Melting and Crystallization Behavior of Ag(I)Coordination Polymers

Chinmoy Das,[1] Satoshi Horike,[1,2] Osamu Yamada[1]

[1] AIST-Kyoto University Chemical Energy Materials Open Innovation Laboratory, National Institute of Advanced Industrial Science and Technology (AIST), Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501, Japan

[2] Institute for Integrated Cell-Material Sciences, Institute for Advanced Study, Kyoto University, Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501, Japan

Keywords: Ag(I) Coordination Polymers (CPs), Melting CP, Crystallization, XAFS Analysis

1. Background

Coordination polymer (CP) is an organic-inorganic hybrid material that self-assembles from metal ions and cross-linkable organic ligands. Until now, nitrile-ligand-based CPs have been utilized in various field of applications, such as gas adsorption / separation, ion conduction and many more by the virtue of their structural design. We synthesized 1D Ag(I)-based CP (Ag-BPCN) by using biphenyl carbodinitrile ligand (*BPCN*). We succeeded in synthesizing terphenyl carbodinitrile ligand (4,4”-TPCN) through Suzuki-Miyaura coupling. We isolated another Ag(I)-based CP (Ag-TPCN). The degas/de-solvated structure of both Ag-BPCN and Ag-TPCN compounds were melt at 282 ^{o}C. In addition, we observed crystallization phenomena during cooling process from the melting state for both the compounds in Ar atmosphere (through Differential Scanning Calorimetry). We performed hard X-ray XAFS analysis to understand the local geometry and structural features of Ag(I) in the crystalline CPs to correlate with the single crystal X-ray structure.

2. Experiments

Ag-BPCN-d-Crys. and Ag-TPCN-d-Crys. compounds are degassed state and moisture sensitive, so the sample preparation was carried out in Ar-filled glovebox. The calculated amount of samples and boron nitride were used to make 10 mm diameter pellet for XAFS analysis. The measurement was carried out at Aichi Synchrotron Radiation Center through a Hard X-ray beamline (BL11S2). XANES and EXAFS measurements were performed.

3. Results and Discussion

XAFS analysis has been an important and powerful characterization technique for understanding the structure of crystalline and glass CP.[1] The Ag K-edge XANES spectra for Ag-BPCN-d-Crys. (**1**) and Ag-TPCN-d-Crys. (**2**) were performed and analyzed (Fig. 1A). The hard X-ray beam was sufficient to excite the electron from the core K-shell for all these Ag(I) CPs to understand their electronic structure. A sharp transition around 25513 eV is due to the electronic transition from core 1s (K) shell to the higher shell 5p was observed for both of them. It was confirmed that the oxidation state (electronic structure) retained in +1 for both the CPs. On the other hand, Fourier transformed Ag *K*-edge extended X-ray absorption fine structure (EXAFS) profiles (Fig. 1B) show that the first coordination environment of Ag-BPCN-d-Crys. and Ag-TPCN-d-Crys. are not identical suggesting that the coordination environment around Ag(I) were different for both structures which support their X-ray structures.

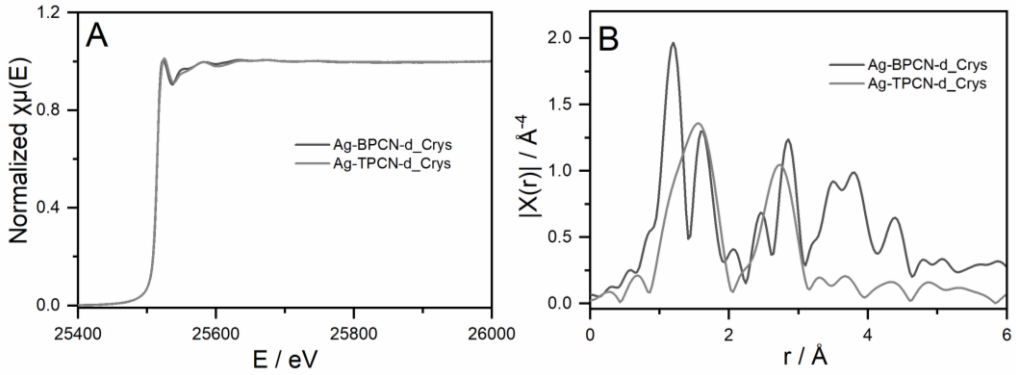

Figure 1. Ag K-edge XANES and Fourier transformed Ag *K*-edge EXAFS spectra of **1** and **2**.

4. References

1. Horike, S. *et al.* Stable melt formation of 2D nitrile-based coordination polymer and hierarchical crystal–glass structuring. *Chem. Commun.*, **2020**, *56*, 8980-8983.