Supporting information for

Template-directed proton conduction pathway in a coordination framework

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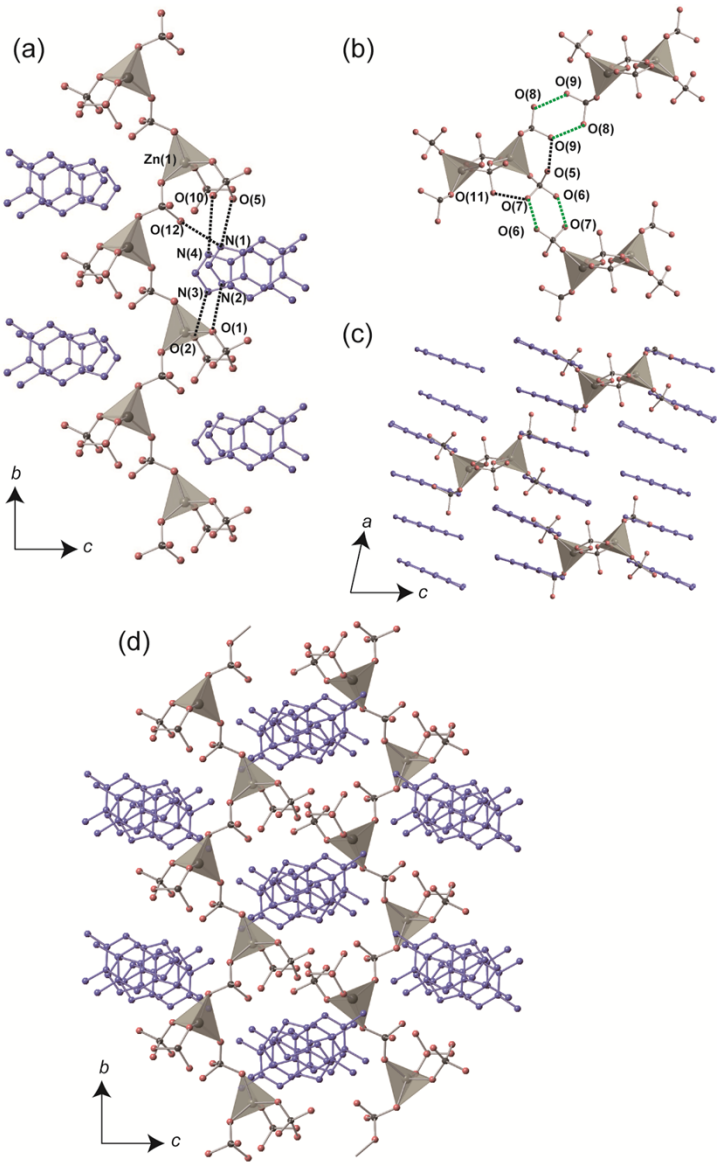

Fig. S1 (a) Crystal structure of $[Zn(H_2PO_4)_2(HPO_4)]\cdot(H_2dmbim)_2$ (**1**) at -50 °C. (b), (c) Three 1-D chains along *b* axis. (d) Packing structure of **1** along *a* axis. The H_2dmbim^+ ions are highlighted as purple and hydrogen atoms were omitted. The H_2dmbim^+ ions are omitted in (b). Intra- and intermolecular H-bonds are shown as dot line. In particular, interchain H-bonds are shown as green dot line. [Color coding: Grey: Zn and P, pink: O, purple: N and C.]

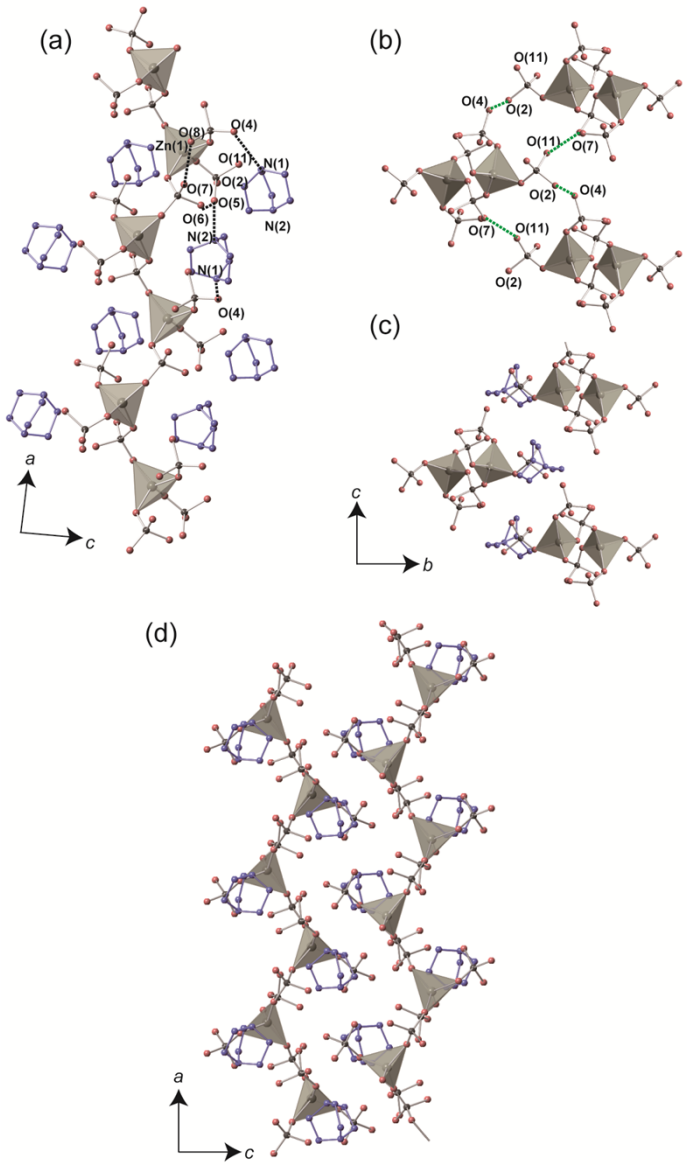

Fig. S2 (a) Crystal structure of $[Zn(H_2PO_4)_2(HPO_4)]\cdot H_2dabco$ (**2**). (b), (c) Three 1-D chains along *a* axis. (d) Packing structure of **2** along *b* axis. The H_2dabco^+ ions are highlighted as purple and hydrogen atoms were omitted. The H_2dabco^+ ions are omitted in (b). Intra- and intermolecular H-bonds are shown as dot line. In particular, interchain H-bonds are shown as green dot line. [Color coding: Grey: Zn and P, pink: O, purple: N and C.]

