, electrical, and magnetic properties, and thus controlling the orders using external stimuli leads to drastic switching of the various functions. In addition, symmetry and dimensionality in materials have great influence on the material properties. Especially, asymmetricity brings chiroptical responses, nonlinear optical phenomena, ferroelectricity, and other functions. In this context, molecular self-assembly into ordered structures is useful because it proceeds spontaneously to give sophisticated functions. Additionally, the flexibility of the self-assembly structures brings room for order and structure changes responsive to external stimuli. Chromism, which is a color change of compounds induced by external stimuli, is also a notable phenomenon because it has been applied to a diversity of fields such as sensing. While it sometimes results from changes in the self-assembly structures, it has been utilized to alter the self-assembly behaviors and functions.

In this dissertation, self-assembly and chromism have been focused on in terms of controlling various orders including symmetry and dimensionality. Consequently, unique properties in asymmetric molecular assemblies have been developed, which are drastically manipulated by stimuli such as heat, vapor, and light.

In Chapter 2, formation of supramolecular coil-like wires of chiral-lipid-packaged chloro-bridged platinum complexes is reported, which results from thermochromic behavior according to the one-dimensional chain dissociation and reconstruction. Surprisingly, compared to the bulk crystal, the coil-like wires show a significant bandgap decrease, and the bandgap is smallest among MX-type chloro-bridged platinum complexes which have ever been reported. This finding brings an interesting perspective that nanowire formation significantly influences electronic states of one-dimensional metal complexes. In addition, the nanowires are a metastable state and gradually turns into the most stable crystalline state. Contrary to the homochiral samples, the racemic mixture gives colorless crystals with negligible intermetal interactions, instead of the supramolecular wires.

In Chapter 3, near-infrared supramolecular vapochromic absorption changes are reported. The chromic phenomena are found in a chiral-liquid-packaged iodo-bridged platinum complex, which easily form cast films. The color changes between indigo and red are reversible and induced by polar organic solvent and water vapors. The absorption peak shift is over 1,000 nm, and it is the largest among vapochoromism under ambient conditions. The vapochromic behavior is strongly associated with the water of crystallization, which is eliminated by the organic vapors and recovered by water vapor. The dehydration and hydration drastically change the lipid packaging style and thus the intermetal distance, i.e., the mixed-valence characteristic. Besides vapor stimuli, heating removes the water of crystallization and great changes in the color and packing structure. These results indicate the lipids receive chemical and physical inputs to amplify and transfer them to the coordination chains. Therefore, lipid-packaging is a practical methodology for developing film-forming functional materials responsive to external stimuli.

In Chapter 4, photo-controlling asymmetric orientation of an arylazopyrazole derivative based on photoisomerization is reported. Because the arylazopyrazole displays a significant difference of water solubility between the *trans*- and *cis*-isomers, photoillumination with the aqueous *cis* solution precipitates the *trans* polar crystalline films at the air-water interface. Moreover, the arylazopyrazole shows photoinduced phase transition between the *trans* polar crystals and the *cis* isotropic liquid, which is applied to optical control of the second-order nonlinear property. These discoveries open new rich functions of photoresponsive materials.

Chapter 5 summarizes this dissertation and describes future perspectives about development of external-stimulus-based ordering control.