

Electronic Supplementary Information (ESI)

Enantioselective Sorption of Alcohols in a Homochiral Metal-Organic Framework

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1. General Methods.

All chemicals were purchased from Aldrich and Fisher and used without further purification. $[\text{Zn}_2(\text{bdc})(S\text{-lac})(\text{dmf})]\cdot\text{DMF}$ (**1**·DMF) was prepared as described earlier [1]. Optical rotation was measured on the Autopol VI automatic polarimeter at 20 °C, 589 nm in the 10 cm, 6 mL sample cell. The TGA plots were recorded on the TG 209 F1 apparatus in an Ar atmosphere at the heating rate of 10 °C/min. Thermogravimetric and Differential Scanning Calorimetric (TG-DSC) analyses were carried out at a ramp rate of 10 °C/min in a N₂ flow (20 mL/min) with the Setaram Labsys Evo instrument. TG-DSC data were processed with the computer program Calisto (v1.075). Both TG and DSC baselines were corrected by subtraction of predetermined baselines recorded under identical conditions without a sample. ¹H NMR spectra were recorded on the Bruker Advance III 400MHz spectrometer. The elemental CHN analysis was carried out on EURO EA 3000. Chromatograms were recorded on the Thermo Separation Products (TSP) and the Agilent Technologies 1260 Infinity equipped with the Daicel Chiralcel OD or OD-H (4.6mm x 250mm) column. The single crystal diffraction data were collected at 100 K on the ADSC Quantum 210 CCD diffractometer with synchrotron radiation ($\lambda=0.80000$ Å) at Macromolecular Crystallography 6B1, Pohang Accelerator Laboratory (PAL), Pohang, South Korea. Powder X-ray diffraction (PXRD) data were collected with Cu-K α radiation ($\lambda = 1.54056$ Å) on the Philips PW 1830 instrument equipped with a PW 1820 vertical Bragg–Brentano powder goniometer and a PW 1710 control unit.

2. Procedure for enantioselective sorption and determination of enantiomeric excess values by polarimetry.

In a typical sorption experiment, **1**·DMF (1.8 g) was soaked in neat racemic 1-phenyl-1-ethanol (10 mL) or neat racemic 1-phenyl-1-propanol (10 mL). After the mixture was stirred with vortex for 48 h, supernatant was separated by centrifugation. The liquid phase was then carefully transferred into a polarimeter cell to measure optical rotation. Sorption kinetic curves for 1-phenyl-1-ethanol and 1-phenyl-1-propanol were obtained from the repetitive measurements of optical rotation by the above mentioned procedure (**Fig. S1**).

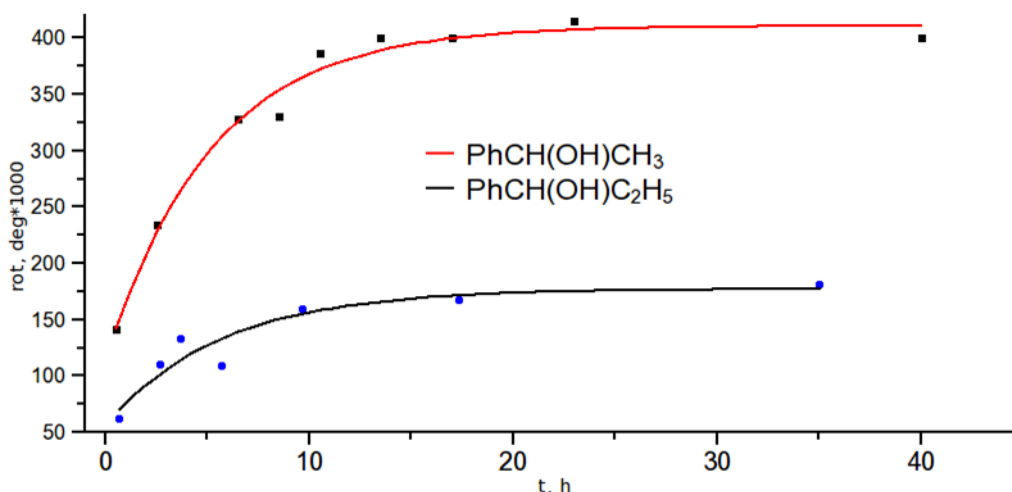


Fig. S1 The time-dependent change in optical rotation for 1-phenylethanol (red) and 1-phenyl-1-propanol (black) in the presence of $[\text{Zn}_2(\text{bdc})(\text{S-lac})(\text{dmf})]$ (**1**).

