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## Studies on phase/structure transformable copper coordination polymers using bis(trifluoromethanesulfonyl)imide anion

(ビス (トリフルオロメタンシルホニル) 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 behaviors 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 ( $\text{NTf}_2^-$ ), which is one of common anions in ionic liquids (ILs), as a key building block. I expected that the delocalized negative charges, low electric polarizability, and flexible structure with two revolving axes in the  $\text{NTf}_2^-$  anion contribute to the weaker intermolecular interactions and a variety of structures to form target transformable CPs with a high probability. This thesis consists of seven chapters, including the introduction to phase/structure transformations (chapter 1)

In chapter 2, I designed a flexible one-dimensional CP **1**, and demonstrated a visualization of interactions between components of ILs and absorbed  $\text{CO}_2$  by this CP as shown in Fig. 1. Analysis of the structure of a  $\text{CO}_2$ -loaded crystal using single-crystal X-ray diffraction analysis indicated that  $\text{CO}_2$  interacts with both fluorine and oxygen atoms of  $\text{NTf}_2^-$  anions in a *trans* rather than *cis* conformation about the S-N bond. Theoretical analysis of the structure of the  $\text{CO}_2$ -loaded crystal indicates that dispersion and electrostatic interactions exist between  $\text{CO}_2$  and the framework. The overall results provide important insight into understanding and improving the  $\text{CO}_2$  adsorption properties of ILs.

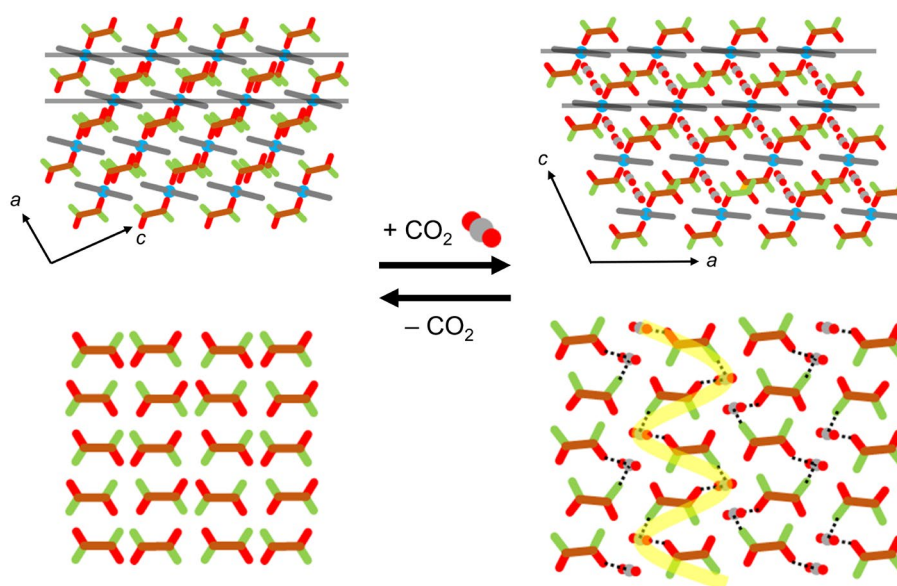


Fig. 1. Schematic views of structural transformations occurring in the CO<sub>2</sub> absorption process by CP **1**.

In chapter 3, I investigated the effect of uptake/release of coordinated molecules on gate-sorption behavior in flexible CP **1**, in which NTf<sub>2</sub><sup>-</sup> anions are weakly constrained by metal ions. A series of small organic molecules that can coordinate to the metal ions were introduced to make an impact on the structure (CP **1**·G). After removing coordinated guest molecules, the decrease in crystallite sizes and the slight change in coordination skeleton are observed as shown in Fig. 2, and NTf<sub>2</sub><sup>-</sup> anions coordinate to the metal ions instead of coordinated guest molecules. CO<sub>2</sub> adsorption/desorption isotherms for CP **1** are affected after uptake and release of coordinated molecules, while they keep almost the same adsorption amount for CO<sub>2</sub>.

