Electronic Supplementary Information (ESI)

Formation of Zeolite-like Zinc 1,3,5-Benzenetriphosphonate Open-Frameworks by Topotactic Pillaring of Anionic Layers

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Experimental details:

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Selective cation exchange experiment.

Selectivity in adsorption of alkali metal cations on ZBP-NH_4 was evaluated using a mixture of standard nitrate solutions of Na^+, K^+, Rb^+, and Cs^+ cations for ICP measurement. All the standard solutions were purchased from Fulka, and all of the solutions were mixed and diluted, preparing a solution containing approximately 2 ppm for each element. In 20 mL of the mixed cation solution 47.3 mg of ZBP-NH_4 was dispersed, and stirred for 3 days at an ambient temperature. The initial concentration C_i of the solution, approximately 2 ppm for each element, and the final concentration C_f after adsorption of the cations on ZBP-NH_4 were measured using ICP-MS on an Agilent 7500c spectrometer. The distribution coefficient K_d was calculated according to the following equation.[1]

$$K_\mathrm{d}(\mathrm{mL\ g^{-1}}) = \frac{(C_\mathrm{i} - C_\mathrm{f})}{C_\mathrm{f}} \times \frac{V_\mathrm{solution}(\mathrm{mL})}{m_\mathrm{solid}(\mathrm{g})}$$

Powder X-ray crystal structure solutions and refinements.

High resolution powder X-ray diffraction data of ZBP-M (M: K, Rb, and Cs) and ZBP-NH_4 were collected on a transmission-geometry diffractometer with a Debye-Scherrer camera having imaging plate (IP) at the BL02B2 of SPring-8 (Hyogo, Japan) using powder samples loaded in 0.5 mm glass capillaries. All the diffraction patterns of ZBP-M phases were successfully indexed in orthorhombic unit cells without unindexed reflections by using NTREOR[2] implemented in EXPO2009 software[3] and were refined in the Le Bail method[4] in EXPO2009, confirming that all of them are single phases with orthorhombic unit cells. The similarity in the refined cell parameters suggested that these phases are isomorphous.

Details in model building and refinement in each compound are explained individually in the following sections. The models were refined to reach convergence in the Rietveld method using Rietan-FP.[5] The final crystallographic parameters are listed in Table 1 in the article, and the Rietveld plots are shown in Fig. S1-S4. The final structures were visualized using VESTA.[6] Effective window sizes are estimated based on atomic coordinates using an oxygen radius of 1.35 Å.

ZBP-K: The systematic absences (*hkl*: $h+k+l = 2n+1$) suggested a body-centered lattice. A comparison of the lattice parameter between ZBP-K and ZBP-TMA it was estimated that there were two ZBP layers stacking to the direction of the c-axis in a unit cell. Since no mirror planes perpendicular to a ZBP layer should not be allowed supposing preserved ZBP layers, and the systematic absences (*hk*0: $h, k = 2n+1$) was not observed, the possible candidates for the space group were tentatively limited to

*I*2*c*m, *Iba*m, *Ic*2m, and *Iba*2. Among these space groups only *Iba*2 gave a set of reasonable Zn, P, and several O positions that correspond to the topology of a ZBP layer by the direct method in EXPO2009. The missing atoms of the ZBP layer, mainly C and H atoms of the benzene ring, are modeled using Accelrys Materials Studio software. In the direct method another peak of high intensity was also found in the interlayer space. Although it was initially thought to be a potassium atom, further investigation revealed that it might be a zinc atom, because the refinement suggested that site needed more electrons than the assumed potassium atom and the site is tetrahedrally surrounded by phosphonate oxygen atoms with reasonable distances as Zn-O bonds. Therefore, the interlayer site was assigned to a zinc atom, and potassium and water positions were found in an electron density map generated by the difference Fourier synthesis. The water molecules were treated as a virtual atom assuming an atom scattering factor corresponding to H_2O. The Rietveld refinement was performed using the initial model in software Rietan-FP.[5] Split pseudo-Voigt profile function and 11th Legendre-polynomial background function were used in the refinement. Since considerable anisotropic broadening was observed probably owing to thin plate-like crystallites, the anisotropic broadening parameters assuming the anisotropic broadening axis as the *c*-axis were also refined to obtain better fitting result. Soft geometrical restraints for interatomic distances (Zn–O: 1.95 Å, P–O: 1.53 Å, P–C: 1.79 Å, C–C: 1.40 Å, C–H: 0.93 Å) and angles (tetrahedral O–Zn–O and O–P–O(C): 109.47°, Zn–O–P (2-coordinated O): 130°, Zn–O–Zn(P) (3-coordinated O): 120°, C–C–C(H): 120°) were applied throughout the refinement. To reduce the number of parameters and stabilize the refinement, the isotropic atomic displacement parameters for similar atoms were constrained to be the same. All positional parameters were refined to convergence with progressively less penalty parameter on the restraints. The R_{wp} value finally converged to 0.0078, though the resulting low R_{wp} value is owing to high background of the diffraction data. Although the framework topology can be modeled also in centrosymmetric space group *Ibam* at the highest symmetry, the refinement in *Ibam* did not reach comparably low R_{wp} to the result in *Iba*2. Therefore, it was concluded that *Iba*2 was more suitable.

