

Supplementary Information

Guest-dependent single-crystal-to-single-crystal transformations in porous adamantane-bearing macrocycle

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General Information

All solvents and reagents were obtained from commercial suppliers including TCI Co., Ltd., Wako Pure Chemical Industries Ltd., Sigma-Aldrich Co., and Cambridge Isotope Laboratories, Inc. and were used without further purification. Macrocycles (**1**, **2**) were synthesized according to the previous literature.¹ All air-sensitive reactions were carried out under an argon atmosphere. IR spectra were recorded on a Jasco FT/IR-6300. ¹H and ¹³C NMR spectra were recorded on a Bruker AV400 spectrometer at room temperature in CDCl₃ with tetramethylsilane as the reference standard. X-ray crystallographic data were collected using a Bruker D8 VENTURE diffractometer with CuK α radiation. Column chromatography was performed by using Wakogel C-200, and thin-layer chromatography was carried out on 2.0 mm Merck precoated silica gel glass plates. Gel permeation chromatography was performed using recycling preparative HPLC (LC-9204, Japan Analytical Industry Co., Ltd.) and a JAIGEL H series column (Japan Analytical Industry Co., Ltd.). The Mercury CSD 4.1.0 software program was used to calculate the voids. The Hirshfeld surfaces and 2D fingerprint plots were generated using the CrystalExplorer17 program.²

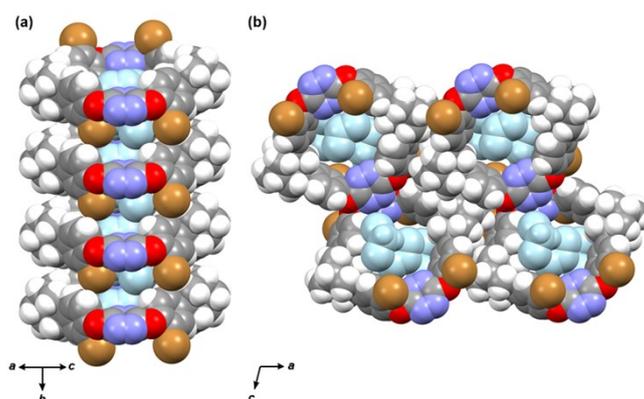


Fig. S1 Packing diagram of **1** and dichloromethane in crystal **1a**; (a) side view of tubular structure and (b) top view of the network structure. Dichloromethane molecules were shown in light blue.

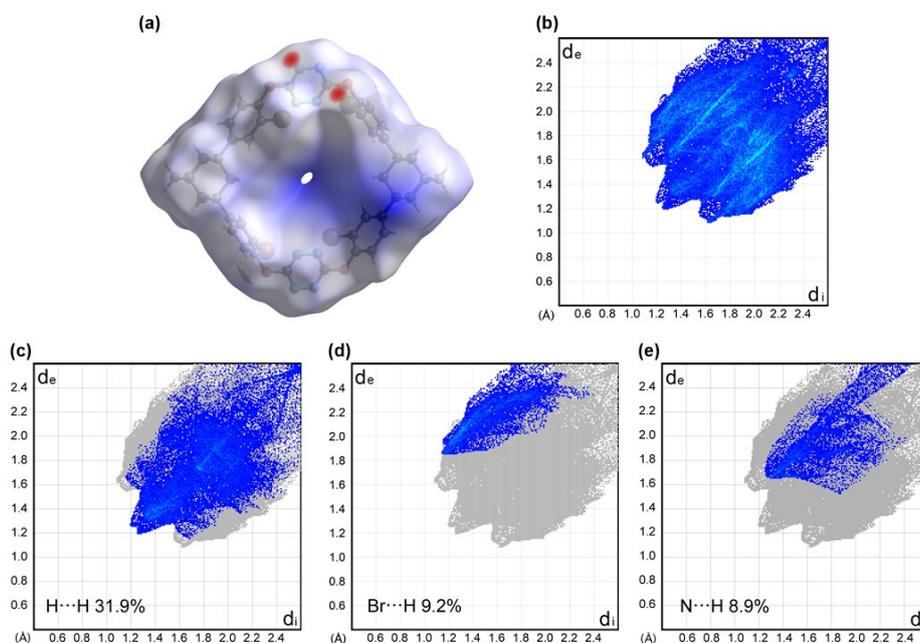


Fig. S2 Hirshfeld surface mapped with d_{norm} (a) and 2D fingerprint plot (b) of **1** in crystal **1c**. 2D fingerprint plots focusing on the specific interactions of **1** in crystal **1c** (c–e).

