Supporting information for

Investigation of post-grafted groups of a porous coordination polymer and its proton conduction behavior

Munehiro Inukai, Satoshi Horike, Daiki Umeyama, Yuh Hijikata, and Susumu Kitagawa

Materials

All chemicals employed were obtained from commercial suppliers and used without futher purification. $[Zn_2(2,5\ DHTP)]_n$ (DHTP = dihydroxyterephthalic acid) was prepared as previously described.[1] 500 mg of dried **1** and 257 mg of histamine were immersed in 25 ml of toluene and refluxed at 115 °C for 14 hours under flowing N_2 gas. Then, the yellow microcrystalline solid was recovered by filtration and washed three times with fresh toluene. The obtained solid was dried at 150 °C under vacuum for 4 hours.

Physical measurements

Liquid state ^1H NMR spectrum was recorded on a JEOL 500 MHz spectrometer. X-ray powder diffraction (XRPD) data were collected on a Rigaku RINT 2000 Ultima diffractometer with CuKα radiation. Thermogravimetry analysis (TGA) in the temperature range of 303 ~ 773 K was performed using a Rigaku TG8120 under flowing nitrogen with 10 K min^{-1} and 4 K min^{-1} ramp rate. AC Impedance measurement were recorded using a Solartron SI 1260 Impedance/Gain-Phase analyzer over frequency range 1 Hz–1 MHz with input voltage amplitude of 100 mV. The pelletizing powder **1-His** was put in a measurement cell and dried 100 °C under vacuum for 24 hours before measurement. The measurements were carried out in the cell under N_2 atmosphere. ZView software was used for fitting of impedance profiles by means of an equivalent circuit to obtain the resistance values.

Solid-state NMR measurements

All solid state NMR measurement were performed on a 9.4 T Bruker solid- state NMR instrument with an ADVANCE III 400 MHz spectrometer and a double resonance 4 mm magic angle spinning (MAS) probe. ^{1}H-^{13}C heteronuclear correlation (HETCOR) with frequency switched Lee-Goldburg (FSLG) homonuclear decoupling was carried out. The HETCOR spectrum was obtained using a recyle deley of 3 s with a spinning rate of 14 kHz. FSLG period and contact time of ^{1}H-^{13}C cross-polarization were 10.21 μs and 2 ms, respectively. Carbon signals were acquired under two-pulse phase modulating (TPPM) proton decoupling. Variable temperature natural abundance ^{15}N CP-MAS spectra were obtained using a recyle deley of 5 s with a spinning rate of 14 kHz (at 30, 60 °C) and 8 kHz (at 110 °C). ^{15}N chemical shifts were referenced to NH_4Cl at 40.7 ppm. Variable temperature ^{1}H MAS spectra were obtained using a recyle deley of 20 s with a spinning rate of 10 kHz.

Details of calculation

The structure of isolated histamine was optimized by Gaussian 09 Revision C.01[2] with 6-311G(d) and B3LYP level. We constructed a model structure using the optimized structure of histamine and the X-ray crystal structure of **1**. The histamine was introduced to the 1D channel which was cut out from **1**. We performed the quench dynamics using Forcite module implemented in Material Studio 6.0 Package (Accelrys Inc., San Diego, CA). Universal Force Field and NVT constant condition were applied.[3] N, V, and T were the number of particles, volume and temperature of the model system, respectively. Temperature was set at 298 K, and time step and total simulation time were 2.0 fs and 1000 ps, respectively.

