

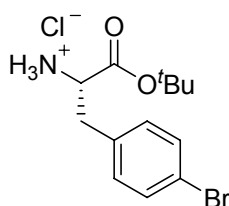
Electronic Supplementary Information

Self-assembled octameric cage constructed by potassium salt of *p*-*tert*-butylcalix[6]arene *p*-bromophenylalanine derivative in solid state

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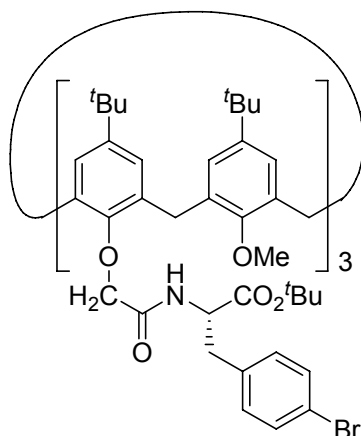
Synthesis

General: Melting points are uncorrected. Optical rotations were measured using a JASCO DIP-360 digital polarimeter. IR absorption spectra (FT: diffuse reflectance spectroscopy) were measured with a Horiba FT-210 IR spectrometer using KBr powder. ^1H NMR spectra were measured with a JEOL JNM-GX500 spectrometer (500 MHz) or a JEOL JNM-AL300 spectrometer (300 MHz). ^{13}C NMR spectra were measured with a JEOL JNM-AL300 spectrometer (75 MHz) or a JEOL JNM-EX270 spectrometer (67.8 MHz). All signals are expressed as ppm downfield from tetramethylsilane used as an internal standard (δ value). The following abbreviations are used: singlet (s), doublet (d), triplet (t), and multiplet (m). Fast atom bombardment (FAB) mass spectra were obtained with JEOL JMS-600H and JEOL JMS-700. Time of flight (TOF) mass spectra were obtained using Applied Biosystems Voyager-DE. Unless stated, all reactions were carried out under N_2 atmosphere. Merck Kieselgel 60 was used as an adsorbent for column chromatography.



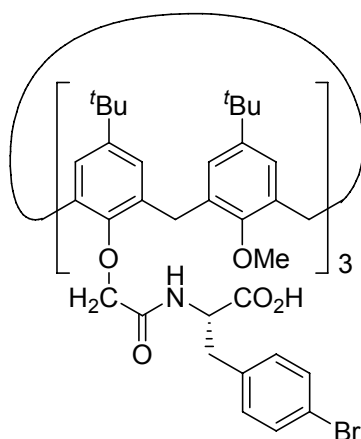
***p*-Bromo-L-phenylalanine *tert*-butyl ester hydrochloride (4).** A sealed tube was charged with *p*-bromo-L-phenylalanine (2.00 g, 8.19 mmol), dioxane (12 mL), conc. H_2SO_4 (2 mL) and liq. 2-methylpropene (ca. 8 mL). After sealing, the mixture was stirred at rt overnight. The reaction mixture was poured onto 50 mL of 2 N NaOH, and the mixture was extracted twice with Et_2O . The solvent was evaporated and the residue was neutralized with 4.0 M HCl–dioxane (2.1 mL) at 0 °C prior to solvent evaporation to

give crude **4**. Pure **4** is a colorless needles (1.57 g, 57%) obtained by recrystallization from MeOH/EtOAc (Found: C, 46.30; H, 5.61; N, 4.18; Br+Cl, 33.97. Calc. for C₁₃H₁₉BrClO₂: C, 46.38; H, 5.69; N, 4.16; Br+Cl, 34.26%); mp 214–215 °C; [α]_D²² +21.3 (*c* 1.00 in MeOH); $\nu_{\max}/\text{cm}^{-1}$ 3439 (NH), 1728 (C=O), 1568 (NH₃⁺); δ_{H} (500 MHz; CD₃OD) 1.43 (9H, s, C(CH₃)₃), 3.15 (2H, d, *J* 7.3, ArCH₂), 4.18 (1H, t, *J* 7.3, NCH), 7.22 (2H, d, *J* 8.5, Ar–H), 7.53 (2H, d, *J* 8.5, Ar–H); δ_{C} (75 MHz; CD₃OD) 28.0 (3C), 37.0, 55.2, 85.4, 122.7, 132.6 (2C), 133.1 (2C), 135.0, 168.9.



