Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Freeze-drying synthesis of an amorphous Zn^{2+} complex and its transformation to a 2-D coordination framework in the solid state

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Synthesis of compounds

All of the chemicals and solvents used in the syntheses were reagent-grade and used without further purification. Synthesis of powder samples of **1**: ZnO (81 mg, 1 mmol), 1,2,4-triazole (138 mg, 2 mmol), and phosphoric acid (85%, 136 μL, 2 mmol) were mixed into a mortar and grinded for 30 minutes. The obtained powder was washed with ethanol three times, and dried at 80 °C 15 h. Synthesis of **1′**: ZnO (81 mg, 1 mmol), 1,2,4-triazole (138 mg, 2 mmol), and phosphoric acid (85%, 136 μL, 2 mmol) were dissolved into distillated water (10 mL) and cooled rapidly with liquid nitrogen. The obtained frozen sample was freeze-dried under 10 Pa for 15 h by EYELA FD-1000.

Synchrotron X-ray analysis

The synchrotron X-ray absorption spectra and total scattering for 1 and **1′** were collected at Aichi Synchrotron Radiation Center on BL5S1 and BL5S2, respectively. X-ray absorption spectra of powder samples were recorded in transmission mode under ambient conditions, using a Si(111) double crystal monochrometer. The phonon energy was calibrated with the pre-edge peak observed in Zn K-edge XANES spectrum of Zn foil. The data were processed with IFEFFIT.[1] Fourier transformation was k^3-weighted in the k range from 3.0 to 13.0 $Å^{-1}$. The X-ray total scattering were collected at $\lambda = 0.614$ Å with a large Debye-Scherrer camera and imaging plate converting the Q range from 0.3 to 15.6 $Å^{-1}$. The correction of the data for Compton scattering, multiplicative contributions, and Fourier transformation were performed with PDFgetX3.[2] A Gauss window ($\exp[-BQ^2]$, $B = 0.009$) 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 an average number density and $g(r)$ is a pair distribution function. $G(r)$ is directly obtained from the Fourier transform of S(Q), and a value of atomic number density is not necessary in $G(r)$. We employed $G(r)$ rather than $g(r)$ to investigate the structural ordering range of 1’ by comparing with that of 1 because the dropping-off of amplitudes in $G(r)$ means the structural disorder and the structural coherence.

Other physical measurements

Thermogravimetry analysis (TGA) was obtained using a Rigaku TG8120 under flowing nitrogen with 10 K min^{-1} ramp rate. Differential scanning calorimetry (DSC) was carried out with a Mettler Toledo DSC822e/200 at the heating rate of 10 K min^{-1}. Variable-temperature powder X-ray diffraction (PXRD) data were collected on a Rigaku RINT 2200 Ultima diffractometer with CuKα radiation. SEM observations were performed with a JEOL Model JSM-6700F SEM system operating at 10.0 kV. Solid-state ^{31}P and ^{13}C cross polarization magic angle spinning nuclear magnetic resonance spectra were recorded on a Bruker ADVANCE 400MHz spectrometer, The spinning rate for cross polarization magic angle spinning spectra was 6 kHz for ^{31}P and ^{13}C. The profile of ^{13}C-NMR was fitted with Lorentzian as follows;

$$f(\mathrm{x}) = 2ab/\pi\{(x-x_c)^2+b^2\}$$

where a is amplitude, b is half width at half maximum, and x_c is maximum position. The fitting results for **1′** were shown in Figure S4 and Table S1.

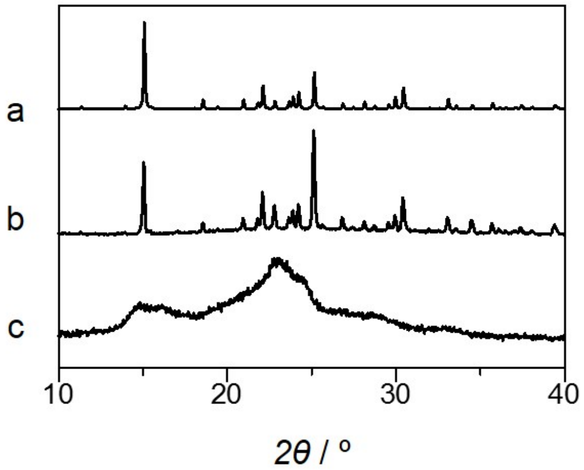

Figure S1. PXRD patterns of (a) simulated pattern of **1**, (b) **1′** after applied pressure of 2 MPa, and (c) as-synthesized **1′**.

