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学位論文題目	Studies on Gas Sorption, Dielectric, and SHG Responses of One-Dimensional Copper Coordination Complexes by Control in the Intermolecular Interactions (一次元鎖型銅錯体の分子間相互作用の制御によるガス吸着、誘電およびSHG応答に関する研究)
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論文内容要約

Dimensional controls and physical properties of metal-coordination complexes have been achieved by chemical designs of central metal and ligand structure. The metal-coordination complexes have been widely examined in terms of electrical, magnetic, and optical materials through the chemical design for generating functions. Among them, one-dimensional (1D) metal coordination complexes have been attracted much attentions to clarify a correlation between the crystal structure and physical property. In the 1D MX chain and MMX chain compounds (M and X are metal and halogen atoms, respectively), a high electrical conductivity has been observed at room temperature. On the other hand, the fabrication of 1D quantum magnets and its physical properties have been extensively examined in the chemically designing single chain magnets, whereas the gigantic third-order non-linear optical response has been also confirmed in the 1D mixed-valence chain compound. In these 1D complexes, chemical control of the interchain interactions played an important role in forming the ideal 1D structures and novel physical responses.

The gas-sorption properties have been widely examined in the metal coordination complexes, where the three-dimensional lattice with void space realized a large surface area and permanent porosity. Chemically designed surface area in the porous metal coordination complexes is much larger than those of the conventional gas adsorption materials such as activated carbons and zeolites. Among them, some kinds of gas-adsorption metal coordination complexes showed a unique gas-sorption properties coupled with the structural flexibility of crystal lattice. Although a sufficient void space was not confirmed in the as-grown crystal of 1D metal coordination complexes, the structural phase transition generated the void space for gas adsorption property. The precise chemical controls of weak van der Waals type intermolecular interactions play an essential role for realizing structural flexibility and gas-sorption properties.

The 1D metal coordination complexes have a potential to realize new functional materials of gas adsorption, electric, magnetic, and optical properties by the controls of intermolecular interactions. At present, the study to clarify a correlation between the gas-sorption and electric property has not been carried out in 1D metal coordination complexes enough. In addition, rational synthetic methods of the gas adsorption or SHG active 1D metal coordination complexes as well as precise structural evaluation of the intermolecular interactions have not been examined enough. The molecular motion within crystals of 1D metal coordination complexes is also one of

the interesting research targets to design gas adsorption and dielectric response of molecular materials. In this thesis, the author tried several approaches for controls of chemical and physical properties such as gas sorption, dielectric, and SHG activity, through the chemical modification of the intermolecular interactions in the 1D copper coordination complexes.

In chapter 2, the author tried to realize a coupling system of two kinds of physical functions between gas-sorption and dielectric properties. Molecular motions of polar substituted ligands in the 1D copper-coordination complexes through gas sorption were expected to achieve dielectric response. Four kinds of substituted benzoate ligands (RBA), *m*-fluorobenzoate, 2,3-difluorobenzoate, *m*-methylbenzoate, and *m*-chlorobenzoate, were introduced into the paddle-wheel copper-coordination structures to form $[\text{Cu}_2(\text{RBA})_4(\text{pz})]_n$ complex, where pyrazine (pz) ligands were axially coordinated to form the 1D copper coordination complexes of $[\text{Cu}_2(\text{RBA})_4(\text{pz})]_n$. From the crystal structural analyses, difference in the interchain interactions such as $\pi \cdots \pi$ and dipole-dipole interactions was confirmed in each crystal, and the number of crystallization solvents and the void volume were different to each other. These differences affected the gate-opening pressure and adsorption-desorption hysteresis in the CO_2 sorption isotherms at 195 K. These kinds of CO_2 sorption behavior was typically observed in gate-opening mechanism with structural phase transition through gas sorption. Temperature-dependent ϵ_1 under a vacuum condition did not show any anomaly, whereas the ϵ_1 under the CO_2 environment showed the anomaly corresponding to CO_2 sorption processes around room temperature. Especially in the ϵ_1 responses at room temperature of copper-coordination complexes bearing *m*-fluorobenzoate and 2,3-difluorobenzoate ligands were approximately 1.5 times larger than those at 210 K. The molecular motions accompanying the CO_2 desorption were discussed from the CO_2 gas-sorption isotherms at 273 and 298 K, temperature-modulated differential scanning calorimetry (DSC) under CO_2 flow, and the dielectric anomaly. The isotherms at 273 and 298 K revealed that the complexes bearing *m*-fluorobenzoate and 2,3-difluorobenzoate ligands showed gas-sorption behavior at these temperatures. Thermal anomalies around room temperature in DSC measurement under CO_2 flow were consistent with molecular motion biased by CO_2 desorption. As a result, dielectric anomaly at room temperature were induced by molecular motions through CO_2 desorption.

