Electronic Supplementary Information (ESI)

Room-Temperature Proton Transport and Its Effect on Thermopower in Solid Ionic Semiconductor, $TTFCOONH_4$

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Table of contents

1. Structure determination from PXRD analysis

The quality of the present data is much better than that of previous data due to the careful treatment of sample preparation. We can detect many weak peaks at low angle region in the present data. Twenty peak positions of seemingly isolated Bragg reflections in low angle region were evaluated from the powder diffraction data of $TTFCOONH_4$. The cell parameters were determined by DICVOL06[S1] by using the positions. The determined cell parameters were different from previous study.[18] The length of the *a*-axis is almost twice and the *b*-axis is almost half to the previous cell length. We determined more reliable cell parameters from high-quality powder diffraction data. The space group was uniquely determined as $P2_1/n$ from reflection conditions.

The powder data of $TTFCOONH_4$ were collected at the 100 K and 300 K for investigation of thermal stabilities. The N_2 gas flow type temperature device was utilized to control the temperature of the sample. The peak shape, width and intensity of 300 K data are almost identical to those of 100 K data.

The crystal structure of $TTFCOONH_4$ at 100 K has been determined by the structure solution system based on genetic algorithm (GA).[S2] The total number of degrees of freedom of $TTFCOONH_4$ is 8 including 5 positional parameters, 3 orientation parameters, and 1 torsion angles for two independent molecules. The orientation parameters of NH_4^+ molecule did not determined in this process. The GA analysis was carried out using the program accelerated by graphic processing unit (GPU). The reliability factors of final Rietveld refinement were R_{wp} = 1.9 % and R_I = 5.8 % with d > 0.94680 Å d-spacing range which are satisfactory for accurate structure solution.

