

Electronic Supporting Information

**Channel structure for guest inclusion based on hexameric assembly of
thiacalix[4]arene analogue**

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Supporting Information Comprises:

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2. Crystal data and structure determination for the hexameric assembly 2

Crystal data and structure determination for the hexameric assembly **2**.

Table S1 Crystal data and structure refinement for the hexameric assembly **2**.

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Figure S1 Thermogravimetric analysis (TGA) of hexameric assembly **2**.

1. Materials and Experimental Methods:

1. Synthesis of de-*tert*-butylthiacalix[4]arene

De-*tert*-butylthiacalix[4]arene was obtained by de *tert*-butylation reaction from *p*-*t*Bu-thiacalix[4]arene¹ which was prepared according to our previously reported procedures². ¹H NMR spectra were taken on a Bruker DPX 300, and measured using tetramethylsilane as an internal standard and CDCl₃ as a solvent, unless otherwise noted.

2. Synthesis of brominated-thiacalix[4]arene

Brominated-thiacalix[4]arene was obtained by bromination reaction from De-*tert*-butylthiacalix[4]arene which was prepared according to our previously reported procedures^{1c}. ¹H NMR spectra were taken on a Bruker DPX 300, and measured using DMSO as a solvent, unless otherwise noted. Describe below the detail procedure for the synthesis of brominated-thiacalix[4]arene: To a suspension of de-*tert*-butylthiacalix[4]arene (3.0 g, 6 mmol) in acetone (180 mL) was added *N*-Bromosuccinimide (5.3 g, 29.6 mmol) to the solution. After 24 hours stirring, the brominated-thiacalix[4]arene was filtered off and washed with CHCl₃ (1×100ml). The filtered product was dried under vacuum (0.01 mmHg) at 70°C for 24h, brominated-thiacalix[4]arene (3.003 g, 3.69 mmol, 61.5%) was obtained.

3. Synthesis of brominated at upper rim and propyl etherified at lower rim of thiacalix[4]arene (1)

To a suspended solution of Brominated-thiacalix[4]arene (2.1 g, 2.58 mmol) in acetone (150 mL) and cesium carbonate (6.4 g, 4.9 mmol) was added. The suspension was refluxed for 20 min and 1-iodopropane (4 mL, 27.6 mmol) was added to the solution. The reflux was maintained for 24 h under nitrogen and the solvent was evaporated to dryness. The powder was dissolved in CHCl₃ (30 mL) and treated with 2N-HCl (30 mL) and water (2×30 mL). The organic phase was dried over non-hydrous Na₂SO₄ and concentrated under reduced pressure, washed with ethanol and filtered. The filtered product was chromatographed on silica gel using *n*-hexane-CHCl₃ (2:1) as an eluting solvent. Eluted fractions were collected and evaporated off to give a white powder. Recrystallization from CHCl₃-hexane(1:1 v/v) afforded colorless crystalline product (1.1g, 1.12 mmol, 43.4%, total yield 27%).

Supplementary References:

1. (a) Y. Higuchi, M. Narita, T. Niimi, N. Ogawa, F. Hamada, H. Kumagai, N. Iki, S. Miyano, C. Kabuto, *Tetrahedron*, 2000, **56**, 4659; (b) C. Kabuto, Y. Higuchi, T. Niimi, F. Hamada, N. Iki, N. Morohashi, S. Miyano, *J. Incl. Phenom. Macrocycl. Chem.*, 2002, **42**, 89; (c) O. Kasyan, D. Swierczynski, A. Drapailo, K. Suwinska, J. Lipkowski, V. Kalchenko, *Tetrahedron Lett.*, 2003, **44**, 7167.
2. (a) Y. Kondo, K. Endo, N. Iki, S. Miyano, F. Hamada, *J. Incl. Phenom. Macrocycl. Chem.*, 2005, **52**, 45; (b) Y. Kondo and F. Hamada, *J. Incl. Phenom. Macrocycl. Chem.*, 2007, **58**, 123.