ZBP-Rb: The extinction suggested that body-centered lattice is not plausible in spite of assumed similar topology to ZBP-K. In obtaining an initial structural model selection of an appropriate space group was not straightforward because there were too many plausible space groups in the primitive cell and unambiguous determination of the space group was difficult owing to overlapping reflections. Therefore, Le Bail fitting was automatically repeated with all the space groups up to orthorhombic with all the possible axis settings using space group search routine of FOX software[7] to find space groups giving best fitting results. By eliminating space groups in which ZBP layer cannot be topologically included or Z is less than 8 among space groups giving lowest GoF (or R_{wp}) values, primitive cells belonging to the maximal non-isomorphic subgroups of *Iba*m, the highest possible symmetry of framework of ZBP-K as above-mentioned, proved to remain as candidates. Therefore, these space groups P*bcn*, P*bcm*, and P*ccn* were examined. The atomic coordinates of the framework atoms were modeled from those of ZBP-K and rubidium cation and water oxygen atoms were found in electron density distribution map determined by the maximum entropy method (MEM)[8] using program PRIMA.[9] The further refinement was performed using Rietan-FP in a manner similar to ZBP-K. Among these candidates only P*ccn* resulted in a somewhat successful convergence with lower R_{wp} value. However, refinement assuming one Rb site at a similar position to the K site in ZBP-K still left considerable difference between the observed and calculated patterns, and an attempt to refine the site occupancies of Rb and water sites resulted in lowering of the Rb occupancy to *ca.* 70% and increasing of the occupancy of a water site more than 100% accompanied with lower R_{wp} value. Therefore, the second Rb site was introduced and the sum of the occupancies of the two Rb sites was constrained to 1. The site occupancies of water sites were also constrained to the site occupancy of the coordinating cation considering chemical validity. Finally the R_{wp} value converged to 0.0076 with a chemically feasible model.

ZBP-Cs: Similarly to ZBP-Rb the extinction suggested that body-centered lattice is not plausible and there were again difficulty in determining an appropriate space group. Therefore, almost the same procedure as ZBP-Rb was attempted and the space group search of FOX software was used to find candidates of the space group. Rietveld refinements were attempted using space groups P*bcn* and P*bcm*, which gave best Le Bail fitting results and belong to the maximal non-isomorphic subgroups of *Iba*m. The initial atomic coordinates of the framework were obtained by modeling based on those of ZBP-K and the cation and water positions were found in MEM-generated electron density distribution map using PRIMA. The structural model in P*bcn* resulted in better fit and it was again necessary to assume two cation sites to reach satisfactory convergence similarly to ZBP-Rb. The sum of the occupancies of the two Cs sites was constrained to 1 and the site occupancies of water sites were also constrained to the site occupancy of the coordinating cation considering chemical validity. Finally the R_{wp} value converged to 0.0115 with a chemically feasible model.

ZBP-NH$_4$: Since the XRD pattern closely resemble that of ZBP-K and the assumed extinction was the same as the case of ZBP-K, the atomic coordinates of the framework of ZBP-K were used as an initial model assuming I*bam*, the same space group as ZBP-K. The cation and water positions were found in MEM-generated electron density distribution map using PRIMA. Finally the R_{wp} value converged to 0.0075.

