# 学位論文の要約

題目　Studies on Multi-Dimensional and Consecutive Structural Transformations Based on Coordination Polymers

（配位高分子を基盤とした多次元ならびに逐次構造変換に関する研究）

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序論

It is well established that dimensionality of atomic or molecular arrangements through chemical bonds plays a crucial role in determining the physical properties of solids. Thus, it is apparent that dimensional/structural transformation has the potential to control a wide range of physical properties. Coordination polymers (CPs), which are built by coordinative self-assembly of metal ions or nodes and multidentate organic ligands, show diverse supramolecular architectures leading to 1D, 2D, and 3D skeletons. They are a promising platform for investigating dimensional transformations because the coordination bonds are generally weaker than covalent bonds. To date, considerable studies related to dimensional transformations have been reported in CPs. However, the reversible multi-dimensional transformation and the consecutive structure transformation under the same condition have not been realized. In this thesis, a multi-dimensional transformation system was established based on Cu-BDC because the Cu(II) ($S$ = 1/2) ions are sensitive to dimensionality change and bidentate terephthalate ($BDC^{2-}$) ligands have diverse coordination manner. A reversible 1D/2D/3D dimensional transformation was realized in Cu-BDC through removal or exchange of the solvent molecules. During the process of 2D Cu-BDC to 1D Cu-BDC, a consecutive transformation which included a unique 2D-to-2D structural transformation was observed. Furthermore, two kinds of consecutive structural transformations were achieved by changing the temperature. This thesis aims to control the physical and chemical properties through dimensional/structural transformation.

## 1. Reversible One- to Two- to Three-Dimensional Transformation in Cu(II) Coordination Polymer

A reversible transformation between 1D, 2D, and 3D is demonstrated for the first time in coordination polymers comprising Cu(II) ions and bidentate terephthalate ($BDC^{2-}$). 1D uniform chains were reversibly transformed into 2D layers with the construction of Cu-paddlewheels by eliminating

water molecules. 2D/3D reversible transformation was achieved by removing/rebinding *N*,*N*-dimethylformamide coordinated to the paddlewheels. These dimensional transformations significantly changed chemical and physical properties such as gas sorption and magnetism. Although the uptake in open-framework 1D and 2D Cu-BDC was insignificant, pronounced absorption was observed for 3D Cu-BDC. Drastic difference in magnetic behavior is consistent with their coordination structures; uniform 1D chain of Cu(II) in 1D Cu-BDC and 2D sheet based on Cu(II)-paddlewheel dimers in 2D Cu-BDC. Ferromagnetic behavior observed in air-exposed 3D Cu-BDC is attributed to the 3D structure formed by the connection of 2D sheets.

## 2. Drastic Structural Transformation in Two-Dimensional Assemblies in Coordination Polymer

A 2D-to-2D (2D: two-dimensional) structural transformation accompanying bond rearrangement and coordination environment change in a coordination polymer (CP) comprised of copper(II) ions and terephthalate ($BDC^{2-}$) ligands is demonstrated for the first time. When immersed in water, a free-standing membrane of 2D Cu(BDC)(DMF) (**Cu-1**; DMF: *N*,*N*-dimethylformamide) transforms into 2D $Cu(BDC)(H_2O)_2$ (**Cu-2**) while maintaining its highly oriented layered structure. In the 2D sheet, paddlewheel-type Cu(II) dimers coordinated with four bidentate BDC ligands in a square-planar array to form **Cu-1**, were released to form uniform aqua-bridged Cu(II) chains, which are cross-linked with each other by unidentate BDC ligands, in **Cu-2**. The present facile approach to implement the 2D-to-2D transformation accompanied by bond rearrangement, which is characteristic of CPs, causes a significant change in the in-plane electronic and protonic behavior, as evidenced by in situ magnetic and proton conductivity measurements.

## 3. Temperature-controlled consecutive reactions in multi-dimensional transformation system

Multi-dimensional structural transformations of two-dimensional (2D) Cu-BDC, [Cu(BDC)(DMF)] ($H_2BDC$: terephthalic acid; DMF: *N*,*N*-dimethylformamide), were investigated in the kinetic viewpoint. We found two kinds of consecutive transformations when stirring 2D Cu-BDC in water at different temperatures; one being the transformation to one-dimensional (1D) Cu-BDC, $[Cu(BDC)(H_2O)_2]\cdot H_2O$, through an intermediate phase, $[Cu(BDC)(H_2O)_2]$ (IM), at room temperature and the another being the transformation to three-dimensional (3D) Cu-BDC, $[Cu_2(OH)_2(BDC)]$, through the same intermediate phase at 70 ℃. The kinetics of consecutive reactions were discussed using in-situ XRD and Raman measurements.