Supporting Information

for

Templated dynamic cryptophane formation in water

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Experimental Procedures:

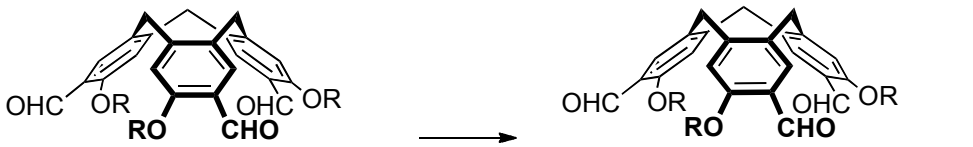
Cryptophane 6:

A solution of cyclotribenzylene **1** [1] (17.5 mg, 40 μmol) was suspended in $CDCl_3$ (4.4 mL). A few beads of molecular sieves (3Å) were added, followed by ethylene-1,2-diamine (5.2 μL, 80 μmol) and TFA (20 μL of 1% solution in $CDCl_3$). The mixture was stirred at room temperature overnight, after which all of **35** had dissolved. The solution was filtered and the solvent evaporated to yield **6** quantitatively as a yellowish solid. X-ray quality crystals of **6** were obtained by dissolving about 3 mg of **6** in CH_2Cl_2/CH_3OH (2:1) and slow evaporation of the solvent at room temperature. Spectroscopic data: ^{1}H NMR ($CDCl_3$; 500 MHz, 25 ^{o}C): δ_H 8.41 (s, 6H, C*H*N), 7.80 (s, 6H, Ar-*H*), 6.84 (s, 6H, Ar-*H*), 4.60 (d, 6H, *J* = 13.4 Hz, ArCH_{ax}H), 4.17 (d, 6H, *J* = 10.1 Hz, NC*H*H), 3.79 (d, 6H, *J* = 10.1 Hz, NC*H*H), 3.61 (d, 6H, *J* = 13.4 Hz, ArCH_{eq}H); ^{13}C NMR ($CDCl_3$; 125 MHz, 25 ^{o}C): δ_C 157.56, 157.15, 144.00, 130.51, 128.15, 122.66, 112.06, 63.60, 55.60, 36.20. MALDI-TOF: *m/z* 961.4695 ([**6**+H]$^+$, 961.46 (calcd. for $[C_{60}H_{61}N_6O_6]^+$))

Reference:

1. D**.** Xu and R. Warmuth, *J. Am. Chem. Soc.*, 2008, **130**, 7520.

Cyclotribenzylene 35:



1: R = CH_3 **35**: R = $CH_2COOC(CH_3)_3$

A solution of **1** (125 mg, 0.281 mmol) and anhydrous LiCl (1.35 g, 32 mmol) in anhydrous DMF (15 mL) was refluxed under argon for 20.5 hrs, after which time the NMR spectrum of the crude products ($CDCl_3$, 25 ^{o}C) showed complete ether cleavage. After the reaction mixture had cooled to room temperature, the solvent was removed under reduced pressure. The residual oil, was

treated with water (30 mL) and 1N aq. HCl (50 mL). The precipitated crude product was filtered off, washed with water (10 mL) and methanol (10 mL) and dried at high vacuum. It was used for the next step without further purification and dissolved in anhydrous DMF (5 mL) under argon. Cs_2CO_3 (600 mg, 1.84 mmol) and *tert.* butyl bromoacetate (0.3 mL, 2.03 mmol) was added to the solution. After stirring at room temperature for 24 hrs, the solvent was removed under reduced pressure. The residue was partitioned between water and CH_2Cl_2. The organic layer was washed with brine and dried over $MgSO_4$. After removing of the solvent, the crude product was chromatographed on silicagel. **35** was eluted with CH_2Cl_2/ethyl acetate (9:1) and obtained as a white solid (119.5 mg, 57% yield based on **1**). Spectroscopic data: ^{1}H NMR ($CDCl_3$; 500 MHz, 25 ^{o}C): δ_H 10.42 (s, 3H, C*H*O), 7.80 (s, 3H, Ar-*H*), 6.87 (s, 3H, Ar-*H*), 4.69 (d, 3H, *J* = 13.7 Hz, ArCH_{ax}H), 4.59 (s, 9H, OCH_2), 3.71 (d, 3H, *J* = 13.7 Hz, ArCH_{eq}H), 1.50 (s, 27H, C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$; 100 MHz, 25 ^{o}C): δ_C 189.14, 167.19, 159.48, 147.67, 131.46, 129.99, 124.68, 114.45, 83.15, 66.26, 37.04, 28.24. MALDI-TOF: *m/z* 767.2777 ([**35**+Na]$^+$, 767.3038 (calcd. for $[C_{42}H_{48}O_{12}Na]^+$))

Water-soluble cyclotribenzylene 9

Cyclotribenzylene **35** (50 mg, 62 μmol) was dissolved in the minimum amount of dichloromethane (3 mL), and an excess of pure trifluoroacetic acid (3 mL) was added. The reaction was stirred overnight with a stopper on the flask. The solvent was pumped off under vacuum. Dichloromethane (5 mL) was added and evaporated under vacuum to remove residual trifluoroacetic acid. The solid residue was dried overnight under vacuum at 100 ^{o}C to yield **9** as a white solid (34.6 mg, 97 %). Spectroscopic data: ^{1}H NMR (300 MHz, DMSO-*d6,* 25°C) δ_H: 13.06 (3H, sb, COO<u>H</u>), 10.28 (3H, s, C<u>H</u>O), 7.94 (3H, s, <u>Ar</u>-CHO), 7.41 (3H, s, <u>Ar</u>-OCH_2), 4.92-4.78 (9H, m, <u>H</u>$_{ax}$ & OC<u>H</u>$_2$), 3.84 (3H, m, <u>H</u>$_{eq}$). ^{13}C NMR (100 MHz, DMSO-*d6,* 25°C) δ_c: 188.55 (H<u>C</u>=O), 169.54 (<u>C</u>=O), 158.67 (<u>Ar</u>-OCH_2), 148.52 (<u>Ar</u>-CH_2), 131.80 (<u>Ar</u>-CH_2), 129.93 (Ar), 123.68 (<u>Ar</u>-CHO), 115.08 (Ar), 65.15 (O<u>C</u>H$_2$), 35.04 (<u>C</u>H$_2$). MALDI-TOF: *m/z* 599.11502 ([**9**+Na]$^+$, 599.11600 (calcd. for $[C_{30}H_{24}NaO_{12}]^+$)). HPLC: Vydac RP-C_{18}, mobile phase: buffered H_2O ($(NH_4)_2CO_3$)/acetonitrile; gradient: t_0 = 9/1 -> t_{20min} = 6/4 -> t_{25min}= 9/1; flow = 1 mL min^{-1}, λ = 280 nm, t_R = 10.44 min.