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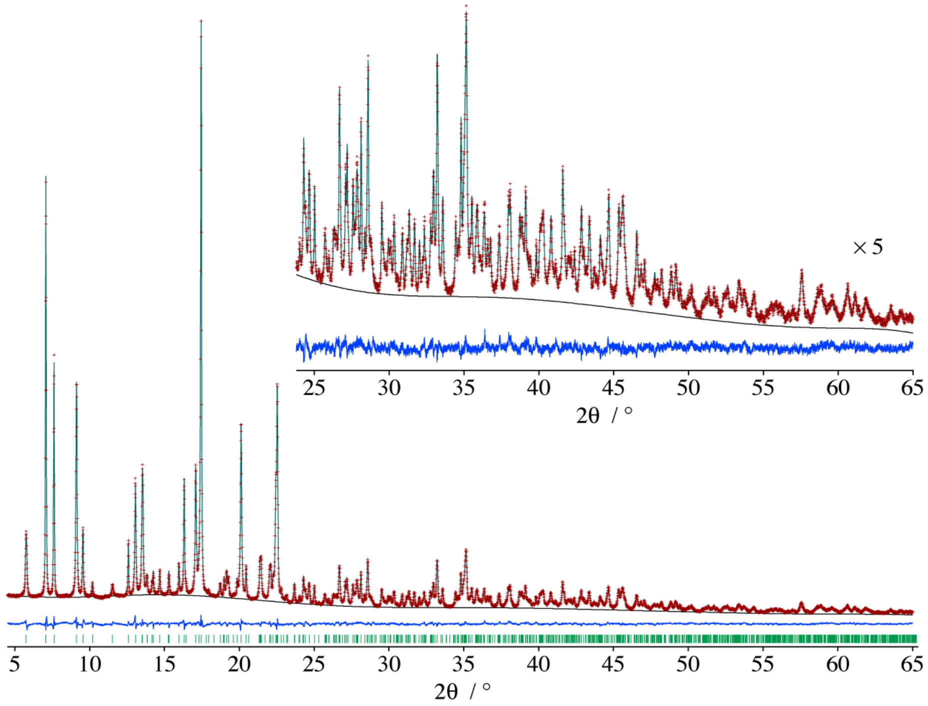

Fig. S1 Rietveld plot of ZBP-K. Observed (red dots), calculated (green line), and difference (blue line) plots with baseline (black line).

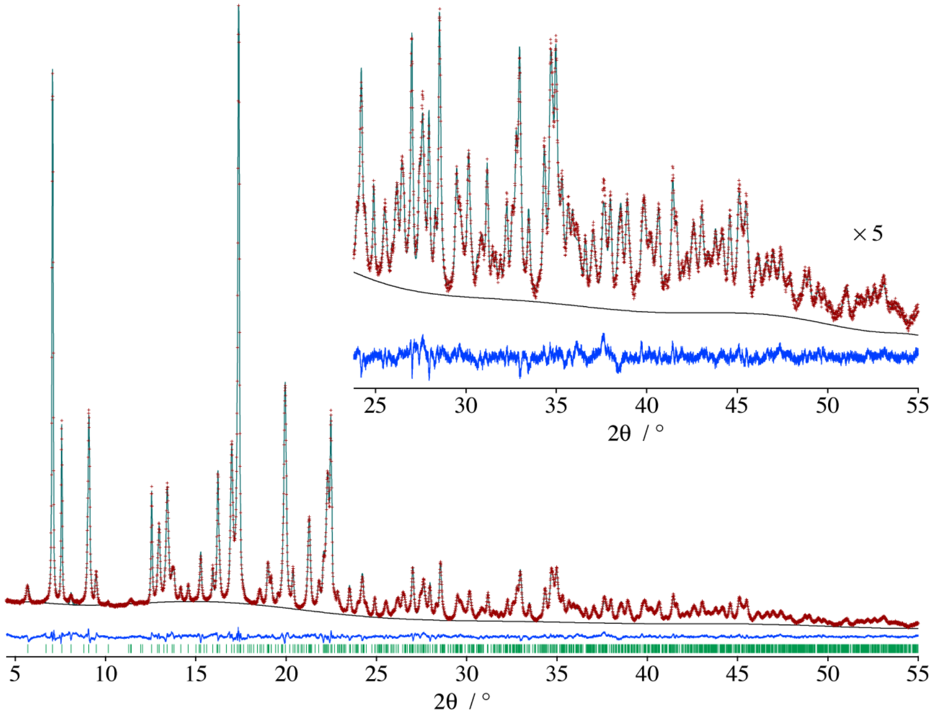

Fig. S2 Rietveld plot of ZBP-Rb. Observed (red dots), calculated (green line), and difference (blue line) plots with baseline (black line).

