Supplementary Information

Dimeric structures of ketones and esters in porous adaptive crystals of adamantane-containing macrocycle

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The composition of macrocycles and guests in crystals by ^{1}H NMR analyses

Crystal **1e** (2.0 mg) were immersed in each guest (1.0 mL) for 24 h at room temperature. The resulting crystals **1a**–**d** were collected, and dried under air for 0.5 h on a filter paper. The crystals were dissolved in $CDCl_3$ followed by ^{1}H NMR analyses (Fig. S1–4). The composition of crystals was estimated from the integral ratios of the signal of the proton at δ 2.38 ppm of **1** and the corresponding protons of the guest molecules. The molar ratio of macrocycles and each guest was indicated to be approximately 1:2 for crystals **1a**–**d**, respectively.

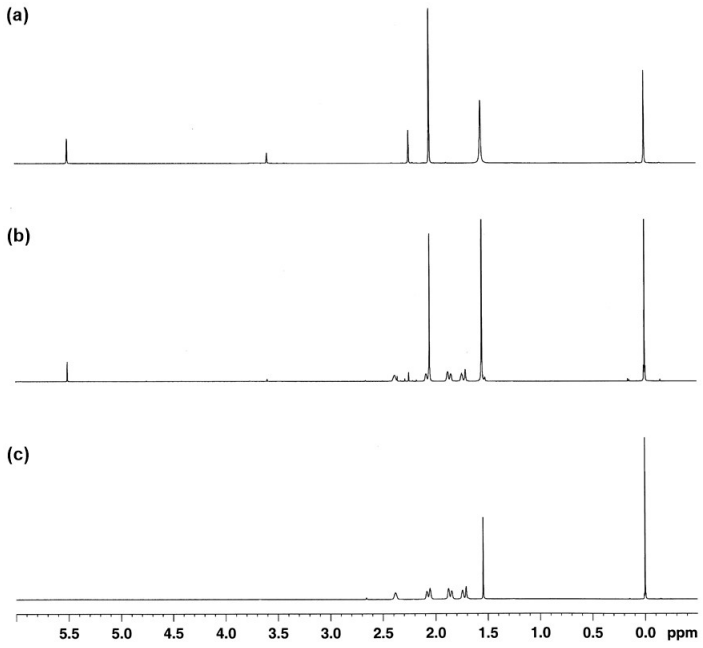

Fig. S1 Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$); (a) acetylacetone, (b) crystal **1a**, and (c) macrocycle **1**.

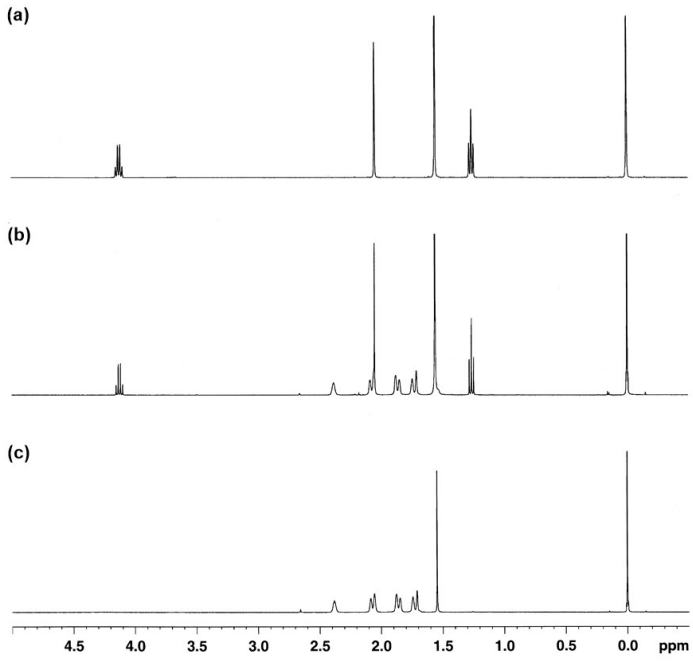

Fig. S2 Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$); (a) ethyl acetate, (b) crystal **1b**, and (c) macrocycle **1**.