CH_2Cl_2 complex of cryptophane 8 (Procedure A)

The cyclotribenzylene **9** (1.5 mg, 2.6 μmol) was suspended in D_2O (0.5 mL) and dissolved by adding 2N NaOD in D_2O solution (6 μL). Distillated ethylenediamine was introduced (0.313 mg, 5.2x10^{-3} mmol) following by dichloromethane (3 μL) as template. A solution of sodium acetate in D_2O (4mM; 10 μL) was added as reference. The reaction was completed after 2hours. Spectroscopic data: ^{1}H NMR (500 MHz, D_2O*,* 25°C) δ_H: 8.54 (6H, s, C<u>H=N</u>), 7.73 (6H, s, <u>Ar</u>-

CH=N), 6.68 (6H, s, Ar-OCH_2), 4.67 (6H, d, H_{ax}, $J^2_{Hax-Heq}$ = 15.9), 4.64 (6H, d, OCH_2, J^2_{H-H} = 13.9), 4.36 (6H, d, H_{eq}, $J^2_{Heq-Hax}$ = 15.9), 4.22 (6H, d, N-CH_2, J^2_{H-H} = 9.7),

3.88 (6H, d, N-CH_2, J^2_{H-H} = 10.4), 3.6 (6H, d, OCH_2, J^2_{H-H} = 15.9), 0.98 (2H, s, CH_2Cl_2). ^{13}C NMR (125 MHz, D_2O, 25°C) δ_c: 176.81 (C=O), 158.76 (CH=N), 156.45 (Ar-OCH_2), 145.17 (Ar-CH_2), 131.31 (Ar-CH_2), 128.14 (Ar), 121.54 (Ar-CH=N), 112.78 (Ar), 67.11 (OCH_2), 61.36 (N-CH_2), 35.36 (CH_2). MALDI-TOF: *m/z* 1313.3142 ([**8**-2Na^++3H]$^+$, 1313.3314 (calcd. for [$C_{66}H_{57}N_6Na_3O_{18}$]$^+$)).

2-Norbornylene complex of cryptophane 10

Prepared according to **procedure A** from **9** (1.5 mg, 2.6 μmol) and 1,4-butanediamine (0.464 mg, 5.2x10^{-3} mmol) with 2-norbornylene as template. Spectroscopic data: ^1H NMR (500 MHz, D_2O, 25°C) δ_H: 8.49 (6H, s, CH=N), 7.84 (6H, s, Ar-CH=N), 6.7 (6H, s, Ar-OCH_2), 4.72 (6H, d, OCH_2, J^2_{H-H} = 13.6), 4.43 (6H, d, H_{ax}, $J^2_{Hax-Heq}$ = 15.8), 4.17 (6H, d, H_{eq}, $J^2_{Heq-Hax}$ = 15.8), 3.94 (6H, m, N-CH_2), 3.72 (6H, d, OCH_2, J^2_{H-H} = 13.6), 3.44 (6H, m, N-CH_2), 1.68 (6H, m, N-CH_2-CH_2), 1.47 (6H, m, N-CH_2-CH_2), 2.77 (2H, s, guest), 0.05 (1H, m, guest), -0.06 (1H, m, guest), -0.88 (1H, m, guest), -1.01 (1H, m, guest), -1.47 (1H, m, guest), -1.67 (1H, m, guest), -1.77 (1H, m, guest), -1.9 (1H, m, guest); MALDI-TOF: *m/z* 1309.4407 ([**10**-6Na^++7H]$^+$, 1309.4976 (calcd. for [$C_{72}H_{73}N_6O_{18}$]$^+$)).

Cryptophane 11

Prepared according to **procedure A** from **9** (1.5 mg, 2.6 μmol) and *p*-xylenediamine (0.710 mg, 5.2x10^{-3} mmol) with ferrocene as template and 10 μL of a sodium acetate solution (4mM) as reference. The reaction was completed after 2hours at 353K. Spectroscopic data: ^1H NMR (500 MHz, D_2O, 25°C) δ_H: 8.67 (6H, s, CH=N), 7.89 (6H, s, Ar-CH=N), 7.14 (12H, s, Ar-diamine), 6.73 (6H, s, Ar-OCH_2), 5.06 (6H, d, OCH_2, J^2_{H-H} = 12.6), 4.54 (6H, d, OCH_2, J^2_{H-H} = 12.6), 4.14 (6H, d, H_{ax}, $J^2_{Hax-Heq}$ = 15.7), 4.04 (6H, d, H_{eq}, $J^2_{Heq-Hax}$ = 15.7), 3.72 (6H, d, N-CH_2, J^2_{H-H} = 9.7). MALDI-TOF: *m/z* 1607.2279 ([**11**+Na]$^+$, 1607.3711 (calcd. for [$C_{84}H_{66}N_6Na_7O_{18}$]$^+$)).

Binding Studies

For the binding experiments, a known amount of CTB **9** was dissolved in D_2O in a NMR tube. 10μL of a sodium acetate solution (4 mM in D_2O) was added as an internal integration standard followed by recording an ^1H NMR spectrum (spectrum 1). After addition of 2 equivalents of ethylene-1,2- diamine **5**, the pD was adjusted to pD ~ 11 via the addition of 2N NaOD in D_2O, followed by the addition of excess CH_2Cl_2. After two hours of equilibration at room temperature

a second ^{1}H NMR spectrum was recorded (spectrum 2). K was determined from the total concentration of **9** in spectrum 2 ([**9**]), the integration of the aryl protons of **9** relative to that of the methyl protons of the standard in spectrum 1 ($I_{\mathbf{9}}$) and the integral of free CH_2Cl_2 (I_G) and of the aryl protons of the complex **8**⊙CH_2Cl_2 (I_C) relative to that of the methyl protons of the standard in spectrum 2. The difference between I_C and $I_{\mathbf{9}}$ was taken as the integration of aryl protons in the polymers (I_P):

$$I_P = I_{\mathbf{9}} - I_C$$

$$K(CH_2Cl_2) = 2/3 \times I_C/(I_G \times I_P \times [\mathbf{9}])$$

Binding constants of other guests were determined from competition experiments, in which two guests G1 and G2 were added to a solution of **9** and 2 equivalents of **5** in D_2O at pD ~ 11, of which K(G1) for guest G1 is known. The binding constants for guest 2, K(G2), was determined from the integral of the aryl protons or imine protons of complexes **8**⊙G1 (I_{C1}**)** and **8**⊙G2 (I_{C2}), the integral of the n protons of free guest 1 (I_{G1}) and the integral of m protons of free guest 2 (I_{G2}) in the ^{1}H NMR spectrum of the mixture:

$$K(G2) = K(G1) \times I_{C2} \times I_{G1} \times m / (I_{C1} \times I_{G2} \times n)$$

where m and n are the number of protons of G2 and G1 respectively.

The error of K in both methods is estimated at 10%.