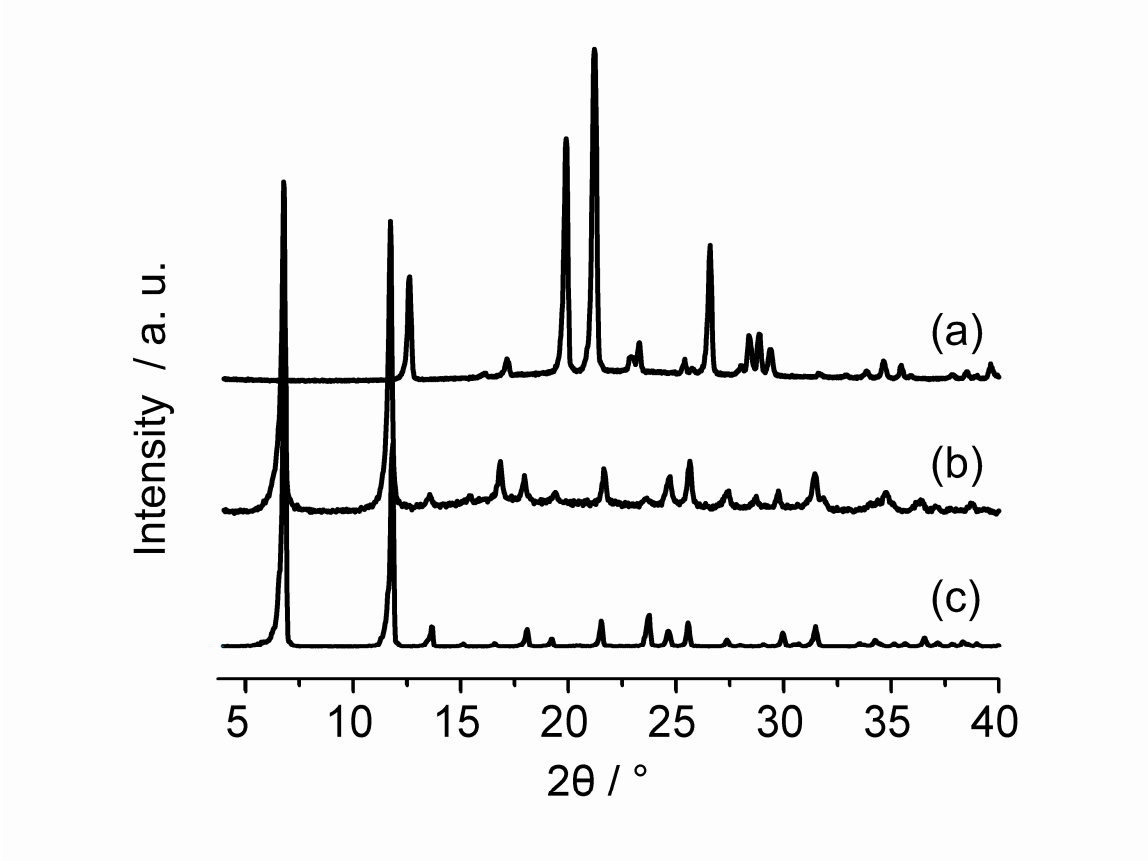

Figure S1. Powder X-ray diffraction patterns of (a) bulk histamine, (b) **1-His,** and (c) **1-DMF**.