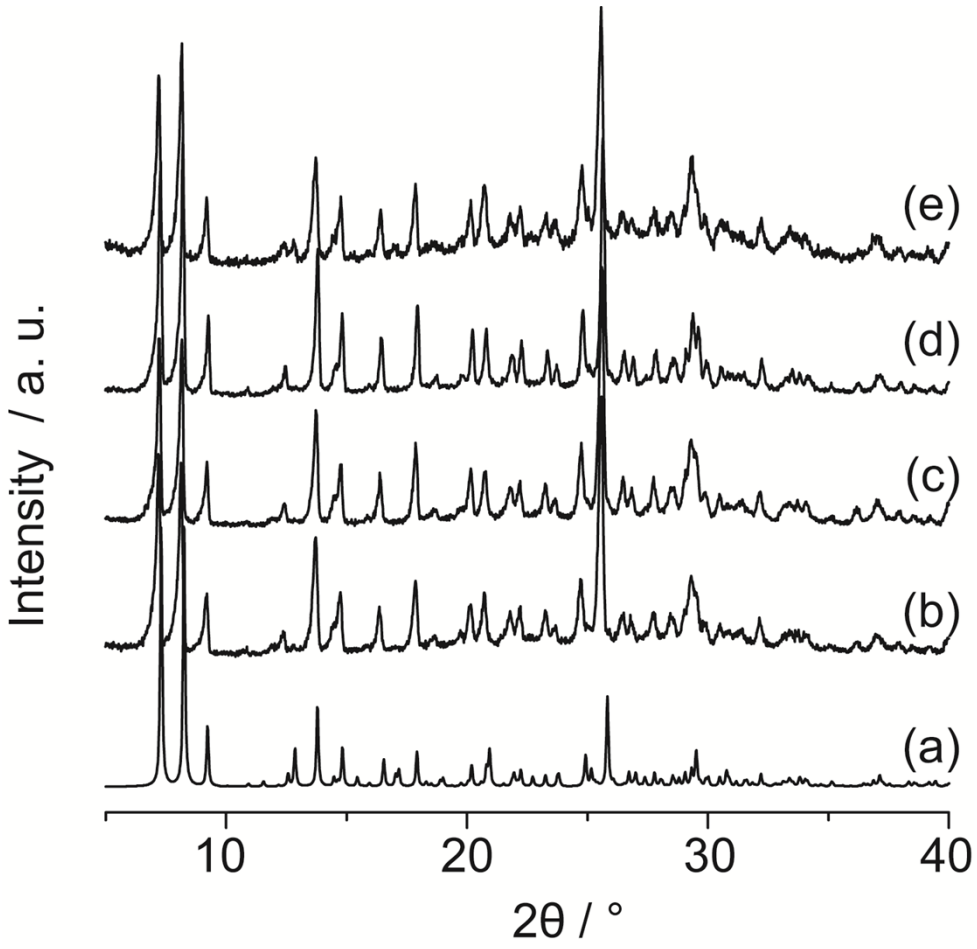

Fig. S3 Powder X-ray diffraction patterns of (a) simulation from the crystal structure of **1**, (b) **1**, (c) deuterated **1** (**1-d**), (d) **1** after humidity exposure (80 °C and 80% relative humidity), and (e) **1** after impedance measurement.

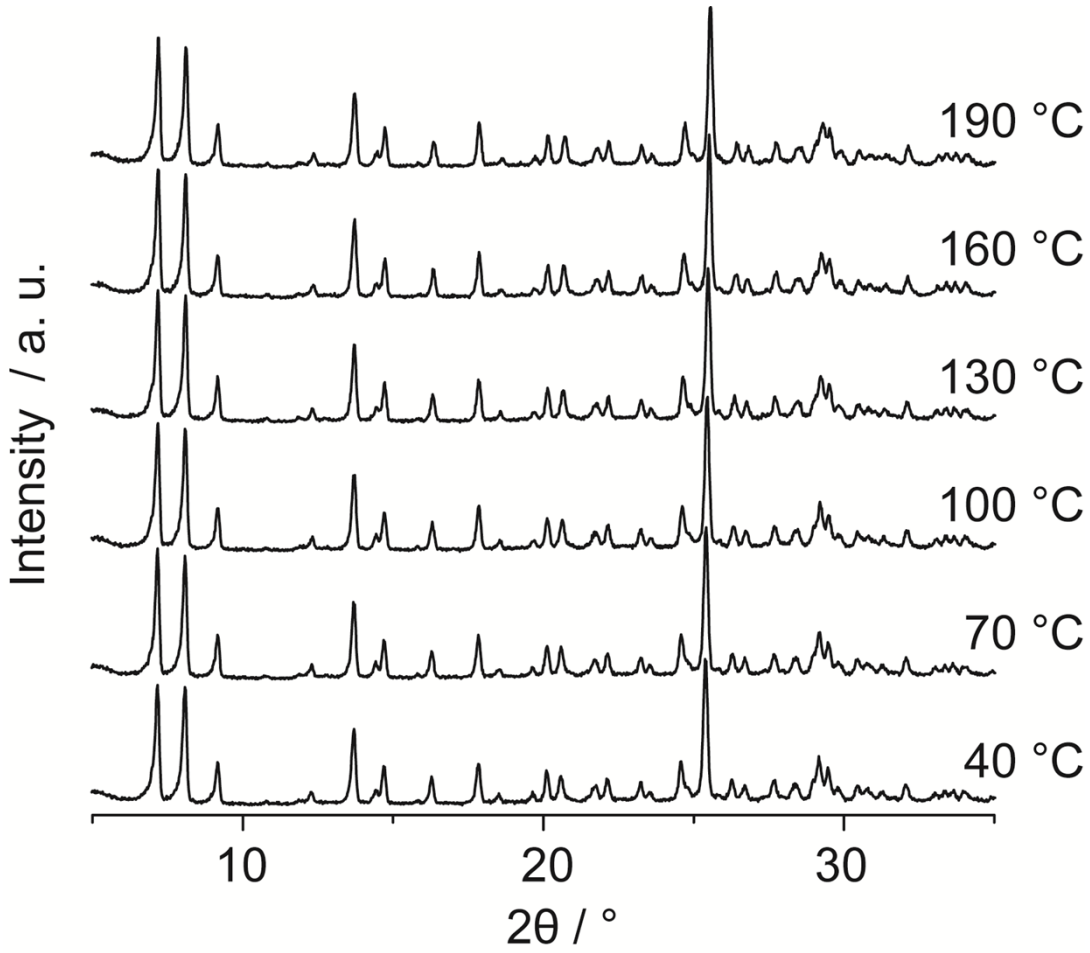

Fig. S4 Powder X-ray diffraction patterns of **1** from 40 to 190 °C under N_2 atmosphere.