NMR Spectra

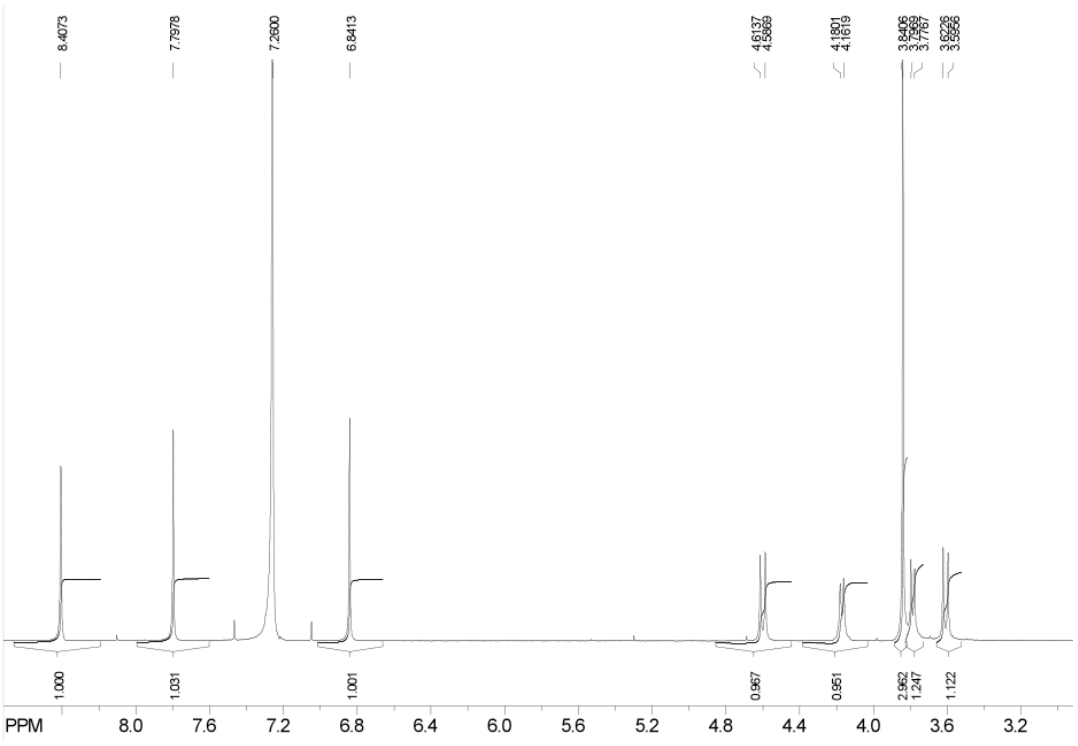


Figure S1: ^{1}H NMR spectrum ($CDCl_3$; 500 MHz, 25 ^{o}C) of **6**.

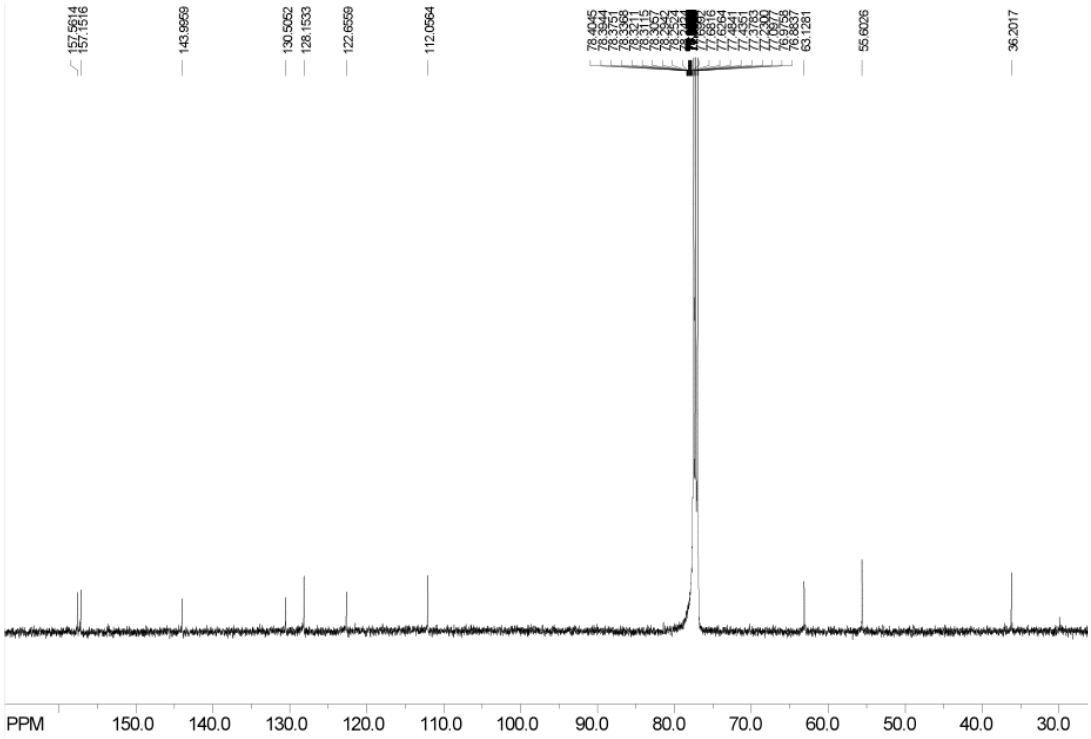


Figure S2: ^{13}C NMR spectrum ($CDCl_3$; 125 MHz, 25 ^{o}C) of **6**.

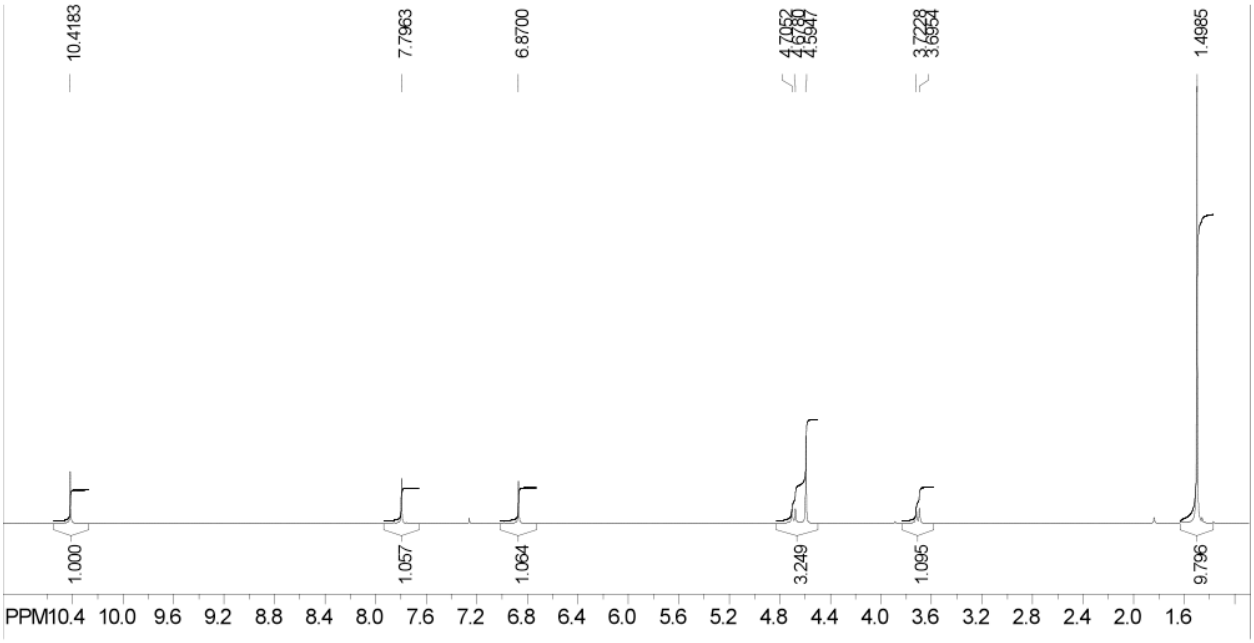


Figure S3: ^{1}H NMR spectrum ($CDCl_3$; 500 MHz, 25 ^{o}C) of **35**.