In the case of 1-phenyl-1-ethanol and 1-phenyl-1-propanol, after the sorption experiments, the adsorbed guest molecules were extracted with methanol (2 mL x 5) from the solid to measure *e.e.* values by polarimetry. The *e.e.* values are almost the same as those obtained with the supernatant, but with the opposite sign. After the extraction experiment the solid was digested in an acid and ^1H NMR spectra were taken, which confirmed near complete removal of the guest from pores.

Enantiomeric excess was calculated by the following formula:

$$ee = \frac{R - S}{R + S}$$

$$[\alpha]_{589}^{20} = \frac{\alpha}{l \times C}, \text{ where:}$$

$[\alpha]$ = specific rotation

α = observed rotation

l = cell length

C = concentration of optically active isomer

$R - S = C$

$R + S$ = the amount of guest molecules found in the framework

The enantiomeric excess values for other aliphatic alcohols described in this paper were determined by the same procedure. The *e.e.* values for 1-phenyl-1-ethanol and 1-phenyl-1-propanol obtained by this method were also confirmed by HPLC.

3. Procedure for Enantioselective Sorption and Determination of enantiomeric excess values by HPLC.

To determine enantiomeric excess value by HPLC, **1**·DMF (20 mg, 38 μmol) was added to racemic 1-phenyl-1-ethanol (11.67 μL , 2.5eq) in a 2 mL tube. The mixture was kept for 2 d at room temperature. Centrifugation of the mixture gives a clear solution which was analyzed by HPLC. In case of 1-phenyl-1-propanol sorption experiment, the same procedure was used except for **1**·DMF (15 mg, 28 μmol) and racemic 1-phenyl-1-propanol (12 μL , 3.1eq).

1-phenyl-1-ethanol: *e.e.*_s 20 % (Eluent: 99% n-Hex and 1% IPA, Flow rate: 0.5mL/min, Injection Volume: 10 μL , Wavelength: 254nm, TSP equipped with Chiralcel OD) $t_{\text{R-PhEtOH}} =$

50 min; $t_{R-PhEtOH} = 69$ min (**Fig. S2a**).

1-phenyl-1-propanol: $e.e.s$ 11 % (Eluent: 95% n-Hex and 5% IPA, Flow rate: 0.5mL/min, Injection Volume: 5 μ L, Wavelength: 254nm, Agilent Technologies 1260 infinity equipped with Chiralcel OD-H) $t_{R-phenylpropanol} = 14$ min; $t_{S-phenylpropanol} = 17$ min (**Fig. S2b**).

The alcohols were in some excess, compared to the amount of crystalline **1**·DMF, therefore the $e.e.$ values, measured for supernatant liquids, were recalculated for the $e.e.$ values in the solid. The following formula has been used:

$$e.e.s = e.e.l \times \frac{(v_l - v_s \times n)}{v_s \times n}, \text{ where :}$$

$e.e.l$ = the enantiomeric excess, measured by HPLC in liquid phase (%)