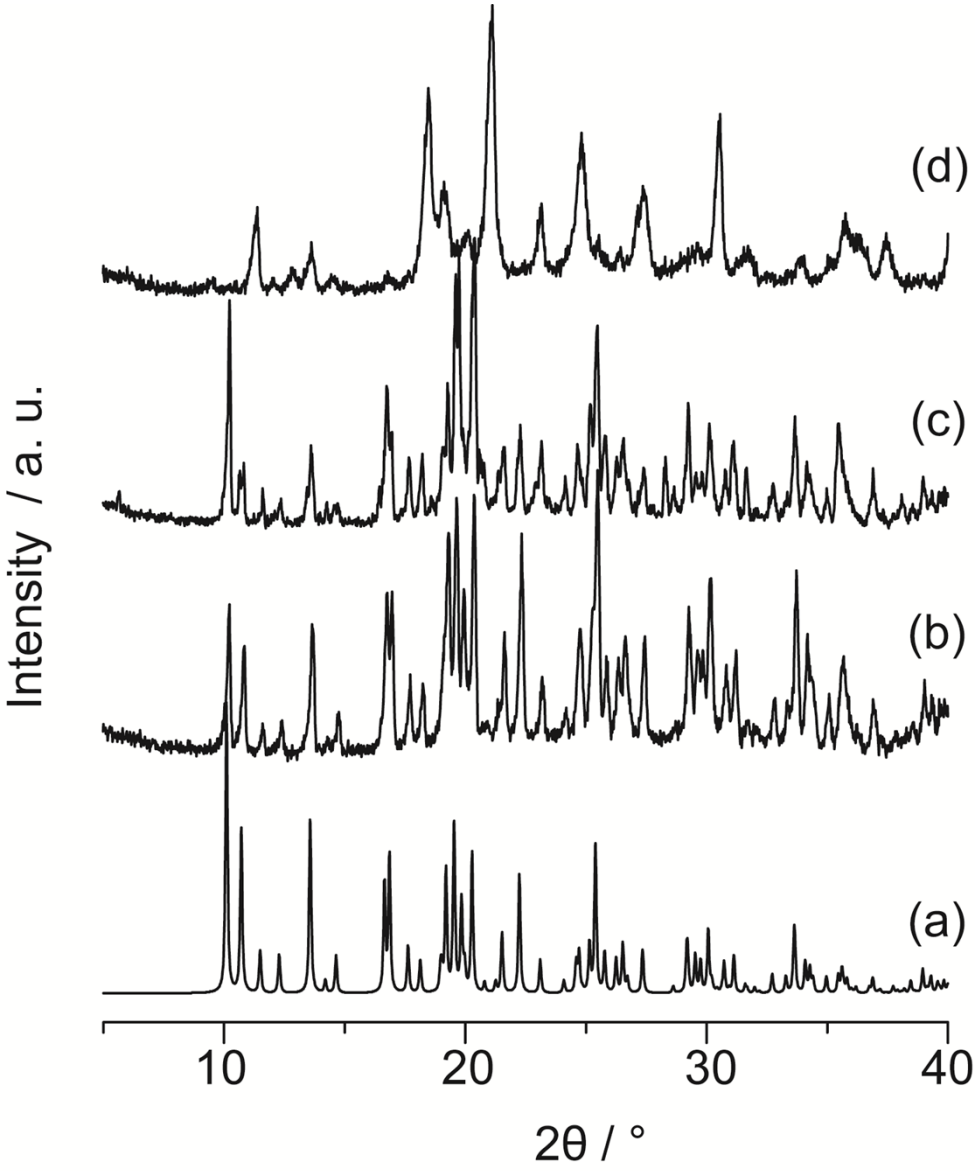

Fig. S5 Powder X-ray diffraction patterns of (a) simulation from the crystal structure of **2**, (b) **2**, (c) **2** after humidity exposure (80 °C and 80% relative humidity), and (d) **2** after heating at 180 °C for 6 h under N_2 flow.