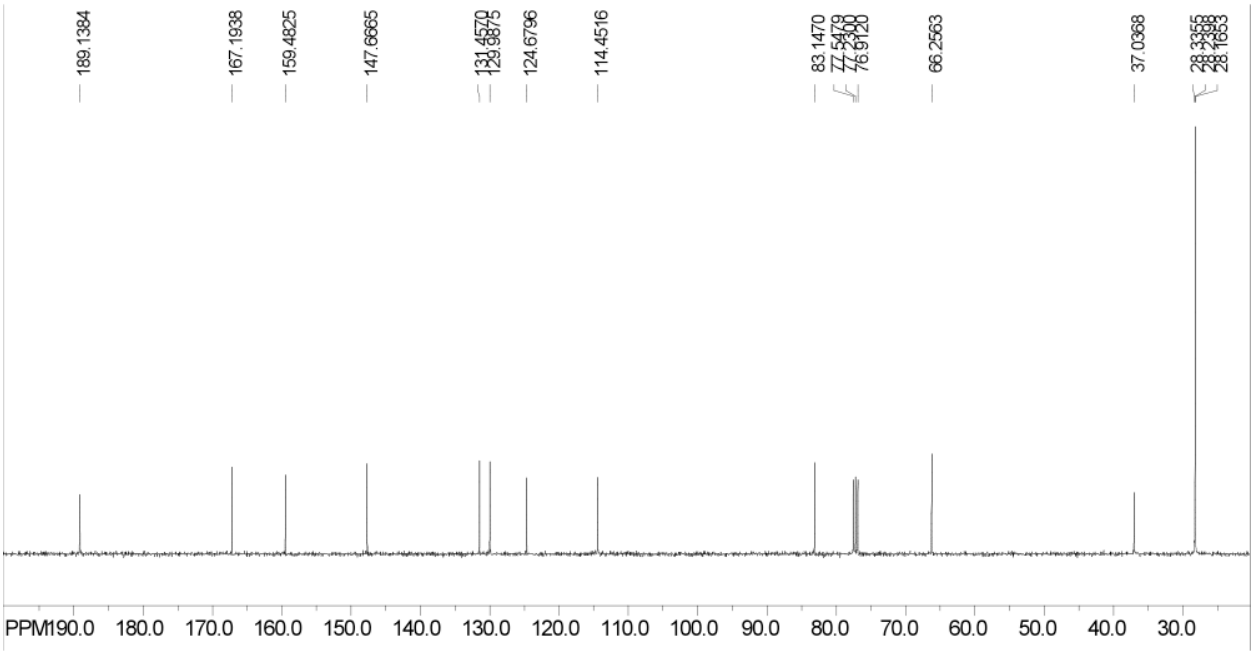


Figure S4: ^{13}C NMR spectrum ($CDCl_3$; 100 MHz, 25 ^{o}C) of **35**.

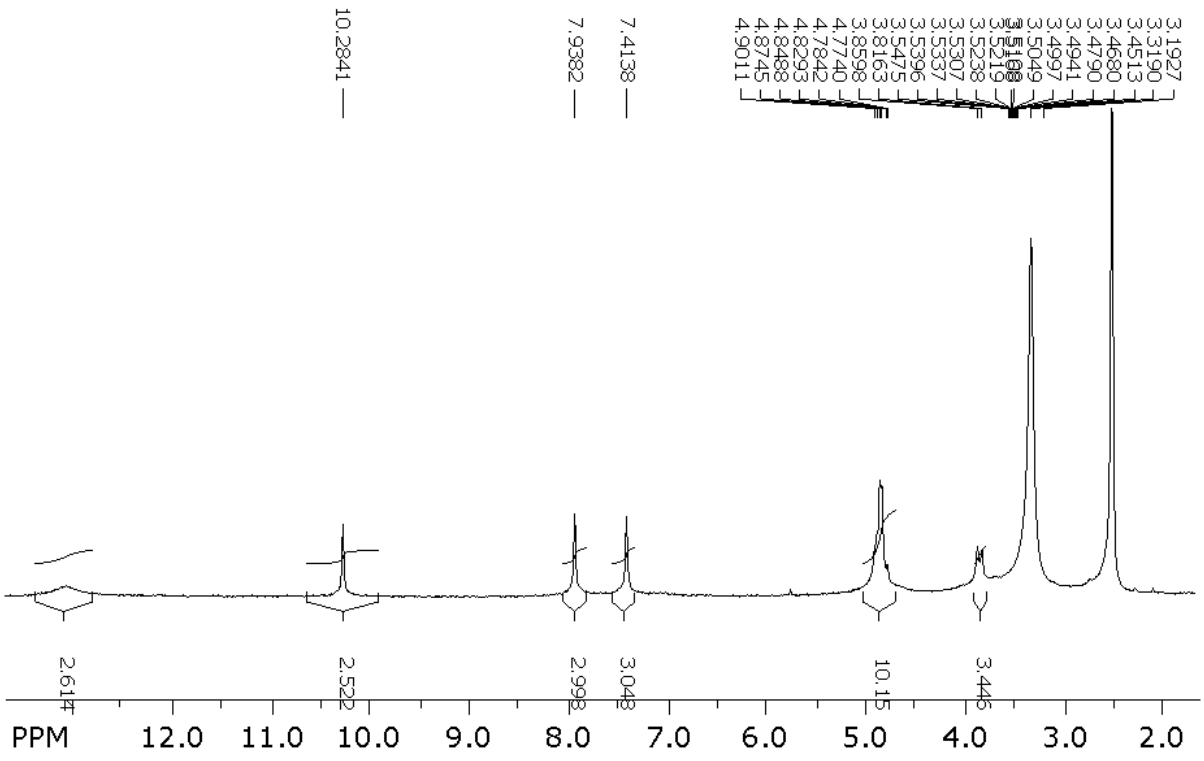


Figure S5: ^{1}H NMR spectrum (500 MHz, $DMSO_{d6}$, 25^{o}C) of **9**.

