# Electronic Supplementary Information for

# A second-order nonlinear optical material with 5-fold interpenetrating diamondoid framework based on two achiral precursors: spontaneous resolution to absolute chiral induction

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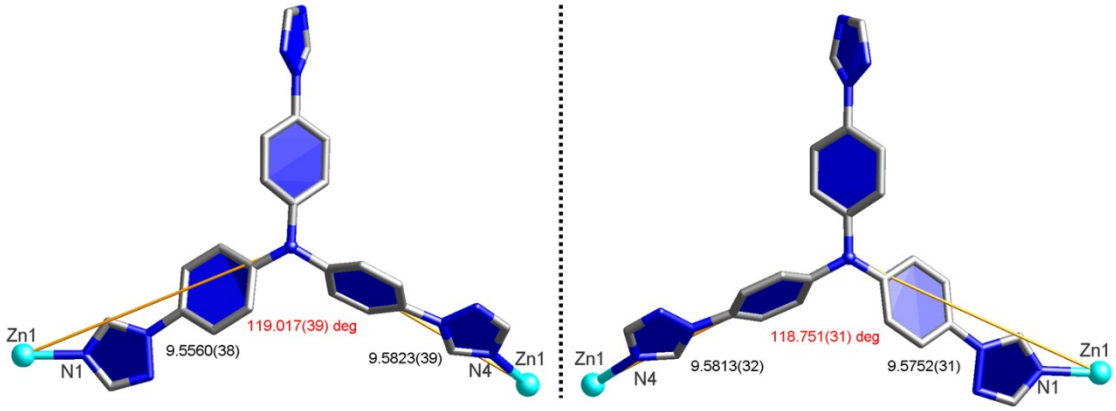