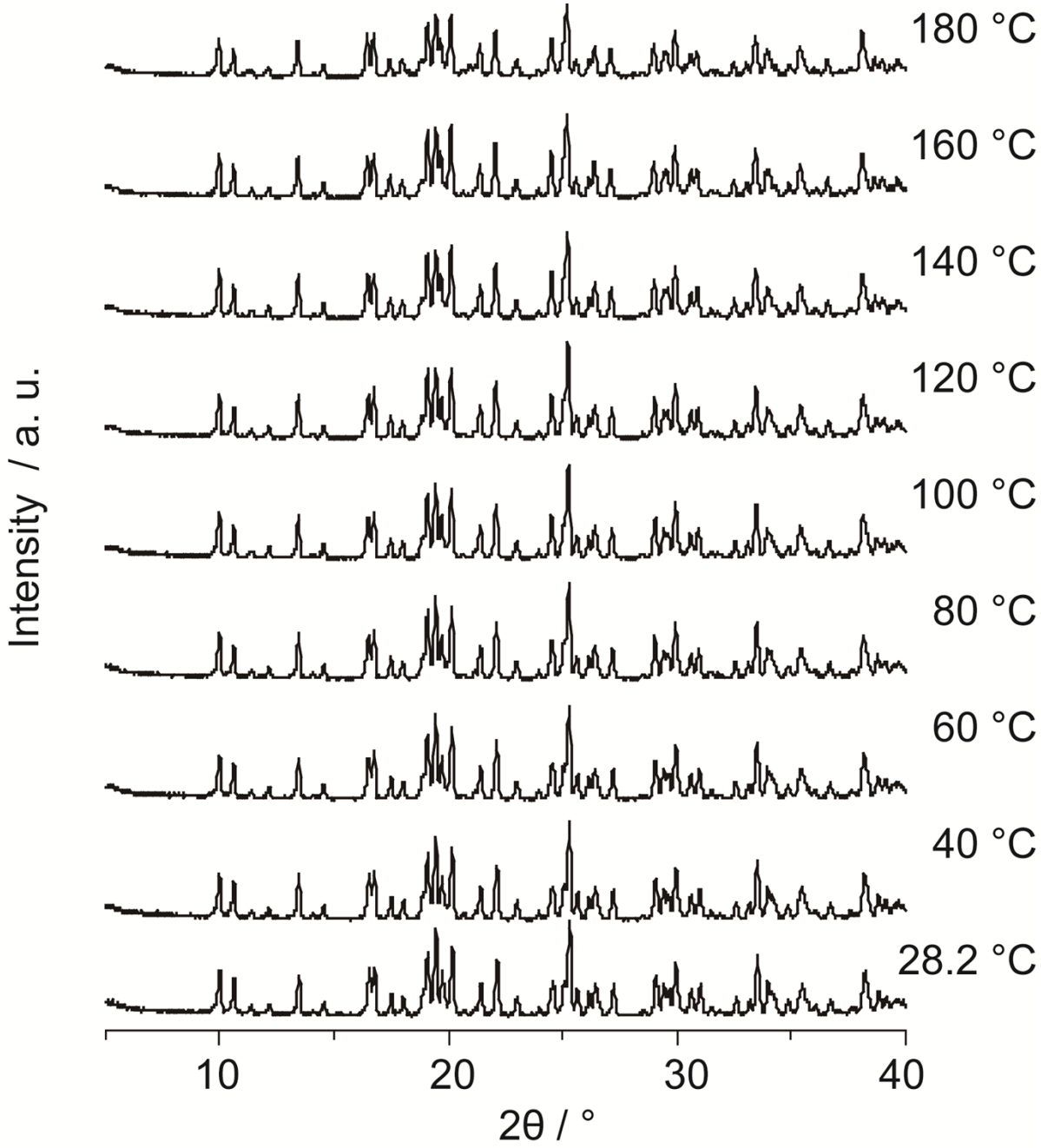

Fig. S6 Powder X-ray diffraction patterns of **2** from 28 °C to 180 °C under N_2 atmosphere.

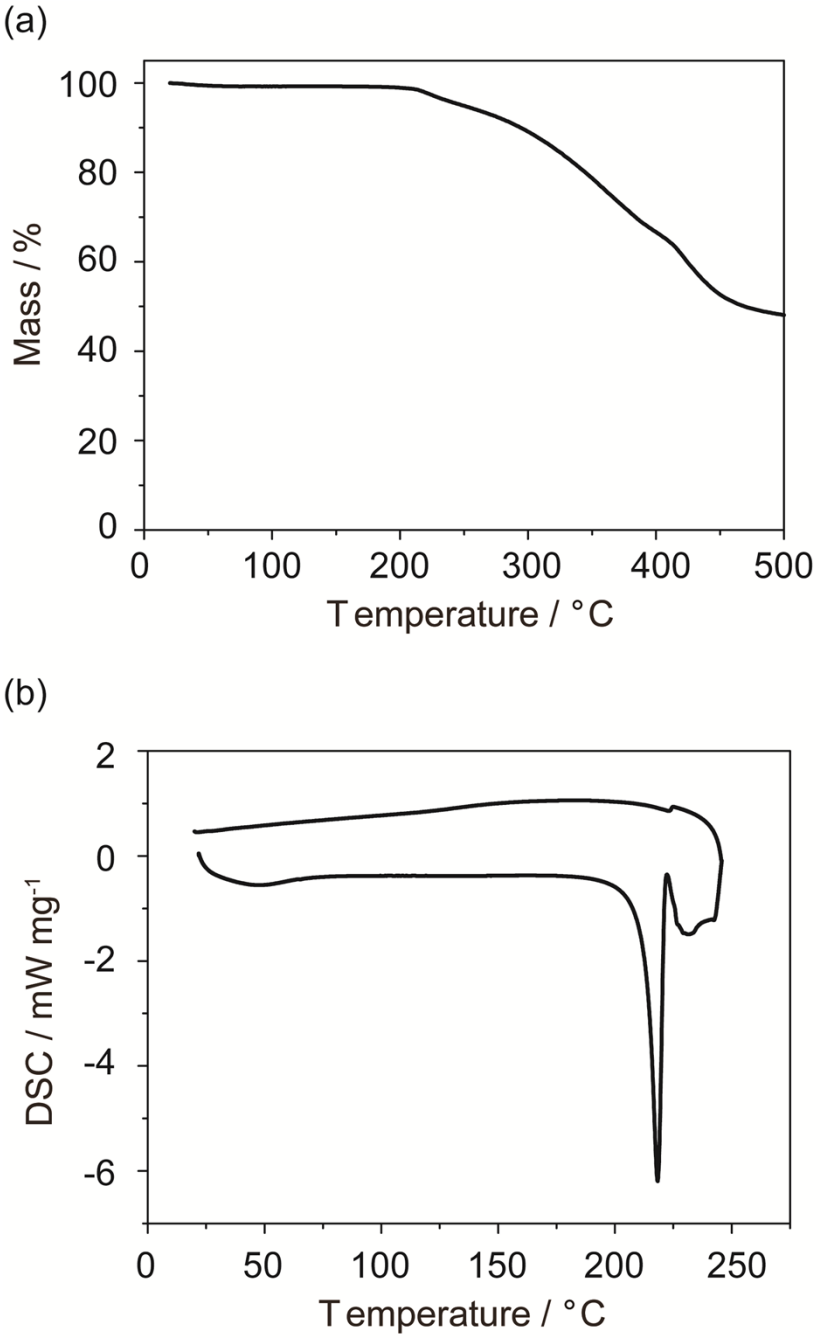

Fig. S7 (a) Thermogravimetric analysis (TGA) of **1** from 25 °C to 500 °C and (b) differential scanning calorimetry (DSC) profile of **1** from 20 °C to 250 °C.

