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Supporting Information for

Formation of coordination polymer glass by mechanical milling: dependence on metal ions and molecular doping for H^+ conductivity

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Synthesis of crystalline [M(1,2,4-triazole)$_2$(H$_2$PO$_4$)$_2$] (MTz).

All chemicals and solvents used in the synthesis were of reagent grade and used without further purification.

[Cr(1,2,4-triazole)$_2$(H$_2$PO$_4$)$_2$] (CrTz):

Powder samples or single crystal of CrTz were obtained by solvothermal reaction under Ar atmosphere. 1,2,4-triazole (5526 mg, 80 mmol), and phosphoric acid (85%, 5470 μL, 80 mmol) were mixed into 100 mL round flask and stirred for 10 minutes at 100°C, then evacuated for 8 hours at 85°C. The obtained dehydrated sample was ground by mortar and dissolved in deoxidized MeOH (1670.6 mg, 20 mL) under Ar atmosphere. The obtained solution was mixed with deoxidized MeOH solution of $CrCl_2$ (100 mM, 10 mL) in 50 mL glass vial. The vial was tightly sealed with a Teflon-lined cap and heated in a programmable oven at 80 °C for two days. Green-colored single crystals were collected. Powder samples were obtained by grinding the single crystals after washing with MeOH under Ar atmosphere.

[Mn(1,2,4-triazole)$_2$(H$_2$PO$_4$)$_2$] (MnTz): Powder samples of MnTz were obtained by solid state grinding of Mn(OAc)$_2$·4H$_2$O (1225.4 mg, 5 mmol), 1,2,4-triazole (690.07 mg, 10 mmol) and phosphoric acid (85%, 670 µL, 10 mmol) Single crystal of MnTz was synthesized under same ratio: Mn(OAc)$_2$·4H$_2$O (24.5 mg, 0.1 mmol), HTz (13.8 mg, 0.2 mmol), and phosphoric acid (85%, 13.4 µL, 0.2 mmol) in 1986.6 µL ethanol were mixed in a 4 mL glass vial. The vial was tightly sealed with a Teflon-lined cap and heated in a programmable oven at 120 °C for three days. Colorless single crystals were collected.

[Fe(1,2,4-triazole)$_2$(H$_2$PO$_4$)$_2$] (FeTz): Powder samples or single crystal of FeTz were obtained by solvothermal reaction under Ar atmosphere. 1,2,4-triazole (5526 mg, 80 mmol), and phosphoric acid (85%, 5470 µL, 80 mmol) were mixed into 100 mL round flask and stirred for 10 minutes at 100°C, then evacuated for 8 hours at 85°C. The obtained dehydrated sample was ground by mortar and dissolved in deoxidized MeOH (1670.6 mg, 20 mL) under Ar atmosphere. The obtained solution was mixed with deoxidized MeOH solution of FeCl$_2$ (100 mM, 10 mL) in 50 mL glass vial. The vial was tightly sealed with a Teflon-lined cap and heated in a programmable oven at 80 °C for two days. Light blue-colored single crystals were collected. Powder samples were obtained by grinding the single crystals after washing with MeOH.

[Co(1,2,4-triazole)$_2$(H$_2$PO$_4$)$_2$] (CoTz): Powder samples of CoTz were obtained by solid state grinding of Co(OAc)$_2$·4H$_2$O (1245.4 mg, 5 mmol), HTz (690.07 mg, 10 mmol) and phosphoric acid (85%, 670 µL, 10 mmol) Single crystal of CoTz was synthesized under same ratio: CoCl$_2$·6H$_2$O (23.8 mg, 0.1 mmol), HTz (13.8 mg, 0.2 mmol), and phosphoric acid (85%, 13.4 µL, 0.2 mmol) in 1986.6 µL ethanol were mixed in a 4 mL glass vial. The vial was tightly sealed with a Teflon-lined cap and heated in a programmable oven at 120 °C for three days. Orange colored single crystals were collected.

[Cd(1,2,4-triazole)$_2$(H$_2$PO$_4$)$_2$] (CdTz): Powder samples were synthesized according to the previous report (W. Chen, et al. *Angew. Chem. Int. Ed.*, **2016**, 55, 5195.).