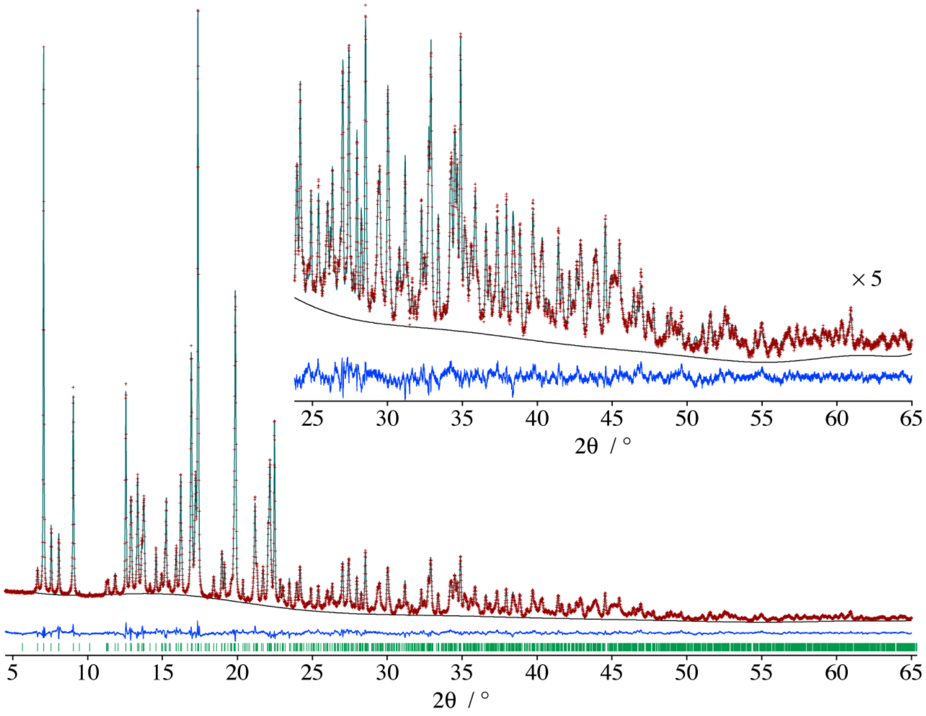

Fig. S3 Rietveld plot of ZBP-Cs. Observed (red dots), calculated (green line), and difference (blue line) plots with baseline (black line).