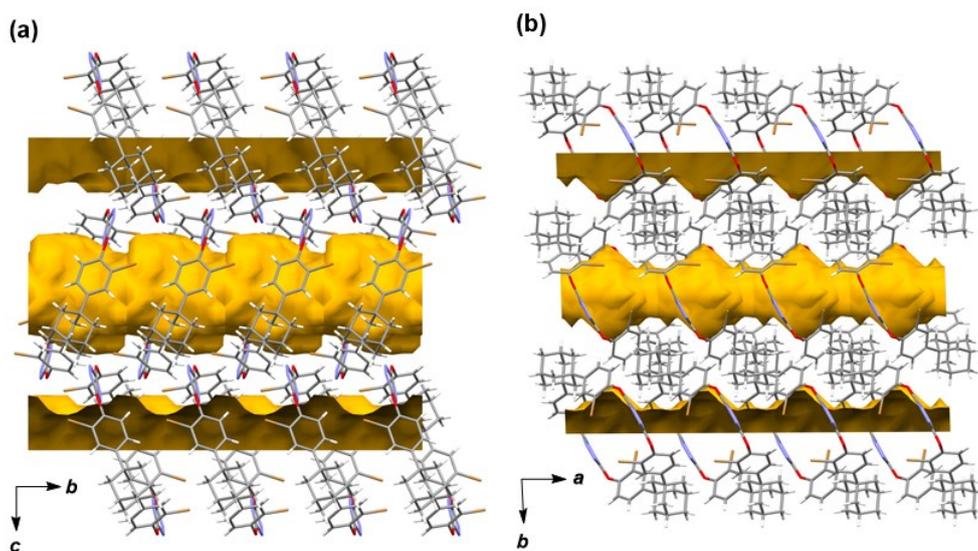


Fig. S3 Calculated voids of crystals (a) **1b** and (b) **1c** with a side view.

Quantitative determination for the composition of **1** and guests (**3** and **4**) in crystals **1d** and **1e** by the ^1H NMR measurements

The crystals **1c** (1.0 mg) were soaked in styrene (**3**) or ethylbenzene (**4**) (0.2 mL) for 24 h at room temperature. The resulting crystals (**1d** and **1e**) were collected, washed with a small amount of diethyl ether, and dried under air for 1 h on a filter paper. The inclusion crystals were dissolved in CDCl_3 followed by the ^1H NMR measurements. These experimental procedures were performed on three times. The stoichiometry of the crystals was estimated based on the integral ratios of the signal of the aromatic proton at δ 7.57 ppm of **1** and the corresponding protons of the guest molecules. As a result, the molar ratio of **1** and guests was indicated to be an average of approximately 1 : 1 for crystals **1c** and **1d**.

