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. 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. 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 $\rho_0$ 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;

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

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 I’ (pink) and the fitted curve (grey).

Table S1. Results of fitting the $^{13}$C-NMR spectrum for I’ with one Lorentzian.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
<th>Standard error / %</th>
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<tbody>
<tr>
<td>$a$</td>
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<td>$b$</td>
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<td>$x_c$</td>
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References