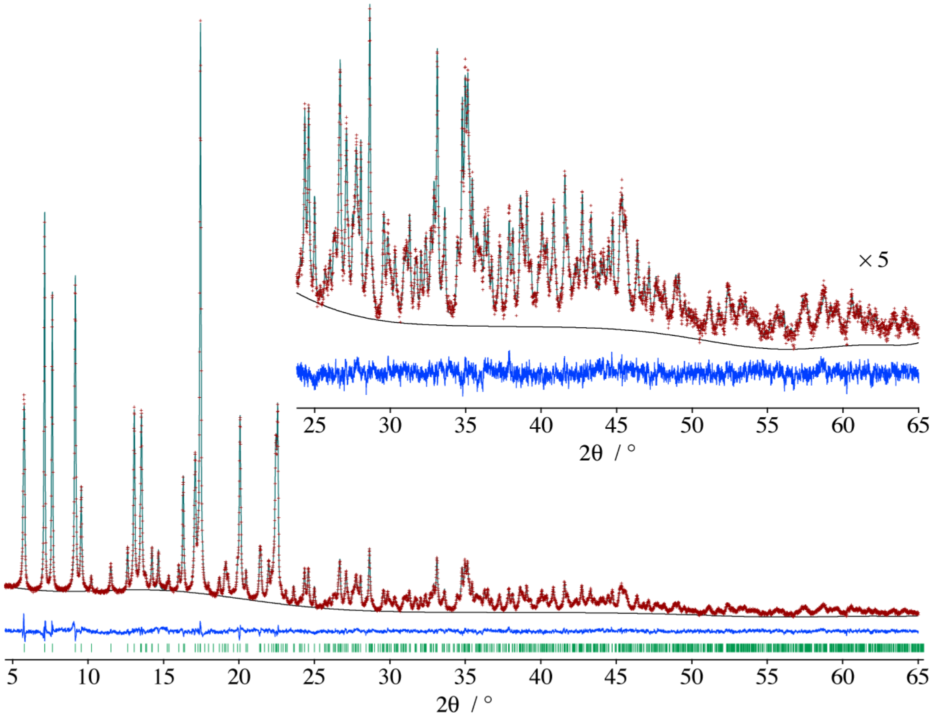

Fig. S4 Rietveld plot of ZBP-NH_4. Observed (red dots), calculated (green line), and difference (blue line) plots with baseline (black line).

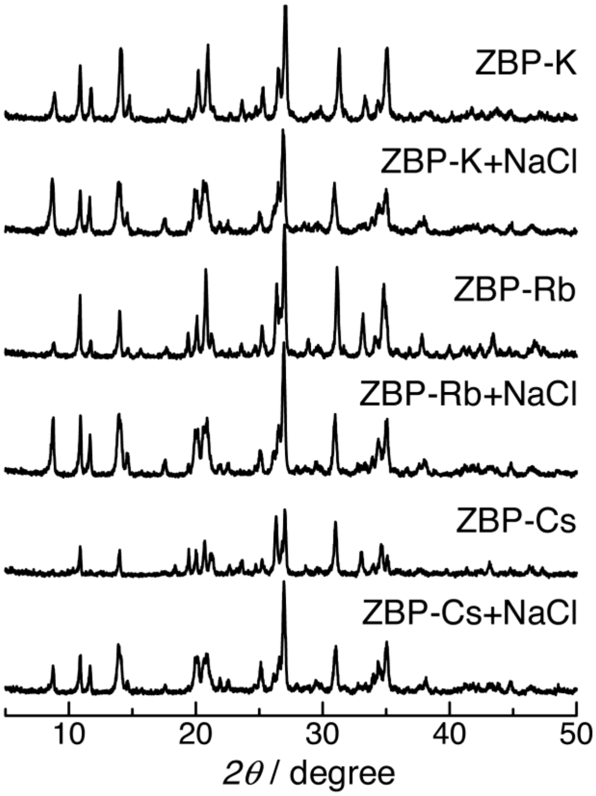

Fig. S5 XRD patterns of ZBP-K, ZBP-Rb, and ZBP-Cs reacted with an aqueous NaCl solution.