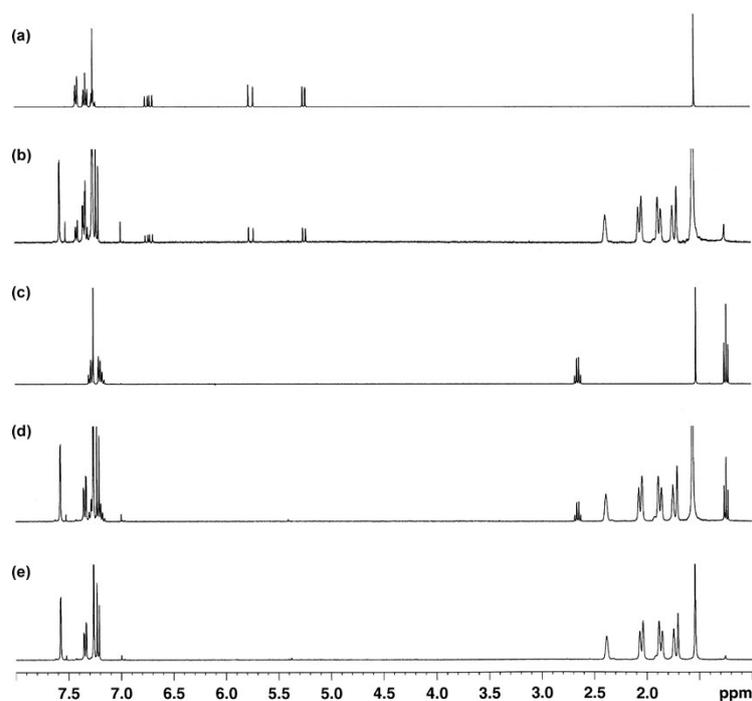


Fig. S4 ^1H NMR spectra (400 MHz, CDCl_3); (a) styrene (**3**), (b) crystal **1d**, (c) ethylbenzene (**4**), (d) crystal **1e**, and (e) macrocycle **1**.

Single crystal X-ray diffraction experiment for crystal **1b**

The crystals **1a** (5.0 mg) were soaked in diethyl ether (20.0 mL) at room temperature. After for 12 h, the solution was removed by filtration. This procedure was repeated on three times to afford crystal **1b**. The pink prismatic crystal **1b** (0.050 × 0.100 × 0.100 mm³) was immersed in Paraton-N oil and placed in the N₂ cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE, CuK α : λ = 1.54178 Å). Absorption correction was performed by an empirical method implemented in SADABS.³ Structure solution and refinement were performed by using SHELXT-2014/5⁴ and SHELXL-2018/3⁵.

C₅₂H₅₀Br₄N₈O₅, *M*_r = 1186.64; monoclinic, space group *P*2₁/*n*, *Z* = 2, *D*_{calc} = 1.490 g·cm⁻³, *a* = 16.1540(15), *b* = 7.1493(7), *c* = 23.597(2) Å, β = 103.890(3)°, *V* = 2645.5(4) Å³, 37077 measured and 5170 independent [*I* > 2 σ (*I*)] reflections, 338 parameters, 37 restraints, final *R*₁ = 0.0461, *wR*₂ = 0.1361, *S* = 1.083 [*I* > 2 σ (*I*)]. CCDC 2014531.

All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23, and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. The diethyl ether molecule (C1a, C2a, C3a, C4a, and O1a) which is located on the crystallographic symmetry position was firstly refined with the free variable and finally refined with PART -n fixing the site occupancy factor to be 0.5. These atoms were refined by PART applying with DANG, DELU, DFIX, SIMU, and SUMP.