2. Molecular orbital calculation

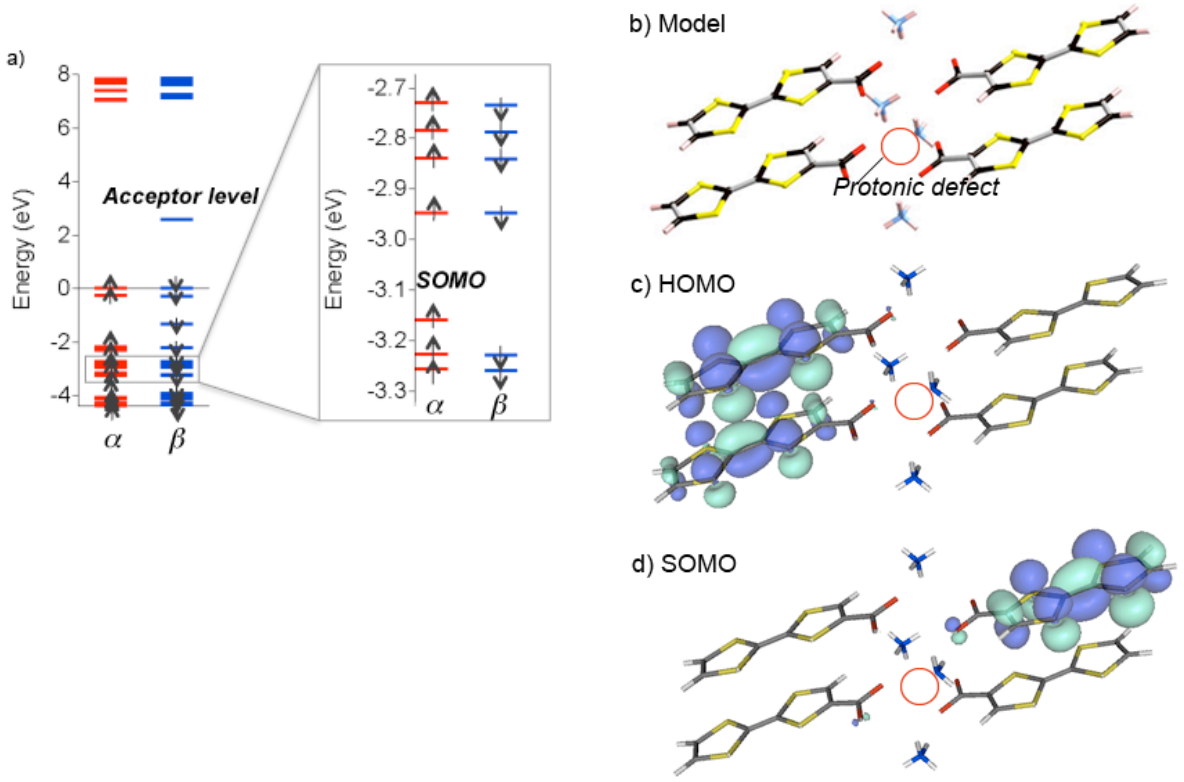

Figure S1. Molecular orbital calculation. a) Energy level for 4 molecular pair with one protonic defect at doublet state with neutral charge, which was evaluated at UHF/6-31G* level of theory. The lowest occupied molecular orbital (LUMO) of beta orbital corresponds to an acceptor level, providing semiconducting properties to the system. This lowered LUMO is derived from embedded singly occupied molecular orbital (SOMO). b) A cluster model used for the calculation. c) HOMO picture, which delocalize over molecules. d) SOMO picture, which is localized on one molecule.

3. Frequency dependence in AC conductivity

a. **b.**

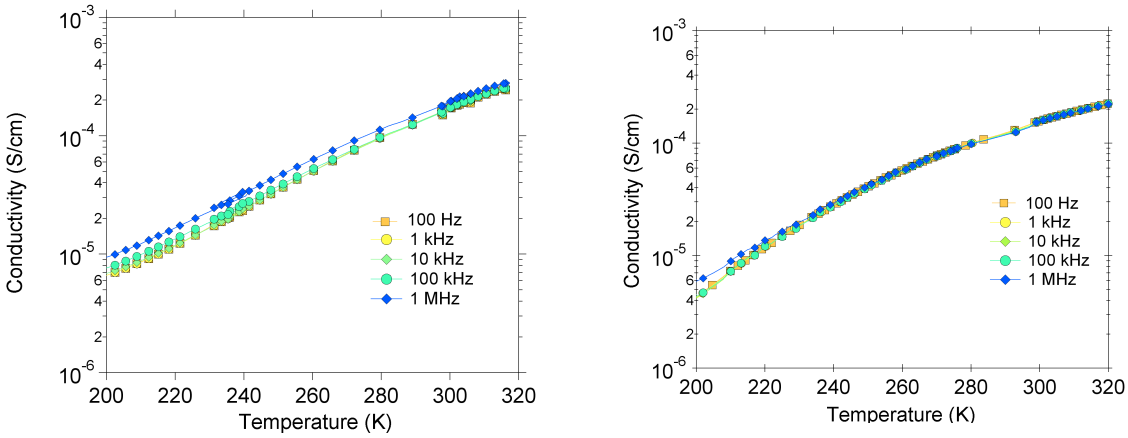

Figure S2. Ac conductivity with a frequency range of 100 Hz-1 MHz from 220 to 320 K, measured with a two-probe method. a. $TTFCOONH_4$ and b. $TTFCOOND_4$.