**Fig. S1** The conformation of TTPA ligand of **Δ-1** and **Λ-1**

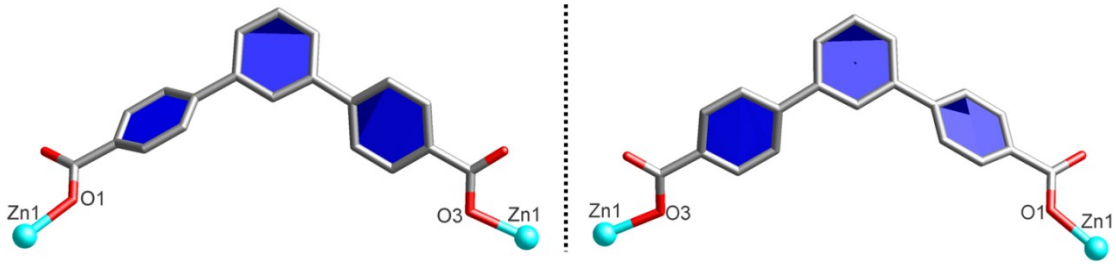


**Fig. S2** The coordination modes of auxiliary ligands in **Δ-1** and **Λ-1**

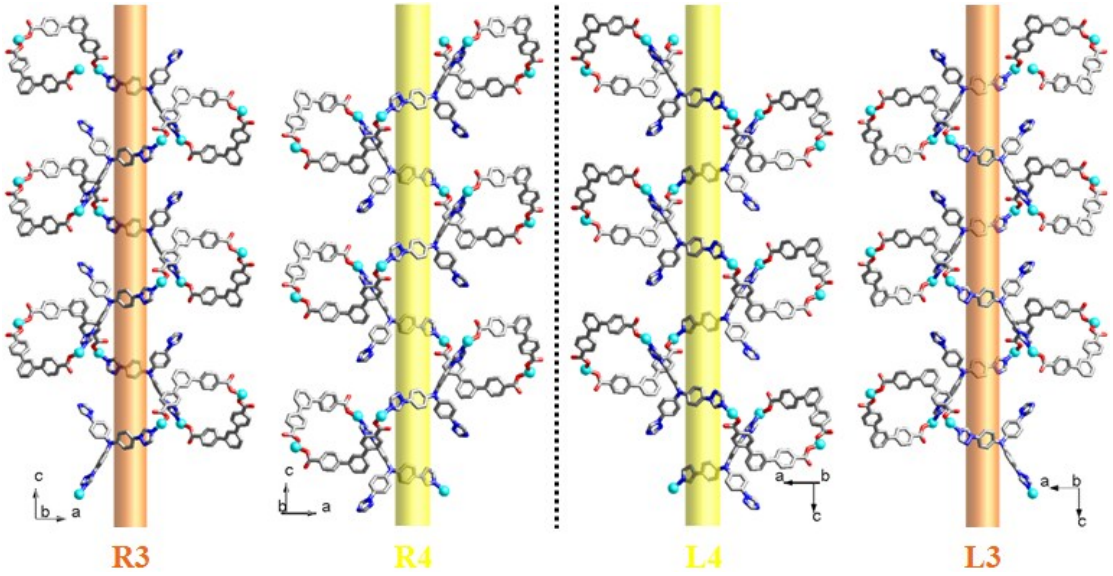


**Fig. S3** Two kinds of left- or right-handed helical chains labeled R3 and R4 constructed by Zn(II) ions, TTPA and $TPDC^{2-}$ ligands in **Δ-1** (left) and labeled L3 and L4 in **Λ-1** (right)

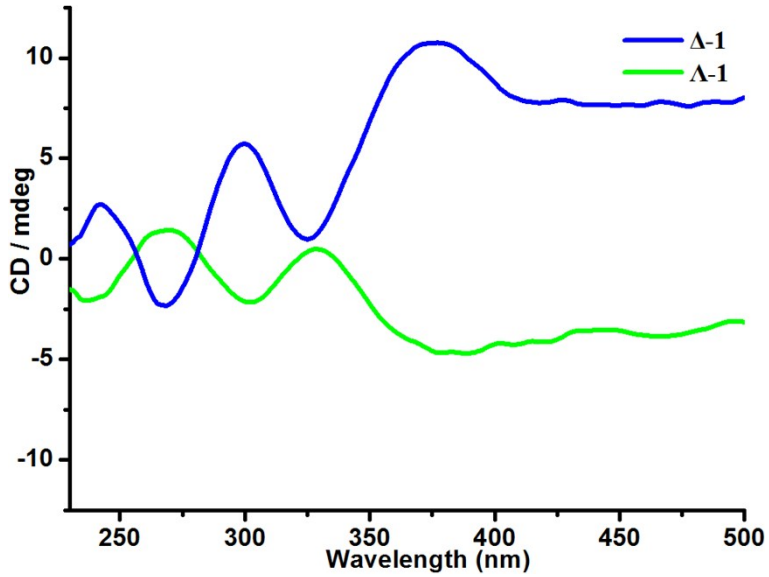


**Fig. S4** The solid-state CD spectra of **Δ-1** and **Λ-1** induced by (*S*)- or (*R*)-propane-1,2-diol respectively show the opposite Cotton effects