Ball milling treatment: Solvent-free ball milling was conducted using Fritsch Pulverisette 7 planetary ball-milling apparatus with zirconia vessel and balls. The degassed crystalline powder (400 mg) of MTz (M = Cr, Mn, Fe, Co, Cd) or CdTz + 0.05/0.10dabco (5/10 mg) was milled at room temperature with different milling time under Ar atmosphere. The volumetric capacity of the pot was 20 mL and 10 balls with a diameter of 10 mm were used for the milling. The rotation speed of the solar disk was set to 400 rpm. We took care to alternate milling periods (5 minutes) with pause periods (20 minutes) in order to limit overheating of the sample. Milled samples were collected under Ar atmosphere. Elemental analysis for CdTz’-0.10dabco: (Expected)

C = 12.12, H = 2.48, N = 19.06. (Observed) C = 12.35, H = 2.61, N = 18.88.

Single crystal X-ray diffraction and structure analysis: Single crystal X-ray diffraction measurements were performed using a Rigaku AFC10 diffractometer with Rigaku Saturn Kappa CCD system equipped with a MicroMax-007 HF / Varimax rotating-anode X-ray generator with confocal monochromated MoKα radiation. Crystal structures were solved by a direct method (ShelXT 2014/5) and refined by full matrix least-squares refinement using SHELXL 2018/1.

Powder X-ray diffraction: Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku SmartLab diffractometer with CuKα radiation. Variable temperature PXRD were performed on powder samples of CrTz' and MnTz' in the temperature range between 25 and 150 °C at the heating rate of 10 °C min^{-1} by use of SPring-8 on BL02B2 beamline. The samples for X-ray total scattering measurements were sealed in a silica glass capillary under Ar atmosphere.

Pair distribution function analysis: The X-ray total scattering measurements for MnTz and MnTz' were performed at SPring-8 on BL02B2 beamline. Samples for X-ray total scattering measurements were sealed in a silica glass capillary under Ar atmosphere. The data were collected at 25 °C using a large Debye−Scherrer camera with an imaging-plate-type detector and imaging plate converting the Q (= $4\pi sin\theta/\lambda$) range from 0.5 to 20 Å^{-1}. The incident beam was monochromated at λ = 0.35314 Å. The correction of the data for Compton scattering, multiplicative contributions, and Fourier transformation were performed with PDFgetX3. A Gauss window ($\exp[-BQ^2]$, B = 0.015) was applied before converting the structure functions into PDFs to suppress truncations errors. Reduced pair distribution function $G(r)$ is defined as follow;

$$G(r) = 4\pi r\rho_0\{g(r) - 1\},$$

where ρ_0 is the average number density and $g(r)$ is the pair distribution function. $G(r)$ is directly obtained from the Fourier transformation of $S(Q)$, and the value of atomic number density is not necessary in $G(r)$.

X-ray adsorption fine structure analysis: The X-ray absorption spectra (XAS) of the Mn^{2+} of MnTz were collected at the beamline BL5S1 at Aichi Synchrotron Radiation Center. The powder samples were mixed with boron nitride with a given amount and ground for 10 minutes and pressed at 1000 kgN for 3 minutes by a standard 10 mm die under Ar atmosphere. XASs in the energy region of the Mn K-edge were measured in transmission mode with a double-crystal monochromator and ion chambers and processed using the IFEFFIT library. Fourier transformation was k^3-weighted in the k range from 3 to 12 Å^{-1}.

$$\chi(k) = S_0^{\,2}\sum\frac{N_j f_j(k) exp[-2k^2\sigma_j^{\,2}]}{kr_j^{\,2}}\sin[2k_j r_j + \delta(k)]$$

where r is distance from the target to neighboring atom, N is coordination number of the neighboring atom, and σ^2 is Debye-Waller factor. The photoelectron wavenumber k is given as $k = \sqrt{2m(E - E_0)/\hbar^2}$, $f(k)$ is the scattering amplitude, and $\delta(k)$ is the phase shift. S_0, amplitude reduction factor, was empirically determined from EXAFS of MnTz.