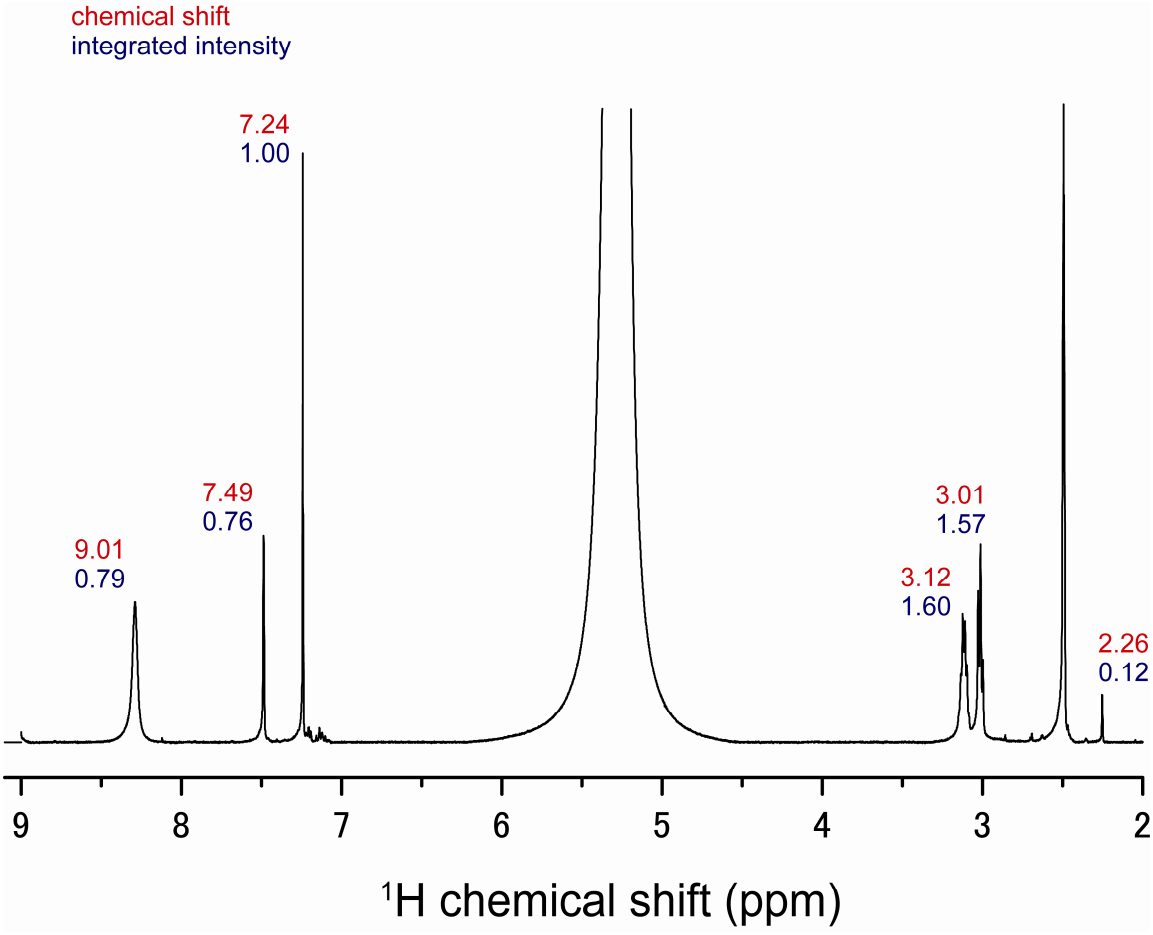

Figure S2. Liquid state ^{1}H NMR spectrum of degradated 1-His. (500 MHz, DMSO-d_6/HCl) δ_H 9.01 ppm (1H, s, N-CH-N, histamine), 7.49 ppm (1H, s, CH-N, histamine), 7.24 ppm (2H, s, -CH-, DHTP), 3.12 ppm (2H, m, -CH2-N, DHTP)), 3.01 (2H, t, J=7.3 Hz, -CH2-, DHTP), 2.26 (3H, s, CH_3, toluene). The peaks of benzene ring of toluene were observed around 7.18 ppm. The peaks of H_2O and DMSO were observed at 5.3 and 2.5 ppm, respectively. The relative integration of histamine peak showed amount of 0.77 loaded histamine per 1 metal site.

