MLF Experimental Report	提出日 Date of Report 2013/05/19
課題番号 Project No. 2012B0259 実験課題名 Title of experiment Characterization of proton conduction mechanism of coordination polymer 実験責任者名 Name of principal investigator Satoshi Horike 所属 Affiliation Kyoto Univ. Grad. School of Engineering	装置責任者 Name of responsible person Takashi Ohhara 装置名 Name of Instrument/（BL No.） BL-18 実施日 Date of Experiment 2013/2/26~3/9

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Proton conductive coordination polymers
（1） $[Zn(HPO_4)(H_2PO_4)_2]\cdot 2HIm$ （HIm＝protonated imidazolium） = compound 1
（2） $Zn(H_2PO_4)_2(124triH)_2$ （124triH= protonated 1,2,4-triazole） = compound 2

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

【Abstract】
We synthesized the single crystals of compound 1 and 2, and performed structural analysis by neutron diffraction at 77 K and 273 K. We determined the precise positions and thermal factors of the hydrogens of the structures at each temperatures.

【Method】
The single crystals are attached on a VT goniometer in a vacuum chamber. The diffraction data were measured under vacuum at 298 K and 77 K.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

【Result】

Both compound 1 and 2 provided diffractions of good quality to analyze the structures. So far we almost succeeded in the structural determination of compound 2 explained as follows.

We considered how the mobile hydrogens of compound 2, which locate on the phosphate and triazole, contribute to its proton conductivity. Compound 2 has 2-D layered crystal structure that result in the anisotropic proton conductivity in conductivity measurement of the single crystal (100 times higher for in-layer than out-of-layer). However, if the compound had a perfect anisotropy, the difference between in-layer and out-of-layer should have been larger. Therefore, we measured the crystal structure of compound 2 and found that the thermal libration of the hydrogen on the triazole was slightly larger than that of hydrogen on the phosphate. We also found from the analysis at 298 K that the thermal factor of the hydrogen on phosphate became much significant and disordered. Because the hydrogen on the triazole has hydrogen-bond interaction perpendicular to the layer at 298 K, the triazole, which bridges the zinc ions of compound 2, librates to give a certain value of the out-of-layer proton conductivity. Although we concluded that the main conduction path is phosphates aligned in the layer based on the X-ray structural analysis, the neutron diffraction data revealed the precise positions and thermal libration of hydrogens and explained the in-layer proton conductivity.

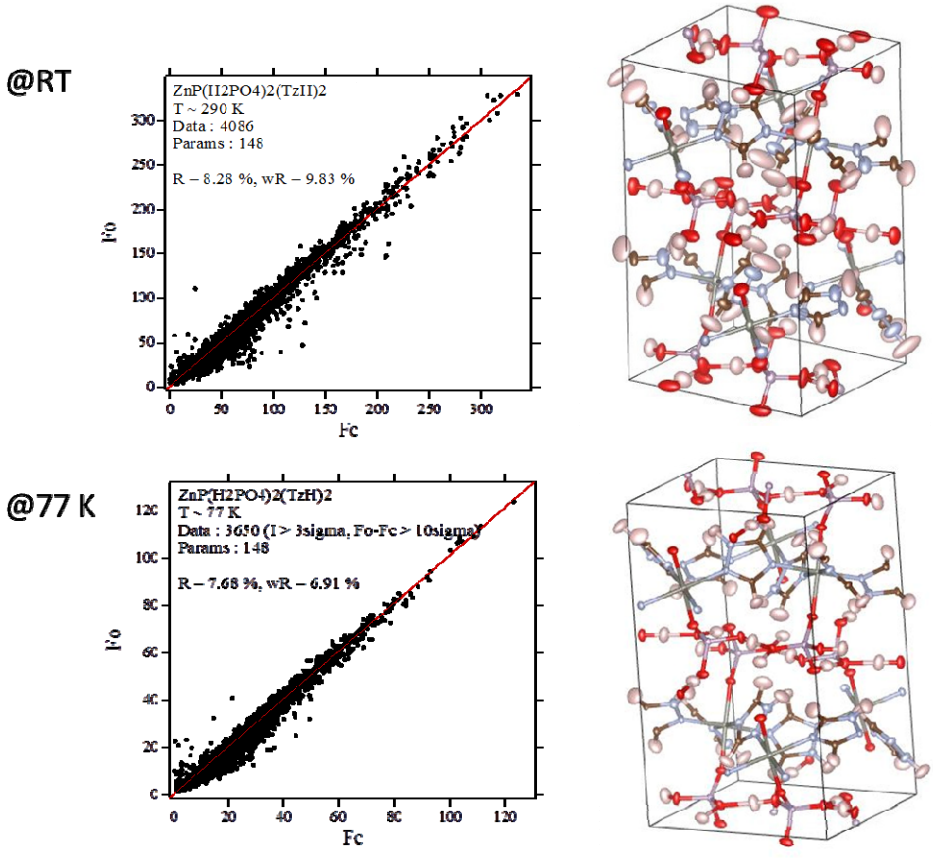

Figure: F_o-F_c plots and crystal structures of $Zn(H_2PO_4)_2(124triH)_2$ (compound 2) at 298 K and 77 K.