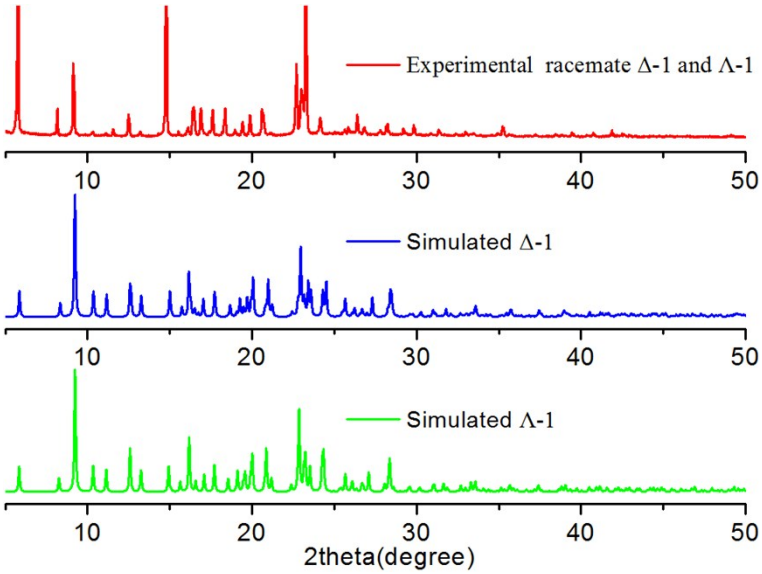


**Fig. S5** Powder X-ray diffraction patterns of racemate **Δ-1** and **Λ-1**

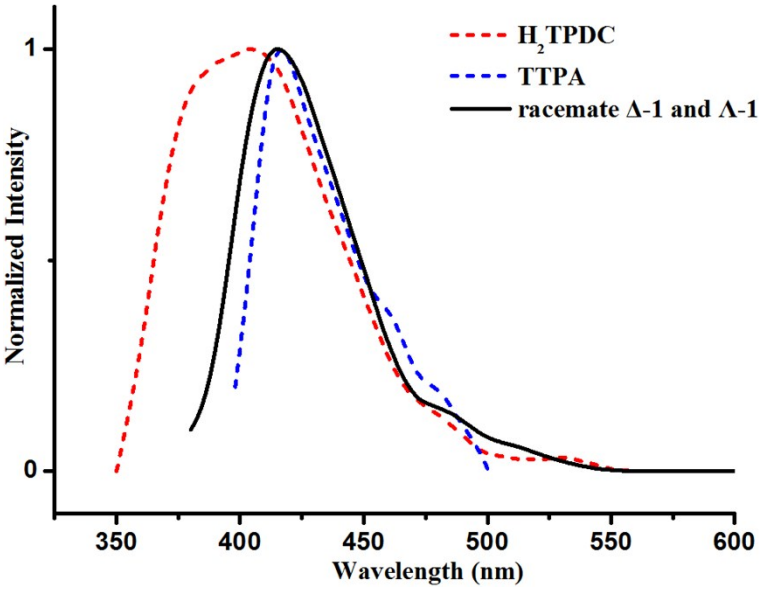


**Fig. S6** Photoluminescence emission spectra of racemate **Δ-1** and **Λ-1** at room temperature

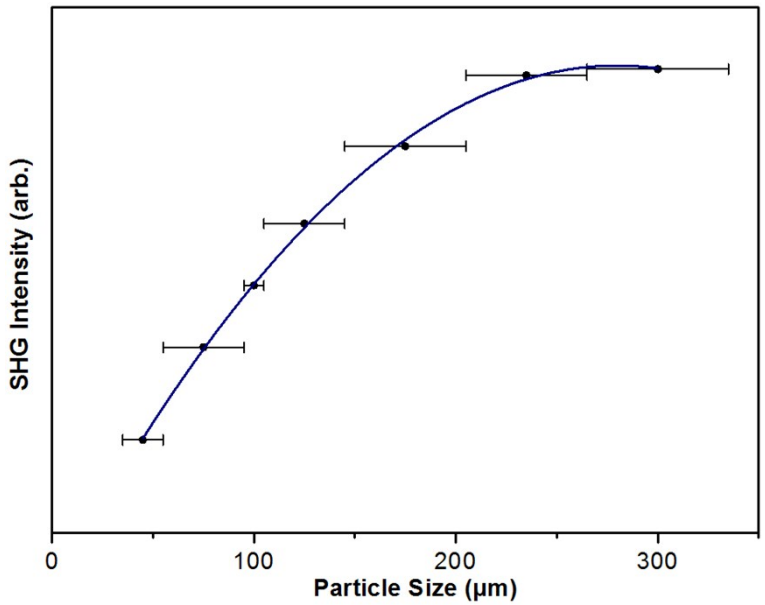


**Fig. S7** Phase-matching curve for racemate **Δ-1** and **Λ-1**. The curve drawn is to guide the eye and not a fit to the data.

**Materials and methods**

All chemicals and solvents except TTPA and $H_2$TPDC ligand were of reagent-grade quality from commercial sources and were used without further purification. The tritopic ligand tris(4-(1*H*-1,2,4-triazol-1-yl)phenyl)amine (TTPA) was prepared by the copper-catalyzed carbon-nitrogen bond cross-coupling reaction between tris(4-bromophenyl)amine and 1,2,4-triazole using Ullmann condensation methods based on previous literature with proper modifications.[S1] The V-shaped ligand (1,1':3',1''-terphenyl)-4,4''-dicarboxylic acid ($H_2$TPDC) was prepared by the tetra(triphenylphosphine) palladium(0)-catalyzed Suzuki coupling reaction between 1,3-dibromobenzene and (4-(methoxycarbonyl)phenyl)boronic acid and further hydrolysis based on previous literature with proper modifications.[S2] The IR absorption spectra of these complexes were recorded in the range of 400-4000 $cm^{-1}$ by means of a Nicolet (Impact 410) spectrometer with KCl pellets. Element analyses (C, H, N) were carried out on a Perkin-Elmer model 240C analyzer. PXRD measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu-*Kα* radiation (λ = 0.15418 nm), in which the X-ray tube was operated at 40 kV and 30 mA. Thermogravimetric analysis was performed on a Perkin Elmer thermogravimetric analyzer from room temperature to 800 °C with a heating rate of