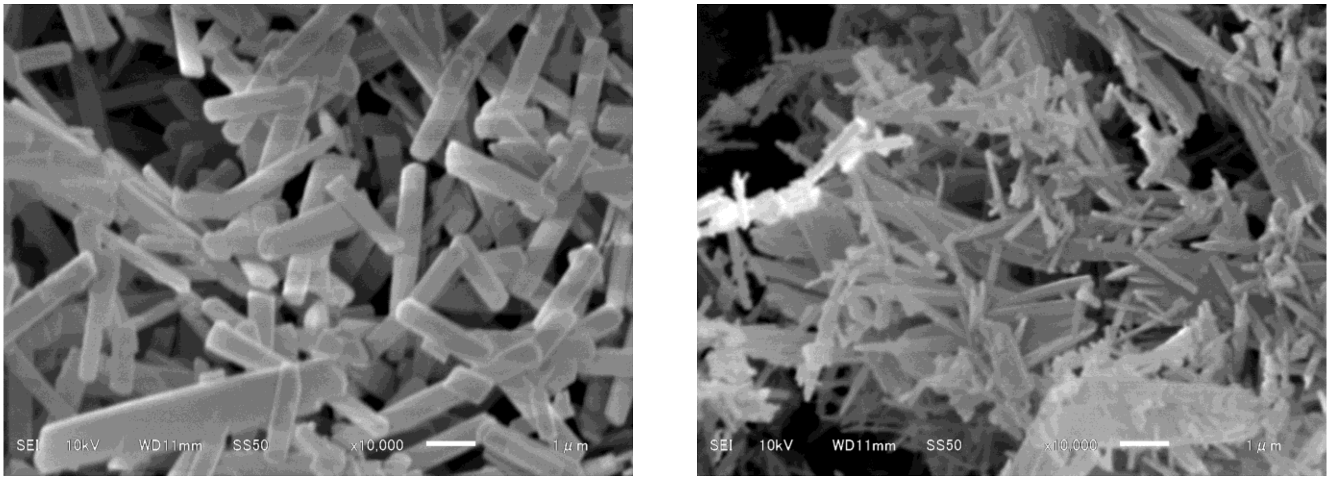

Fig. S6 SEM images of starting ZBP-bpy (left) and formed ZBP-K (right) by cation-exchange reaction.