Thermal property measurements: Thermogravimetric analysis (TGA) was performed using a Rigaku Thermo plus TG 8120 apparatus in the temperature range between 25 and 500 °C with Ar or N_2 gas flow (50-60 mL min^{-1}) and at the heating rate of 10 °C min^{-1} inside Ar or N_2-filled glove box. TGA combined with mass spectrometry were performed on a Rigaku Thermo plus EVO II equipped with ThermoMass Photo/S by using electron impact ionization method. The measurement was performed from 25 to 500 °C with heating rate of 10 °C min^{-1} under a flow of Helium. Differential scanning calorimetry (DSC) was carried out with a Hitachi DSC7200 at the heating rate of 10 °C min^{-1}. Sample preparations for DSC were conducted under Ar.

Solid-state NMR: Solid-state NMR experiments were performed on JNM-ECZ600R spectrometer (JEOL RESONANCE Inc., Japan) at 14.01 T with a ^{1}H resonance frequency of 599.7 MHz, equipped with a 1.0 mm double resonance MAS probe (JEOL RESONANCE Inc, Japan). 1D ^{1}H and ^{31}P/^{113}Cd spectra were measured by echo pulse sequence and cross polarization magic angle spinning (CP-MAS) sequence, respectively. All 2D HETCOR spectra were measured by ^{1}H-detected ^{1}H/X cross polarization heteronuclear single quantum coherence (CP-HSQC) sequence at a MAS rate of 70 kHz.(Nishiyama, Y.; Kobayashi, T.; Malon, M.; Singappuli-Arachchige, D.; Slowing, I. I.; Pruski, M., Studies of minute quantities of natural abundance molecules using 2D heteronuclear correlation spectroscopy under 100 kHz MAS. *Solid State Nuclear Magnetic Resonance*, **2015**, 66–67, 56-61.) The 2D ^{1}H DQ/^{1}H SQ were acquired by BaBa-xy16 sequence (K. Saalwächter, F. Lange, K. Matyjaszewski, C.-F. Huang, R. Graf, *Journal of Magnetic Resonance*, **2011**, 212, 204-215.) All spectra were processed with the Delta software (JEOL RESONANCE Inc., Japan).

Conductivity measurement: AC impedance analysis was performed on powders of each samples without modification. The powders (ca. 25-30 mg) were pressed at 500 kgN for 3 minutes by a standard 5 mm die and sandwiched between two gold electrodes under Ar atmosphere. Measurements were performed using an impedance and gain-phase analyzer (Solartron SI 1260 Impedance/Gain-Phase analyzer) over frequency range 1 Hz -1 MHz with an input voltage amplitude of 30 mV, and temperature range is 30 to 150 °C and the heating rate is 1.3 °C min^{-1}. Measurement cell was filled with Ar at atmospheric pressure before recording the measurements. ZView software was used to fit impedance data sets by means of an equivalent circuit simulation to obtain the resistance values.

Table S1. Parameters of crystal structures and bond lengths (Å) of metal(II) and nitrogen from 1,2,4-triazole of [M^{2+}(1,2,4-triazole)$_2$(H_2PO_4)$_2$] (MTz, M = Cr, Mn, Fe, Co).

Compound	**CrTz**	**MnTz**	**FeTz**	**CoTz**
CCDC deposit number	1830937	1830938	1830939	1830940
Formula	$C_4H_{10}N_6O_8P_2Cr_1$	$C_4H_{10}N_6O_8P_2Mn_1$	$C_4H_{10}N_6O_8P_2Fe_1$	$C_4H_{10}N_6O_8P_2Co_1$
MW (g mol^{-1})	384.12	387.06	387.97	391.05
Temperature (K)	213	173	213	223
Wavelength (Å)	0.71075	0.71075	0.71075	0.71075
Theta range (°)	3.1448-27.1454	3.1465-27.4855	3.1782-27.4739	3.2162-27.4623
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$	*Pbcn*	*Pbcn*	*Pbcn*
a **(Å)**	15.303(3)	8.708(2)	8.603(2)	8.477(3)
b **(Å)**	8.7095(19)	9.681(3)	9.609(3)	9.531(3)
c **(Å)**	9.695(2)	15.573(4)	15.328(5)	15.479(5)
β (°)	91.626(5)	90	90	90
V (Å^3)	1291.6(5)	1312.8(6)	1267.1(6)	1250.6(7)
Z	4	8	8	8
ρ (g cm^{-3})	1.975	1.958	2.034	2.077
μ (mm^{-1})	1.186	1.301	1.496	1.682
Number of collected/independent reflection	9795/2507	9788/1497	9440/1451	8989/1421
R_1, wR_2 [I > 2σ(I)]	0.0479, 0.1245	0.0326, 0.0790	0.0377, 0.0785	0.0256, 0.0669
R_1, wR_2 (all data)	0.0522, 0.1297	0.0383, 0.0820	0.0467, 0.0827	0.0271, 0.0681
GOF	1.089	1.127	1.122	1.085
Metal-N from 1,2,4-triazole (Å)	2.138-2.343	2.224-2.283	2.181-2.190	2.129-2.167