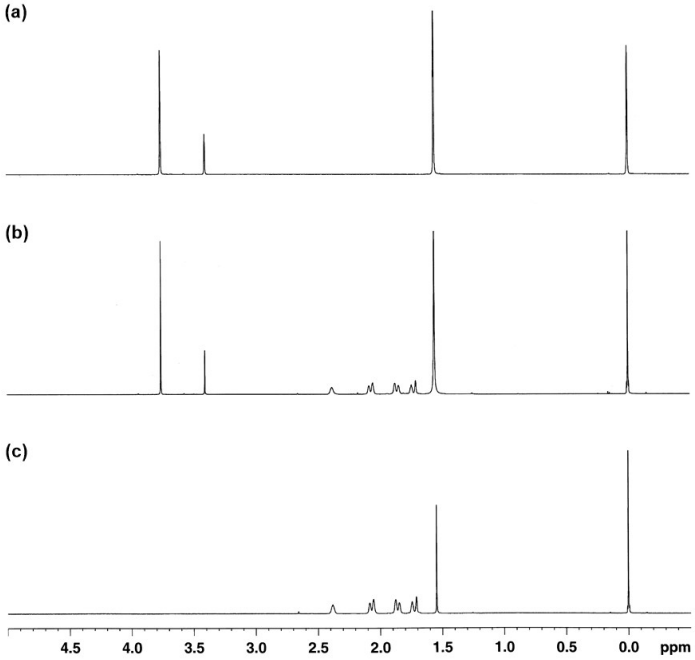

Fig. S3 Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$); (a) dimethyl malonate, (b) crystal **1c**, and (c) macrocycle **1**.

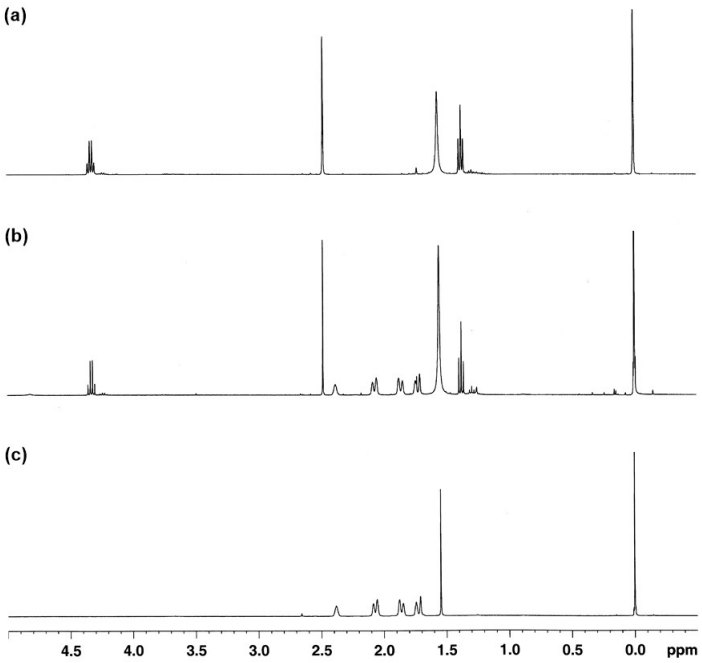

Fig. S4 Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$); (a) ethyl pyruvate, (b) crystal **1d**, and (c) macrocycle **1**.

Single crystal X-ray diffraction experiment for crystal 1a

A colorless prismatic crystal (0.100 × 0.050 × 0.050 mm^3), obtained from the crystal **1e** soaked with acetylacetone for 24 h at room temperature, was immersed in Paraton-N oil and placed in the N_2 cold stream at 100 K. Data were collected using diffractometer with a CMOS detector (Bruker D8 VENTURE, CuKα: λ = 1.54178 Å). Absorption correction was performed by an empirical method implemented in SADABS.[1] Structure solution and refinement were performed by using SHELXT-2018/2[2] and SHELXL-2019/2[3].

$C_{62}H_{60}Br_4N_4O_8$, Mr = 1308.78; monoclinic, space group $P2_1/c$, Z = 2, D_{calc} = 1.582 $g{\cdot}cm^{-3}$, a = 11.3262(17), b = 15.883(2), c = 16.168(2) Å, β = 109.122(6)°, V = 2748.1(7) $Å^3$, 39054 measured and 5356 [$I > 2\sigma(I)$], 5761 [all] independent reflections, 358 parameters, R_1 = 0.0345, wR_2 = 0.0924, S = 1.026 [$I > 2\sigma(I)$], R_1 = 0.0369, wR_2 = 0.0945, S = 1.026 [all]. CCDC 2365042.