2. Crystal data and structure determination for the hexameric assembly 2

Crystal data and structure determination for the hexameric assembly 2: C₂₄₀H₂₆₄Br₂₄O₂₄S₂₄, *M* = 6219.79, size = 0.35 × 0.3 × 0.3 mm, trigonal, space group *R*-3c, colorless prism, *a* = *b* = 30.7287(12) Å, *c* = 23.7570(12) Å, γ = 120.00°, *U* = 19427.2(15) Å³, *Z* = 3, μ = 3.961 mm⁻¹, *T* = 100(2) K, Mo-K α radiation (λ = 0.71075 Å), 50935 measured reflections, 3952 unique reflections (*R*_{int} = 0.0623), 3214 observed reflections (*I* > 2.00 σ (*I*)), 233 parameters, *R*₁ = 0.0377, *wR*₂ = 0.0862, Final GOF = 1.071. The structure of **2** were solved by direct methods using *SHELXS-97*³ and refined by full-matrix least-squares on *F*² using the *SHELXL-97*⁴ program. The non-hydrogen atoms were refined anisotropically. The disordered carbon atoms of two cyclohexane molecules were refined isotropically. One cyclohexane molecule (C19A and C19B) was refined as disordered molecule, occupancy of which was fixed at 0.78 and 0.22, respectively. Other cyclohexane molecule (C20 and C21) was refined as disordered molecule, occupancy of which was fixed at 0.75 and 0.25, respectively. Hydrogen atoms of cyclohexane molecules were refined with constraints and thiacalixarene hydrogen atoms were geometrically calculated. Crystallographic data of the crystals have been deposited at the Cambridge Crystallographic Data Center in CIF format CCDC no 785498.

Supplementary References:

3. Sheldrick, G. M. *SHELXS-97* Program for solution of crystal structures, University of Göttingen, Germany, 1997.
4. Sheldrick, G. M. *SHELXL-97* Program for refinement of crystal structures, University of Göttingen, Germany, 1997.

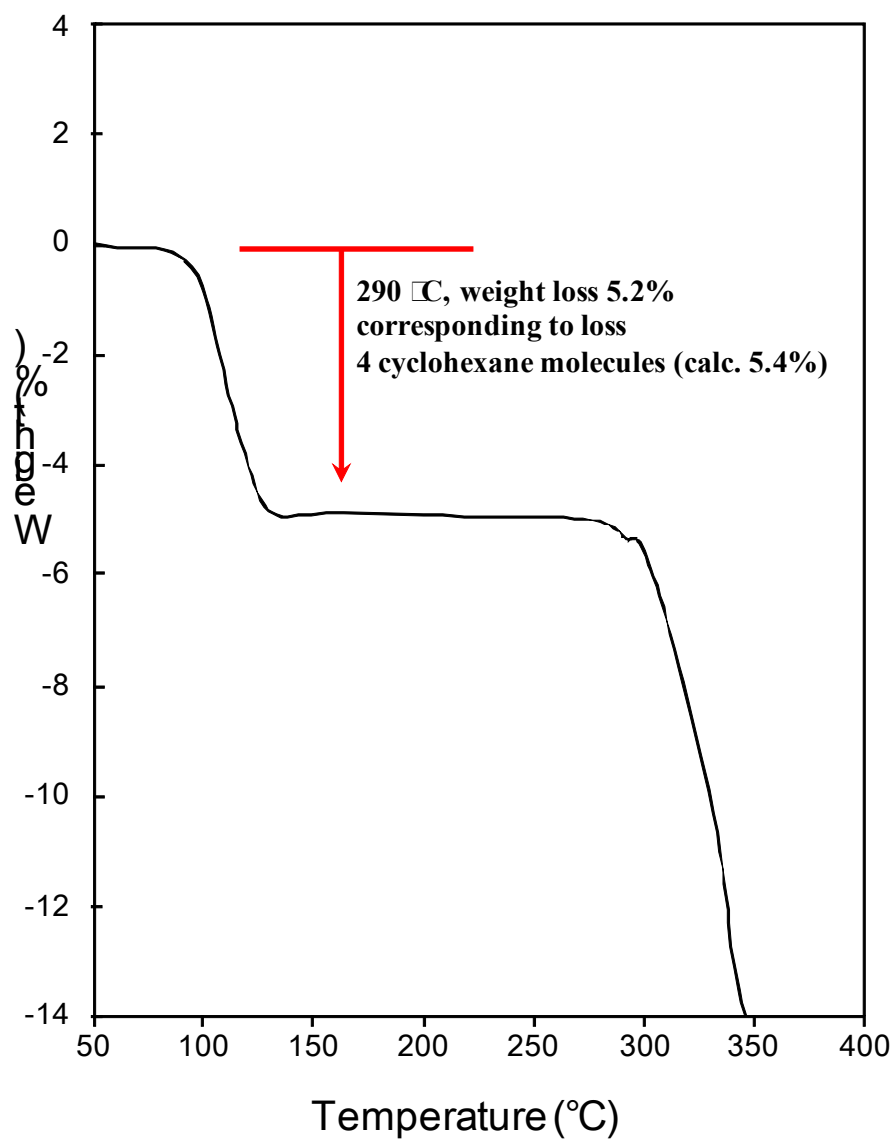
Supplementary Table S1 Crystal data and structure refinement for the hexameric assembly **2**.