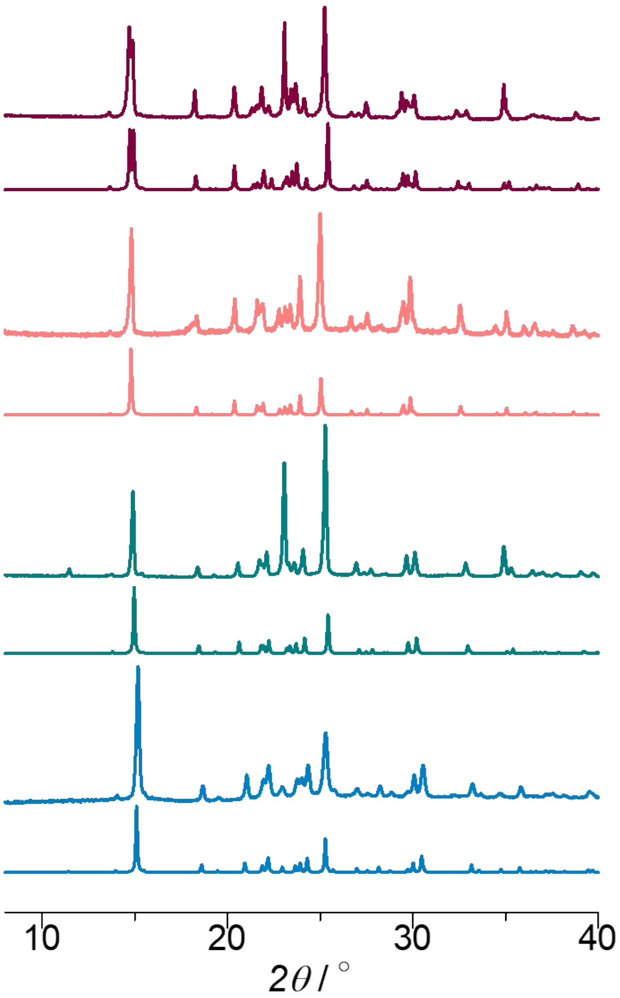

Figure S1. PXRD patterns of (upper) as-synthesized and (bottom) simulation from crystal structure for CrTz (dark red), MnTz (pink), FeTz (green), CoTz (blue)).

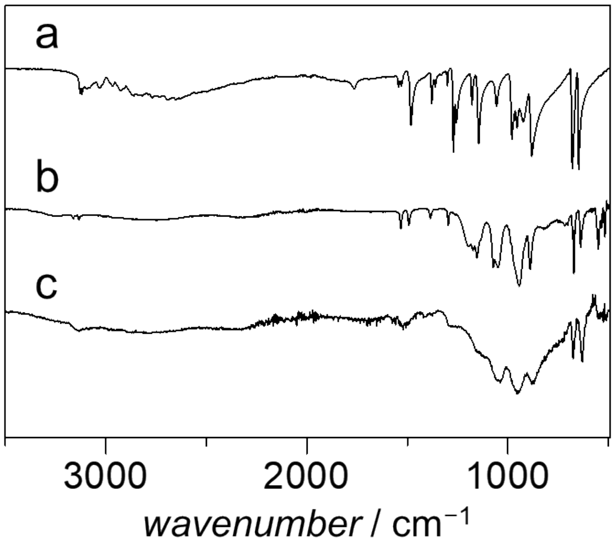

Figure S2. IR spectra of (a) 1,2,4-triazole (b) MnTz (c) MnTz' under Ar atmosphere.