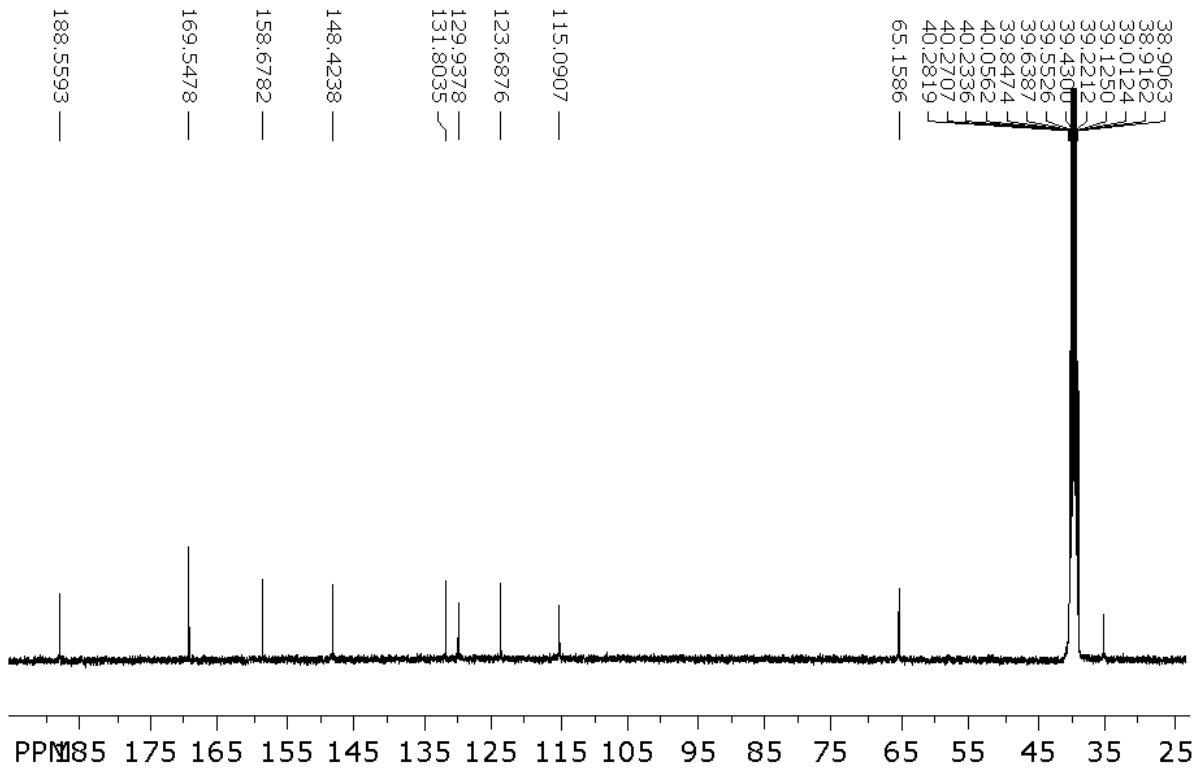


Figure S6: ^{13}C NMR spectrum (100 MHz, $DMSO_{d6}$, 25^{o}C) of **9**.

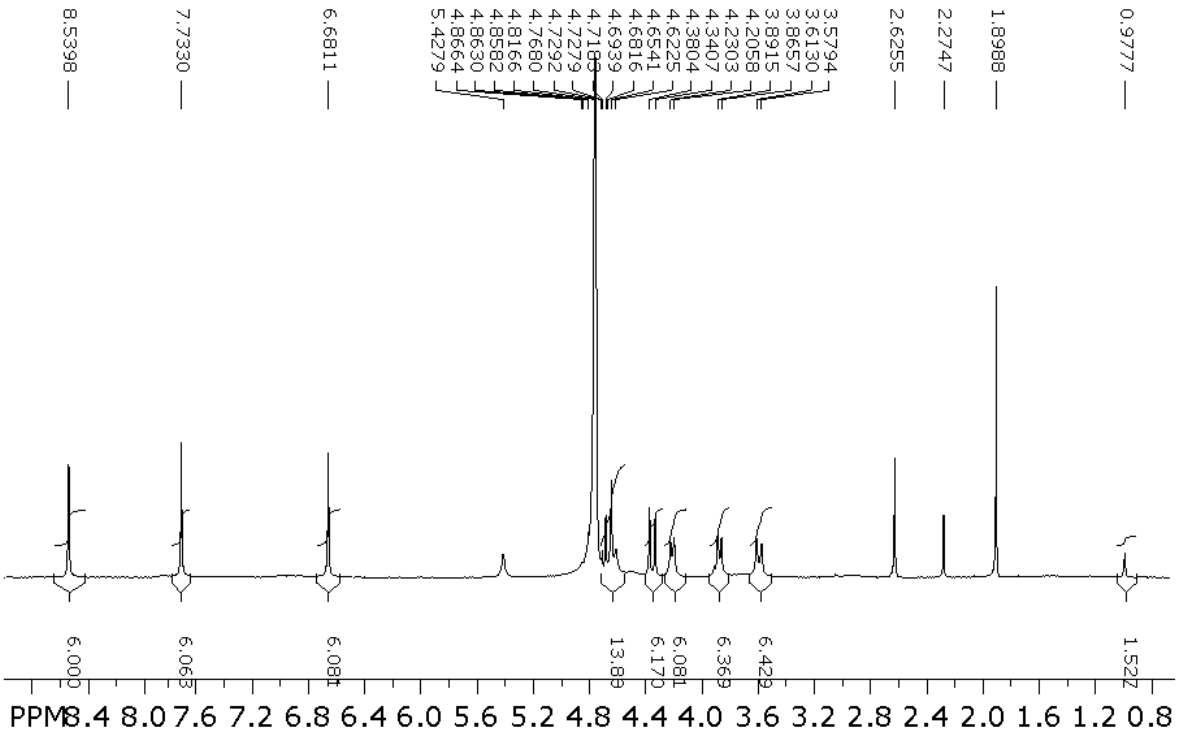


Figure S7: ^{1}H NMR spectrum (500 MHz, D_2O, NaOD, pD 12; 25°C) of **8**⊙CH_2Cl_2.

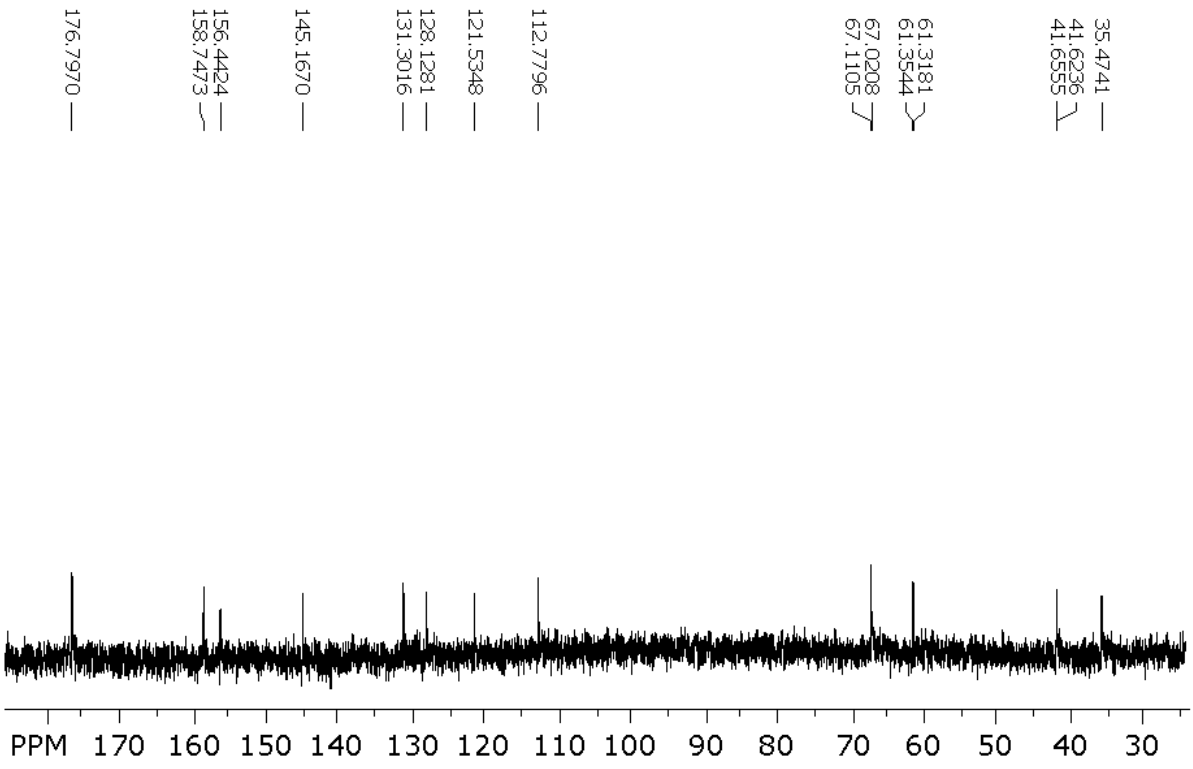


Figure S8: ^{13}C NMR spectrum (500 MHz, D_2O, NaOD, pD 12; 25°C) of **8**⊙CH_2Cl_2.