All non-hydrogen atoms were refined anisotropically. The O-H hydrogen atom was assigned from the difference Fourier map, and refined. Another hydrogen atoms were geometrically placed 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.

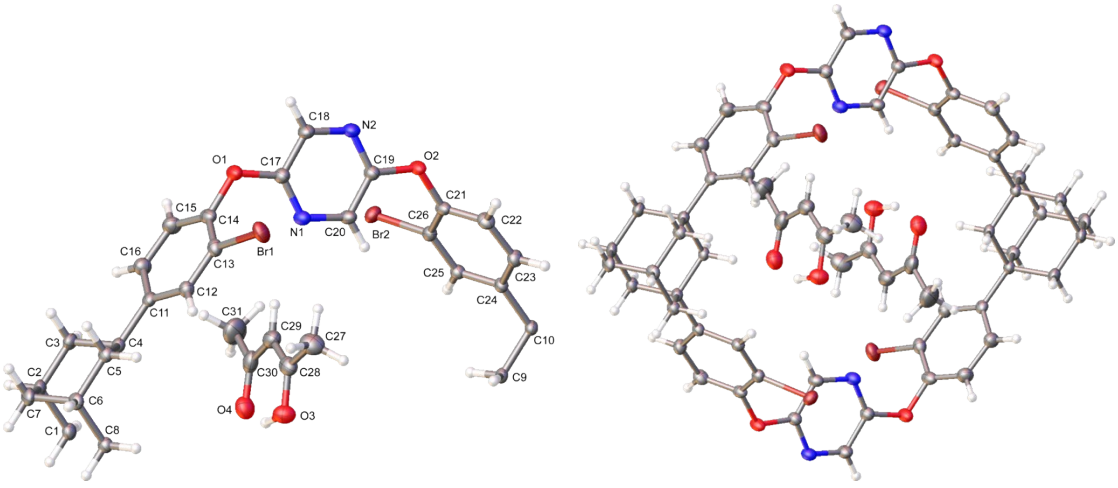

Fig. S5 Ortep drawing of **1** and acetylacetone in crystal **1a** (50% probability). Left: asymmetric unit. Right: one complete unit.

Single crystal X-ray diffraction experiment for crystal 1b

A colorless prismatic crystal (0.100 × 0.100 × 0.100 mm^3), obtained from the crystal **1e** soaked with ethyl acetate for 24 h at room temperature, was immersed in Paraton-N oil and placed in the N_2 cold stream at 100 K. Data were collected using diffractometer with a CMOS detector (Bruker D8 VENTURE, CuKα: λ = 1.54178 Å). Absorption correction was performed by an empirical method implemented in SADABS.[1] Structure solution and refinement were performed by using SHELXT-2018/2[2] and SHELXL-2019/2[3].

$C_{60}H_{60}Br_4N_4O_8$, *M*r = 1284.76; monoclinic, space group $P2_1/c$, Z = 2, D_{calc} = 1.582 $g{\cdot}cm^{-3}$, a = 11.6223(18), b = 15.384(2), c = 15.956(3) Å, β = 109.037(5)°, V = 2696.9(7) $Å^3$, 37945 measured and 5290 [$I > 2\sigma(I)$], 5570 [all] independent reflections, 345 parameters, R_1 = 0.0328, wR_2 = 0.0910, S = 1.060 [$I > 2\sigma(I)$], R_1 = 0.0342, wR_2 = 0.0927, S = 1.060 [all]. CCDC 2365043.

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically placed 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.