5,11,17,23,29,35-Hexa-tert-butyl-37,39,41-trimethoxycalix[6]arene-38,40,42-tris-oxyacetyl-N-p-bromo-L-phenylalanine tert-butyl ester (5). PyProp·PF₆ (1.74 g, 3.74 mmol) was added to a mixture of calix[6]arene derivative **3** (1.49 g, 1.25 mmol), diisopropylethylamine (1.99 mL, 11.6 mmol), and amino acid **4** (1.26 g, 3.74 mmol) in DMF (25 mL). The whole was stirred at rt for 20 h. The mixture was diluted with Et₂O and washed sequentially with 1 N NaOH, water, 10% citric acid, and water. The solution was dried over Na₂SO₄, and the solvent was evaporated. The crude residue was chromatographed on silica gel eluting with hexane–CHCl₃–EtOAc (3:1:1) to give **5** (2.00 g, 78%) as a colorless powder (Found: C, 67.36; H, 7.22; N, 2.00; Br, 11.42. Calc. for C₁₁₄H₁₄₄Br₃N₃O₁₅: C, 67.25; H, 7.13; N, 2.06; Br, 11.77%); mp 114–116 °C; [α]_D²³ +10.0 (*c* 1.00 in CHCl₃); $\nu_{\max}/\text{cm}^{-1}$ 3421 (NH), 1740 (CO₂R), 1686 (CONH); δ_{H} (500 MHz; CDCl₃) 0.78 (27H, s, C(CH₃)₃), 1.40 (27H, s, C(CH₃)₃), 1.42 (27H, s, C(CH₃)₃), 2.30 (9H, s, OCH₃), 3.04 (3H, dd, *J* 7.9 and 14.0, ArCH₂CHN), 3.18 (3H, dd, *J* 6.1 and 14.0, ArCH₂CHN), 3.26 (3H, d, *J* 15.3, ArCH₂Ar), 3.45 (3H, d, *J* 15.3, ArCH₂Ar), 4.26 (3H, d, *J* 15.3, ArCH₂Ar), 4.29 (3H, d, *J* 14.6, OCH₂CO), 4.43 (3H, d, *J* 15.3, ArCH₂Ar), 4.56 (3H, d, *J* 14.6, OCH₂CO), 4.88 (3H, ddd, *J* 6.1, 7.9 and 8.5, NCH), 6.59 (3H, s, Ar–H), 6.63 (3H, s, Ar–H), 7.04 (6H, d, *J* 8.5, Ar–H), 7.17 (6H, d, *J* 8.5, Ar–H), 7.27 (6H, m, Ar–H), 7.51 (3H, d, *J* 8.5, NH); δ_{C} (75 MHz, CDCl₃) 27.9 (9C), 29.7 (3C), 30.1

(3C), 31.0 (9C), 31.6 (9C), 33.9 (3C), 34.2 (3C), 37.5 (3C), 53.0 (3C), 60.1 (3C), 71.2 (3C), 82.2 (3C), 120.7 (3C), 123.6 (3C), 124.1 (3C), 127.9 (3C), 128.5 (3C), 131.0 (6C), 131.4 (6C), 132.0 (3C), 133.0 (6C), 133.2 (3C), 135.2 (3C), 146.2 (3C), 146.7 (3C), 150.4 (3C), 154.4 (3C), 168.3 (3C), 169.7 (3C).