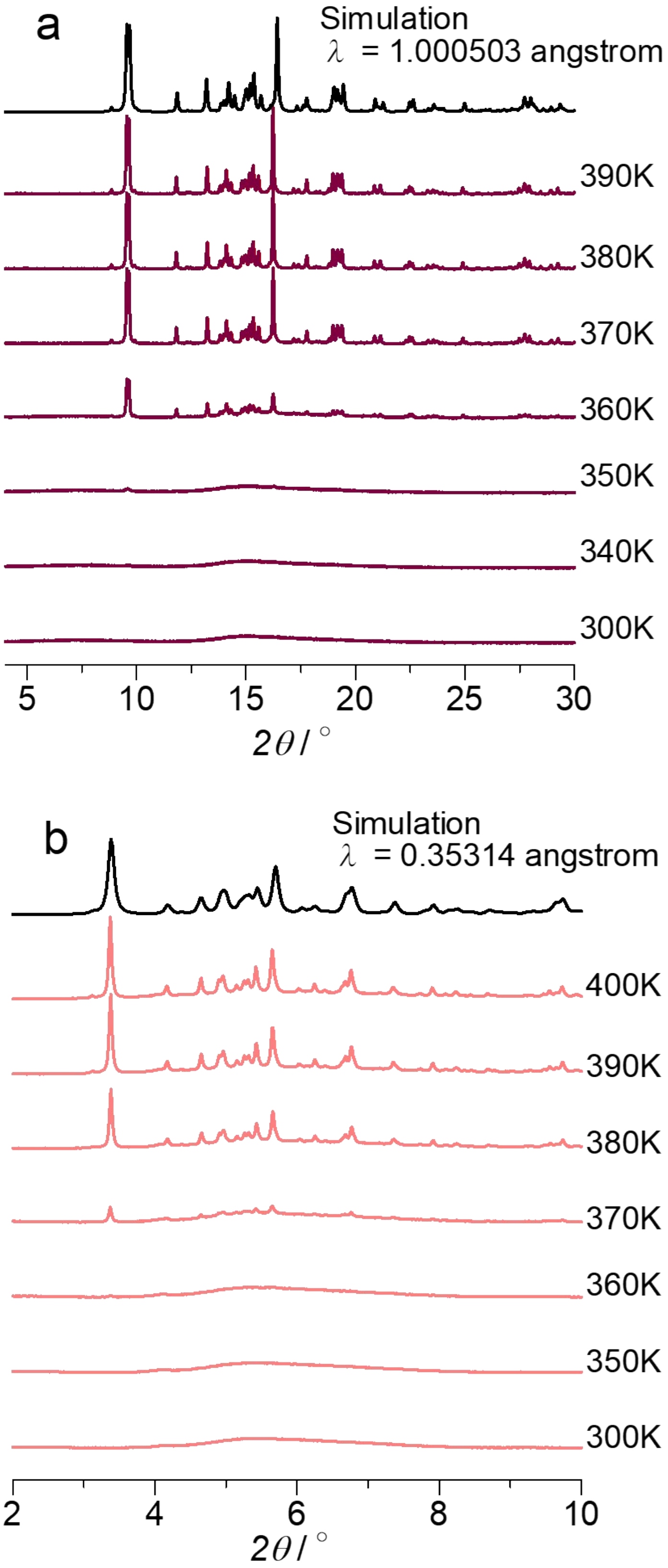

Figure S3. Temperature dependent PXRD patterns of (a) CrTz’ (b) MnTz’ to observe crystallization to CrTz’’ and MnTz’’.

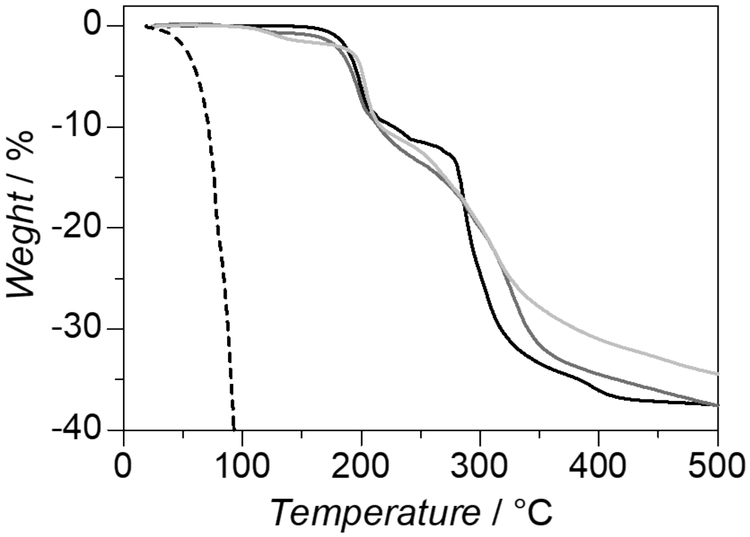

Figure S4. TGA profiles of (black) CdTz, (dark gray) CdTz', (light gray) CdTz'-0.10dabco, (dot) dabco. Heating rates are 10 °C min^{-1}.

