学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Studies on phase/structure transformable copper coordination polymers using bis(trifluoromethanesulfonyl)imide anion
（ビス（トリフルオロメタンスルホニル）イミドアニオンを用いた相転移あるいは構造変化できる銅配位高分子に関する研究）

Phase/structure transformations are almost everywhere in people's lives and have been well investigated from the melting of ice to the origin of superconductivity. Coordination polymers (CPs), a kind of crystalline solid constructed from metal ions and organic ligands, own a high diversity and flexibility of structures, which makes CPs good candidates for functional phase/structure transformable materials. However, designing phase/structure transformable CPs remains a challenge. In this thesis, I tried to synthesize a variety of phase/structure transformable CPs with a bulky and flexible fluorinated anion, bis(trifluoromethanesulfonyl)imide (NTf_2^-), which is one of common anions in ionic liquids (ILs), as a key building block. It was expected that the delocalized negative charges, low electric polarizability, and flexible structure with two revolving axes in the NTf_2^- anion contribute to weak intermolecular interactions and a variety of structures to form target transformable CPs with a high probability.

Chapter 1 reviewed the researches on phase/structure transformable CPs and explained the background to the idea of this research and the purpose of the research.

Chapter 2 described a visualization of interactions between an NTf_2^- anion and adsorbed CO_2 using a flexible one-dimensional (1D) CP $[Cu(NTf_2)_2(bpp)_2]$ (**1**), in which bpp is 1,3-bis(4-pyridyl)propane. Analysis of the structure of a CO_2-loaded crystal using single-crystal X-ray diffraction analysis revealed that CO_2 interacts with both fluorine and oxygen atoms of NTf_2^- anions in a *trans* rather than *cis* conformation. Theoretical analysis indicated that dispersion and electrostatic interactions exist between CO_2 and the framework. The overall results provided important insight into understanding and improving the CO_2 absorption properties of ILs.

Chapter 3 described the effect of uptake/release of coordinated guest molecules on CO_2 gate-adsorption behaviors in the flexible 1D CP **1**. A series of small organic molecules that can coordinate to Cu(II) ions was introduced to **1** to make an impact on the original skeleton. After removing the coordinated guest molecules, particle sizes of the crystallites became smaller proved by scanning electron microscope images, and negligible structural changes were observed by powder X-ray diffraction analysis. CO_2 adsorption/desorption isotherms were affected after the uptake and release of coordinated molecules, while they kept almost the same adsorption amounts for CO_2.

Chapter 4 described a synchronous change in fluid space and encapsulated NTf_2^- anions in a flexible three-dimensional (3D) CP $\{[Cu(bib)_{2.5}]\cdot 2NTf_2\}$ (**3**) containing an organic bridging ligand bib (bib = 1,4-bisimidazole butane) with a conformationally flexible tetramethylene unit. The combined results of DSC measurements, single-crystal X-ray diffraction analysis and impedance spectroscopy demonstrated that **3** encapsulating NTf_2^- anions contains fluid space and it undergoes a crystal-to-crystal phase transition in association with a synchronous change in the conformations of both the bib ligand and the NTf_2^- anion.

Chapter 5 described a 3D CP liquid and glass using **3**. **3** had the lowest melting point and glass transition temperature among all 3D CPs that can melt without decomposition that benefited from its flexible cationic and anionic skeleton. The 3D coordination framework was retained after the amorphization. The ionic conductivity of the glass was several times higher than that of its crystal at the same temperature.

Chapter 6 described a variety of structure/phase transformations using a two-dimensional CP $\{[Cu(bip)_2(DMSO)_2]\cdot 2NTf_2\}$ (**4**·2DMSO), in which bip and DMSO are 1,3-bisimidazole propane and dimethyl sulfoxide. **4**·2DMSO irreversibly converted to a 1D chain structure in association with the recombination of coordination environment after removing coordinated DMSO molecules. In addition, the desolvated 1D **3** showed phase transformations at high temperature region.

Chapter 7 summarized my thesis. Thanks to the NTf_2^- anion's characteristics mentioned above, a variety of phase/structure transformable CPs were developed with the aid of other building blocks. The strategy of introducing bulky and flexible fluorinated anions including the NTf_2^- anion to CPs will not only break with the stereotype images for CPs, CPs are crystalline, but also provide guest-responsive CPs showing interesting chemical and physical properties.