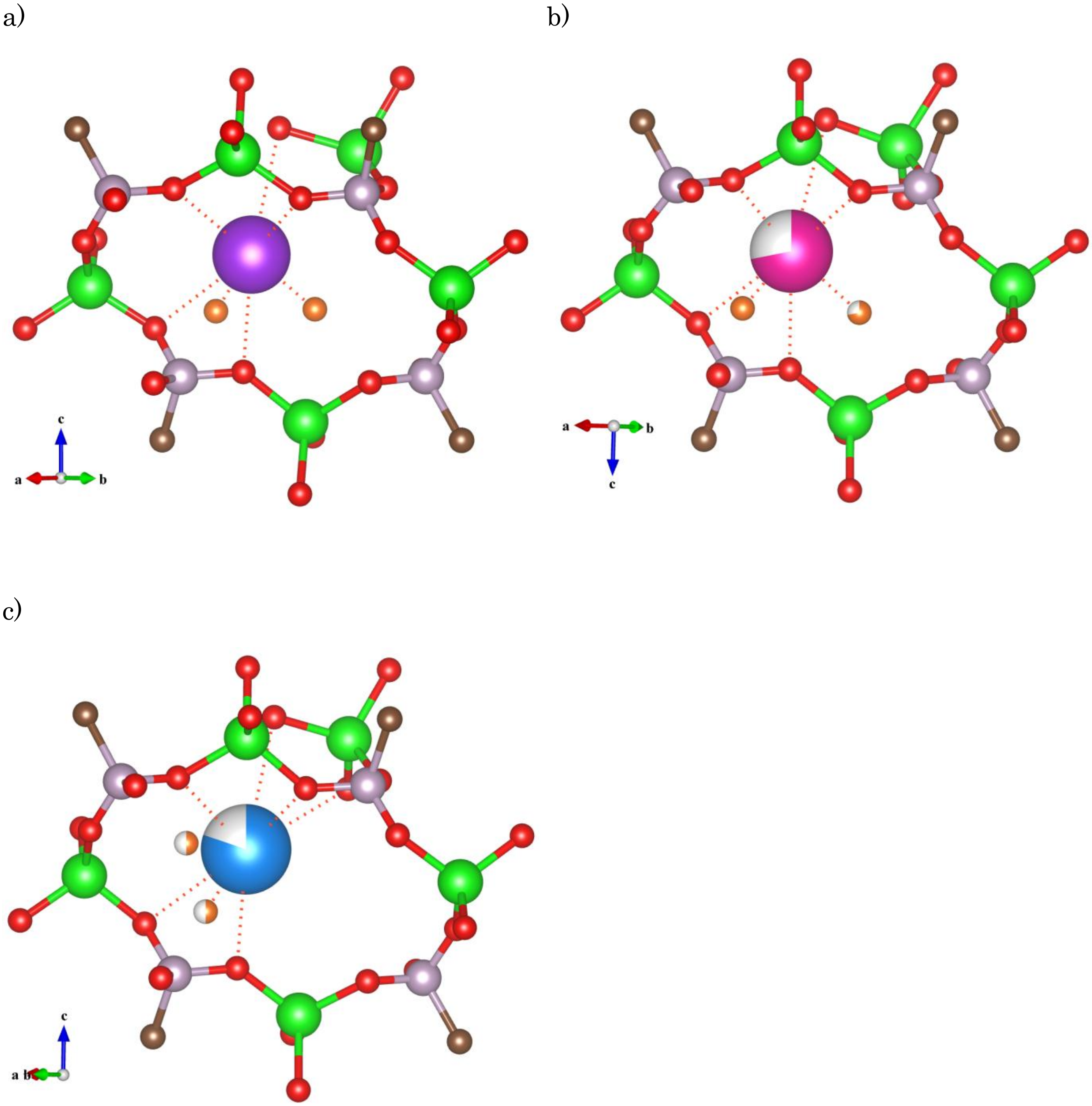

Fig. S7 The 8-membered ring and cation coordination in (a) ZBP-K, (b) ZBP-Rb, and (c) ZBP-Cs. Brown lines, and green, pale violet, violet, magenta, sky-blue, and orange spheres denote C–C bonds, and Zn, P, K, Rb, Cs, and O (water) atoms. In partly filled spheres meaning partly occupied sites, circle graphs express the occupancies of elements.