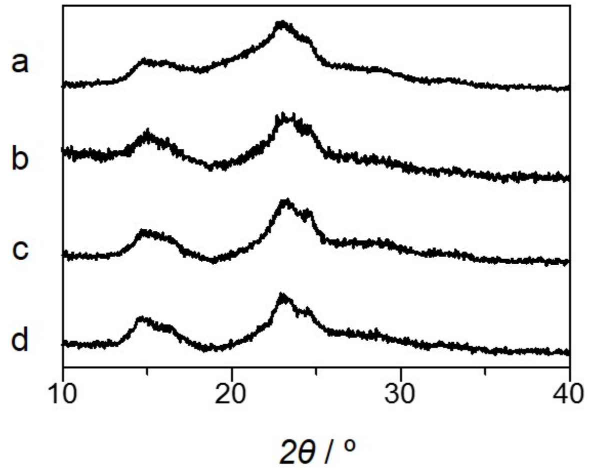

Figure S2. PXRD patterns of **1′** (a) as-synthesized, and kept under ambient condition (b) after 2 days, (c) after 3 days, and (d) six weeks.

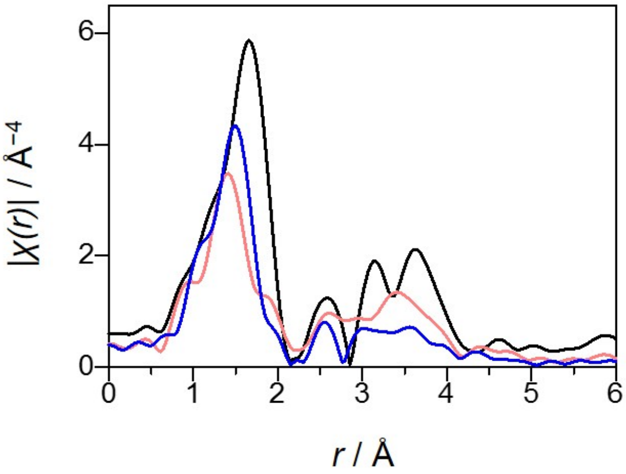

Figure S3. FT-EXAFS spectra of **1** (black), **1′** (pink), and melt-quenched glass state (blue) at 25 °C.

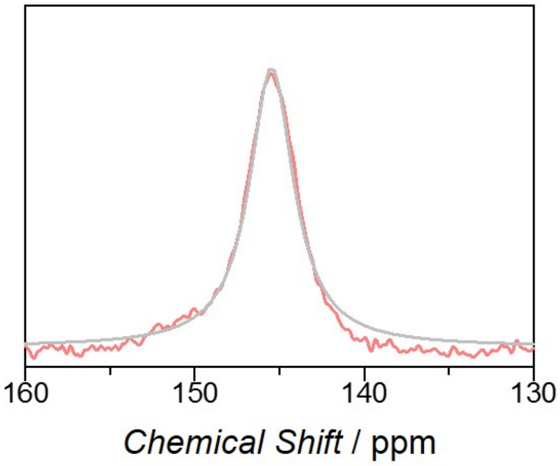

Figure S4. Solid-state ^{13}C-NMR spectra for **1′** (pink) and the fitted curve (grey).

Table S1. Results of fitting the ^{13}C-NMR spectrum for **1′** with one Lorentzian.

parameter	value	Standard error / %
a	6.879×10^6	0.3287
b	3.150	0.4676
x_c	145.5	0.00345

References

1. B. Ravel and M. Newville, *J. Synchrotron Radiat.*, 2005, **12**, 537-541.
2. P. Juhás, T. Davis, C. L. Farrow and S. J. L. Billinge, *J. Appl. Crystallogr.*, 2013, **46**, 560-566.