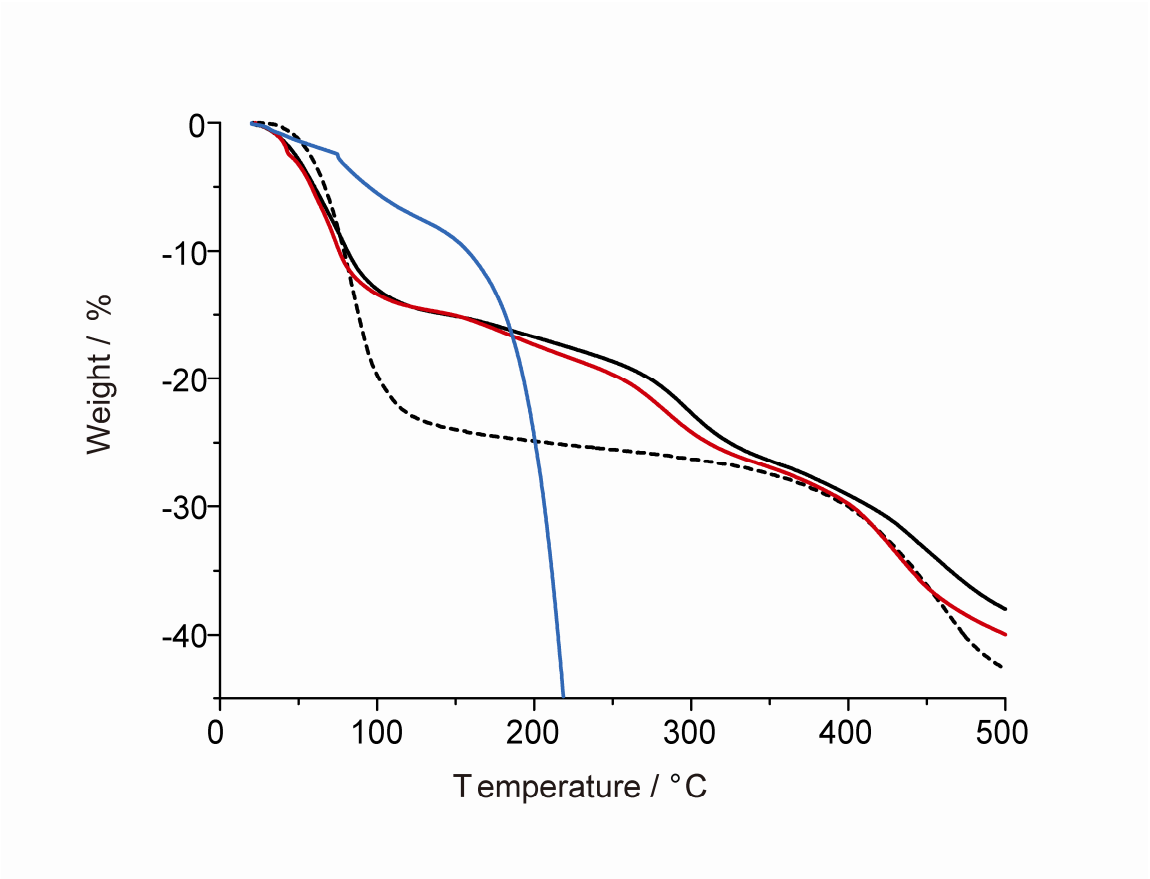

Figure S3. Thermogravimetric analysis for **1** (dash line), **1-His** (solid line), bulk histamine (blue solid line) with 10 K/min rate, and **1-His** (red solid line) with 4 K/min ramp rate. The weight loss of 1 and 1-His from R.T. to 100 ºC is attributed to water molecule which was adsorbed from air during the preparation of TG measurement.

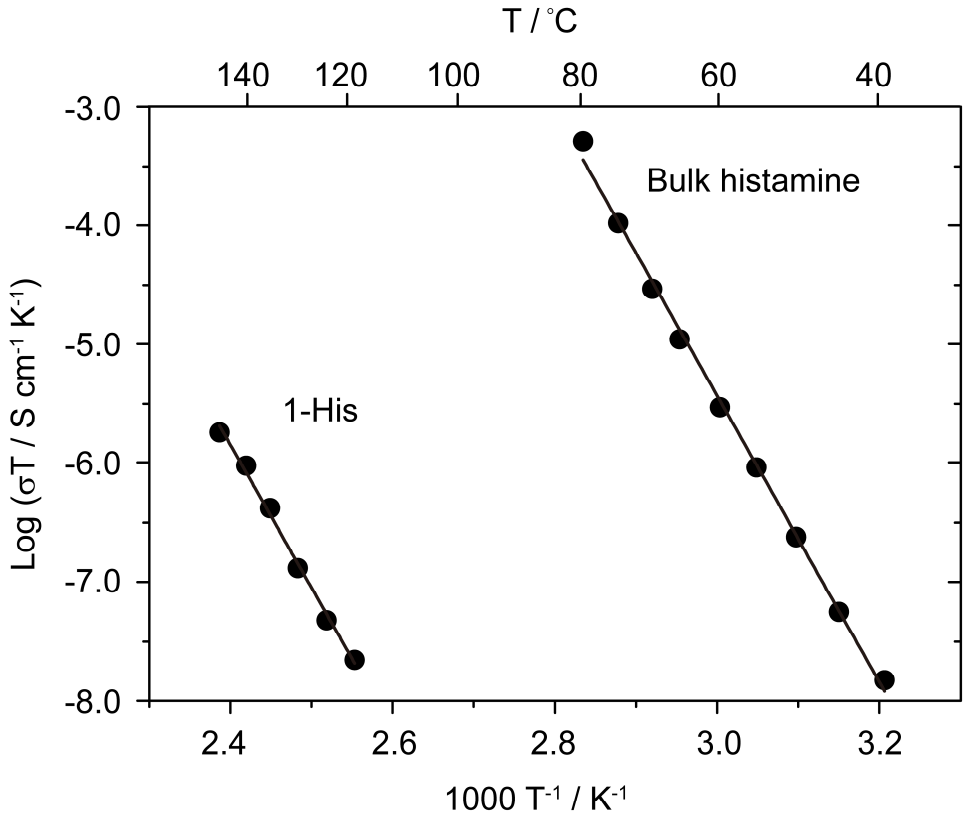

Figure S4. Arrhenius plots of anhydrous conductivity of **1-His** and bulk histamine from 40 to 146 °C.