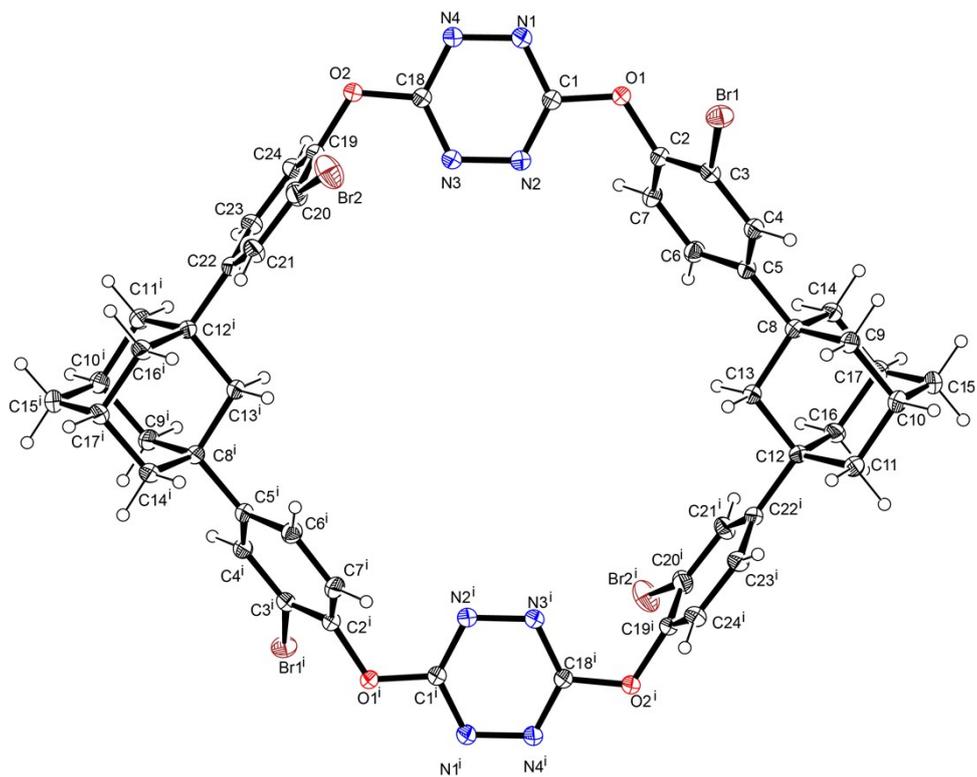


Fig. S5 Ortep drawing of **1** in crystal **1b** (30% probability).

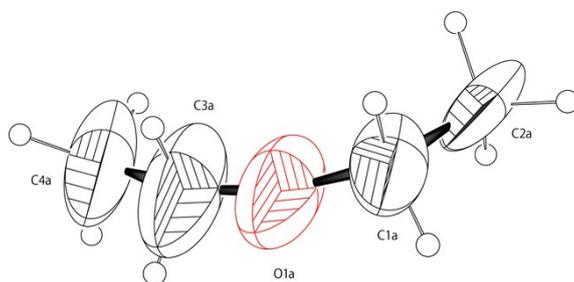


Fig. S6 Ortep drawing of guest molecule in crystal **1b** (30% probability).

Single crystal X-ray diffraction experiment for crystal **1c**

The crystals **1b** were treated under the vacuum for 24 h at 100 °C to afford crystal **1c**. The pink prismatic crystal **1c** ($0.200 \times 0.100 \times 0.100$ mm³) was immersed in Paraton-N oil and placed in the N₂ cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE, CuK α : $\lambda = 1.54178$ Å). Absorption correction was performed by an empirical method implemented in SADABS.³ Structure solution and refinement were performed by using SHELXT-2014/5⁴ and SHELXL-2018/3⁵.

C₄₈H₄₀Br₄N₈O₄, *Mr* = 1112.52; monoclinic, space group *P*2₁/*c*, *Z* = 2, *D*_{calc} = 1.522 g·cm⁻³, *a* = 7.6473(12), *b* = 14.096(2), *c* = 22.535(4) Å, β = 91.643(4)°, *V* = 2428.2(7) Å³, 33751 measured and 5051 independent [*I* > 2 σ (*I*)] reflections, 290 parameters, final *R*₁ = 0.0410, *wR*₂ = 0.1258, *S* = 1.284 [*I* > 2 σ (*I*)]. CCDC 2014532.

All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 23, and 43) with Uiso values constrained to 1.2/1.5 Ueq of their parent atoms.