5,11,17,23,29,35-Hexa-*tert*-butyl-37,39,41-trimethoxycalix[6]arene-38,40,42-tris-oxyacetyl-*N*-*p*-bromo-*L*-phenylalanine (2). A solution of **5** (30 mg, 14.7 μ mol) in CF₃CO₂H (0.45 mL) was stirred at rt for 8 h. After the solvent was evaporated, the residue was chromatographed on silica gel eluting with CHCl₃–MeOH–AcOH (97:3:3) to give **1** (25.3 mg, 92%) as a colorless powder (Found: C, 64.50; H, 6.47; N, 2.16; Br, 12.34. Calc. for C₁₀₂H₁₂₀Br₃N₃O₁₅·2H₂O: C, 64.35; H, 6.57; N, 2.21; Br, 12.59%); mp 148–150 °C; $[\alpha]_D^{23} +9.0$ (*c* 1.00 in CHCl₃); $\nu_{\max}/\text{cm}^{-1}$ 3500–3000 (OH), 3402 (NH), 1738 (CO₂H), 1678 (CONH); δ_{H} (300 MHz; CDCl₃) 0.77 (27H, s, C(CH₃)₃), 1.40 (27H, s, C(CH₃)₃), 2.17 (9H, s, OCH₃), 3.17 (3H, d, *J* 14.7, ArCH₂Ar), 3.12–3.20 (3H, m, ArCH₂CHN), 3.30–3.37 (3H, m, ArCH₂CHN), 3.39 (3H, d, *J* 15.0, ArCH₂Ar), 4.24 (3H, d, *J* 14.7, ArCH₂Ar), 4.35 (3H, d, *J* 15.0, ArCH₂Ar), 4.39 (3H, d, *J* 14.8, OCH₂CO), 4.52 (3H, d, *J* 14.8, OCH₂CO), 5.03 (3H, m, NCH), 6.53 (3H, br s, CO₂H), 6.66 (6H, s, Ar–H), 7.03 (6H, d, *J* 8.3, Ar–H), 7.17 (6H, d, *J* 8.3, Ar–H), 7.26 (6H, s, Ar–H), 7.98 (3H, d, *J* 7.3, NH); δ_{C} (67.8 MHz; CDCl₃) 29.5 (3C), 29.8 (3C), 31.0 (9C), 31.7 (9C), 34.1 (3C), 34.4 (3C), 36.7 (3C), 52.9 (3C), 59.8 (3C), 70.9 (3C), 121.0 (3C), 123.7 (3C), 124.0 (3C), 127.8 (3C), 128.5 (3C), 131.0 (6C), 131.4 (6C), 132.0 (3C), 132.6 (3C), 133.2 (3C), 133.5 (3C), 134.5 (3C), 146.0 (3C), 146.8 (3C), 149.6 (3C), 154.0 (3C), 169.3 (3C), 174.5 (3C); TOF-MS: *m/z* = 1868.75 ([M+H]⁺ requires 1868.78), 1890.85 ([M+Na]⁺ requires 1890.76), 1904.36 ([M+H+2H₂O]⁺ requires 1904.81), 1926.11 ([M+Na+2H₂O]⁺ requires 1926.79).

X-ray diffraction statistics

Table S1. X-ray diffraction statistics for **1a**. Values in parentheses are for the highest-resolution shell.

	Remote (high energy)	Peak	Inflection	Remote (low energy)
space group	<i>R</i> 3			
crystal system	rhombohedral			
X-ray wavelength (Å)	0.7000	0.9194	0.9200	0.9230
<i>a</i> (Å)	43.05	43.06	43.07	43.08
<i>b</i> (Å)	43.05	43.06	43.07	43.08
<i>c</i> (Å)	43.17	44.17	44.17	44.17
α (°)	90			
β (°)	90			
γ (°)	120			
Resolution (Å)	50–1.16 (1.20–1.16)	28.49–1.50 (1.58–1.50)	28.50–1.50 (1.58–1.50)	28.50–1.50 (1.58–1.50)
All reflections	60089	24665	24706	24212
Unique reflections	10543	4757	4769	4763
R_{merge} (%)	6.4 (14.4)	6.8 (7.6)	8.7 (7.0)	7.5 (5.5)
Completeness (%)	99.9 (100.0)	97.2 (85.3)	97.5 (85.0)	97.1 (83.1)
mean $I/\sigma I$	23.1	20.1	18.4	24.6

Table S2. X-ray diffraction statistics for **1b**. Values in parentheses are for the highest-resolution shell.

	Remote (high energy)	Peak	Inflection	Remote (low energy)
space group	<i>R</i> 3			
crystal system	rhombohedral			
X-ray wavelength (Å)	0.9100	0.9194	0.9198	0.9220
<i>a</i> (Å)	43.22	43.21	43.21	43.22
<i>b</i> (Å)	43.22	43.21	43.21	43.22
<i>c</i> (Å)	43.40	43.40	43.40	43.40
α (°)	90			
β (°)	90			
γ (°)	120			
Resolution (Å)	50–1.05 (1.09–1.05)	50–1.05 (1.09–1.05)	50–1.05 (1.09–1.05)	50–0.95 (0.98–0.95)
All reflections	75273	74966	74947	97012
Unique reflections	14081	14071	14027	18434
R_{merge} (%)	8.6 (67.3)	9.7 (65.4)	6.6 (38.7)	3.8 (39.1)
Completeness (%)	99.8 (100.0)	99.7 (100.0)	99.5 (100.0)	96.6 (72.7)
mean $I/\sigma I$	19.3	19.2	24.1	29.2