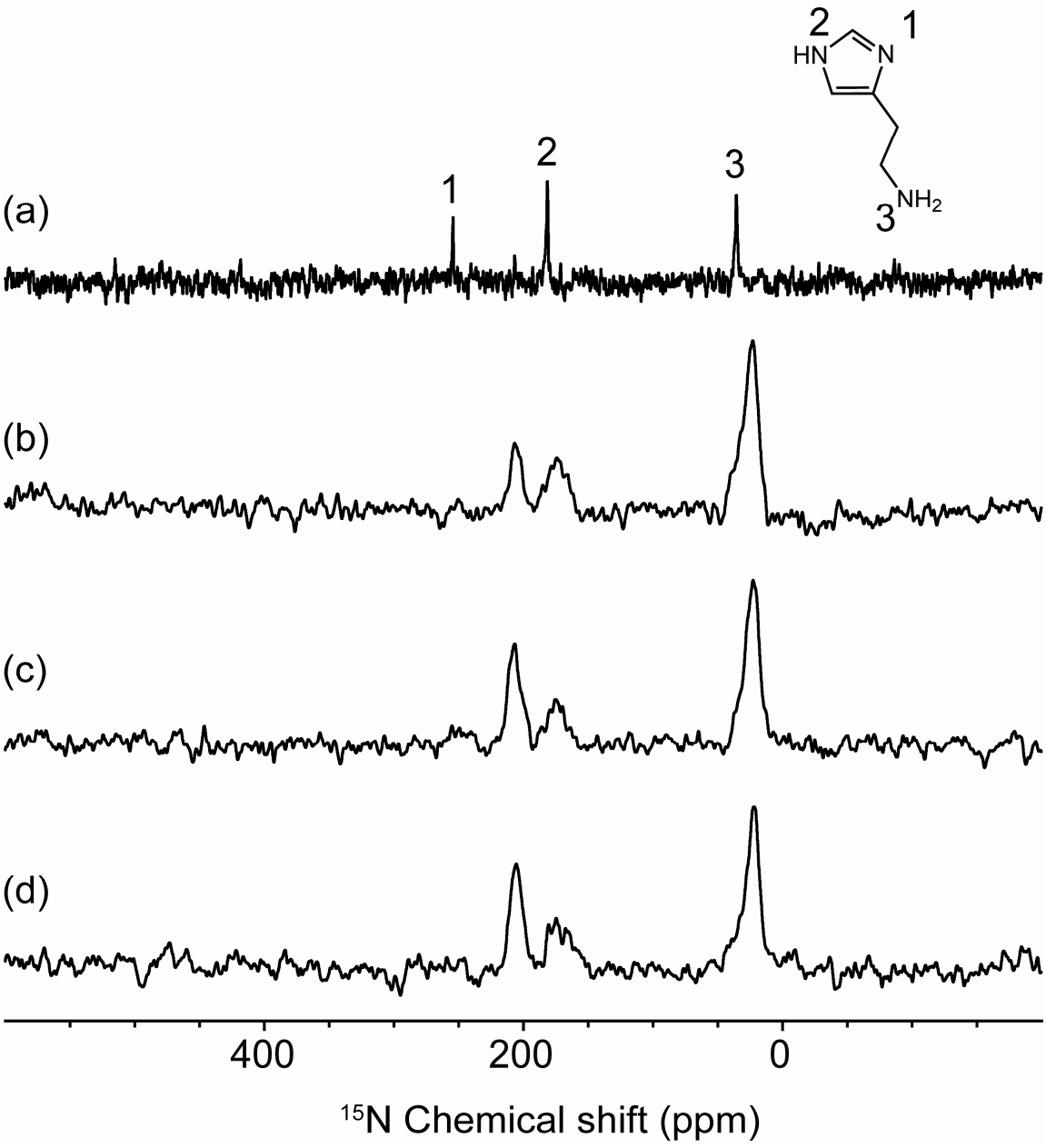

Figure S5. ^{15}N CP-MAS spectra of (a) bulk histamine at 298 K, **1-His** at (b) 298, (c) 333, and (d) 383 K.