20 K·min$^{-1}$ under $N_2$ atmosphere. Luminescent spectra were recorded with a SHIMAZU VF-320 X-ray fluorescence spectrophotometer at room temperature. The sieved urea powders were used as reference materials to assume the effect. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate a SHG signal. The backscattered SHG light was collected by a spherical concave mirror and passed through a filter that transmits only 532 nm radiation. The powder samples (50mg) were ground and sieved into particle size ranges (< 55, 55-95, 95-105, 105-145, 145-205, 205-265, and 265-335 μm).

**Crystal structure determination**

Single crystals of **Δ-1** and **Λ-1** were prepared by the methods described in the synthetic procedure. Their crystal structures were determined by single-crystal X-ray analyses. Data collections were performed using a Bruker D8 Venture diffractometer with Mo-*Kα* radiation with an *φ–ω* mode (λ = 0.71073 Å). The structures were solved with direct methods using the SHELXTL program[S3] and refined anisotropically with SHELX2016 using full-matrix least-squares procedures. In the crystal X-ray structure analysis, some residual electron densities of **Δ-1** and **Λ-1** were observed within the pores, and assignment to specific molecules cannot be made. They were removed by the SQUEEZE routine in PLATON.

**Preparation of the Δ-1 and Λ-1**

**Synthesis of racemate Δ-1 and Λ-1.** A mixture of TTPA (4.46 mg, 0.01 mmol), $H_2$TPDC (3.19 mg, 0.01 mmol), and $Zn(NO_3)_2{\cdot}6H_2O$ (14.85 mg, 0.05 mmol) was dissolved in 4 mL of DMA/$H_2O$ (2:2, v/v). The final mixture was placed in a Teflon vessel (12 mL) under autogenous pressure and heated at 85 °C for 3 days and then cooled to room temperature over 24 h. Colorless rod-shaped crystals of **Δ-1** and **Λ-1** were obtained, dried in air and collected in 42% yield (based on Zn(II) salt).

**Synthesis of Δ-1.** A mixture of TTPA (4.46 mg, 0.01 mmol), $H_2$TPDC (3.19 mg, 0.01 mmol), (*S*)-propane-1,2-diol (21 mg, 0.02 ml) and $Zn(NO_3)_2{\cdot}6H_2O$ (14.85 mg, 0.05 mmol) was dissolved in 4 mL of DMA/$H_2O$ (2:2, v/v). The final mixture was placed in a Teflon vessel (12 mL) under autogenous pressure and heated at 85 °C for 3 days

and then cooled to room temperature over 24 h. Colorless rod-shaped crystals of **Δ-1** were obtained, dried in air and collected in 39% yield (based on Zn(II) salt).

**Synthesis of Λ-1.** A mixture of TTPA (4.46 mg, 0.01 mmol), $H_2$TPDC (3.19 mg, 0.01 mmol), (*R*)-propane-1,2-diol (21 mg, 0.02 ml) and $Zn(NO_3)_2 \cdot 6H_2O$ (14.85 mg, 0.05 mmol) was dissolved in 4 mL of DMA/$H_2O$ (2:2, v/v). The final mixture was placed in a Teflon vessel (12 mL) under autogenous pressure and heated at 85 °C for 3 days and then cooled to room temperature over 24 h. Colorless rod-shaped crystals of **Λ-1** were obtained, dried in air and collected in 37% yield (based on Zn(II) salt).

Elemental analysis calcd. for $C_{96}H_{80}N_{22}O_{11}Zn_2$ (%): C, 62.37; H, 4.36; N, 16.67. Found: C, 62.33; H, 4.29; N, 16.88. IR (KBr, $cm^{-1}$): 3447w, 3113w, 1623s, 1605vs, 1558w, 1521vs, 1363s, 1311m, 1277s, 1210w, 1183s, 1145m, 1051w, 1016w, 999w, 974s, 954w, 837m, 799w, 774m, 708w, 673m, 654m, 545m (Fig. S8).