$e.e.s$ = the enantiomeric excess in solid phase (%)

v_l = the amount of substrate (mol)

v_s = the amount of sorbate (mol)

n = the number of guest molecules per formula unit

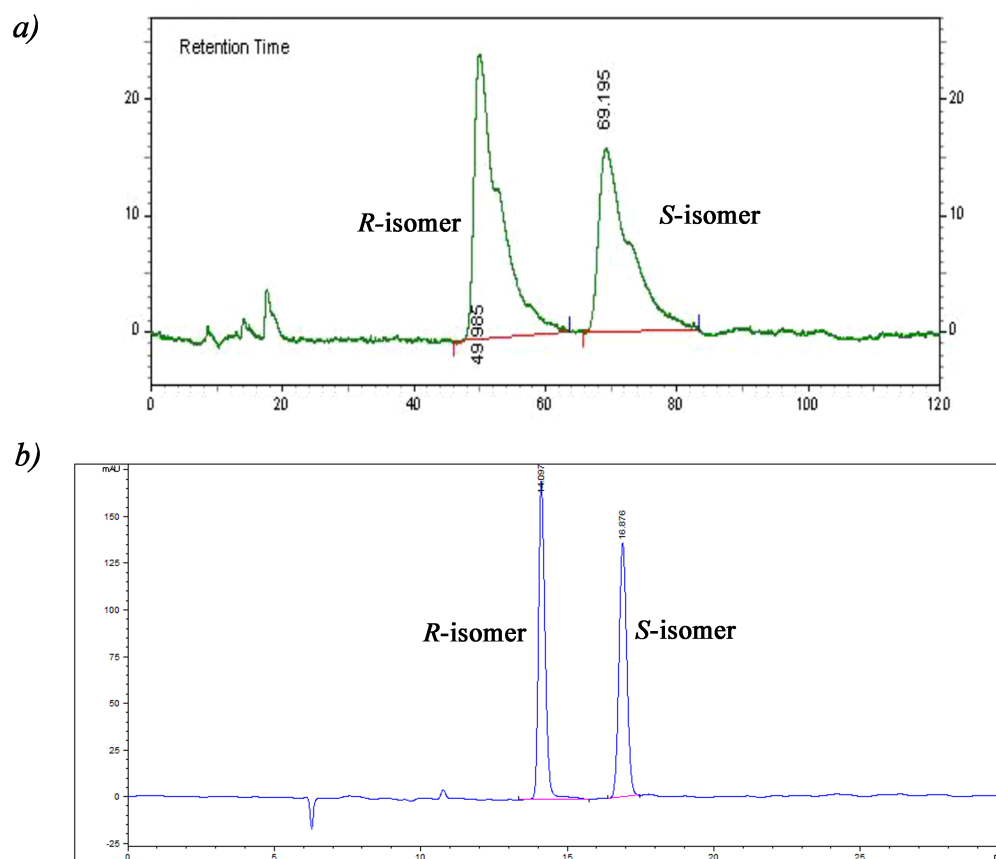


Fig. S2 A Chromatogram of 1-phenylethanol (a) obtained by normal phase HPLC on Chiralcel OD column and 1-phenyl-1propanol (b) obtained by normal phase HPLC on Chiralcel OD-H column

4. Stability of the framework **1**

The overall stability of the framework **1** upon sorption of the aromatic alcohols was confirmed by powder XRD (**Fig. S3-S4**). The splitting and shifting of some peaks are explained by partial flexibility of the framework after the inclusion of bulky guests. Powder X-ray diffraction plots of **1** saturated with aliphatic alcohols show similar features and support

the framework rigidity during the enantioselective sorption experiments.