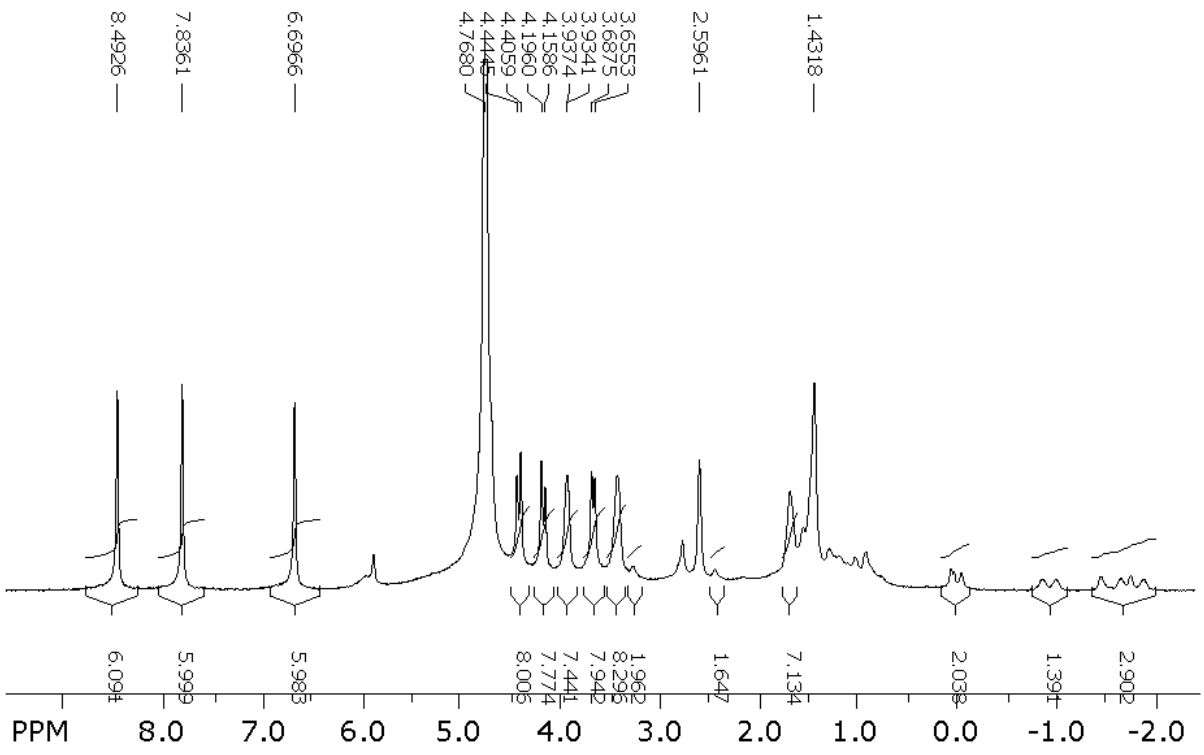


Figure S9: ^{1}H NMR spectrum (500 MHz, D_2O, NaOD, pD 12; 25^{o}C) of **10⊙22**

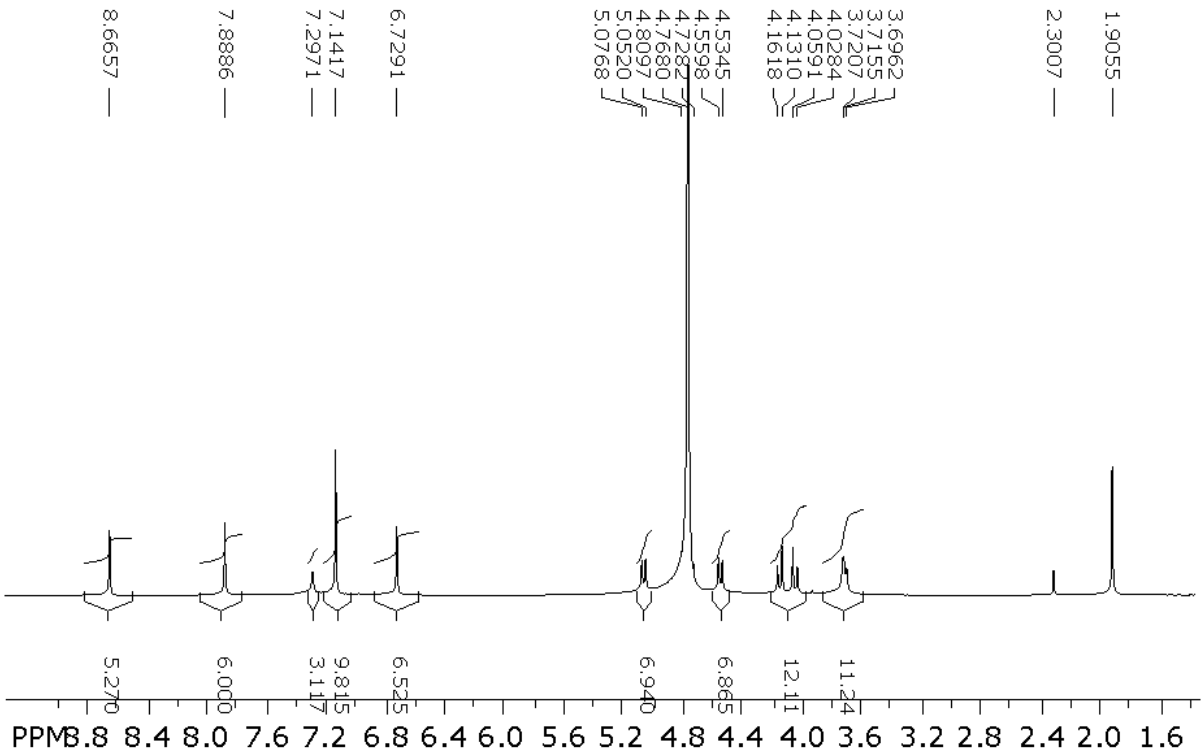


Figure S10: ^{1}H NMR spectrum (500 MHz, D_2O, NaOD, pD 12; 25^{o}C) of **11**

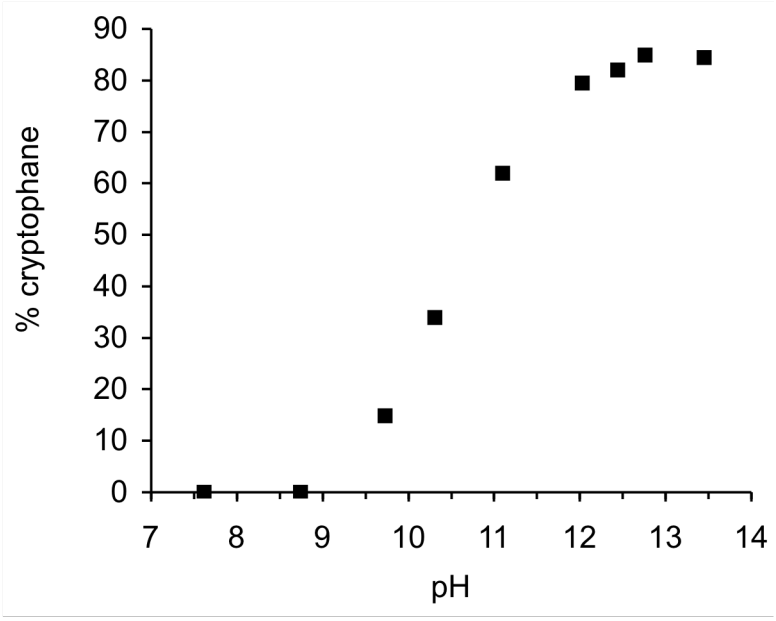


Figure S11: pH profile for the formation of **8**⊙CH_2Cl_2.