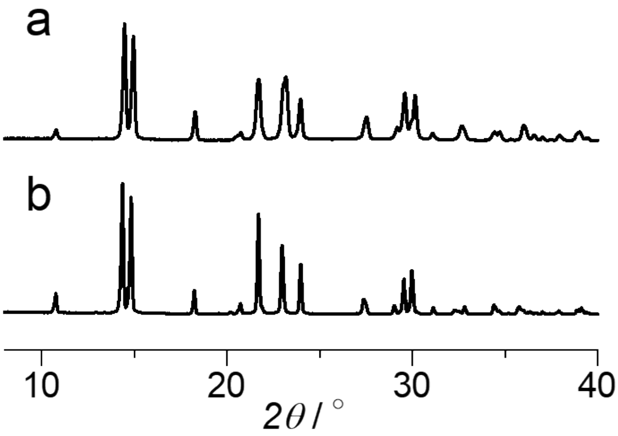

Figure S5. PXRD patterns of (a) CdTz''-0.10dabco and (b) CdTz.

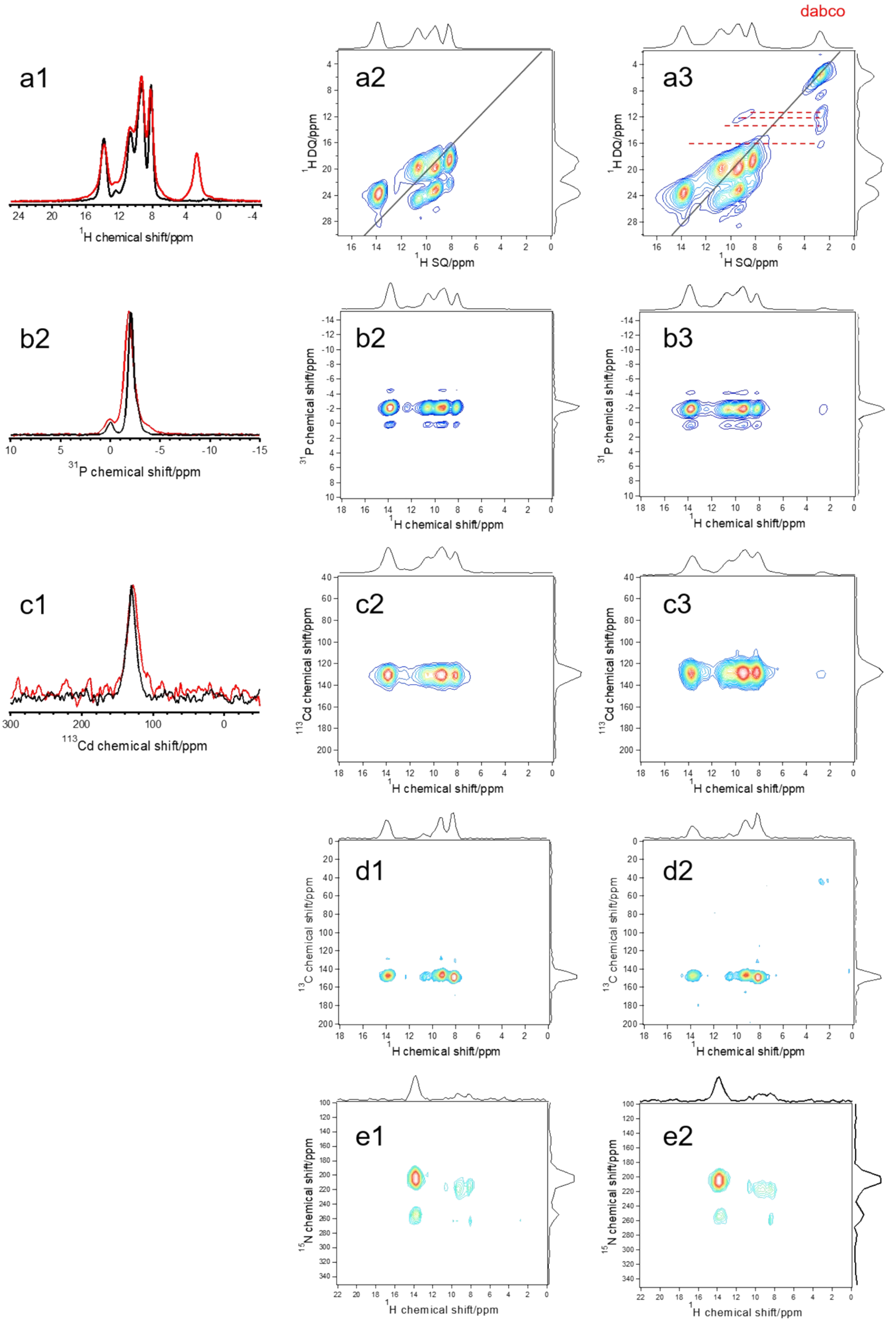

Figure S6. Solid-state NMR spectra. (a1) 1D ^{1}H echo spectra of (black) CdTz and (red) CdTz''-0.10dabco. 2D ^{1}H DQ/^{1}H SQ spectrum of (a2) CdTz and (a3) CdTz''-0.10dabco. (b1) 1D ^{31}P CPMAS spectra of (black) CdTz and (red) CdTz''-0.10dabco. 2D ^{1}H-^{31}P HETCOR spectrum of (b2) CdTz and (b3) CdTz''-0.10dabco. (c1) 1D

^{113}Cd CPMAS spectra of (black) CdTz and (red) CdTz''-0.10dabco. 2D ^{1}H-^{113}Cd HETCOR spectrum of (c2) CdTz and (c3) CdTz''-0.10dabco. 2D ^{1}H-^{13}C HETCOR spectrum of (d2) CdTz and (d3) CdTz''-0.10dabco. 2D ^{1}H-^{15}N HETCOR spectrum of (d2) CdTz and (d3) CdTz''-0.10dabco. All spectra were measured at a contact time of 10 ms.