In chapter 3, the author focused on controls in intermolecular interactions and gas-sorption properties by chemical modification, and precise evaluation of intermolecular interactions in the 1D copper-coordination complexes. Many reports have pointed out distinctive gas-sorption properties of metal-coordination complexes were derived from structural flexibilities. However, relationship between them was unclear because of difficulty in evaluation of structural flexibility (host-host interactions). Taking an advantage of gas-sorption behavior of 1D copper-coordination complexes, chemical modification of substitution on *para*-position of benzoate ligand was expected to realize gas-adsorptive packing structures in the absence of sufficient void space. These structures were capable of controlling both structural flexibility and gas sorption property. Therefore, four kinds of 1D copper-coordination complexes of $[\text{Cu}_2(p\text{-RBA})_4(\text{pz})]_n$ (*p*-RBA = *p*-chlorobenzoate, *p*-bromobenzoate, *p*-iodobenzoate, and *p*-methoxybenzoate) were prepared. X-ray structural analyses revealed that the intermolecular interactions between the 1D copper-coordination chains (adsorption host framework) were associated with gas-sorption behavior because sufficient void space to include crystallized solvent was not

confirmed in structural lattice of each as-grown crystal. The differences in CO₂ and N₂ gas-sorption isotherms at 195 and 77 K, respectively, were observed. 1D copper coordination complexes with *p*-chlorobenzoate, *p*-bromobenzoate, and *p*-methoxybenzoate showed CO₂ sorption properties, whereas the complex with *p*-iodobenzoate did not adsorb CO₂ molecule in the lattice. Only 1D coordination complexes of [Cu₂(*p*-chlorobenzoate)₄(pz)]_n showed N₂ sorption behavior. The chemical design of the substituted group was useful to adjust the gas-sorption properties. To evaluate interchain interactions precisely, Hirshfeld surface analysis were performed on structural unit of [Cu₂(*p*-RBA)₄(pz)₂]. From the comparison of Hirshfeld surfaces with dnorm mapping, the increasing in the size of X-atom expanded the atomic contact area less than the sum of van der Waals radii between neighboring two atoms. This increasing in the interchain interactions corresponded to the decrease in the gas-sorption property. Therefore Hirshfeld surface analysis was useful techniques to evaluate the relationship between the intermolecular interactions and gas-sorption properties.

In chapter 4, the author proposed designing strategy of the intermolecular interactions and polar crystal for realization of the SHG active optical crystals. Polarity of crystals plays an important role in controlling physical functions such as non-linear optical response, pyroelectricity, piezoelectricity, and/or ferroelectricity. However, crystal design of polar crystals by achiral molecular compounds and coordination complexes was not developed enough. Herein, the author focused on asymmetrical copper-coordination [Cu(*p*-RBA)₂(pyridine)₂(H₂O)] complexes with the permanent dipole moment. These copper-coordination complexes were self-assembled to hydrogen-bonded 1D chain structure with polar moment parallel to the chain. Substitutions on *para*-position of benzoate ligand were expected to control interchain-interactions, and formation of parallel arrangement of the polar 1D chains were enabled to form crystals with polar space group. Six kinds of complexes were prepared by using the ligands of *p*-fluorobenzoate, *p*-chlorobenzoate, *p*-bromobenzoate, *p*-iodobenzoate, *p*-methylbenzoate, and *p*-methoxybenzoate, and its single crystal X-ray structural analyses, DFT calculation, second harmonic generation (SHG) measurements, and thermogravimetric analyses were examined to clarify the correlation of polar crystal formation and the magnitude of the intermolecular interactions. The formation of polar 1D chain was observed in all crystals through the intermolecular O-H•••O⁻ (carboxylate) hydrogen-bonding interactions, and each chain was assembled to the polar two-dimensional (2D) layer through the weak C-H•••O⁻ van der Waals interaction between the neighboring polar chains. Polar crystals were obtained using *p*-RBA ligands with R = Cl, Br, I, and OCH₃. In contrast, apolar crystals were grown from complexes containing *p*-RBA ligands with R = F and CH₃. Weak interlayer halogen (X)•••π and multipoint C-H•••π interactions played important roles in forming parallel arrangements of polar 2D layers and polar crystals, but there were no effective intermolecular interactions between the polar 2D layers in apolar [Cu(II)(*p*-fluorobenzoate)₂(pyridine)₂(H₂O)] and [Cu(II)(*p*-methylbenzoate)₂(pyridine)₂(H₂O)] crystals. The difference of intermolecular interactions in the polar and apolar crystals was consistent with the thermogravimetric analyses, where the thermal stabilities of polar crystals were higher than those of the apolar ones. The realization of the polar molecular arrangement was explained by the stabilization energies between the polar 2D chains, and the energy above ~4.18 kJ mol⁻¹ was one of the indicators to form the polar arrangement in this system. The SHG activities of the polar crystals were about 0.7 times larger than that of sucrose. Although dipole moments by theoretical calculation were different in