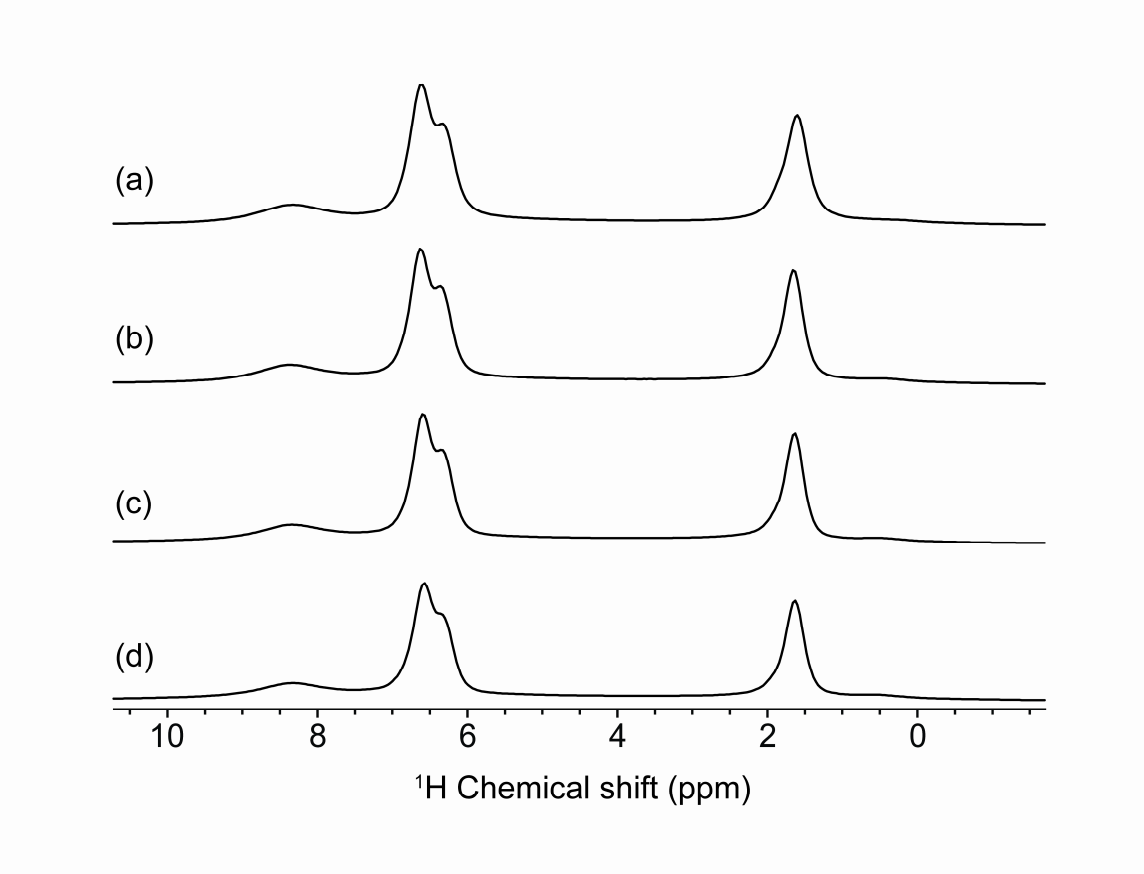

Figure S6. ^{1}H MAS spectra of **1-His** at (a) 298, (b) 333, (c) 363 and (c) 383 K.

Acknowledgement

Computation time was provided by the Super Computer Laboratory, Institute for Chemical Research, Kyoto University.

References

1. Rosi, N. L.; Kim, J.; Eddaoudi, M.; Chen, B. L.; O'Keeffe, M.; Yaghi, O. M., *J. Am. Chem. Soc.* 2005, **127**, 1504.

2. Gaussian 09, Rev. C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

3. Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A.; Skiff, W. M., *J. Am. Chem. Soc.* 1992, **114**, 10024.