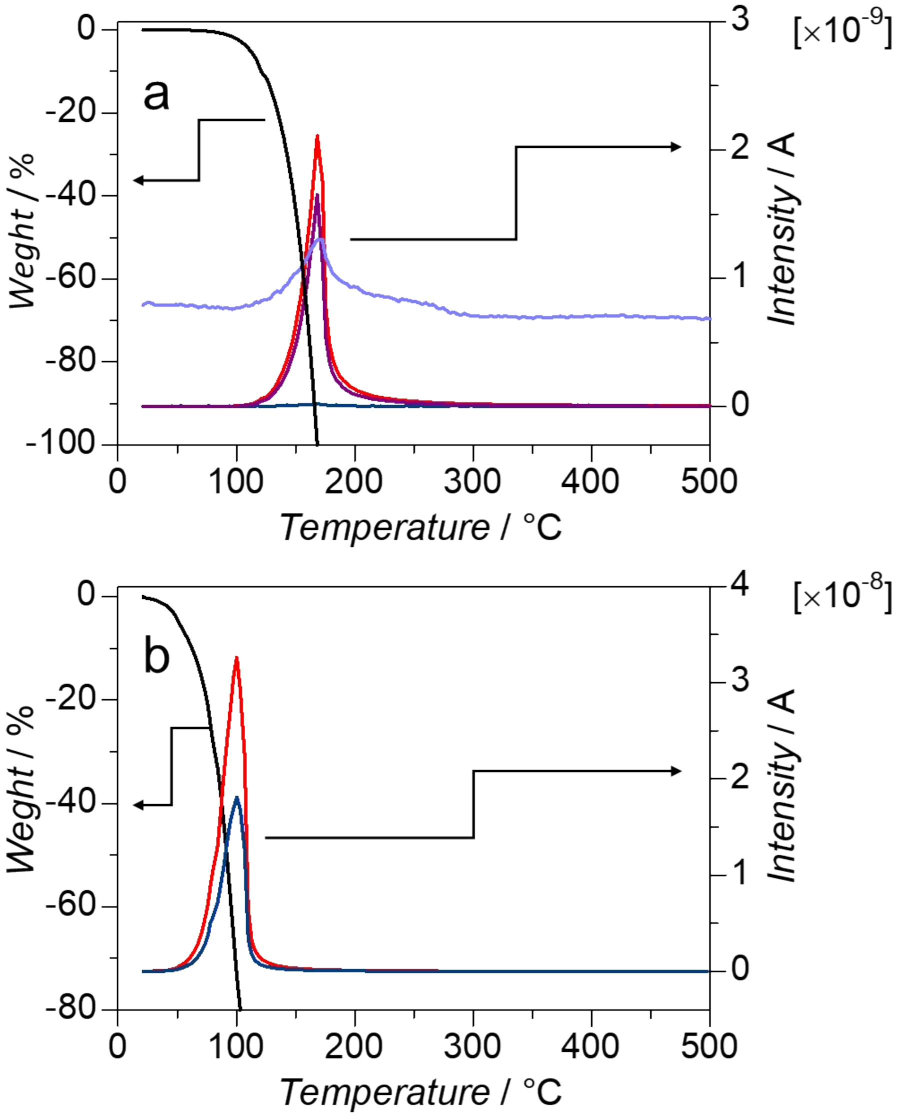

Figure S7. TGA-MS profiles of (a) 1,2,4-triazole (b) dabco. *mz* = 18 (pale purple), 42 (red), 55 (dark