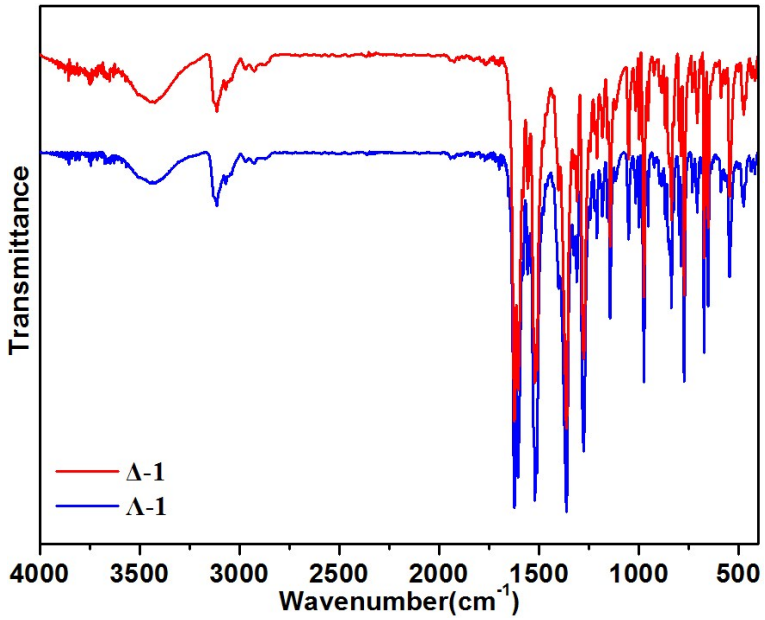


**Fig. S8** IR spectra of **Δ-1** and **Λ-1**

**Table S1** A summary of the crystal data and refinement results for 30 randomly selected crystals with space group $P2_12_12_1$ through the spontaneous resolution