Crystallographic data for **6**⊙CH_2Cl_2

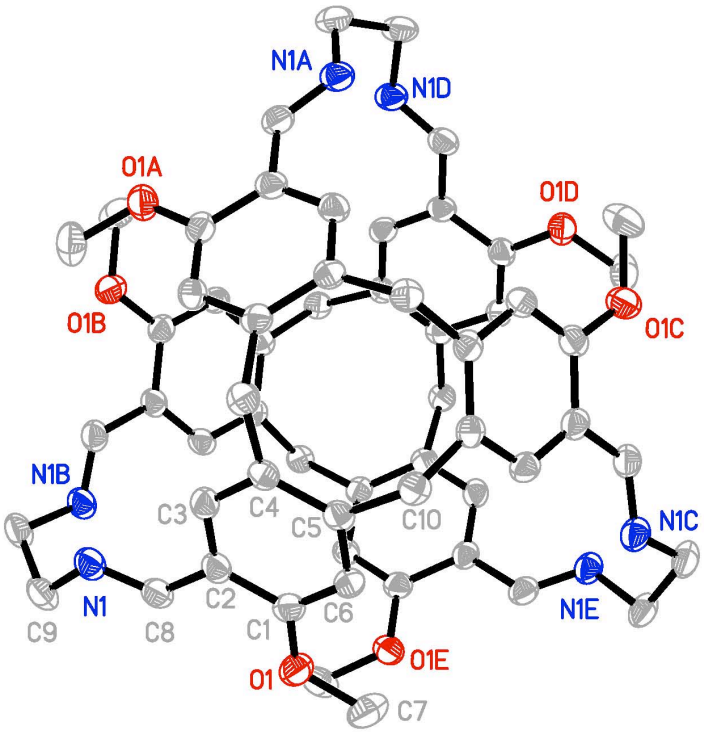


Figure S12: ORTEP representation of **6**⊙CH_2Cl_2 with atom labeling. Solvent is excluded.

Table S1. Crystal data and structure refinement for cryptophane complex **6**⊙CH_2Cl_2.

Identification code	cryptophane	
Empirical formula	C66 H72 Cl12 N6 O6	
Formula weight	1470.70	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	R32	
Unit cell dimensions	a = 16.2073(7) Å	α= 90°.
	b = 16.2073(7) Å	β= 90°.
	c = 23.4757(18) Å	γ = 120°.
Volume	5340.4(5) $Å^3$	
Z	3	
Density (calculated)	1.372 Mg/m^3	
Absorption coefficient	0.520 mm^{-1}	
F(000)	2286	
Crystal size	0.24 x 0.15 x 0.07 mm^3	
Theta range for data collection	2.26 to 30.54°.	
Index ranges	-18<=h<=23, -22<=k<=23, -21<=l<=30	
Reflections collected	7840	
Independent reflections	3444 [R(int) = 0.0254]	
Completeness to theta = 30.54°	96.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.964 and 0.885	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3444 / 6 / 163	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0564, wR2 = 0.1213	
R indices (all data)	R1 = 0.0772, wR2 = 0.1327	
Absolute structure parameter	0.02(10)	
Largest diff. peak and hole	0.680 and -0.582 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for cryptophane. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	3542(2)	354(2)	598(1)	34(1)
O(1)	3274(1)	2687(1)	679(1)	37(1)
C(1)	2625(2)	1931(2)	997(1)	29(1)
C(2)	2686(2)	1096(2)	974(1)	28(1)
C(3)	2055(2)	328(2)	1303(1)	28(1)
C(4)	1363(2)	341(2)	1648(1)	26(1)
C(5)	1298(2)	1167(2)	1658(1)	26(1)
C(6)	1938(2)	1959(2)	1338(1)	28(1)
C(7)	3230(2)	3538(2)	715(1)	44(1)
C(8)	3405(2)	1063(2)	607(1)	31(1)
C(9)	4267(2)	422(2)	202(1)	38(1)
C(10)	547(2)	1265(2)	1994(1)	28(1)
C(11)	993(2)	4326(2)	1667	42(1)
Cl(1)	1094(1)	5436(1)	1573(1)	82(1)
C(20)	3333	6667	639(3)	78(2)
Cl(21)	4362(5)	7614(4)	248(4)	63(2)
Cl(22)	2515(5)	6924(5)	258(4)	70(2)
C(30)	0	0	319(5)	51(3)
Cl(31)	-756(6)	229(8)	-69(5)	75(3)
Cl(32)	989(5)	232(6)	-24(5)	77(3)

Table S3. Bond lengths [Å] and angles [°] for cryptophane.

N(1)-C(8)	1.275(3)	C(9)-C(9)#2	1.517(5)
N(1)-C(9)	1.459(3)	C(9)-H(9A)	0.9900
O(1)-C(1)	1.370(3)	C(9)-H(9B)	0.9900
O(1)-C(7)	1.419(3)	C(10)-C(4)#3	1.524(3)
C(1)-C(6)	1.390(3)	C(10)-H(10A)	0.9900
C(1)-C(2)	1.407(3)	C(10)-H(10B)	0.9900
C(2)-C(3)	1.384(4)	C(11)-Cl(1)#4	1.737(2)
C(2)-C(8)	1.472(3)	C(11)-Cl(1)	1.737(2)
C(3)-C(4)	1.391(3)	C(11)-H(11)	0.9900
C(3)-H(3)	0.9500	C(11)-H(12)	0.9900
C(4)-C(5)	1.395(3)	C(20)-Cl(22)	1.813(8)
C(4)-C(10)#1	1.524(3)	C(20)-Cl(21)	1.850(8)
C(5)-C(6)	1.399(3)	C(20)-H(21)	1.037(3)
C(5)-C(10)	1.524(3)	C(20)-H(22)	0.760(8)
C(6)-H(6)	0.9500	C(30)-Cl(32)	1.660(10)
C(7)-H(7A)	0.9800	C(30)-Cl(31)	1.711(9)
C(7)-H(7B)	0.9800	C(30)-H(31)	0.971(7)
C(7)-H(7C)	0.9800	C(30)-H(32)	0.971(7)
C(8)-H(8)	0.9500		