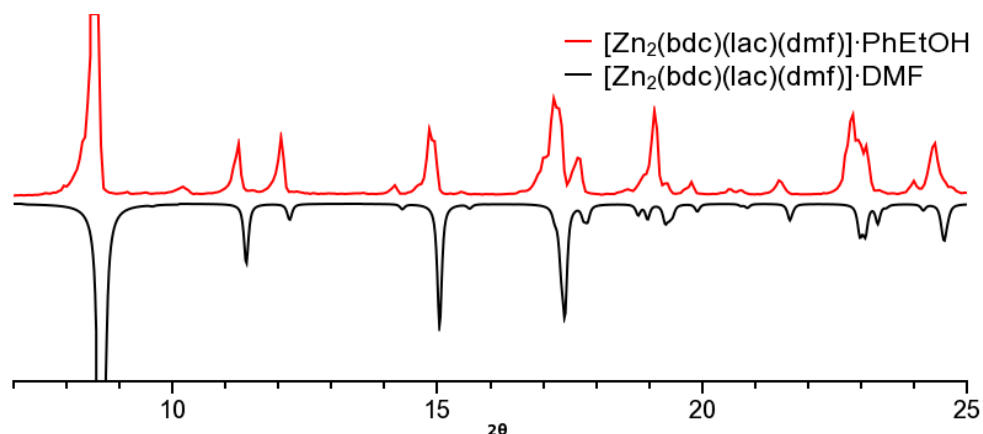


Fig. S3 Powder X-ray diffraction patterns for as-synthesized [Zn₂(bdc)(S-lac)(dmf)]·DMF (black) and [Zn₂(bdc)(S-lac)(dmf)]·PhEtOH (red).

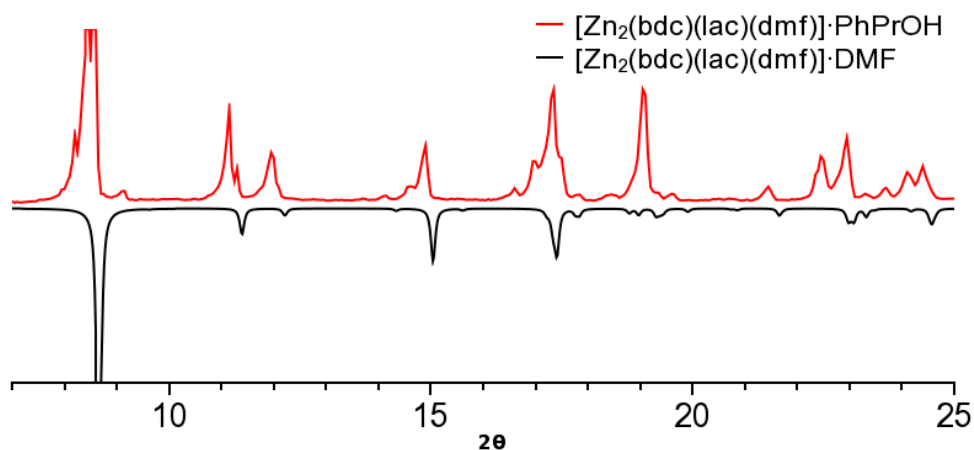


Fig. S4 Powder X-ray diffraction patterns for as-synthesized [Zn₂(bdc)(S-lac)(dmf)]·DMF (black) and [Zn₂(bdc)(S-lac)(dmf)]·PhPrOH (red).

5. Chemical Composition of Host-Guest Complexes.

The alcohol-exchanged solid samples **1**·guest were carefully dried and their composition was established by combination of ¹H-NMR, elemental analysis (**Table S1**) and TGA (**Fig. S5-S8**). These data support the proposed compositions. All the analytical methods showed the amount of adsorbed 1-phenyl-1-propanol less than 1 per formula unit of the framework, which is apparently due to the large size of the substrate.

For ¹H NMR experiments, several crystals were placed in D₂O (0.5 mL). After the addition of a small amount of sodium deuterioxide, the mixture was sonicated until all the solid dissolved and then several drops of CD₃OD were added to dissolve all the organic components. The ratio of the components in the digested solid was determined by the integral ratio of the peaks from guest alcohols and lactic acid (q, 3.98-4.02 ppm, 1H; d, 1.21-1.96 ppm, 3H) and/or terephthalic acid (s, 7.73 ppm, 4H).

The thermogravimetric analysis (TGA) were carried out at the heating rate of 10 °C/min in an Ar atmosphere with the TG 209 F1 apparatus. The weight loss supported the proposed compositions for each sample.

Table S1 Chemical (CHN) analysis (found and calculated) for different substrates.

