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Supporting information for

Glass formation via structural fragmentation of a 2D coordination network

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Materials. All reagents and chemicals were obtained from commercial sources, of reagent grade, and used without further purification. The CP, $[Zn(H_2PO_4)_2(HTr)_2]_n$ (**1**) was prepared in a powder form using a previously described method.[1]

X-ray absorption spectra. The synchrotron x-ray absorption spectra (XAS) for **1** and **1′** were collected at the Aichi Synchrotron Radiation Center (Aichi SR) on BL5S1. XASs in the energy region of the Zn K-edge were measured in transmission mode with a Si(111) double-crystal monochromator and ion chambers and processed using the IFEFFIT library.[2] Fourier transformation was k3-weighted in the k range from 3.0 to 12.0 Å^{-1}. The RDF of **1′** was fitted by a model in which the zinc ions are surrounded by four oxygen atoms (Fig. S1). The following equation was used to calculate and fit RFD of **1′**:

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

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 **1** (crystalline state) as 1.0704. EXAFS spectrum of **1′** was fitted in r range from 1.0 to 2.0 Å. The final values of these parameters are summarized in Table S1.

X-ray total scattering. X-ray total scattering measurements were performed using powder samples of **1** and **1′** that were loaded in 1 mm quartz capillaries and mounted on a PANalytical Empyrean diffractometer equipped with a Ag X-ray tube (λ = 0.56086 Å). These data were corrected for background, Compton, and multiple scattering and beam attenuation by the sample container using the GudrunX package.[3] The normalized structure factor $F(Q)$ was converted to the PDF in the form of the $D(r)$ function as defined by Keen.[4] The measured PDF of **1** was fitted on the basis of the crystal structure of **1** using the PDFGui program[5] to assign the correlation peaks of the PDF (Fig S2).

Reverse Monte Carlo model construction and refinement. Starting models for RMC refinement was constructed by using the Amorphous Cell module implemented in Accelrys Materials Studio 6.0.[6] Fifty molecules of $[Zn(H_2PO_4)_2(HTr)_2]$ were placed in a 25.1281 × 25.1281 × 25.1281 Å^3 cubic cell with $P1$ symmetry, and relaxed for 50 ps as an NVT ensemble via MD simulations using the Forcite module with Universal force field (UFF).[7] Using the 2 × 2 × 2 supercell of the resulting atomic configuration, the program RMCProfile[8] was then used to fit calculated $D(r)$ and $F(Q)$ intensities simultaneously to the experimentally observed patterns by randomly moving atoms in the amorphous cell. Potentials-based bond distance and angle restraints were implemented in order to preserve the tetrahedral arrangements around zinc and phosphorus atoms and the connectivity of the 1,2,4-trialzole rings. We used Morse potentials and harmonic cosine potentials implemented in RMCProfile for bond and angle restraints as follows, respectively;

$$E_B = D[1 - exp(- \alpha(r - r_0))]^2$$

$$\mathrm{E}_A = \frac{1}{2}\mathrm{K}\left(\cos\theta - \cos\theta_0\right)^2$$

where r_0 is the equilibrium bond distance, θ_0 is the equilibrium angle, and D and K are the potential depths. Following the MM3 molecular mechanics force field model,[9] α was set as 2.55 Å^{-1} for all atom pairs. The values of parameters for bond and angle restraints are listed in Table S2. We also used closest-approach constraints for all atom pairs. The refined structure is shown in Fig. S3.

Differential scanning calorimetry. The differential scanning calorimetry (DSC) was carried out with a DSC6220 (SII Nano Technology Inc.) at the heating rate of 10 K min^{-1} with Pt sample pans. The glass transition temperature (T_g) and the value of $\Delta C_p(T_g)$ were determined by using the software Muse Standard Analysis (version 6.2; SII Nano Technology Inc.). The heat capacities of **1** and **1′** were calculated on a reference of a DSC data of sapphire measured under the identical condition.