each crystal, the SHG intensities of all the polar crystals were of similar magnitudes. The SHG intensity was dominated by the difference between the dipole moment values of the ground and excited states. Therefore this parameter was similar for the isostructural polar crystals.

In chapter 5, 1D copper-coordination complexes bearing spherical-shaped rotary ligands were developed, its gas-sorption and dielectric responses were evaluated, and rotational energy barriers of ligands were calculated. Control of molecular motions in solid state was one of the rational approaches to generate physical functions; ferroelectricity induced by cooperative orientation of dipole moment, gas adsorption property through structural phase transition, and so on. Spherical-shaped adamantane molecule was regarded as a structural motif in the molecular design of copper-coordination complexes; herein adamantylcarboxylate (ADCOO) ligand and pz derivatives were utilized for the coordination ligands. The resultant 1D copper-coordination complexes of $[\text{Cu}_2(\text{R-ADCOO})_4(\text{R}'\text{-pz})]_n$ were evaluated in terms of molecular structures, packing structures, theoretical calculations of the rotation barriers, temperature-frequency dependent ε_1 measurement, and CO_2 gas adsorption isotherm. Despite of the formation of 1D chain structure of $[\text{Cu}_2(\text{ADCOO})_4(\text{pz})]_n$ and $[\text{Cu}_2(\text{ADCOO})_4(\text{F-pz})]_n$, the interdigitated 3D assembly structures were observed in both crystals. On the contrary, $[\text{Cu}_2(\text{Cl-ADCOO})_4(\text{pz})]_n$ crystal showed a different packing structure from the former ones, where the parallel 1D arrangement was observed along the *b* axis. The different interchain interactions resulted in the different packing structures, and the usage of Cl-ADCOO ligand changed the dipole-dipole interaction and excluded volume. Unfortunately, the CO_2 adsorption behavior was not observed in all the crystals. The height of activation barriers for the molecular rotation was suppressed by decreasing in the size of the substituted group, and thermally activated molecular motions affected the temperature and frequency dependent ε_1 .

In this thesis, the 1D copper coordination complexes were utilized for one of the fundamental structural motif to control the functions such as gas-sorption property, dielectric constant, and SHG activity through chemical control of the intermolecular interactions. From these trials, the author concluded that both the insight and design for the weak intermolecular interactions played an essential role to develop new functional molecular materials. Further chemical modifications at metal ion and ligand structure will enable us to fabricate sophisticated metal coordination complexes. In the near future, strong coupling system between the gas adsorption and dielectric properties will be realized to design the multi-functionalities. The synergetic behavior between the gas-sorption, dielectric, magnetic, and fluorescent properties will open new field of the molecular materials, and selective gas-sorption polar crystals with SHG activity will also form new optical crystals controllable by the outer stimuli of the gas-sorption. Development of new multi-functional metal-coordination complexes has a potential to fabricate high-density and high-performance functional materials in the next generation.