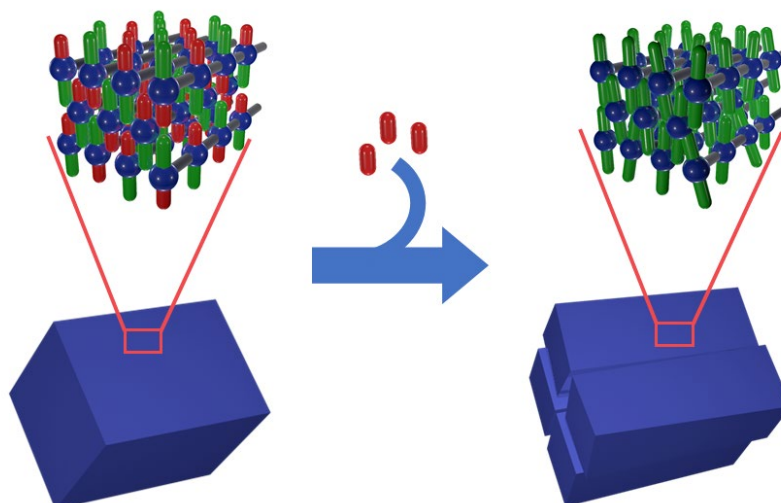


Fig. 2. Schematic views of structural transformations from CP **1·G** to CP **1** after removing coordinated guest molecules.

In chapter 4, I demonstrated a synchronous change in fluid space and encapsulated anions in a flexible three-dimensional CP **3**, containing the organic bridging ligands with conformationally flexible tetramethylene ((CH<sub>2</sub>)<sub>4</sub>) unit. The combined results of DSC measurements, single-crystal X-ray diffraction analysis and impedance spectroscopy revealed that this CP encapsulating NTf<sub>2</sub><sup>-</sup> anions contains fluid space and that it undergoes a crystal-crystal transformation in association with a synchronous change in the conformations of both the organic ligand caused by C-C bond rotation, and the NTf<sub>2</sub><sup>-</sup> anion stemming from rotation about the N-S bond.

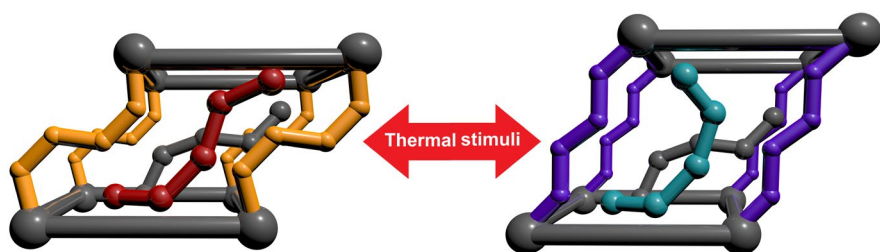


Fig. 3. Schematic views of crystal-crystal transformation in CP **3**.

In chapter 5, I extended the phase transformations in CP **3** from crystal-crystal to

crystal-liquid and liquid-glass. CP **3** owns the lowest melting points ( $T_m$ ), 303 K, and the lowest glass transition temperature ( $T_g$ ), 448 K, among all 3D CPs that can melt without decomposition and the glass-forming ability that can be calculated by  $T_g/T_m$  ratio is 0.68, comparable to those of melt-quenched glasses. Such low  $T_m$  and  $T_g$  are caused by its flexible cationic skeleton and encapsulated  $\text{NTf}_2^-$  anions with flexible structure. The ionic conductivity of the glass state of **3** is several times higher than the crystalline **3** at the same temperature.

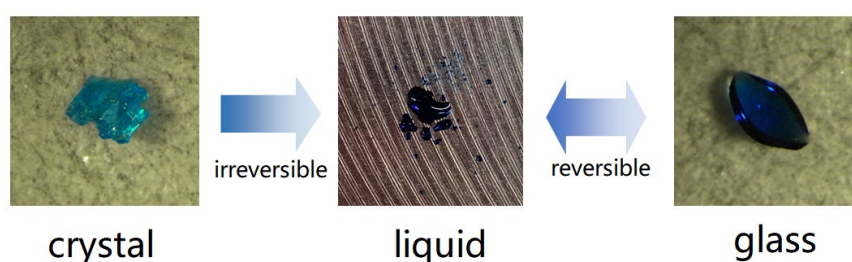


Fig. 4 Multiple phase transformations of CP **3** among crystal, liquid and glass.

In chapter 6, I synthesized a two-dimensional CP, **4**·2DMSO that can irreversibly transform to the 1D chain structure (**4**) after removing coordinated DMSO molecules. Both **4**·2DMSO and **4** were structurally characterized. In **4**·2DMSO, one metal ion coordinates with four organic ligands and two DMSO molecules, while  $\text{NTf}_2^-$  anions are free in the frameworks. In **4**, one metal ion coordinates with four organic ligands and two  $\text{NTf}_2^-$  anions. This structural information revealed that the recombination of not only weak axial coordination bonds, but also normal equatorial coordination bonds occurs during the irreversible 2D to 1D structure transformation. Furthermore, **4** owned reversible and irreversible phase transitions at high temperature region.