| Number | Form | *a* | *b* | *c* | *V* | $R_1$ | $wR_2$ | Flack parameter |
|---|---|---|---|---|---|---|---|---|
| 1 | **Δ-1** | 9.3086(4) | 21.1829(8) | 21.4560(9) | 4230.8(3) | 0.0482 | 0.1052 | 0.036(16) |
| 2 | **Δ** | 9.2648(11) | 21.197(2) | 21.197 | 4163.0(7) | 0.0448 | 0.1006 | 0.030(15) |
| 3 | **Δ** | 9.3151(13) | 21.501(3) | 21.501 | 4306.3(8) | 0.0418 | 0.1099 | 0.003(5) |
| 4 | **Δ** | 9.3132(4) | 21.2184(9) | 21.4352(9) | 4235.8(3) | 0.0413 | 0.0983 | 0.054(13) |
| 5 | **Δ** | 9.3124(12) | 21.510(3) | 21.510 | 4308.6(8) | 0.0441 | 0.1043 | -0.002(7) |
| 6 | **Δ** | 9.3252(11) | 21.347(2) | 21.347 | 4249.6(7) | 0.0539 | 0.1367 | 0.075(17) |
| 7 | **Δ** | 9.3236(9) | 21.363(2) | 21.363 | 4255.0(6) | 0.0413 | 0.0943 | 0.022(13) |
| 8 | **Δ** | 9.3415(17) | 21.585(4) | 21.585 | 4352.3(11) | 0.0427 | 0.1016 | 0.010(7) |
| 9 | **Δ** | 9.3383(9) | 21.423(2) | 21.423 | 4285.7(6) | 0.0398 | 0.0920 | 0.013(5) |
| 10 | **Δ** | 9.3199(9) | 21.456(2) | 21.559(2) | 4311.1(7) | 0.0435 | 0.1015 | 0.003(7) |
| 11 | **Δ** | 9.3308(11) | 21.378(2) | 21.378 | 4264.4(7) | 0.0457 | 0.1011 | 0.032(15) |
| 12 | **Δ** | 9.3067(4) | 21.1746(8) | 21.4360(8) | 4224.3(3) | 0.0465 | 0.1005 | 0.024(15) |
| 13 | **Δ** | 9.3445(11) | 21.421(2) | 21.421 | 4287.7(7) | 0.0464 | 0.0996 | 0.035(15) |
| 14 | **Δ** | 9.3121(12) | 21.297(3) | 21.297 | 4223.7(7) | 0.0418 | 0.0959 | 0.034(14) |
| 15 | **Δ** | 9.3176(4) | 21.1856(8) | 21.4604(9) | 4236.3(3) | 0.0426 | 0.0938 | 0.026(14) |
| 16 | **Λ-1** | 9.3272(10) | 21.377(2) | 21.377 | 4262.5(6) | 0.0414 | 0.0949 | 0.013(13) |
| 17 | **Λ** | 9.3115(11) | 21.498(3) | 21.498 | 4303.5(7) | 0.0424 | 0.1069 | 0.006(5) |
| 18 | **Λ** | 9.3245(11) | 21.527(3) | 21.527 | 4321.2(7) | 0.0440 | 0.1069 | 0.013(6) |
| 19 | **Λ** | 9.316(2) | 21.525(5) | 21.525 | 4316.5(15) | 0.0460 | 0.1118 | 0.019(7) |
| 20 | **Λ** | 9.3369(11) | 21.394(2) | 21.394 | 4273.4(7) | 0.0393 | 0.0921 | 0.021(13) |
| 21 | **Λ** | 9.3266(17) | 21.551(4) | 21.551 | 4331.7(11) | 0.0429 | 0.1012 | 0.008(7) |
| 22 | **Λ** | 9.3249(13) | 21.529(3) | 21.529 | 4322.0(8) | 0.0434 | 0.1019 | 0.011(7) |
| 23 | **Λ** | 9.3199(14) | 21.508(3) | 21.508 | 4311.2(9) | 0.0406 | 0.1013 | 0.007(6) |
| 24 | **Λ** | 9.312(2) | 21.533(4) | 21.533 | 4317.6(13) | 0.0406 | 0.1031 | 0.004(6) |
| 25 | **Λ** | 9.3318(11) | 21.552(3) | 21.552 | 4334.6(7) | 0.0414 | 0.1023 | 0.018(6) |
| 26 | **Λ** | 9.454(11) | 21.73(3) | 22.04(3) | 4527(9) | 0.0403 | 0.1047 | 0.009(5) |
| 27 | **Λ** | 9.3076(11) | 21.509(3) | 21.509 | 4306.1(7) | 0.0389 | 0.1039 | 0.006(5) |
| 28 | **Λ** | 9.3134(4) | 21.1860(9) | 21.4414(9) | 4230.7(3) | 0.0525 | 0.1107 | 0.039(15) |
| 39 | **Λ** | 9.3153(4) | 21.1799(9) | 21.4540(9) | 4232.8(3) | 0.0467 | 0.1032 | 0.037(14) |
| 30 | **Λ** | 9.3072(4) | 21.1778(8) | 21.4460(9) | 4227.1(3) | 0.0416 | 0.0928 | 0.030(13) |

**Table S2** A summary of the crystal data and refinement results for 10 randomly selected crystals with space group $P2_12_12_1$ using a small amount of (*S*)-propane-1,2-diol

| Number | Form | *a* | *b* | *c* | *V* | $R_1$ | $wR_2$ | Flack parameter |
|---|---|---|---|---|---|---|---|---|
| 1 | **Δ** | 9.3090(4) | 21.1827(9) | 21.4422(9) | 4228.2(3) | 0.0465 | 0.0994 | 0.030(15) |
| 2 | **Δ** | 9.3332(10) | 21.435(2) | 21.435 | 4288.4(6) | 0.0366 | 0.0877 | 0.014(5) |
| 3 | **Δ** | 9.3071(3) | 21.2018(8) | 21.4607(8) | 4234.8(3) | 0.0418 | 0.0952 | 0.022(14) |
| 4 | **Δ** | 9.3182(12) | 21.355(2) | 21.355 | 4249.5(7) | 0.0417 | 0.0957 | 0.015(5) |
| 5 | **Δ** | 9.3336(12) | 21.366(2) | 21.366 | 4260.8(7) | 0.0498 | 0.1049 | 0.039(16) |
| 6 | **Δ** | 9.3070(3) | 21.1952(7) | 21.4693(8) | 4235.1(3) | 0.0444 | 0.0987 | 0.024(15) |
| 7 | **Δ** | 9.3361(12) | 21.393(3) | 21.393 | 4273.0(7) | 0.0463 | 0.1011 | 0.021(15) |
| 8 | **Δ** | 9.3030(3) | 21.2026(7) | 21.4416(8) | 4229.3(3) | 0.0430 | 0.0981 | 0.017(14) |
| 9 | **Δ** | 9.3383(11) | 21.414 | 21.414(2) | 4282.4(7) | 0.0395 | 0.0946 | 0.019(14) |
| 10 | **Δ** | 9.3162(6) | 21.1950(14) | 21.4517(16) | 4235.8(5) | 0.0486 | 0.1179 | 0.052(16) |