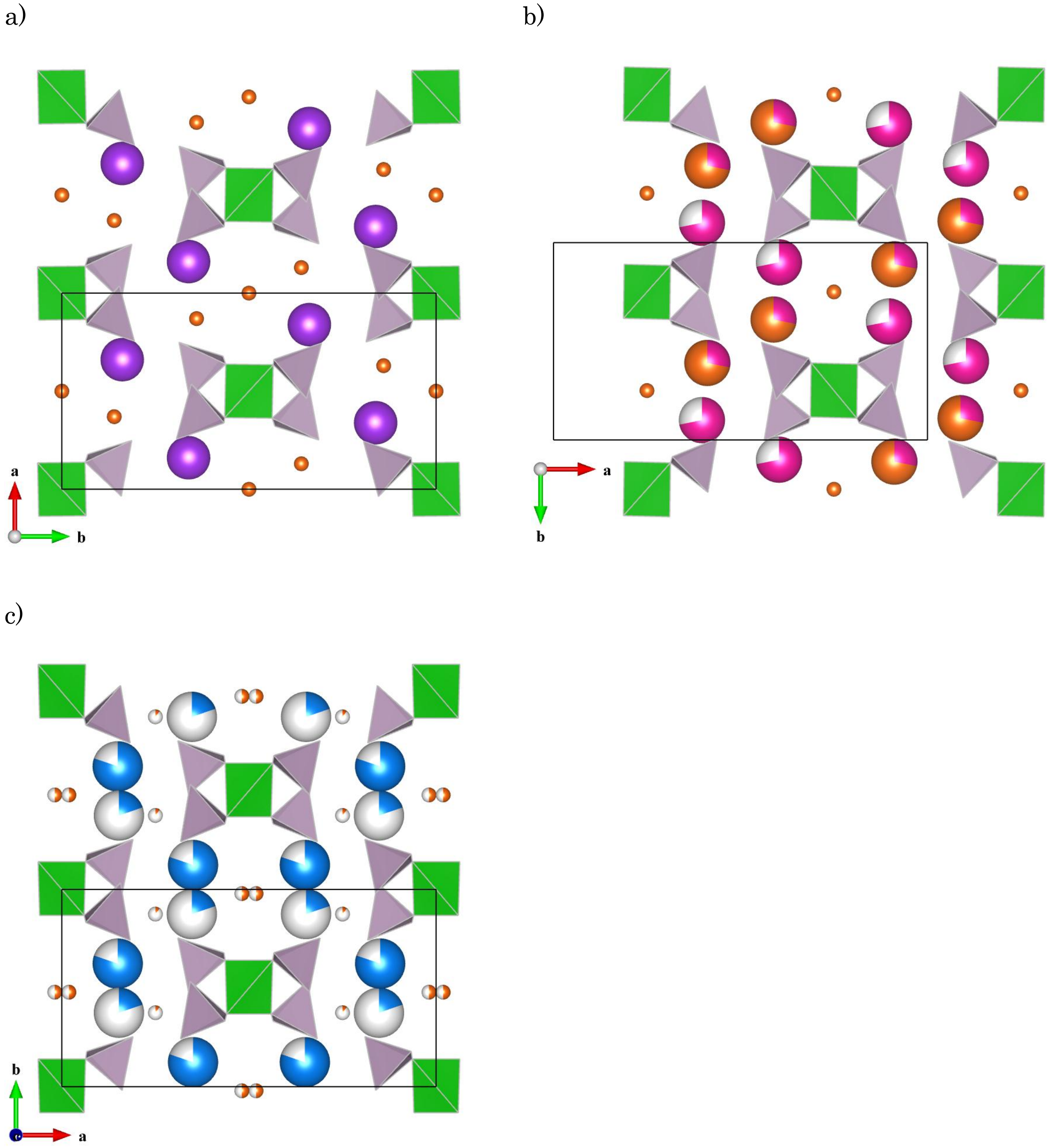

Fig. S8 Structure of the interlayer spaces along 8MR zigzag channels in (a) ZBP-K, (b) ZBP-Rb, and (c) ZBP-Cs. Green and pale violet tetrahedra, brown lines, and violet, magenta, sky-blue, and orange spheres denote ZnO_4 and PCO_3 units, C–C bonds, and K, Rb, Cs, and O (water) atoms. In partly filled spheres meaning partly occupied sites, circle graphs express the occupancies of elements.

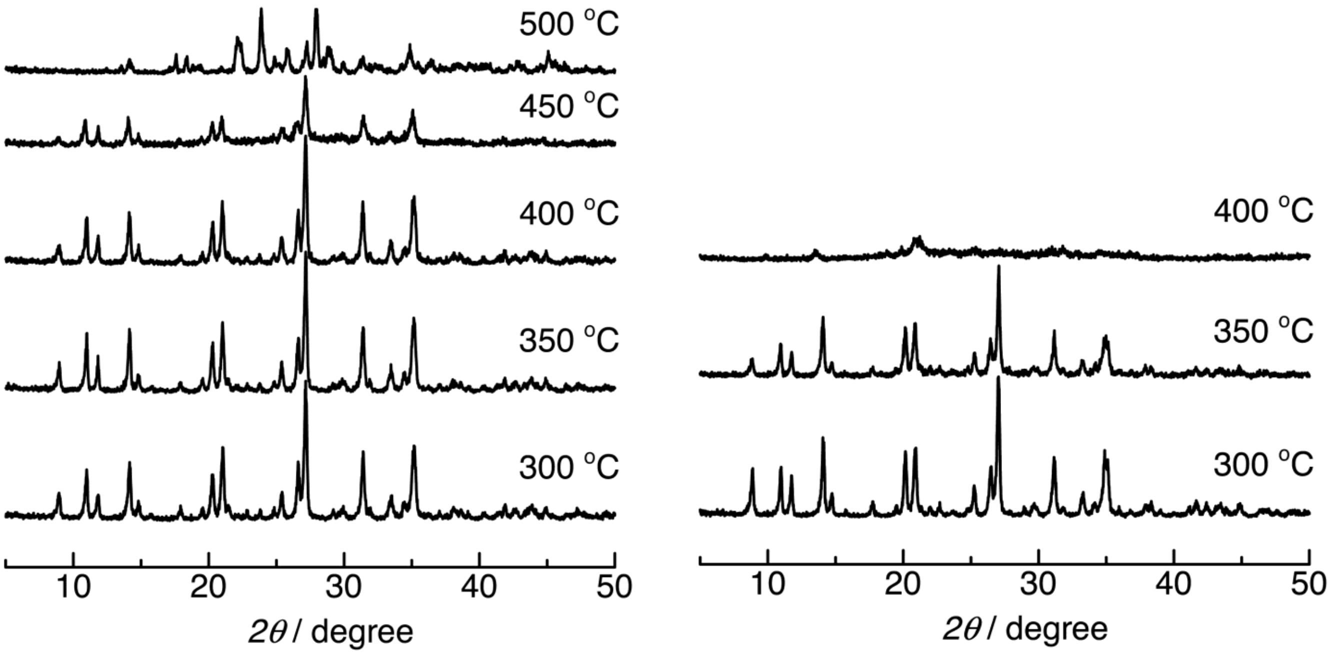

Fig. S9 XRD patterns of heat-treated ZBP-K (left) and ZBP-NH_4 (right).