Formula ^a	Found			Calculated		
	C	H	N	C	H	N
1 ·(Bu)	39.8	4.8	3.1	39.6	4.6	2.6
1 ·(MeBu)	41.8	5.1	3.0	41.9	5.0	2.6
1 ·(PhEtOH) _{0.95}	44.9	4.4	2.6	45.3	4.3	2.4
1 ·(PhPrOH) _{0.75}	44.3	4.5	2.6	44.7	4.3	2.5

^a Bu: 2-butanol; MeBu: 2-methyl-1-butanol; PhEtOH: 1-phenyl-1-ethanol; PhPrOH: 1-phenyl-1-propanol.

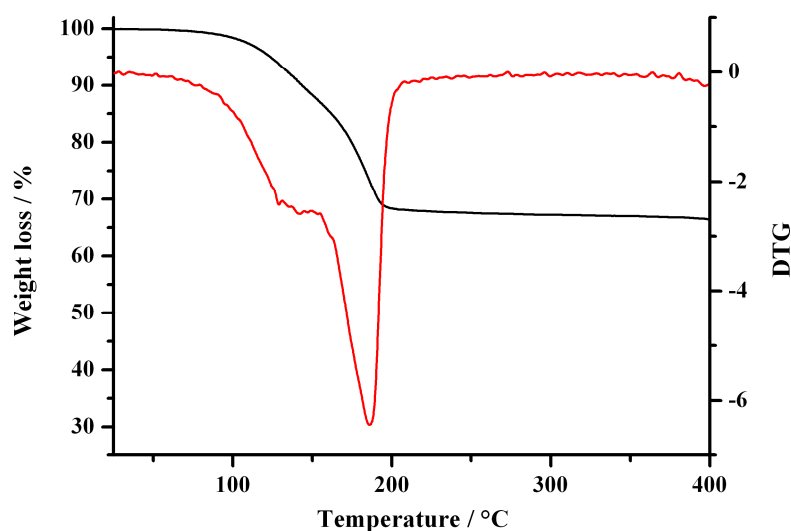


Fig. S5 TGA (black) and DTG (red) curves for **1**·PhEtOH. Found $\Delta m = 33\%$, calculated 33% for DMF+0.95PhEtOH.

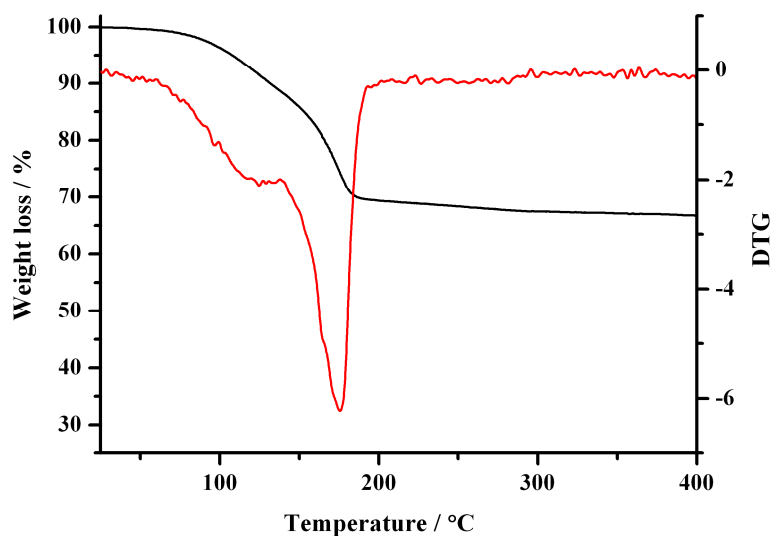


Fig. S6 TGA (black) and DTG (red) curves for **1**·PhPrOH. Found $\Delta m = 33\%$, calculated 31% for DMF+0.75PhPrOH