**Table S3** A summary of the crystal data and refinement results for 10 randomly selected crystals with space group $P2_12_12_1$ using a small amount of (*R*)-propane-1,2-diol

| Number | Form | *a* | *b* | *c* | *V* | $R_1$ | $wR_2$ | Flack parameter |
|---|---|---|---|---|---|---|---|---|
| 1 | **Λ** | 9.3344(14) | 21.371(3) | 21.371 | 4263.2(8) | 0.0432 | 0.0975 | 0.032(14) |
| 2 | **Λ** | 9.3214(12) | 21.329(2) | 21.329 | 4240.7(7) | 0.0412 | 0.0927 | 0.026(13) |
| 3 | **Λ** | 9.3519(14) | 21.400(3) | 21.400 | 4282.6(9) | 0.0516 | 0.1124 | 0.043(16) |
| 4 | **Λ** | 9.3202(12) | 21.352(3) | 21.352 | 4249.0(7) | 0.0464 | 0.1030 | 0.028(15) |
| 5 | **Λ** | 9.3315(12) | 21.389(3) | 21.389 | 4269.1(8) | 0.0422 | 0.0955 | 0.025(14) |
| 6 | **Λ** | 9.3115(12) | 21.302(2) | 21.302 | 4225.5(7) | 0.030(14) | 0.0449 | 0.0986 |
| 7 | **Λ** | 9.3119(3) | 21.1889(8) | 21.4558(8) | 4233.4(3) | 0.0464 | 0.1038 | 0.042(15) |
| 8 | **Λ** | 9.3137(3) | 21.1756(7) | 21.4432(7) | 4229.1(2) | 0.0421 | 0.0948 | 0.008(14) |
| 9 | **Λ** | 9.3062(5) | 21.1780(10) | 21.4485(11) | 4227.2(4) | 0.0433 | 0.0969 | 0.020(14) |
| 10 | **Λ** | 9.3056(5) | 21.2124(12) | 21.4591(12) | 4235.9(4) | 0.0503 | 0.1147 | 0.045(16) |

**Table S4** Selected bond lengths (Å) and angles (°) for **Δ-1** and **Λ-1**

| **Δ-1** | | | |
|---|---|---|---|
| Zn(1)-O(1) | 1.919(3) | Zn(1)-N(1) | 2.001(4) |
| Zn(1)-O(3)#1 | 1.957(3) | Zn(1)-N(4)#2 | 2.034(4) |
| O(1)-Zn(1)-O(3)#1 | 103.89(16) | O(1)-Zn(1)-N(4)#2 | 98.80(15) |

| | | | |
|---|---|---|---|
| O(1)-Zn (1)-N(1) | 120.26(15) | O(3)#1-Zn(1)-N(4)#2 | 109.00(15) |
| O(3)#1-Zn (1)-N(1) | 116.34(15) | N(1)-Zn (1)-N(4)#2 | 106.86(15) |
| | | **Λ-1** | |
| Zn(1)-O(1) | 1.924(3) | Zn(1)-N(1) | 2.000(3) |
| Zn(1)-O(3)#1 | 1.963(3) | Zn(1)-N(4)#2 | 2.040(3) |
| O(1)-Zn(1)-O(3)#1 | 104.13(14) | O(1)-Zn (1)-N(4)#2 | 98.34(14) |
| O(1)-Zn(1)-N(1) | 120.43(12) | O(3)#1-Zn(1)-N(4)#2 | 109.69(13) |
| O(3)#1-Zn(1)-N(1) | 116.11(13) | N(1)-Zn(1)-N(4)#2 | 106.50(13) |

Symmetry codes: #1: − *x* + 3, *y* + 1/2, − *z* + 1/2; #2: − *x* + 1/2, − *y* + 1, *z* + 1/2 for **Δ-1**; #1: − *x* + 2, *y* – 1/2, – *z* + 3/2; #2: − *x* – 1/2, − *y* + 2, *z* + 1/2 for **Λ-1**.

