

Supporting information

Polymorphism in Homochiral Zinc Phosphonates

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Experimental Section

Materials and methods. (S)– or (R)–(1–phenylethylamino)methylphosphonic acid (pempH₂) was prepared by reactions of (S)– or (R)–1–phenylethylamine, diethyl phosphite and paraformaldehyde, according to literature methods.¹ (S)– and (R)–1–phenylethyl-amine were purchased from Aldrich, and all the other starting materials were of reagent grade quality and were obtained from commercial sources without further purification. The elemental analyses were performed in a PE240C elemental analyzer. The infrared spectra were recorded on a VECTOR 22 spectrometer with pressed KBr pellets. The powder XRD patterns were recorded on a Shimadzu XD-3A X-ray diffractometer. CD spectra were measured on a JASCO J-720W spectrophotometer at room temperature. Approximate estimations of the second-order-nonlinear optical intensity were obtained by comparison of the results obtained from a powdered sample (80±150 mm diameter) in the form of a pellet (Kurtz powder test²) with that obtained for urea. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate the SHG signal. The backward-scattered SHG light was collected using a spherical concave mirror and passed through a filter that transmits only 532 nm radiation.

Preparation of 1: A mixture of ZnSO₄·7H₂O (0.1 mmol, 0.0282 g), NaCl (0.05 mmol, 0.0029 g) and *S*–pempH₂ (0.1 mmol, 0.0215 g) in 10 mL of H₂O, adjusted to pH 5.7 with 1 mol/L NaOH, was kept in a Teflon-lined autoclave at 140 °C for 5 days. After cooling to room temperature, colorless plate-like crystals of **1** were obtained. Yield: 31%. Anal.Calcd for C₁₈H₂₅ClN₂O₆P₂Zn₂ (**1**): C, 36.42; H, 4.24; N, 4.72%. Found: C, 36.33; H, 4.19; N, 4.62%. IR (KBr, cm⁻¹): 3429 (w), 3232 (w), 2981(w), 1603(w), 1456(w), 1441(w), 1272(w), 1236(m), 1199(w), 1136(s), 1095(s), 1014(s), 863(w), 761(m), 739(w), 701(m), 646(w), 577(m), 547(w), 495(w).

Preparation of 2: Compound **2** was obtained similarly except that *R*–pempH₂ was

used. Yield: 28%. Anal.Calcd for $C_{18}H_{25}ClN_2O_6P_2Zn_2$ (**2**): C, 36.42; H, 4.24; N, 4.72%. Found: C, 36.21; H, 4.33; N, 4.77%. IR (KBr, cm^{-1}): 3421 (w), 3231 (w), 2981(w), 1602(w), 1456(w), 1441(w), 1272(w), 1236(m), 1199(w), 1136(s), 1095(s), 1004(s), 862(w), 761(m), 739(w), 701(m), 636(w), 577(m), 547(w), 495(w).

Preparation of 3: A mixture of $ZnSO_4 \cdot 7H_2O$ (0.1 mmol, 0.0282 g), *S*-pempH₂ (0.1 mmol, 0.0215 g), NaCl (0.05 mmol, 0.0029 g) and 3-hydroxypiperidine (0.1 mmol, 0.0101 g) in 10 mL of H₂O, adjusted to pH 5.7 with 6 mol/L HCl, was kept in a Teflon-lined autoclave at 140°C for 5 days. After cooling to room temperature, colorless plate-like crystals of **3** were obtained. Yield: 51%. Anal.Calcd for $C_{18}H_{25}ClN_2O_6P_2Zn_2$: C, 36.42; H, 4.24; N, 4.72%. Found: C, 36.31; H, 4.30; N, 4.61%. IR (KBr, cm^{-1}): 3446 (w), 3213 (w), 3031(w), 2875(w), 2360(w), 1589(w), 1454(w), 1383(w), 1275(w), 1168(s), 1133(s), 1103(s), 1052(s), 1007(s), 814(w), 763(m), 739(w), 700(m), 634(w), 612(m), 572(w). Same compound can be obtained by a similar procedure except that 3-hydroxypiperidine is substituted by ethanolamine, tetramethyl ammonium hydroxide, or tetraethylammonium hydroxide. When the reaction temperature is raised to 160 °C, compound **3** can be obtained as a pure phase without the presence of additional organic molecules.

Preparation of 4: Compound **4** was obtained similarly to compound **3** except that *R*-pempH₂ was used. Yield: 49%. Anal.Calcd for $C_{18}H_{25}ClN_2O_6P_2Zn_2$: C, 36.42; H, 4.24; N, 4.72%. Found: C, 36.29; H, 4.21; N, 4.76%. IR (KBr, cm^{-1}): 3440 (w), 3212 (w), 3031(w), 2852(w), 2394(w), 1588(w), 1454(w), 1383(w), 1275(w), 1168(m), 1133(s), 1104(s), 1079(s), 1054(s), 1007(s), 815(w), 763(m), 740(w), 701(m), 633(w), 613(m), 572(w).

Compounds **1-4** can also be prepared without NaCl when $ZnSO_4$ is replaced by $ZnCl_2$.