Complex	2
Empirical formula	$C_{240}H_{264}Br_{24}O_{24}S_{24}$
Formula weight	6219.79
Crystal size / mm	$0.35 \times 0.3 \times 0.3$
Temperature / K	100(2)
Crystal system	trigonal
Space group	$R\bar{3}c$
$a / \text{\AA}$	30.7287(12)
$b / \text{\AA}$	30.7287(12)
$c / \text{\AA}$	23.7570(12)
$\alpha / ^\circ$	90.00
$\beta / ^\circ$	90.00
$\gamma / ^\circ$	120.00
$U / \text{\AA}^3$	19427.2(15)
Z	3
$D_{\text{calcd}} / \text{g cm}^{-3}$	1.595
μ / mm^{-1}	3.961
$F(000)$	9360.0
Reflection collected	50935
Independent reflections (R_{int})	3952 (0.0623)
Data / parameters	3952 / 233
Goodness-of-fit	1.071
R and wR for $I > 2\sigma(I)$	0.0377, 0.0862

3. Vapor adsorption measurement of the guest-free hexameric assembly toward gaseous cyclohexane molecules

The binding isotherms were obtained with a BELSORP 18 automated gas adsorption apparatus. In the sample chamber (ca. 15 mL) maintained at $25.0 \pm 0.1^\circ\text{C}$ was placed the guest-free hexameric assembly (ca. 225 mg), which has been pretreated at 50°C at $< 10^{-3}$ Torr for 7 days just prior to use. The larger gas chamber (176.36 mL) with a pressure gauge was kept at $50 \pm 0.1^\circ\text{C}$. Helium gas at certain pressure was introduced in the gas chamber and was allowed to diffuse into the sample chamber by opening a valve. The change in pressure allowed an accurate determination of volume of the total gas phase. Host-guest complexation was monitored in a similar manner by using a guest cyclohexane vapor in place of helium. The amount of guest adsorbed was calculated readily from the pressure difference ($P_{\text{cal}} - P$), where, P_{cal} is the calculated pressure if there were no guest adsorption, as in the case of helium, and P is the observed equilibrium pressure, as which the change in pressure in 300 sec had become smaller than 1 % of the pressure at the point. All operations were computer-controlled and automatic.

4. Thermogravimetric analysis (TGA) of hexameric assembly



Supplementary Figure S1 Thermogravimetric analysis (TGA) of hexameric assembly **2**.