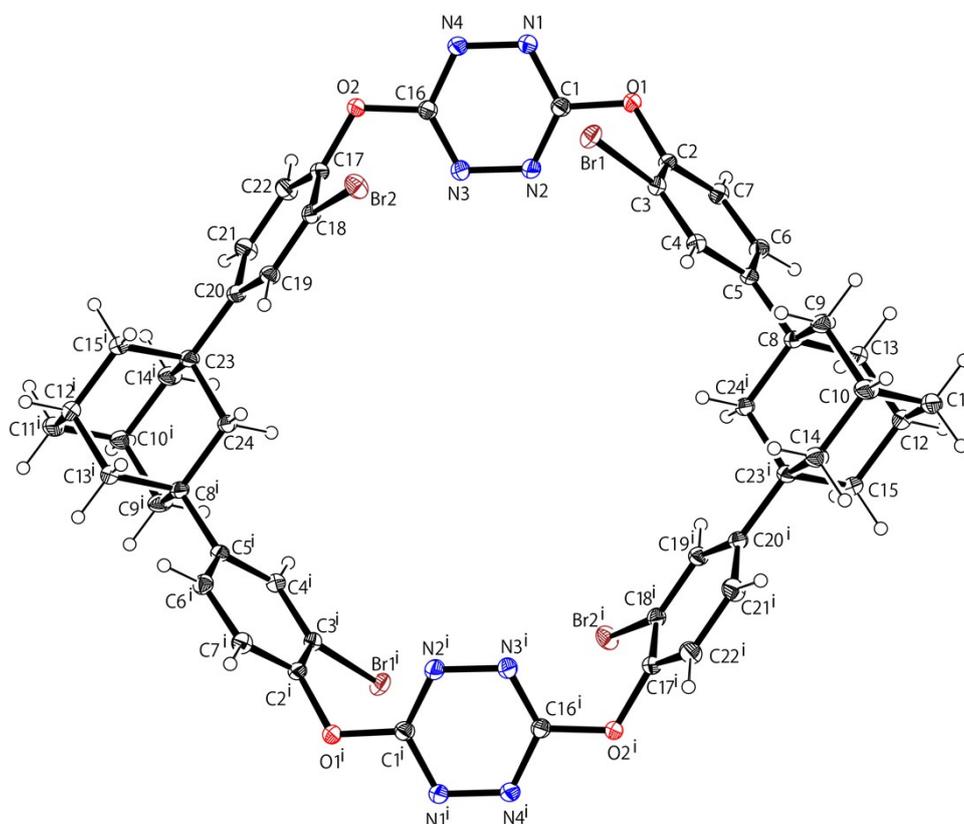


Fig. S7 Ortep drawing of **1** in crystal **1c** (30% probability).

Single crystal X-ray diffraction experiment for crystal 1d

The low diffracting pink prismatic crystal ($0.100 \times 0.100 \times 0.050$ mm³), obtained from the crystal **1c** soaked with styrene for 24 h at room temperature, was immersed in Paraton-N oil and placed in the N₂ cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE, CuK α : $\lambda = 1.54178$ Å). Absorption correction was performed by an empirical method implemented in SADABS.³ Structure solution and refinement were performed by using SHELXT-2014/5⁴ and SHELXL-2018/3⁵.

C₅₆H₄₈Br₄N₈O₄, $M_r = 1216.66$; monoclinic, space group $P2_1/c$, $Z = 2$, $D_{\text{calc}} = 1.666$ g·cm⁻³, $a = 7.6615(6)$, $b = 14.1104(11)$, $c = 22.4415(17)$ Å, $\beta = 91.574(2)^\circ$, $V = 2425.2(3)$ Å³, 35013 measured and 4828 independent [$I > 2\sigma(I)$] reflections, 360 parameters, 32 restraints, final $R_1 = 0.0269$, $wR_2 = 0.0749$, $S = 1.038$ [$I > 2\sigma(I)$]. CCDC 2014533.

All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 23, 43 and 93) with Uiso values constrained to 1.2/1.5 Ueq of their parent atoms. The disordered Br atom was refined with PART n. Occupancy ratio was 35/65 (Br2a / Br2b).

The styrene molecule (C1a, C2a, C3a, C4a, C5a, C6a, C7a, and C8a) which is located on the crystallographic symmetry position was firstly refined with the free variable and finally refined with PART -n fixing the site occupancy factor to be 0.5. These atoms were refined by PART applying with DFIX, DANG, DELU, EADP, FLAT, SIMU, and SUMP.