4. Optical absorption spectra

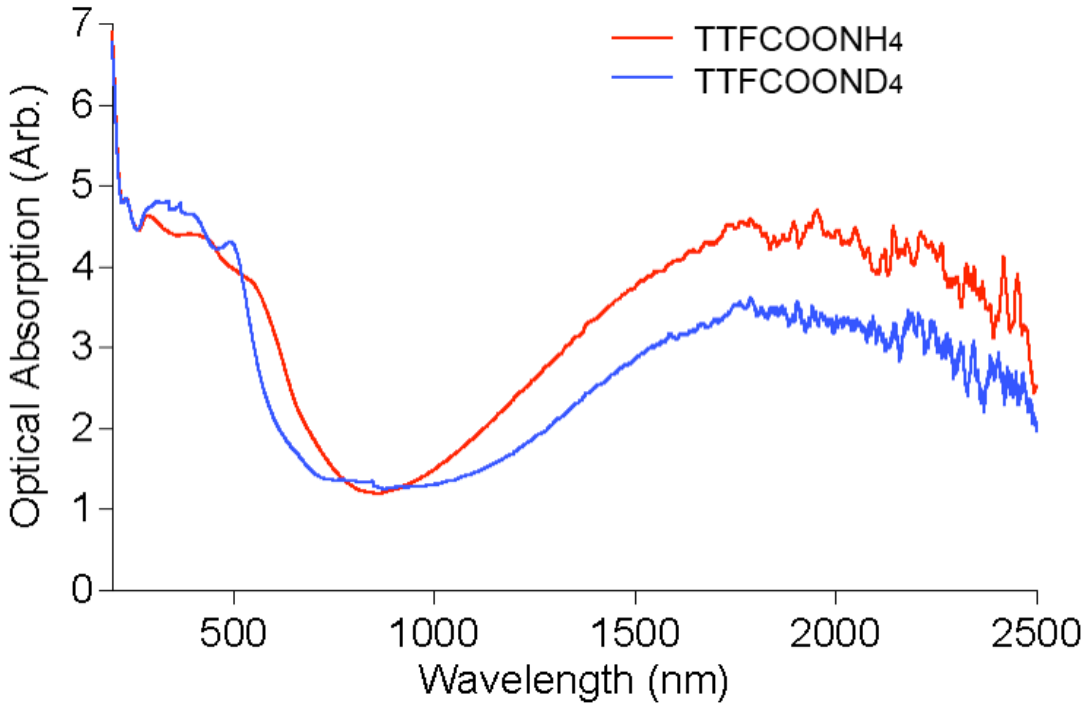

Figure S3. Optical absorption spectra of polycrystalline solids of $TTFCOONH_4$ (red) and $TTFCOOND_4$ (blue) in UV-Vis-NIR region, measured at 300 K.

5. PXRD pattern in $TTFCOONH_4$ and $TTFCOOND_4$

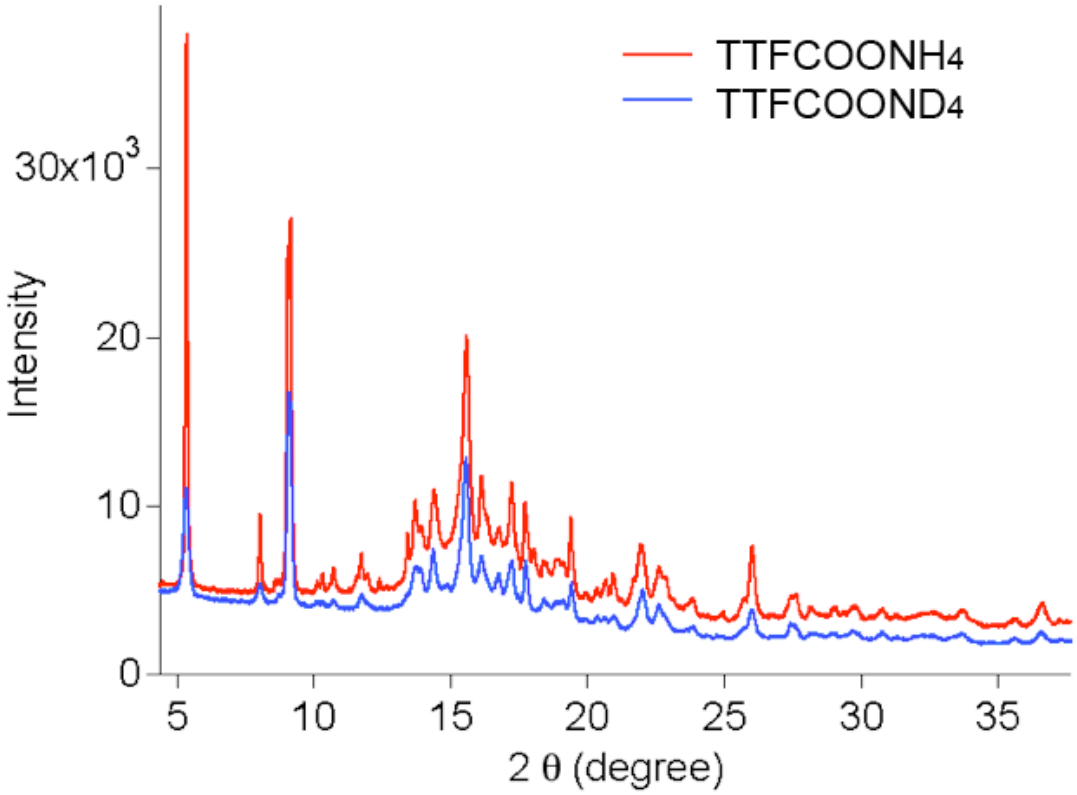

Figure S4. PXRD patterns of $TTFCOONH_4$ (red) and $TTFCOOND_4$ (blue) at 300 K, which are shown from 3 to 50 degrees.

6. References

S1 Boultif, A.; Louër, D. *J. Appl. Cryst.* 2004, 37, 724–731.

S2 Nishibori, E.; Ogura, T.; Aoyagi, S.; Sakata, M. *J. Appl. Cryst.* **2008**, 41, 292-301.