Density functional theory calculations. We performed density functional theory (DFT) calculations to understand the energetics of **1** and **1′**. As a finite model structure for **1**, we adopted a octahedral complex composed of one zinc ion, four equatorial 1,2,4-triazole ligands, and two axial phosphate ligands. All calculations were carried out with Gaussian 09 program.[10] Geometry optimizations and vibrational frequency analyses were performed with M06 functional.[11] For the zinc ions, Stuttgart-Dresden-Bonn (SDD) group basis set are applied, and the core electrons were replaced with SDD effective core potential.[12] 6-311+G(d) was employed for the anionic oxygen atoms that coordinate to the zinc ions, and 6-311G(d, p) was employed for the other atoms. The bond distances in optimized model structures for **1** and **1′** are well accorded with those in the crystal structure of **1** and the RMC structure of **1′**, respectively (Fig S4).

We evaluated the Gibbs free energies for the complex formation for **1** and **1′** on the basis of the reaction shown in Scheme S1. The free energies of the reactions were estimated at 298.15 K, 1 atm. The grand partition functions of these complexes were determined by vibrational frequency analyses, and thus the enthalpies and entropies of the reactions were evaluated.

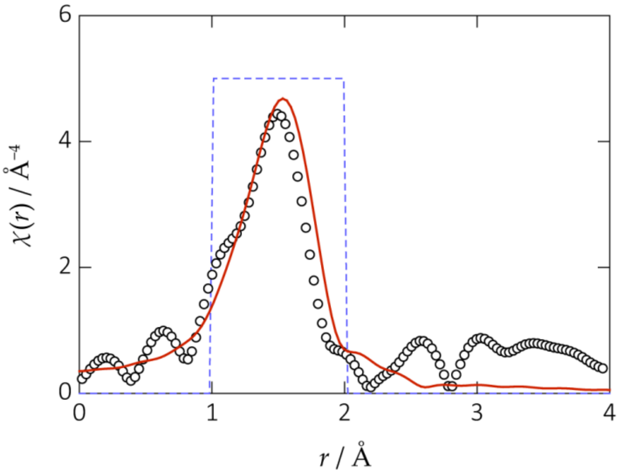

Fig. S1 RDF of **1′** (black circle) and fitting (red line). The fitting range is shown with blue dashed line.

Table S1 Parameters refined by fitting the EXAFS spectrum of **1′**.

Shell	N	r / Å	σ^2 / Å^2	E_0 / eV	R-factor
Zn–O	4.4(8)	2.02(2)	0.014(4)	3.8	0.0208

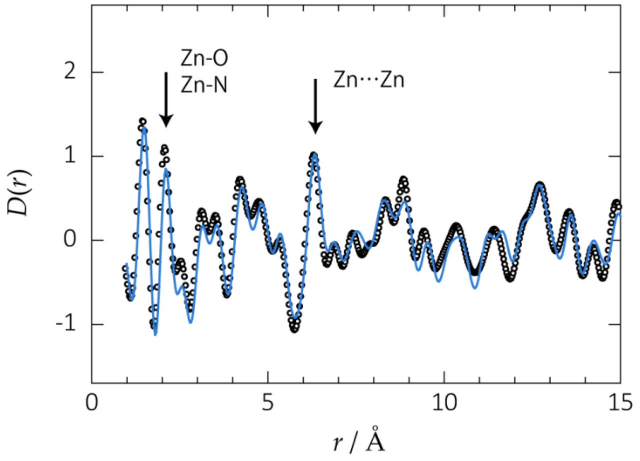

Fig. S2 Experimental PDF of **1** (black circles) and PDFGui fit (blue line). Some of the assigned peaks are indicated by arrows.

Table S2 Parameters for bond and angle restraints applied during RMC refinement.

	D / eV	r_0 / Å	K / eV	θ_0 / degree
O–H	3.731	0.95	–	–
N–H	3.129	1.03	–	–
C–H	2.472	1.10	–	–
P–O	2.736	1.54	–	–
N–C	4.319	1.34	–	–
N–N	4.319	1.34	–	–
Zn–O	1.00	2.00	–	–
Zn–N	1.00	2.00	–	–
O–P–O	–	–	11.235	109.5
N–C–N	–	–	4.993	113.0
C–N–C	–	–	4.993	105.0
C–N–N	–	–	4.993	106.0
O–Zn–O	–	–	5.00	109.5
O–Zn–N	–	–	5.00	109.5
N–Zn–N	–	–	5.00	109.5
H–O–P	–	–	8.738	109.5
H–N–C	–	–	8.364	125.5
H–N–N	–	–	11.235	125.5
H–C–N	–	–	8.364	123.0