**Table S5** Hydrogen bonding distances (Å) and angles (°) for **Δ-1** and **Λ-1**

| D-H···A | d(D-H) | d(H···A) | d(D···A) | ∠(DHA) |
|---|---|---|---|---|
| | | **Δ-1** | | |
| C(1)-H(1)···O(4) #1 | 0.93 | 2.480 | 3.098 | 123.98 |
| C(1)-H(1)···O(5) | 0.93 | 2.580 | 3.373 | 143.51 |
| C(2)-H(2)···O(3) | 0.93 | 2.320 | 3.084 | 139.21 |
| C(3)-H(3)···O(4) #2 | 0.93 | 2.624 | 3.168 | 117.91 |
| C(3)-H(3)···O(5) #3 | 0.93 | 2.563 | 3.417 | 152.87 |
| C(11)-H(11)···O(3) #4 | 0.93 | 2.439 | 3.287 | 151.58 |
| C(17)-H(17)···O(2) #5 | 0.93 | 2.594 | 3.477 | 158.63 |
| C(20)-H(20)···N(6) #6 | 0.93 | 2.657 | 3.501 | 151.25 |
| C(48)-H(48C)···N(9) #7 | 0.96 | 2.680 | 3.552 | 151.35 |
| | | **Λ-1** | | |
| C(1)-H(1)···O(4) #1 | 0.93 | 2.473 | 3.092 | 124.17 |
| C(1)-H(1)···O(5) #2 | 0.93 | 2.592 | 3.379 | 142.76 |
| C(2)-H(2)···O(2) | 0.93 | 2.331 | 3.094 | 139.05 |
| C(3)-H(3)···O(4) #3 | 0.93 | 2.647 | 3.189 | 117.78 |
| C(3)-H(3)···O(5) #4 | 0.93 | 2.557 | 3.415 | 153.68 |

| | | | | |
|---|---|---|---|---|
| C(11)-H(11)···O(3) #5 | 0.93 | 2.438 | 3.284 | 151.27 |
| C(17)-H(17)···O(2) #6 | 0.93 | 2.607 | 3.490 | 158.57 |
| C(20)-H(20)···N(6) #7 | 0.93 | 2.676 | 3.517 | 150.67 |
| C(48)-H(48A)···N(9) #8 | 0.96 | 2.667 | 3.585 | 160.23 |

Symmetry codes: #1; − *x* + 3, *y* + 1/2, − *z* + 1/2; #2: *x* − 5/2, − *y* + 1/2, − *z*; #3: − *x* + 1/2, − *y* + 1, *z* − 1/2; #4: − *x* + 2, *y* + 1/2, − *z* + 1/2; #5: *x* − 1, *y*, *z*; #6: *x* + 1/2, − *y* + 3/2, − *z*; #7: − *x*, *y* − 1/2, − *z* + 1/2 for **Δ**-**1**; #1: − *x* + 2, *y* – 1/2, – *z* + 3/2; #2: – *x* + 1/2, – *y* + 1, *z* + 1/2; #3: *x* – 5/2, – *y* + 5/2, – *z* + 1; #4: *x* – 1, *y* + 1, *z*; #5: – *x* + 1, *y* – 1/2, – *z* + 3/2; #6: *x* – 1, *y*, *z*; #7: *x* + 1/2, – *y* + 3/2, – *z* + 1; #8: *x* + 3/2, – *y* + 1/2, – *z* + 1 for **Λ**-**1**.

## References


S1. Z. Z. Shi, Z. R. Pan, C. L. Zhang and H. G. Zheng, *Dalton Trans.*, 2015, **44**, 16854.

S2. A. M. Johnson, M. C. Younga and R. J. Hooley, *Dalton Trans.*, 2013, **42**, 8394.

S3. Bruker 2000, SMART (Version 5.0), SAINT-plus (Version 6), SHELXTL (Version 6.1), and SADABS (Version 2.03); Bruker AXS Inc.: Madison, WI.