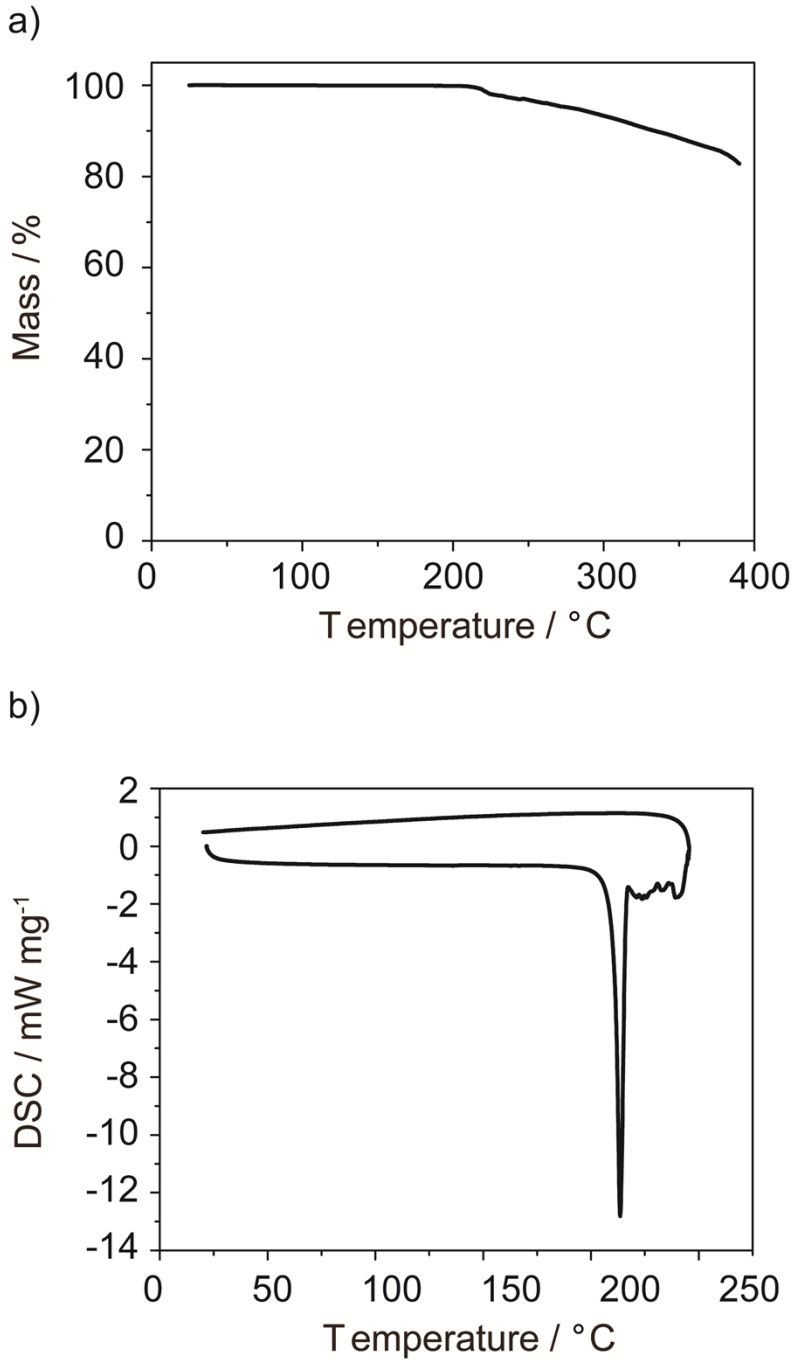

Fig. S8 (a) TGA of **2** from 25 to 400 °C and (b) DSC profile of **2** from 20 °C to 250 °C.

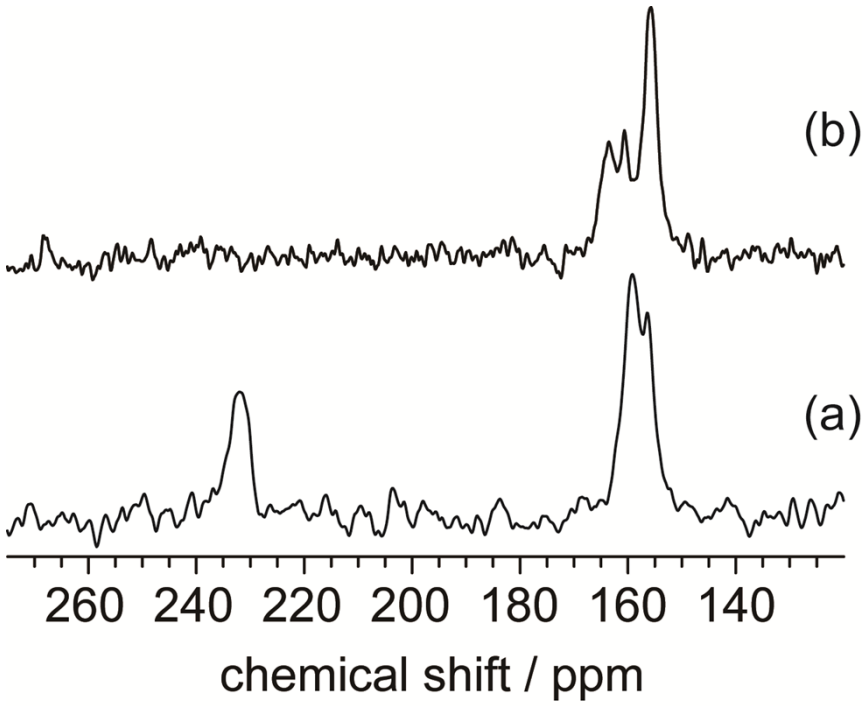

Fig. S9 ^{15}N CPMAS spectra of (a) 5,6-dimethylbenzimidazole (Hdmbim) and (b) **1** at room temperature.

References

(a) M. Munowitz; W. W. Bachovchin; J. Herzfeld; C. M. Dobson; R. G. Griffin, *J. Am. Chem. Soc.* **1982**, 104, 1192–1196; (b) S. Farr-Jones; W. Y. L. Wong; W. G. Gutheil; W. W. Bachovchin, *J. Am. Chem. Soc.* **1993**, 115, 6813–6819.