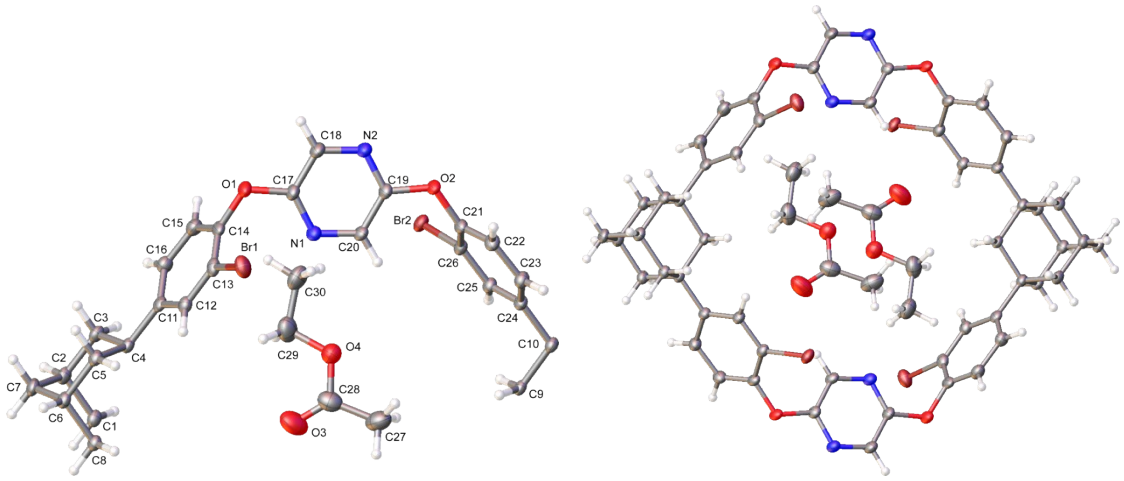

Fig. S6 Ortep drawing of **1** and ethyl acetate in crystal **1b** (50% probability). Left: asymmetric unit. Right: one complete unit.

Single crystal X-ray diffraction experiment for crystal 1c

A colorless prismatic crystal (0.080 × 0.050 × 0.050 mm^3), obtained from the crystal **1e** soaked with dimethyl malonate for 24 h at room temperature, was immersed in Paraton-N oil and placed in the N_2 cold stream at 100 K. Data were collected using diffractometer with a CMOS detector (Bruker D8 VENTURE, CuKα: λ = 1.54178 Å). Absorption correction was performed by an empirical method implemented in SADABS.[1] Structure solution and refinement were performed by using SHELXT-2018/2[2] and SHELXL-2019/2[3].

$C_{62}H_{60}Br_4N_4O_{12}$, Mr = 1372.78; triclinic, space group P-1, Z = 1, D_{calc} = 1.651 g·cm^{-3}, a = 10.8936(10), b = 11.3460(10), c = 12.0159(11) Å, α = 68.692(4), β = 89.676(4), γ = 86.232(4)°, V = 1380.4(2) $Å^3$, 20023 measured and 5184 [$I > 2\sigma(I)$], 5577 [all] independent reflections, 372 parameters, R_1 = 0.0482, wR_2 = 0.1331, S = 1.041 [$I > 2\sigma(I)$], R_1 = 0.0509, wR_2 = 0.1358, S = 1.041 [all]. CCDC 2365044.

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically placed 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.

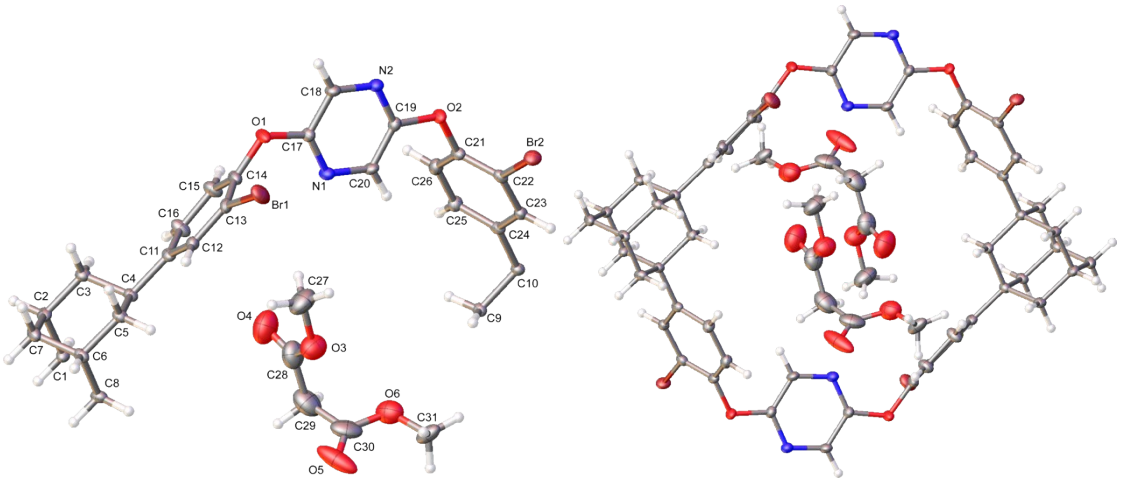

Fig. S7 Ortep drawing of **1** and dimethyl malonate in crystal **1c** (50% probability). Left: asymmetric unit. Right: one complete unit.