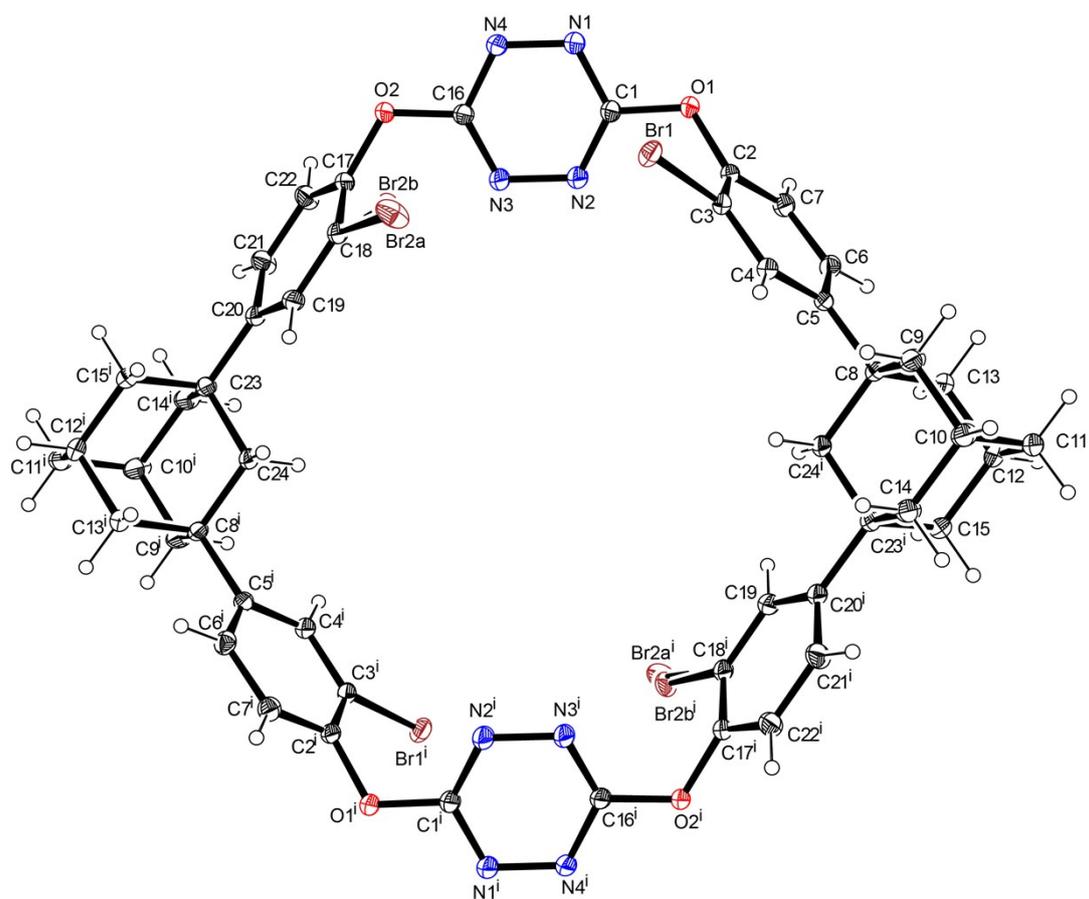


Fig. S8 Ortep drawing of **1** in crystal **1d** (30% probability).

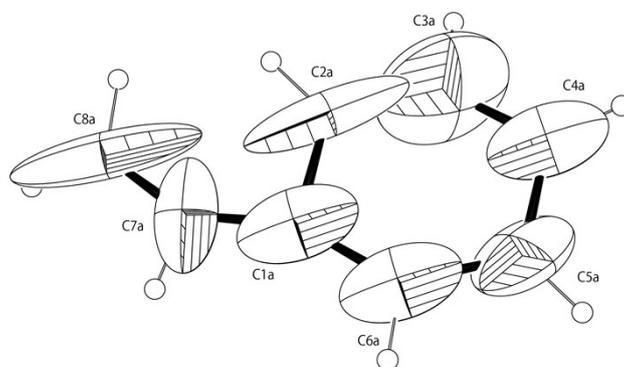


Fig. S9 Ortep drawing of guest molecule in crystal **1d** (30% probability).

Single crystal X-ray diffraction experiment for crystal 1e

The low diffracting pink prismatic crystal ($0.100 \times 0.080 \times 0.080$ mm³), obtained from the crystal **1c** soaked with ethylbenzene for 24 h at room temperature, was immersed in Paratone-N oil and placed in the N₂ cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE, CuK α : $\lambda = 1.54178$ Å). Absorption correction was performed by an empirical method implemented in SADABS.³ Structure solution and refinement were performed by using SHELXT-2014/5⁴ and SHELXL-2018/3⁵.

C₅₆H₅₀Br₄N₈O₄, $M_r = 1218.68$; monoclinic, space group $P2_1/c$, $Z = 2$, $D_{\text{calc}} = 1.651$ g·cm⁻³, $a = 7.6814(17)$, $b = 14.159(3)$, $c = 22.547(5)$ Å, $\beta = 91.184(6)^\circ$, $V = 2451.6(9)$ Å³, 35606 measured and 4945 independent [$I > 2\sigma(I)$] reflections, 373 parameters, 10 restraints, final $R_1 = 0.0297$, $wR_2 = 0.0849$, $S = 1.013$ [$I > 2\sigma(I)$]. CCDC 2014534.

