CROSS TOKAI **Experimental Report** J-PARC	承認日 Date of Approval 2015.2.17 承認者 Approver Takashi Ohhara 提出日 Date of Report 2015.2.17
実験課題番号 Project No. 2013P0906 実験課題名 Title of experiment Project research on structure and dynamics of proton, superionic and amorphous functional materials at BL18 実験責任者名 Name of principal investigator Ryoji Kiyanagi 所属 Affiliation J-PARC, JAEA	装置責任者 Name of Instrument scientist Takashi Ohhara 装置名 Name of Instrument/（BL No.） SENJU/BL18 利用期間 Dates of experiments 2014/3/12 -2014/3/15

1．研究成果概要（試料の名称、組成、物理的・化学的性状を明記するとともに、実験方法、利用の結果得られた主なデータ、考察、結論、図表等を記述してください。

Outline of experimental results (experimental method and results should be reported including sample information such as composition, physical and/or chemical characteristics.

A fluorescent molecular compound, 2-(2'-hydroxyphenyl)benzimidazole (HPBI: Fig. 1), is interested as a candidate of new photo-functional molecular materials because photo-induced excited state intramolecular proton transfer (ESIPT) occurs in this molecule both in solution state and crystalline state and consequently solution, film and crystal of this molecule shows an unique fluorescent property. Recent spectroscopic study of HPBI suggested that the intramolecular proton transfer of HPBI was induced not only by visible light but also by thermal change in crystalline state and the keto-form of HPBI was produced at room temperature [1]. However, there is no evidence of the thermal-induced intramolecular proton transfer of the crystalline HPBI by diffraction technique. In this experiment, the author and co-workers tried to observe the thermal-induced proton transfer by single crystal neutron structure analyses of a HPBI crystal at two different temperatures.

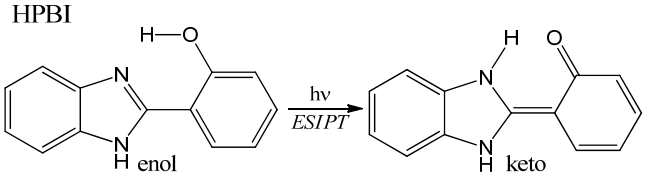

Fig. 1 HPBI molecule (enol- and keto-form)

A single crystal of HPBI with 4.0 x 2.0 x 0.2 mm size was obtained by slow evaporation of ethanol-water solution of the commercially available HPBI. Single crystal neutron diffraction measurements were carried out at 4 K and 298 K by using SENJU (BL18). No obvious structural phase transition was observed between 4 K and 298 K. Space group was $P2_1$ and cell parameters were a=3.739(2) Å, b=22.05(1) Å, c=5.796(3) Å and β=94.429(7)˚ at 4 K. Measurement time and number of measured reflections at 4 K / 298 K were 42 hours (14 orientations x 3 hours) / 45 hours (15 orientations x 3 hours) and 17486 / 7803, respectively.

Structure refinements were carried out by using program JANA2006 [2]. Bragg reflections which intensities were larger than 3σ were used in the refinements. Minimum values of d-spacing were 0.4 Å at 4 K and 0.6 Å at 298 K. Positional parameters and anisotropic displacement parameters of all hydrogen and non-hydrogen atoms were refined without structural restrain. Final R values were 0.105 at 4 K and 0.093 at 298 K.

1．研究成果概要（つづき） Outline of experimental results (continued).

Figure 2 shows the refined structure of HPBI at 4 K (left) and 298 K (right). Bond length, bond angles and anisotropic displacement parameters have reasonable values. The refined structure at 4 K shows the HPBI molecule has the stable enol-form at low temperature. On the other hand, the refined structure at 298 K shows that almost all molecules in a HPBI crystal have the enol-form, not the keto-form, even at room temperature. No peak of hydrogen atom bonding to the nitrogen atom of the O-H…N hydrogen bond was observed in a differential Fourier map of the 298 K data. The interpretation of these results is now in progress.

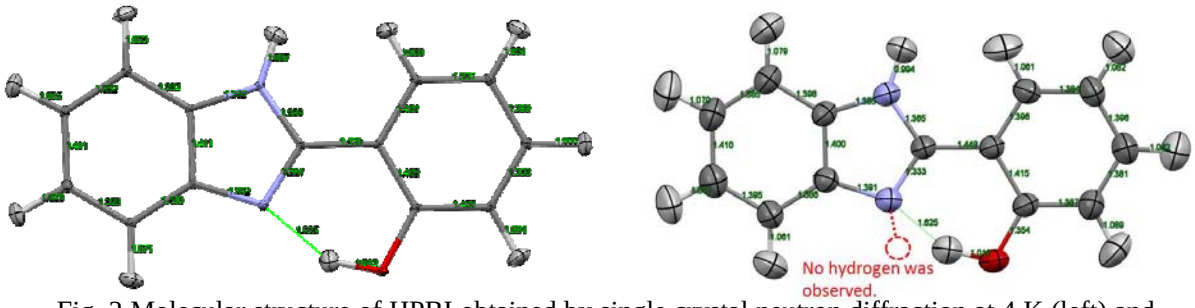

Fig. 2 Molecular structure of HPBI obtained by single crystal neutron diffraction at 4 K (left) and 298 K (right).

References

[1] H. Konoshima, *et al.*, *Chem. Phys. Phys. Chem.*, **2012,** 16448.

[2] V. Petricek, *et al.*, *Z. Kristallogr.*, **229,** 345 (2014).

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