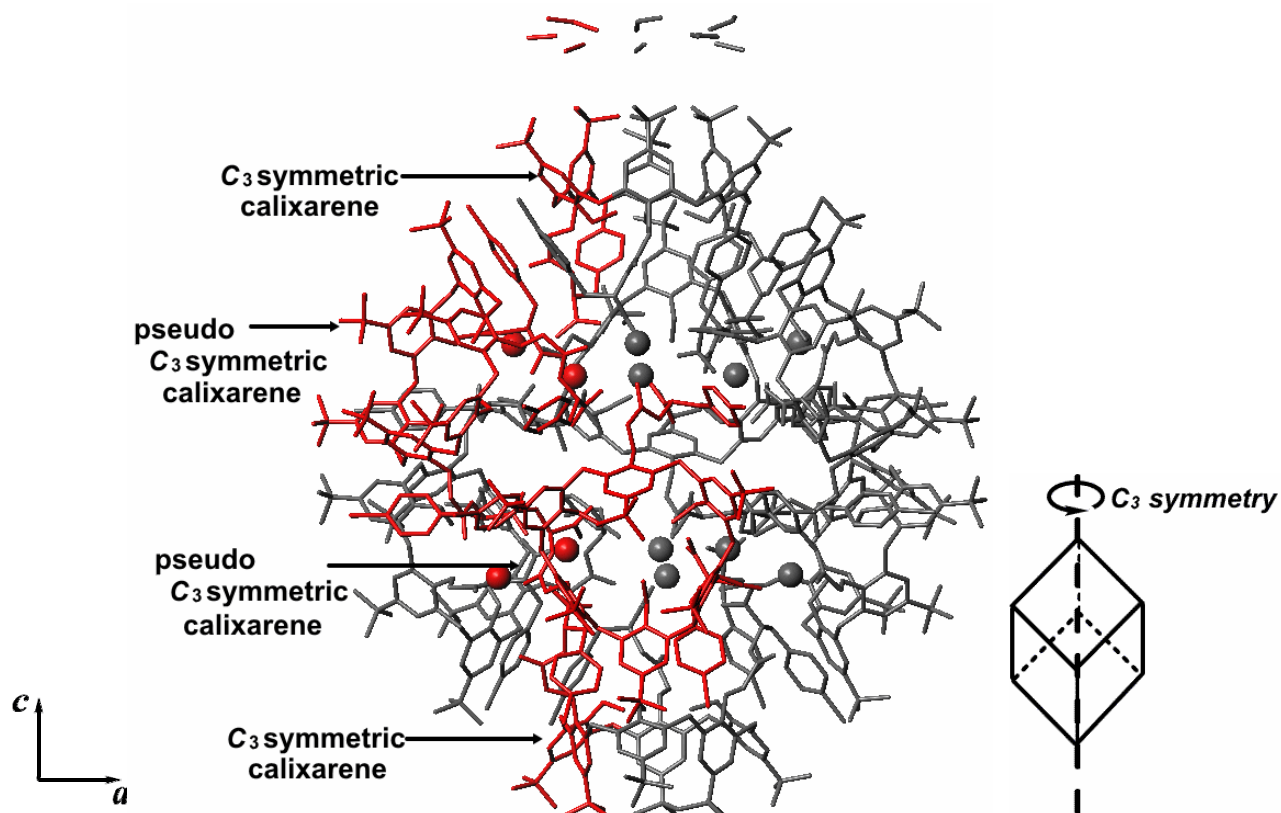


Fig. S1 View of the octamer of **1a** in parallel with an *ac* plate. Red models show the molecules in an asymmetric unit. The sketch of the cubic octamer and 3-fold axis are drawn at bottom right of the figure. Only the red models at the top and bottom correspond to one-third of the calixarene molecule, respectively. Two calixarene derivatives located at the middle of the red models have pseudo C₃ symmetry. The gray moieties are obtained by the symmetry operation of the red models.