Crystal structural determination. Data collections for complexes **1-4** were carried out on a Bruker SMART APEX CCD diffractometer equipped with graphite monochromated $Mo_{K\alpha}$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Hemisphere of data were collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 5s per frame. The data were integrated using the Siemens SAINT program,³ with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Empirical absorption and extinction

corrections were applied. The structure was solved by direct method and refined on F^2 by full-matrix least squares using SHELXTL.⁴ All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were put in calculated positions and refined isotropically with the isotropic vibration parameters related to the non-hydrogen atoms to which they are bonded.

References

- (1) Kabachnik, M. I.; Medved', T. Y.; Kozlova, G. K.; Balabukha, V. S.; Mironova, E. A.; Tikhonova, L. I. *Izvest. Akad. Nauk SSSR, Ser. Khim.* **1960**, 651.
- (2) Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* **1968**, 39, 3798.
- (3) SAINT, Program for Data Extraction and Reduction, Siemens Analytical X-ray Instruments, Madison, WI, **1994–1996**.
- (4) SHELXTL (version 5.0), Reference Manual, Siemens Industrial Automation, Analytical Instruments, Madison, WI, **1995**.

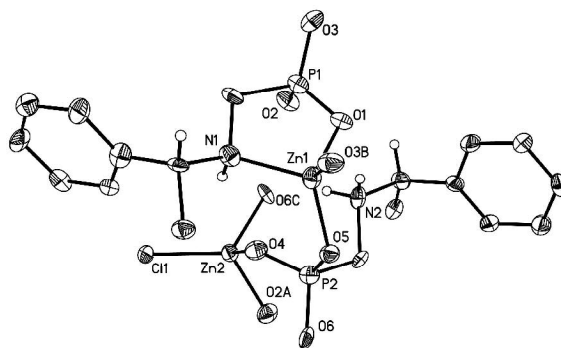


Figure S1 Coordination geometries of zinc in compound **2** with atomic labeling scheme. Thermal ellipsoids are at the 30% probability level. All H atoms except those attached to N and chiral C atoms are omitted for clarity.

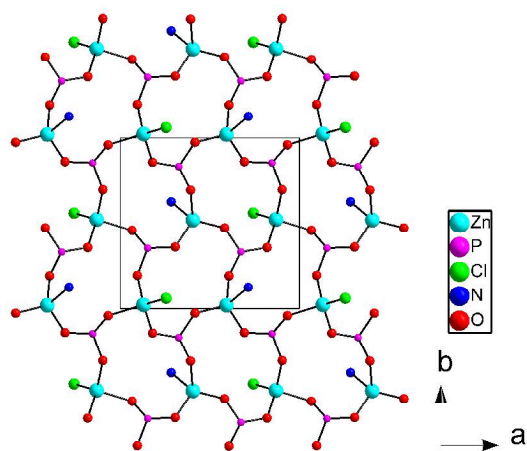


Figure S2 The inorganic layer of **3**

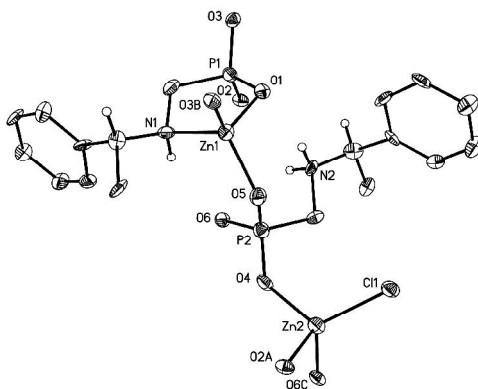


Figure S3 Coordination geometries of zinc in compound **4** with atomic labeling scheme. Thermal ellipsoids are at the 30% probability level. All H atoms except those attached to N and chiral C atoms are omitted for clarity.

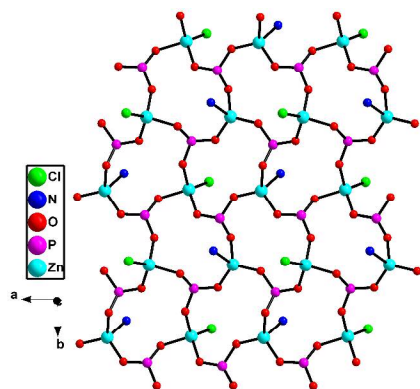


Figure S4 The inorganic layer of **4**

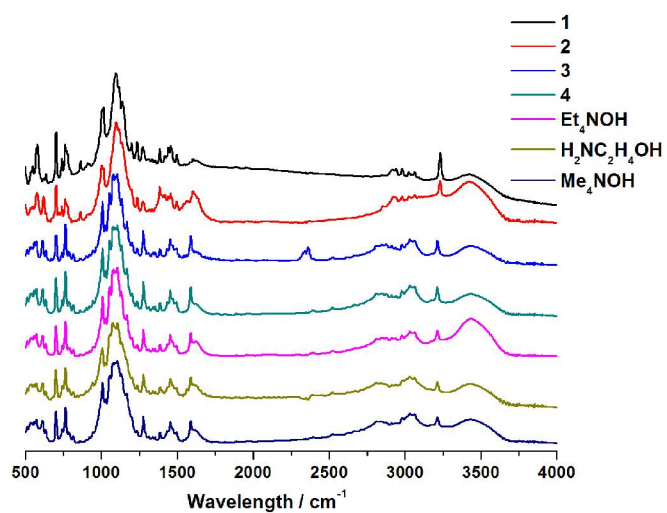


Figure 5 The IR of compounds **1-4**, and **3** prepared at 140°C in the presence of Et₄NOH, Me₄NOH, or H₂NC₂H₄OH.