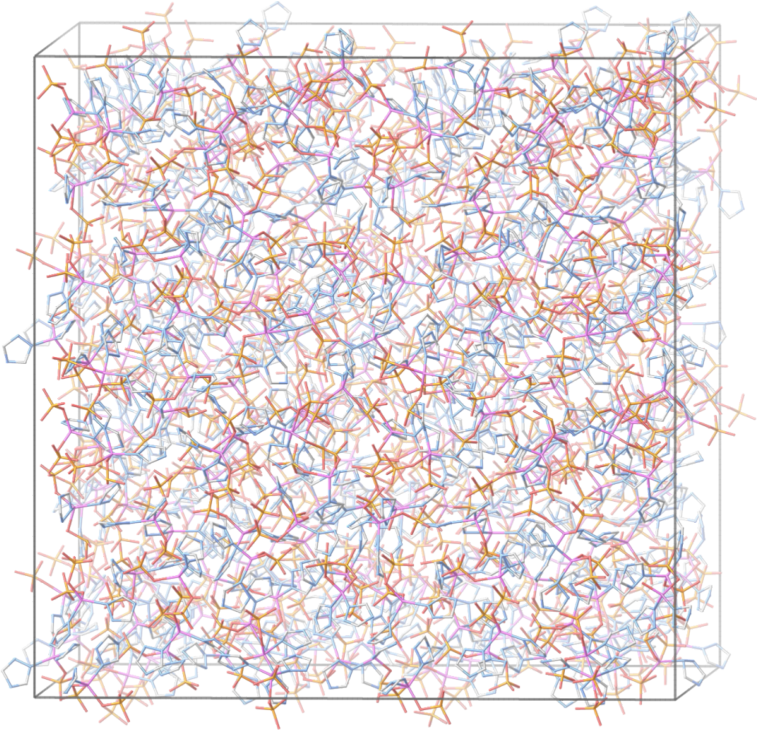

Fig. S3 Structure models for **1′**refined via RMC. H atoms have been omitted for clarity.

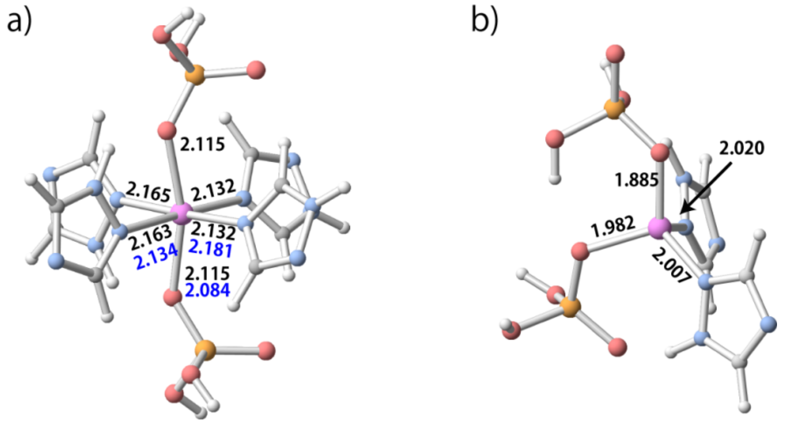

Fig. S4 Structure models for (a) **1′** and (b) **1** obtained by DFT calculations. The calculated (black) and experimental (blue) bond distances (Å) are shown.

Scheme 1 Complex formation reactions of (a) O_h and (b) T_d models for **1** and **1′** considered to estimate the free energy difference between **1** and **1′**.

(a) $Zn^{2+} + 2H_2PO_4^- + 4HTr \rightarrow [Zn(H_2PO_4)_2(HTr)_4]$ ($\Delta_rG(O_h) = -2616$ kJ mol^{-1})

(b) $Zn^{2+} + 2H_2PO_4^- + 2HTr \rightarrow [Zn(H_2PO_4)_2(HTr)_2]$ ($\Delta_rG(T_d) = -2562$ kJ mol^{-1})

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