



Crystal Melting and Vitrification Behaviors of Ag(I) Coordination Polymer

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1. Background

Coordination polymer (CP) is an organic-inorganic hybrid material that self-assembles from metal ions and cross-linkable organic ligands. Until now, 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 succeeded in synthesizing bulky cyanide ligand (pL2) containing Ag(I) based coordination polymer Ag-pL2 (1-a), which melts at 267 °C. In addition, crystalline Ag-pL2-degas (1) can be transformed into glassy Ag-pL2-degas-Glass (1-MIG) by hand-grinding in Ar atmosphere. We performed hard X-ray XAFS analysis to understand the local geometry and structural features of Ag(I) in the crystalline and glass CPs.

2. Experiments

Ag-pL2-degas (1) and Ag-pL2-degas-Glass (1-MIG) compounds are moisture sensitive, so the sample preparation was carried out in Ar-filled glovebox. The as-synthesized 1-a was measured as a standard sample, as the composition of 1 and 1-MIG was similar to 1-a. 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 characterization technique for understanding the structure of glass CP.¹ The Ag K-edge XANES spectra for 1-a, 1 and 1-MIG was 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 25516 eV is due to the electronic transition from core 1s (K) shell to the higher shell 5p was observed for all of them. It was confirmed that the oxidation state (electronic structure) retained in +1 for all three 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 1-a and 1, 1-MIG are also identical.

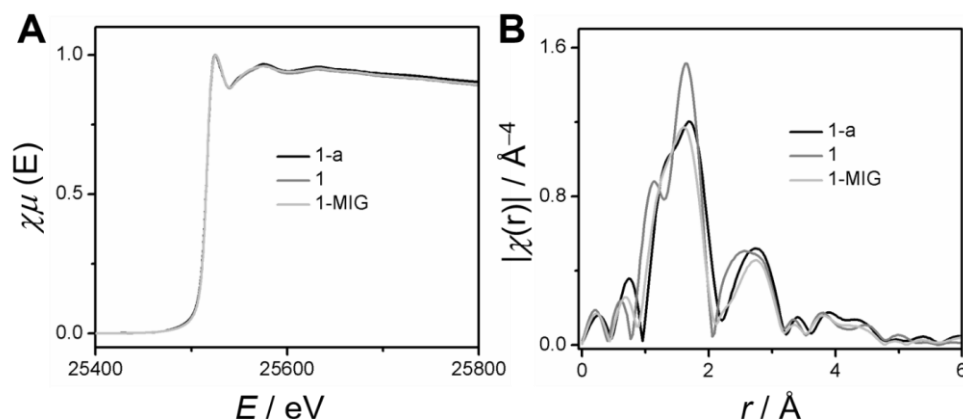


Figure 1. Ag K-edge XANES and Fourier transformed Ag K-edge EXAFS spectra of 1-a, 1 and 1-MIG.

4. References

1. Horike, S. *et al.* Glass Formation of a Coordination Polymer Crystal for Enhanced Proton Conductivity and Material Flexibility. *Angew. Chem., Int. Ed.* **2016**, 55, 5195-5200.