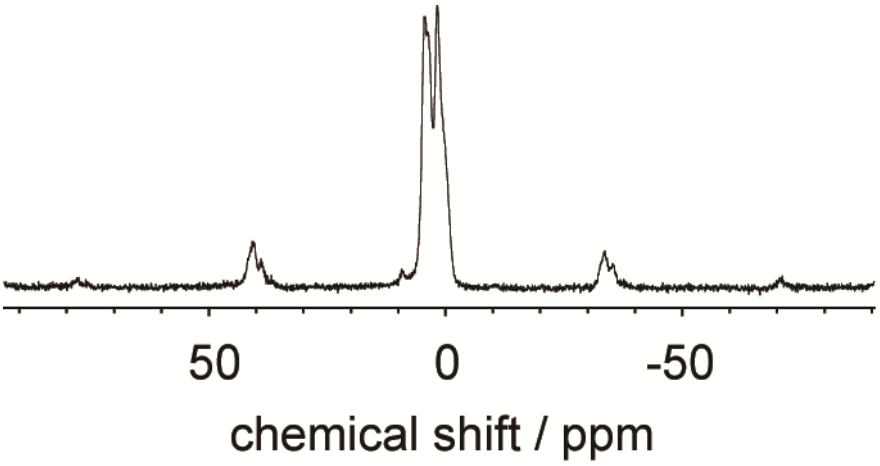

Fig. S10 ^{31}P MAS spectrum of **1** at room temperature. The spectrum does not show a peak at 0 ppm which is assigned to H_3PO_4, suggesting the absence of residual H_3PO_4

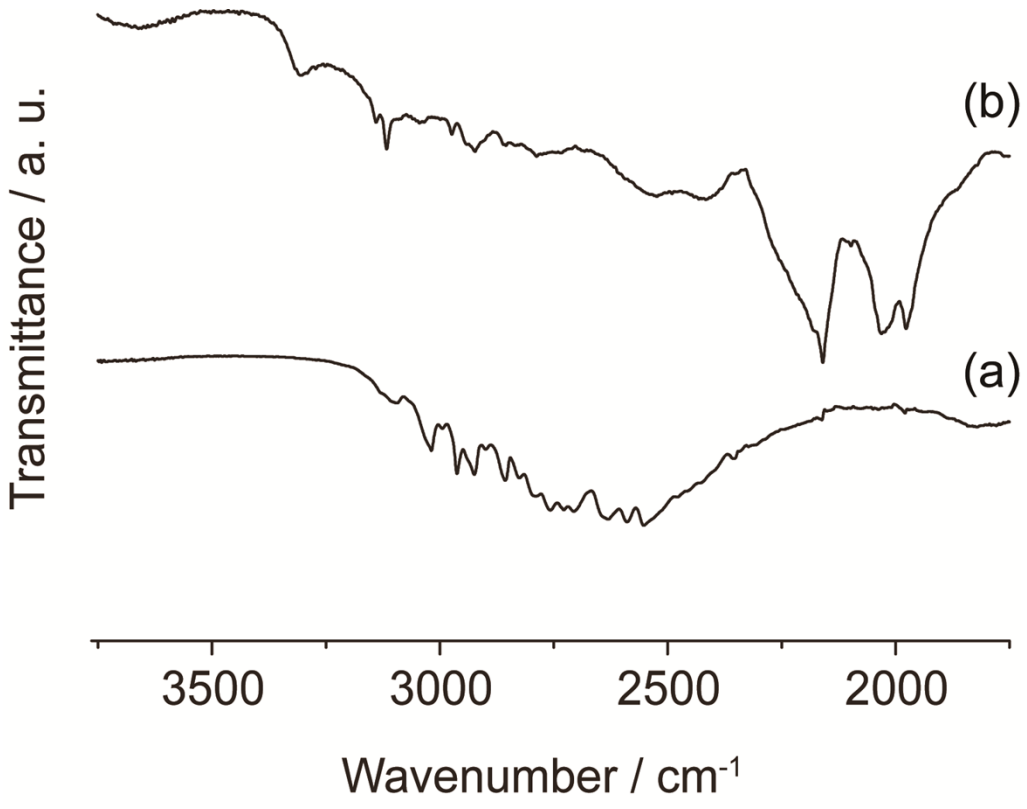

Fig. S11 Infra-red (IR) spectra of (a) Hdmbim and (b) **1** at room temperature. These spectra show N-H stretch band at 2500-3500 cm^{-1}.

References

(a) M. Yamada; I. Honma, *Angew. Chem, Int. Ed.* **2004**, 43, 3688-3691; (b) M. Nakayama; Y. Sugiura; T. Hayakawa; M. Nogami, *Phys. Chem. Chem. Phys*. **2011**, 13, 9439-9444.