blue), 69 (dark purple).

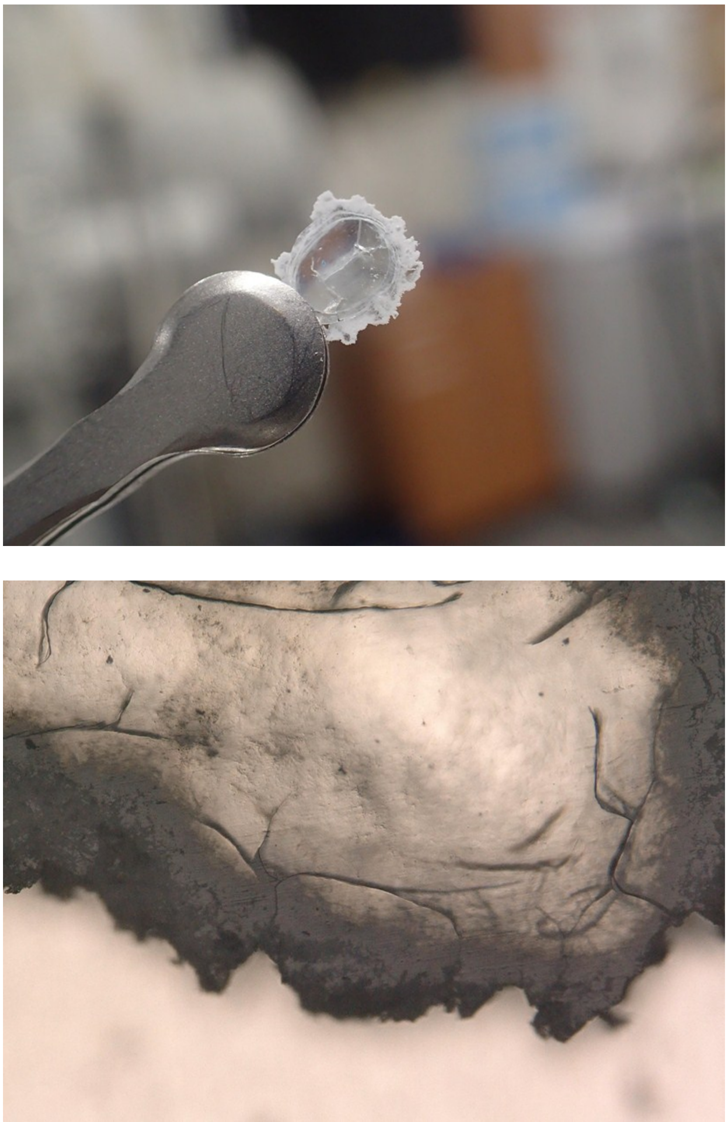

Figure S8. Photos of glass piece of CdTz’ by hot press machine under N_2 atmosphere.