C(8)-N(1)-C(9)	116.1(2)	C(4)-C(5)-C(6)	119.6(2)
C(1)-O(1)-C(7)	116.5(2)	C(4)-C(5)-C(10)	123.8(2)
O(1)-C(1)-C(6)	123.7(2)	C(6)-C(5)-C(10)	116.5(2)
O(1)-C(1)-C(2)	116.6(2)	C(1)-C(6)-C(5)	121.2(2)
C(6)-C(1)-C(2)	119.7(2)	C(1)-C(6)-H(6)	119.4
C(3)-C(2)-C(1)	117.9(2)	C(5)-C(6)-H(6)	119.4
C(3)-C(2)-C(8)	122.5(2)	O(1)-C(7)-H(7A)	109.5
C(1)-C(2)-C(8)	119.6(2)	O(1)-C(7)-H(7B)	109.5
C(2)-C(3)-C(4)	123.4(2)	H(7A)-C(7)-H(7B)	109.5
C(2)-C(3)-H(3)	118.3	O(1)-C(7)-H(7C)	109.5
C(4)-C(3)-H(3)	118.3	H(7A)-C(7)-H(7C)	109.5
C(3)-C(4)-C(5)	118.2(2)	H(7B)-C(7)-H(7C)	109.5
C(3)-C(4)-C(10)#1	118.3(2)	N(1)-C(8)-C(2)	122.7(3)
C(5)-C(4)-C(10)#1	123.5(2)	N(1)-C(8)-H(8)	118.7

C(2)-C(8)-H(8)	118.7	Cl(1)#4-C(11)-H(12)	109.4
N(1)-C(9)-C(9)#2	110.3(2)	Cl(1)-C(11)-H(12)	109.4
N(1)-C(9)-H(9A)	109.6	H(11)-C(11)-H(12)	108.0
C(9)#2-C(9)-H(9A)	109.6	Cl(22)-C(20)-Cl(21)	91.4(4)
N(1)-C(9)-H(9B)	109.6	Cl(22)-C(20)-H(21)	104.5(5)
C(9)#2-C(9)-H(9B)	109.6	Cl(21)-C(20)-H(21)	103.9(5)
H(9A)-C(9)-H(9B)	108.1	Cl(22)-C(20)-H(22)	119.5(4)
C(4)#3-C(10)-C(5)	113.28(18)	Cl(21)-C(20)-H(22)	119.8(4)
C(4)#3-C(10)-H(10A)	108.9	H(21)-C(20)-H(22)	114.4(4)
C(5)-C(10)-H(10A)	108.9	Cl(32)-C(30)-Cl(31)	114.0(8)
C(4)#3-C(10)-H(10B)	108.9	Cl(32)-C(30)-H(31)	116.6(3)
C(5)-C(10)-H(10B)	108.9	Cl(31)-C(30)-H(31)	118.1(3)
H(10A)-C(10)-H(10B)	107.7	Cl(32)-C(30)-H(32)	97.8(4)
Cl(1)#4-C(11)-Cl(1)	111.2(2)	Cl(31)-C(30)-H(32)	99.8(5)
Cl(1)#4-C(11)-H(11)	109.4	H(31)-C(30)-H(32)	106.0(11)
Cl(1)-C(11)-H(11)	109.4		

Symmetry transformations used to generate equivalent atoms:
#1 -x+y,-x,z #2 x-y,-y,-z #3 -y,x-y,z #4 y-1/3,x+1/3,-z+1/3

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for cryptophane. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	28(1)	37(1)	38(1)	-12(1)	-5(1)	18(1)
O(1)	36(1)	28(1)	45(1)	1(1)	9(1)	15(1)
C(1)	26(1)	26(1)	32(1)	-4(1)	-1(1)	10(1)
C(2)	25(1)	31(1)	31(1)	-7(1)	-5(1)	15(1)
C(3)	28(1)	29(1)	32(1)	-6(1)	-7(1)	17(1)
C(4)	24(1)	27(1)	24(1)	-4(1)	-7(1)	12(1)
C(5)	24(1)	28(1)	25(1)	-8(1)	-5(1)	13(1)
C(6)	28(1)	24(1)	31(1)	-7(1)	-4(1)	13(1)
C(7)	50(2)	27(1)	48(2)	0(1)	14(1)	13(1)
C(8)	24(1)	33(1)	35(1)	-6(1)	-2(1)	12(1)
C(9)	25(1)	46(2)	46(2)	-18(1)	-8(1)	20(1)
C(10)	30(1)	28(1)	24(1)	-6(1)	0(1)	14(1)
C(11)	29(1)	29(1)	71(3)	5(1)	-5(1)	16(2)
Cl(1)	82(1)	47(1)	139(1)	6(1)	6(1)	48(1)
Cl(21)	74(4)	33(1)	68(3)	2(2)	-6(3)	17(2)
Cl(22)	119(6)	66(3)	61(3)	17(2)	18(3)	73(4)
Cl(31)	66(5)	110(12)	70(7)	8(6)	-14(5)	59(8)
Cl(32)	58(3)	88(6)	92(4)	7(4)	11(3)	41(4)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for cryptophane.

	x	y	z	U(eq)
H(3)	2096	-236	1292	34
H(6)	1903	2526	1354	33
H(7A)	3722	4026	470	66
H(7B)	3337	3763	1110	66
H(7C)	2601	3413	590	66
H(8)	3782	1592	367	38
H(9A)	4799	435	418	46
H(9B)	4524	1021	-19	46
H(10A)	360	840	2331	33
H(10B)	831	1928	2135	33
H(11)	590	4011	2004	51
H(12)	677	3923	1329	51
H(21)	3237	6042	457	94
H(22)	3333	6667	963	94
H(31)	-276	-553	568	61
H(32)	276	553	568	61

Table S6. Torsion angles [°] for cryptophane.

C(7)-O(1)-C(1)-C(6)	0.8(4)	C(10)#1-C(4)-C(5)-C(10)	-2.9(4)
C(7)-O(1)-C(1)-C(2)	-178.2(2)	O(1)-C(1)-C(6)-C(5)	-179.5(2)
O(1)-C(1)-C(2)-C(3)	178.4(2)	C(2)-C(1)-C(6)-C(5)	-0.5(4)
C(6)-C(1)-C(2)-C(3)	-0.7(4)	C(4)-C(5)-C(6)-C(1)	1.8(4)
O(1)-C(1)-C(2)-C(8)	-1.8(3)	C(10)-C(5)-C(6)-C(1)	-177.3(2)
C(6)-C(1)-C(2)-C(8)	179.1(2)	C(9)-N(1)-C(8)-C(2)	178.8(2)
C(1)-C(2)-C(3)-C(4)	0.6(4)	C(3)-C(2)-C(8)-N(1)	-5.3(4)
C(8)-C(2)-C(3)-C(4)	-179.2(2)	C(1)-C(2)-C(8)-N(1)	174.9(2)
C(2)-C(3)-C(4)-C(5)	0.7(4)	C(8)-N(1)-C(9)-C(9)#2	-123.7(3)
C(2)-C(3)-C(4)-C(10)#1	-179.2(2)	C(4)-C(5)-C(10)-C(4)#3	-92.9(3)
C(3)-C(4)-C(5)-C(6)	-1.8(4)	C(6)-C(5)-C(10)-C(4)#3	86.2(3)
C(10)#1-C(4)-C(5)-C(6)	178.1(2)		
C(3)-C(4)-C(5)-C(10)	177.2(2)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+y,-x,z #2 x-y,-y,-z #3 -y,x-y,z #4 y-1/3,x+1/3,-z+1/3