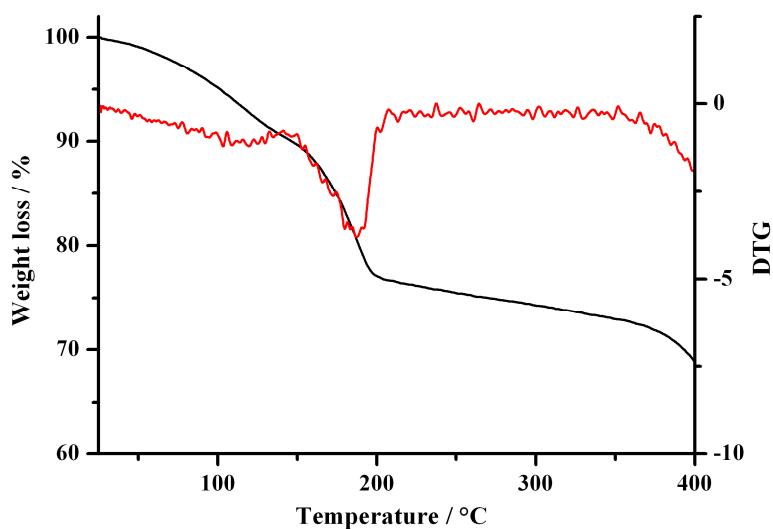


Fig. S7 TGA (black) and DTG (red) curves for 1·Bu. Found $\Delta m = 28\%$, calculated 28% for DMF+Bu.

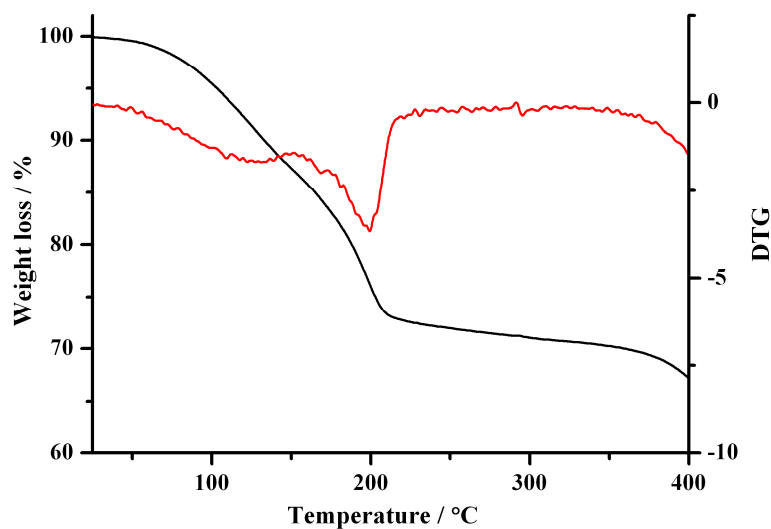


Fig. S8 TGA (black) and DTG (red) curves for 1·Me-Bu. Found $\Delta m = 29\%$, calculated 30% for DMF+MeBu.

6. TG-DSC experiments

Samples of 1·*R*-PhEtOH and 1·*S*-PhEtOH were prepared by soaking 1·DMF (30 mg, 57 μmol) in neat (*R*)-or (*S*)-1-phenyl-1-ethanol (50 μL , 7 eq) for 4 d. The excess 1-phenyl-1-ethanol was removed by filtration and both crystalline samples were dried under the identical conditions (*ca.* 100 $^{\circ}\text{C}$ *in vacuo*) to preserve a similar chemical composition. The thermal decomposition of 1·*R*-PhEtOH and 1·*S*-PhEtOH were analyzed by TG-DSC. The details of

TG-DSC experiments are presented in Table S2 and Fig. S9. The release of PhEtOH and coordinated DMF molecules is indistinguishable therefore we measured the thermal effect in a broad range (100 to 300 °C). The observed heat effects were corrected for the actual guest content (measured by weight loss) in the investigated compounds.