Single crystal X-ray diffraction experiment for crystal 1d

A colorless prismatic crystal (0.120 × 0.08 × 0.08 mm^3), obtained from the crystal **1e** soaked with ethyl pyruvate for 24 h at room temperature, was immersed in Paraton-N oil and placed in the N_2 cold stream at 100 K. Data were collected using diffractometer with a CMOS detector (Bruker D8 VENTURE, CuKα: λ = 1.54178 Å). Absorption correction was performed by an empirical method implemented in SADABS.[1] Structure solution and refinement were performed by using SHELXT-2018/2[2] and SHELXL-2019/2[3].

$C_{60.84}H_{58.15}Br_4N_4O_{9.30}$, *M*r = 1313.86; triclinic, space group *P*-1, *Z* = 1, D_{calc} = 1.588 $g{\cdot}cm^{-3}$, *a* = 10.7974(15), *b* = 11.3923(16), *c* = 12.1371(17) Å, *α* = 67.421(4), *β* = 88.195(5), *γ* = 85.102(4)°, *V* = 1373.5(3) $Å^3$, 20610 measured and 5241 [$I > 2\sigma(I)$], 5621 [all] independent reflections, 364 parameters, 42 restraints, R_1 = 0.0550, wR_2 = 0.1591, *S* = 1.087 [$I > 2\sigma(I)$], R_1 = 0.0574, wR_2 = 0.1610, *S* = 1.126 [all]. CCDC 2365045.

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically placed 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. Although guest ethyl pyruvate molecules were disordered, the major guest structure (88% occupancy) was successfully refined with SIMU. To confirm that guest molecules were fully occupied in the void surrounded by host molecules, the solvent mask was applied to the final structure excluded the guest molecules in OLEX2[4]. (CCDC 2365046) The result is as follows. A solvent mask was calculated and 120 electrons were found in a volume of 414 $Å^3$ in 1 void per unit cell. This is consistent with the presence of $2[C_5H_8O_3]$ per formula unit which account for 124 electrons per unit cell.

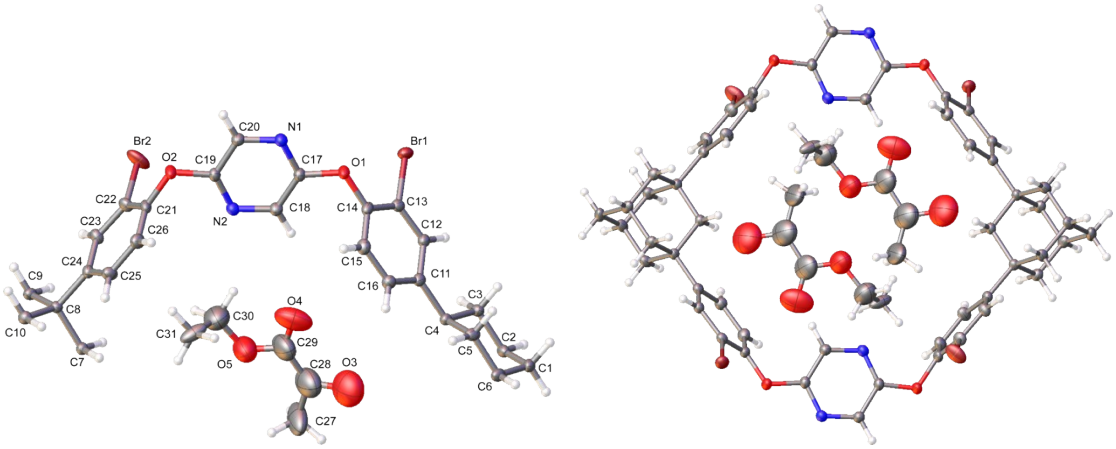

Fig. S8 Ortep drawing of **1** and ethyl pyruvate in crystal **1d** (50% probability). Left: asymmetric unit. Right: one complete unit.

References

(1) G. M. Sheldrick, *SADABS*. University of Göttingen, Germany, 1996.

(2) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3–8.

(3) G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8.

(4) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmanna, *J. Appl. Cryst.,* 2009, **42**, 339–341.