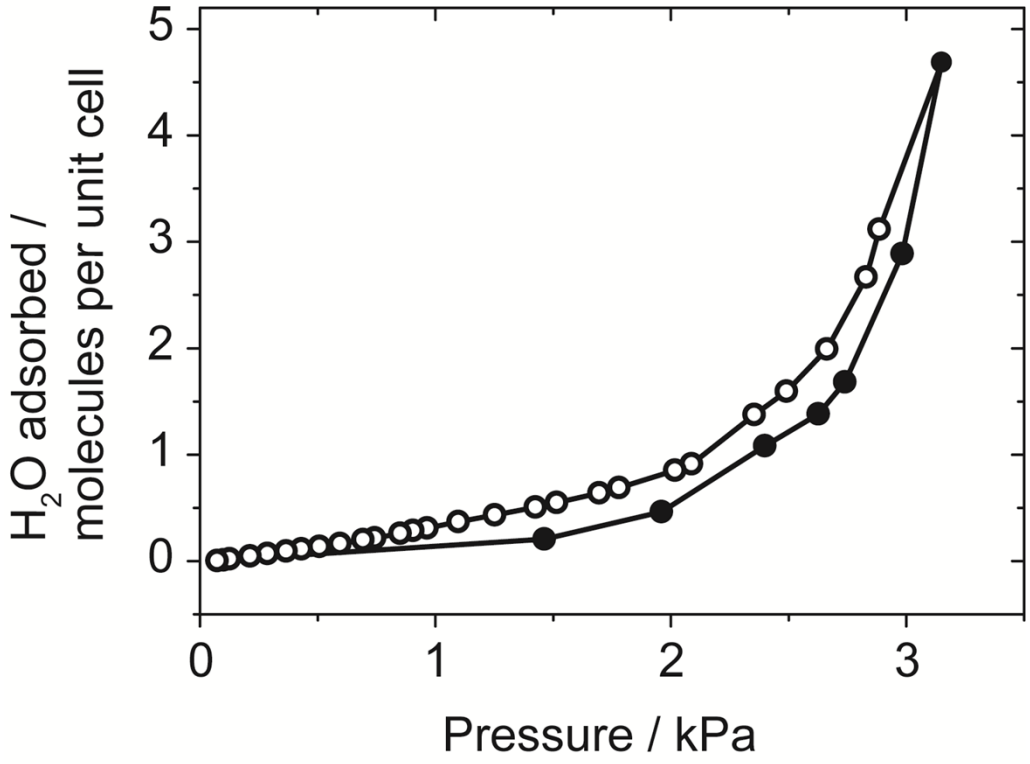

Fig. S12 Adsorption isotherm (closed circles) and desorption isotherm (open circles) of H_2O at 298 K for **1**. The sorption isotherm shows low adsorption and desorption up take until around 2 kPa, suggesting hydrophobicity.

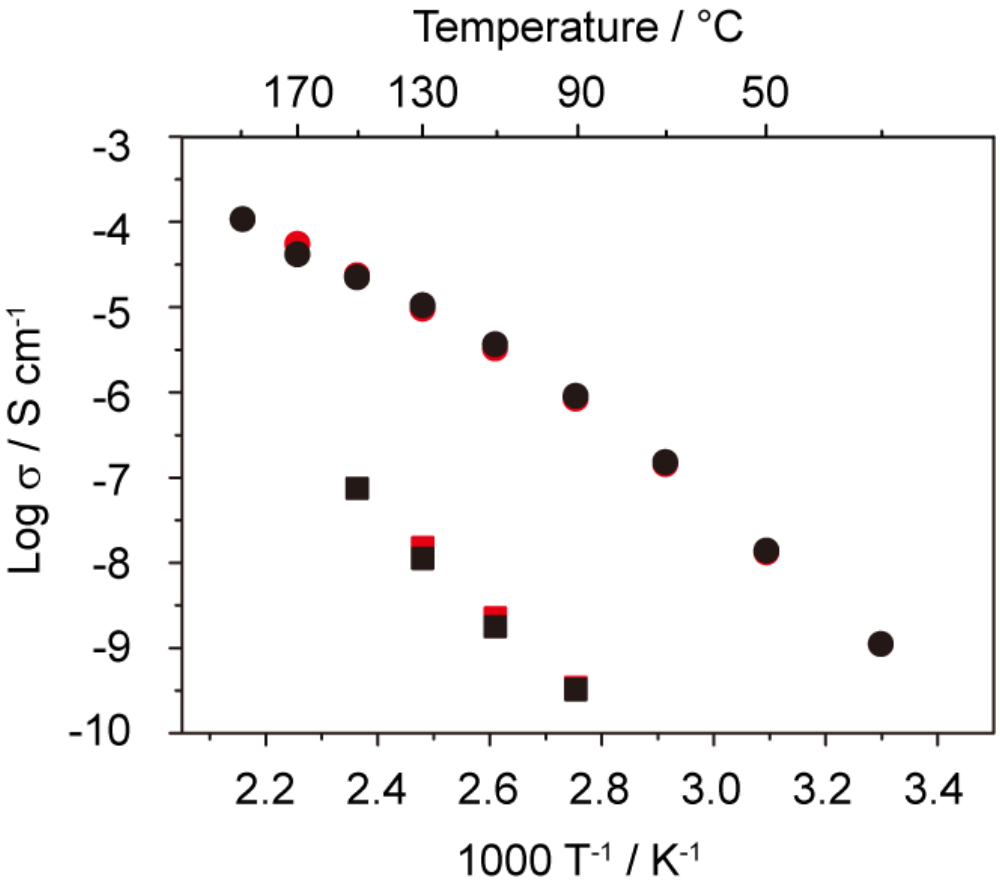

Fig. S13 Arrhenius plots of anhydrous conductivity of **1** in 30–190 °C (circle) and **2** in 90–150 °C (square). Black and Red indicate cooling and heating regime. The proton conductivities in cooling regime are almost coincident with the conductivities in heating process. This indicates thermal stability and reproducibility of proton conduction. The conductivities shown in Fig. 2a are that in heating process.

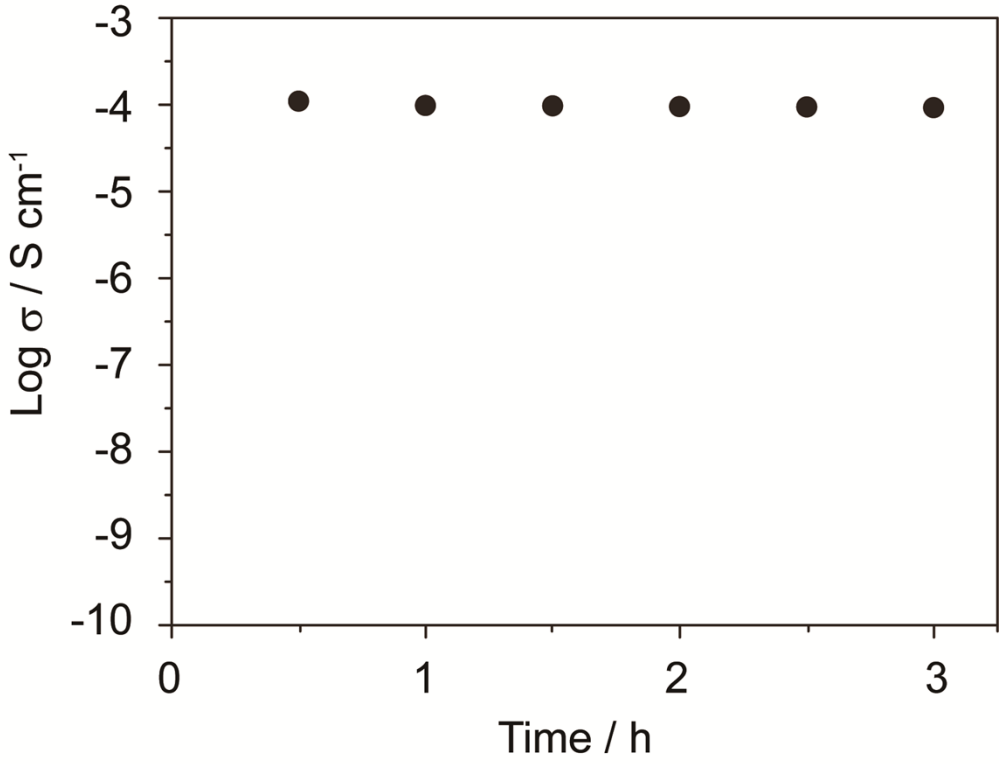

Fig. S14 Time dependence of conductivity of **1** at 190 °C.

