

Formation of a nanometer-thick water layer at high humidity on a dynamic crystalline material composed of multi-interactive molecules

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1 Introduction

Weak intermolecular interactions like hydrogen bond or π - π interaction play a crucial role in biological systems. Especially, multi-interactivity contribute to stabilizing meta-stable intermediates, because the multiple interactions can deepen local minimum potential states well. Therefore, we aimed to implement multi-interactivity into a ligand to achieve self-assembled materials. We designed and synthesized tri(4-pyridyl) hexaazaphenalenyl (TPHAP) anion. The potassium salt form of TPHAP showed unexpected crystalline state under highly hydrated conditions. Here we describe ionic layered structure with a 1.2 nm-thick water layer, and the dynamic structure transformation revealed by X-ray powder diffraction analysis. The ion conductivity of this material changed from insulator to $3.4 \times 10^{-3} \text{ S cm}^{-1}$ depending on humidity conditions.

2 Results and Discussion

We used KTPHAP single crystal powder (1) as an initial material which has 1D-channel structure. The single crystal of KTPHAP is highly hygroscopic: 1g of powder of KTPHAP adsorbs > 70 mL of water. Therefore KTPHAP powder (1) retained its crystallinity after hydration.

We measured the XRPD pattern of fully-hydrated powder (2) which has prepared by hydration of KTPHAP single crystal (1) at 95% RH and 25 °C, for 1 day. The XRPD pattern of (2) showed an irreversible change to dried powder (3) by keeping at 20% RH and 25 °C for 20 s. Notably, the sharp powder pattern of (2) was recovered by rehydration of (3).

The structures were determined by the simulated annealing method in DASH, followed by Rietveld refinement using RIETAN-FP to refine the position of each atom with soft bond-angle restraints for a TPHAP group. We revealed that 1.2 nm water layer form in the fully-hydrated (2) and that 1D water channels form in (3) by dehydration. The structure solutions of (2) revealed four possible models that have monoclinic systems that show good refinement result between the calculated and

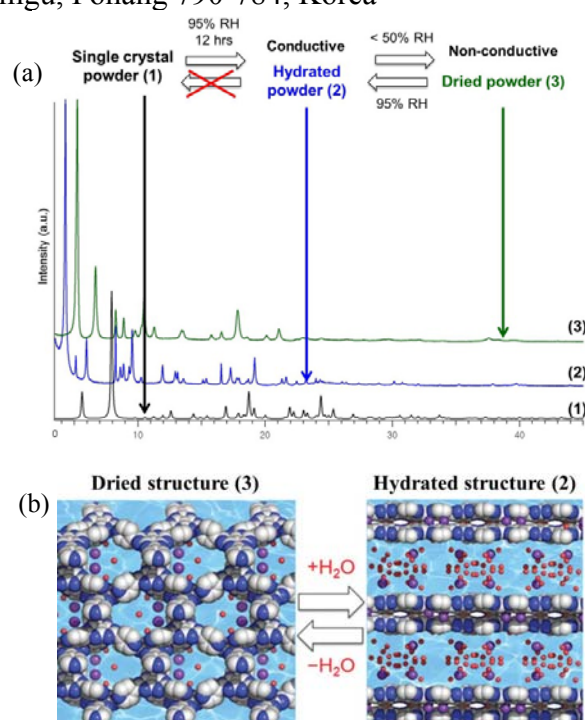


Figure 1 (a) Synchrotron XRPD pattern changes. (b) Reversible structure transformation of KTPHAP system

experimental patterns. Although the precise position determination of disordered water and potassium cation was technically very difficult, all of refinement results showed flat layer structure composed of KTPHAP dimer-like layers forming 1.2 nm-thick water layers. These layers are stabilized by the intermolecular interactions between HAP skeleton and the disorder potassium ions.

In conclusion, we demonstrated high ion conducting structure under the humid condition and insulator structure after dehydration. This result can be useful for development of efficient ionic conductors.

References

[1] Y. Yakiyama *et al.*, *Chem. Commun.*, **2015**, 51, 6821-6831.

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