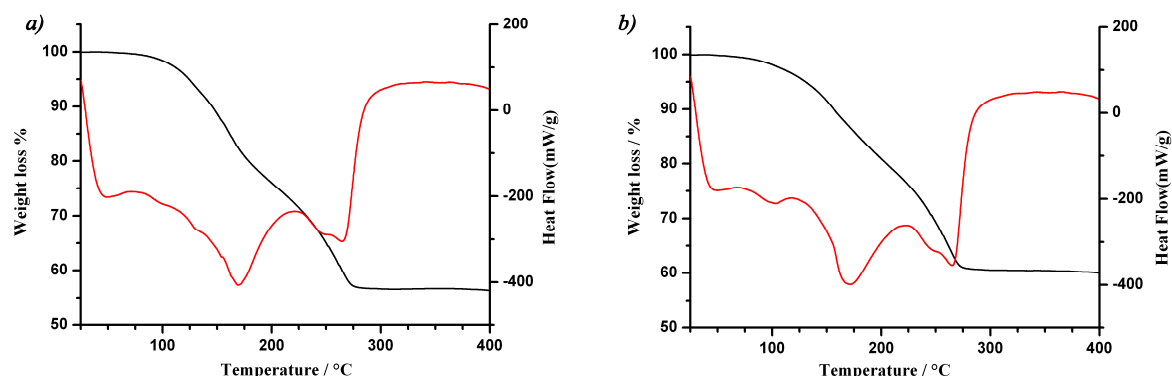


Fig. S9 TG-DSC of phenylethanol included **1**: a) **1·R**-PhEtOH, b) **1·S**-PhEtOH

Table S2 The details of TG-DSC measurements and calculations for from 100 to 300 °C

	Initial weight (mg)	Weight loss (mg)	ΔH_{sample} (J/g)	$\Delta H_{\text{dmf+PhEtOH}}$ (J/g)	$\Delta H_{\text{dmf+PhEtOH}}$ (kJ/mol)
R -isomer	29.6	12.4	371	888	173
S -isomer	27.2	10.2	369	981	192

7. Single Crystal X-ray Diffraction Study

Samples were prepared by soaking as-synthesized **1**·DMF in enantiopure 1-phenyl-1-ethanol for 11 d at room temperature. The diffraction data for colorless rod-shape crystals of as-prepared **1·R**-PhEtOH and **1·S**-PhEtOH were collected at 100 K on an ADSC Quantum 210 CCD diffractometer with synchrotron radiation ($\lambda=0.80000$ Å) at Macromolecular Crystallography 6B1, Pohang Accelerator Laboratory (PAL), Pohang, South Korea. Data reduction and adsorption correction were performed with HKL-2000 package [2]. The structures were solved by direct method, and the refinements were carried out with full-matrix least-squares on F^2 with the SHELXTL package [3] (**Table S3**).

To confirm the consistency of the structural data for the bulk phase, we collected the single-crystal X-ray diffraction data for five randomly selected single crystals for each host-guest compound. The structures were essentially identical. Additionally, X-ray diffraction data were independently collected at room temperature to ensure that host-guest structures at ambient conditions (at which all enantioselective sorption data were obtained) are identical to the low temperature data. We should note here that the important interatomic distances $d(\text{O}_{1\text{R}} \cdots \text{O}_{2\text{B}}) = 3.2926(5)$ Å, $d(\text{O}_{1\text{R}} \cdots \text{O}_{4\text{B}}) = 3.4187(4)$ Å in **1·R**-PhEtOH as well as $d(\text{O}_{1\text{S}} \cdots \text{C}_{3\text{D}}) = 3.2623(6)$ Å in **1·S**-PhEtOH are just about 1% longer than those at low temperature (100 K).