All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23, and 43) with Uiso values constrained to 1.2/1.5 Ueq of their parent atoms. The disordered Br atom was refined with PART n. Occupancy ratio was 77/23 (Br2a / Br2b).

The ethylbenzene molecule (C1a, C2a, C3a, C4a, C5a, C6a, C7a, and C8a) which is located on the crystallographic symmetry position was firstly refined with the free variable and finally refined with PART -n fixing the site occupancy factor to be 0.5. These atoms were refined by PART applying with DFIX, DANG, FLAT, and, SUMP.

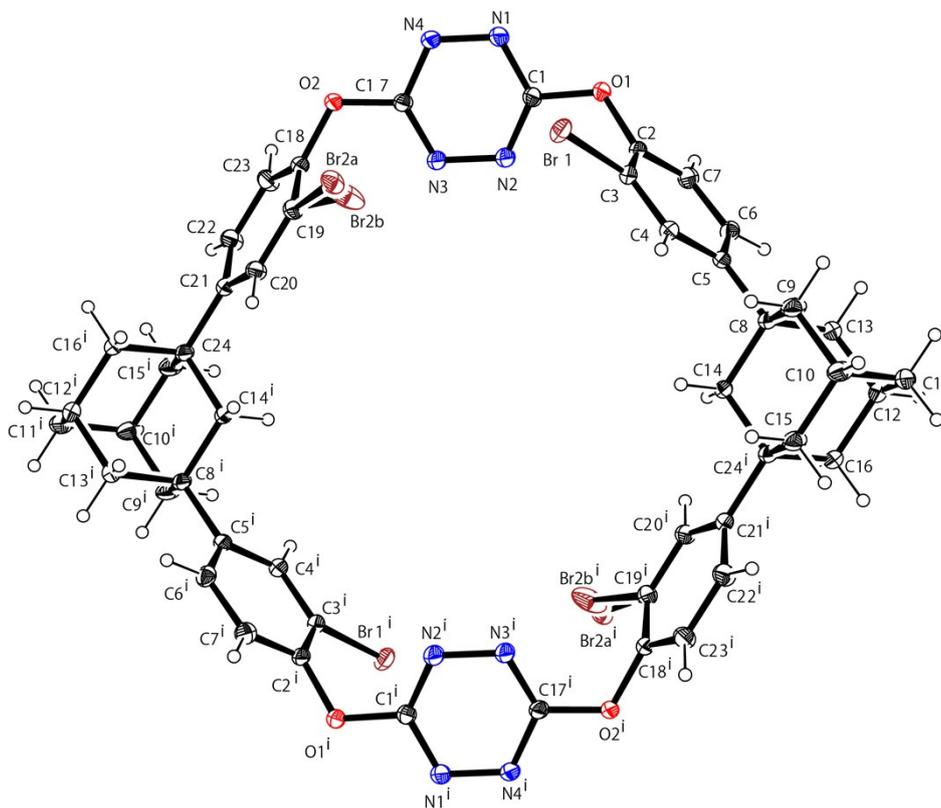


Fig. S10 Ortep drawing of **1** in crystal **1e** (30% probability).

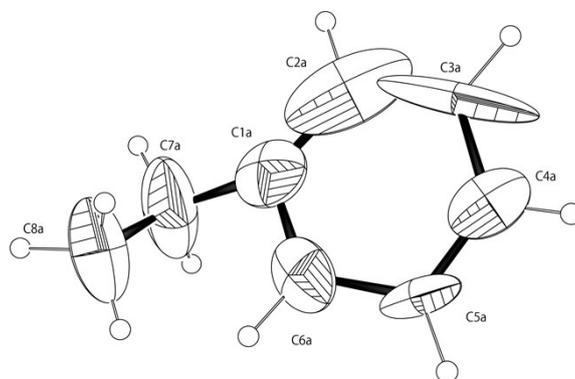


Fig. S11 Ortep drawing of guest molecule in crystal **1e** (30% probability).

References

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