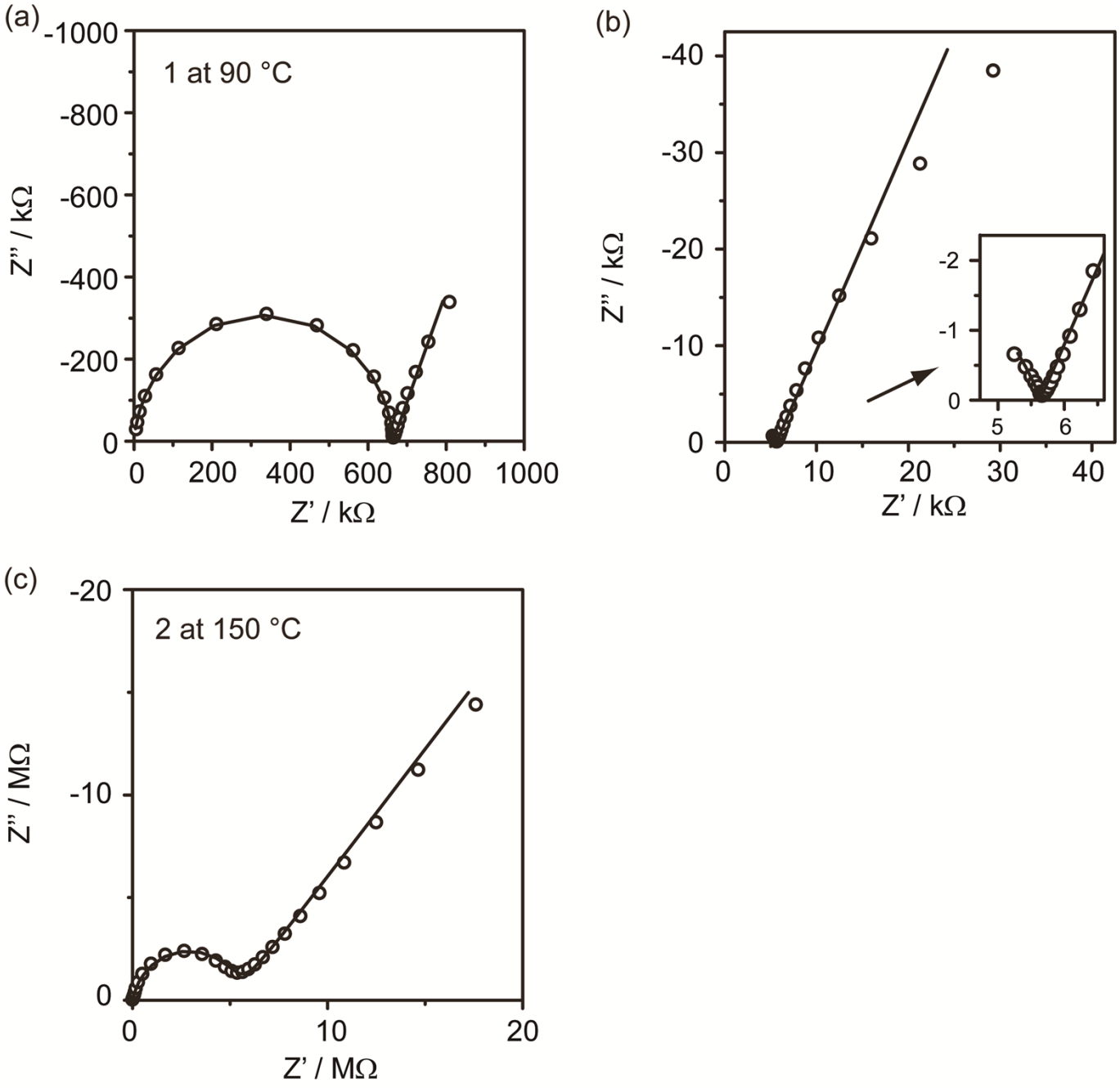

Fig. S15 Nyquist plots of **1** (a) at 90 and (b) 190 °C, and (c) **2** of 150 °C. Circles and lines represent experimental data and simulated values from equivalent circuit $(R_bCPE_b)(CPE_{el})$.

Table S1 Crystallographic data for **1** at -50 and 130 °C.

Formula	$[Zn(H_2PO_4)_2(HPO_4)]\cdot(dmbimH_2)_2$	$[Zn(H_2PO_4)_2(HPO_4)]\cdot(dmbimH_2)_2$
CCDC Deposition number	948865	948866
Temperature	-50 °C	130 °C
Space Group	Monoclinic P 2_1 / n	Monoclinic P 2_1 / n
a / Å	14.184(4)	14.392(3)
b / Å	9.890(2)	9.901(2)
c / Å	19.307(5)	19.266(4)
α / °	90	90
β / °	97.307(4)	97.337(4)
γ / °	90	90
Volume / Å^3	2686.5(12)	2722.8(10)
Z	4	4
R	0.0775	0.0709
*R*w	0.2061	0.2013
GOF	1.100	0.930

Table S2 Inter- and intramolecular H-bond lengths [Å] for 1 at -50 and 130 °C.

Temperature	-50 °C	130 °C
N(1)-O(5)	3.038	3.143
N(1)-O(12)	3.003	3.030
N(2)-O(1)	2.887	2.890
N(3)-O(2)	2.790	2.800
N(4)-O(10)	2.699	2.706
O(6)-O(7)	2.548	2.564
O(8)-O(9)	2.582	2.599
O(5)-O(9)	2.526	2.537
O(7)-O(11)	2.604	2.622

Table S3 Inter- and intramolecular H-bond lengths [Å] for **2**.

N(1)-O(4)	2.717
N(2)-O(5)	2.603
O(2)-O(4)	2.610
O(7)-O(11)	2.534
O(5)-O(6)	2.578
O(7)-O(8)	2.517