学位論文の要約

題目　Studies on the Dimensional Extension of Halogen-Bridged Transition-Metal Chain: Nanotube and Three-Dimensional Network

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序論

The systematically dimensional extension of low-dimensional electronic systems has attracted much attention because it can create new structures and realize unique physical and chemical properties. We focus on halogen-bridged transition-metal chain (MX-chains) systems because their electronic states can be controlled by structural components such as metal ions, halide ions, organic ligands, and counter anions. Recently, dimensional extensions based on MX-chains lead to a variety of interesting structures, such as two-legged MX-ladder, four-legged MX-tube and 2D MX-sheet. However, there are still many topics worth exploring, such as the variation of counter ions and the further 3D extension in MX system. This thesis demonstrates several new dimensional extension structure based on the MX-chain including soluble metal–organic nanotube and 3D networked ladder compounds. The electronic state, physic and chemical properties are well studied.

1. Self-Assembled Crystalline Bundles in Soluble Metal‐Organic Nanotubes

The use of nanotubes in the solution state is crucial not only for the exploration of physical and chemical behaviors at the molecular level but also for application such as thin-film fabrication. Surface modification is generally used to solubilize carbon nanotubes (CNTs) and various synthetic nanotubes; however, this method may affect the surface properties of the original nanotubes, and the detailed crystal structure obtained after modification is unclear. Here, we report the synthesis of a crystalline and soluble metal–organic nanotube consisting of a cationic tubular framework and an anion with a long alkyl chain. The nanotubular structures are formed not only in the solid state but also in the solution state, as confirmed by an X-ray structural analysis, optical measurements, and electron microscopy studies. This nanotube system is realized in different states without any surface modification, which is quite different from typical CNTs and synthetic nanotubes. In addition, self-assembled crystalline bundles are directly observed using transmission electron microscopy (TEM) for the first time in a metal–organic nanotube system. The bundle structures are also confirmed by atomic force microscopy (AFM) observations of thin nanotube films.

2. A Three-Dimensional Extended Metal‑Organic Ladder Compound

Dimensional extensions of one-dimensional (1D) chain system have attracted much attention because their electronic states and physical properties strongly depend on the electronic correlations among chains. As a representative system, transition metal-oxide ladder materials with two-/three-legs are generally studied, but further three-dimensional (3D) extension is difficult for oxide ladder systems due to the extreme synthesis conditions such as high temperature and high pressure. Here, for the first time, we report the successful creation of a 3D extended metal–organic ladder compound, which is exceptional in that it consists of 1D chains (···Pt–I–Pt–I···) and organic ligands as the constituent legs and rungs. The uniqueness of such a 3D networked lattice can be realized unexpectedly by a simple polymerization of a small macrocyclic complex, which is quite different from other dimensional extension in this systems. It is a Pt2+/Pt4+ mixed valence compound, as confirmed by X-ray structural analyses and optical measurements. The out-of-phase Pt2+/Pt4+ arrangement arises from the weak correlation among adjacent legs within ladder, as revealed by diffuse X-ray scattering analyses. This is the first time to experimentally observe the electronic correlations in a 3D extended ladder systems. In addition, this compound shows a high humidity-dependence of proton conducting behavior.

3. Enhanced Proton Conduction in A Three-Dimensional Metal‑Organic Ladder Compound with Dangling Hydroxyl Group

We have synthesized a new 3D extended MX-ladder compound with dangling hydroxyl group. The 3D chiral structure and mixed-valence electronic state were studied using X-ray structural analysis and optical measurements. It is worth noting that the hydroxyl group is not post-modified, but obtained by oxidative polymerization of a macrocyclic complex with a hydroxyl group with iodine. Because of the dangling hydroxyl group, this 3D ladder compound exhibits high proton conductivity, which is an order of magnitude higher than that of the analog without hydroxyl group. This work provides insights into the dimensional extension based on halogen-bridged transition-metal chains and the optimal design of proton conductors.