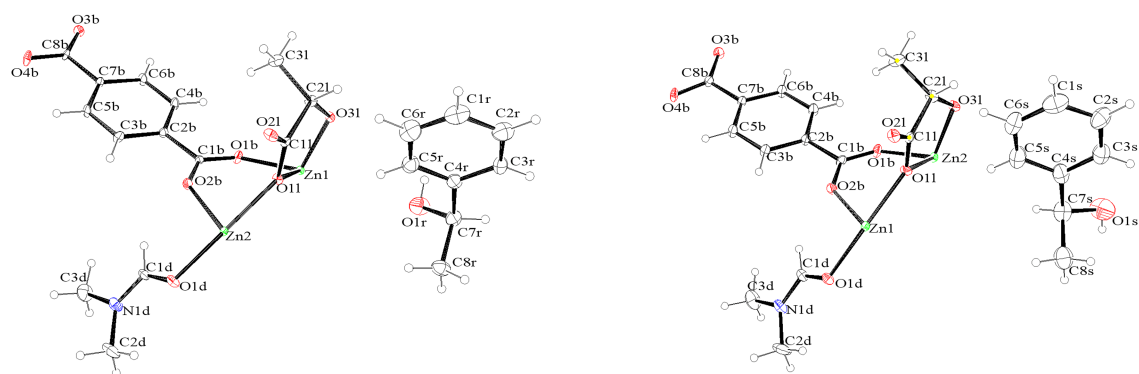


Fig. S10 ORTEP presentation of crystallographically independent parts of host-guest complexes **1·R-PhEtOH** (left) and **1·S-PhEtOH** (right). Thermal displacement parameters are given with 30% probability.

Table S3. Detailed crystal data and structure refinement for **1·R-PhEtOH** and **1·S-PhEtOH**.

Compound	1·R-PhEtOH	1·S-PhEtOH
Empirical formula	C ₂₂ H ₂₅ N O ₉ Zn ₂	
Formula weight	578.17	
Temperature	100 K	
Wavelength	0.80000 Å	
Crystal system	<i>Orthorhombic</i>	
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	<i>a</i> = 10.334(2) Å <i>b</i> = 11.672(2) Å <i>c</i> = 20.341(4) Å α = 90 ° β = 90 ° γ = 90 °	<i>a</i> = 10.337(2) Å <i>b</i> = 11.649(2) Å <i>c</i> = 20.464(4) Å α = 90 ° β = 90 ° γ = 90 °
Volume	2453.5(9) Å ³	2464.2(9) Å ³
Z	4	4
Density (calculated)	1.565 g/cm ³	1.558 g/cm ³
Absorption coefficient	2.005 mm ⁻¹	1.997 mm ⁻¹
F(000)	1184	1184
Crystal size	0.2 x 0.20 x 0.30 mm ³	0.20 x 0.20 x 0.30 mm ³
Theta range for data collection	2.49 to 30.34 °	2.48 to 30.36 °
Index ranges	-13 ≤ <i>h</i> ≤ 13 -14 ≤ <i>k</i> ≤ 14 -24 ≤ <i>l</i> ≤ 24	-13 ≤ <i>h</i> ≤ 3 -14 ≤ <i>k</i> ≤ 14 -25 ≤ <i>l</i> ≤ 25
Reflections collected	16254	17272
Independent reflections	5039 [R(int) = 0.0939]	5155 [R(int) = 0.0620]
Completeness to theta = 30.34°	97.1%	99.2%
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5039 / 0 / 307	5155 / 0 / 307
Goodness-of-fit on F ²	1.136	1.019
Final R indices [I > 2σ(I)]	<i>R</i> ₁ = 0.0479 <i>wR</i> ₂ = 0.1324	<i>R</i> ₁ = 0.0481 <i>wR</i> ₂ = 0.1318
R indices (all data)	<i>R</i> ₁ = 0.0480 <i>wR</i> ₂ = 0.1327	<i>R</i> ₁ = 0.0484 <i>wR</i> ₂ = 0.1323
Absolute structure parameter	0.058(11)	0.006(14)
Largest diff. peak and hole	0.764 and -1.264 e.Å ⁻³	0.693 and -2.220 e.Å ⁻³

References

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3. G. M. Sheldrick, *SHELXTL-97, Program for X-ray Crystal Structure Solution and Refinement*, University of Göttingen, Germany, 1997.