Electronic Supplementary Information for:

Tubular duplex α-cyclodextrin triply bridged with disulfide bonds: synthesis, crystal structure and inclusion complexes.

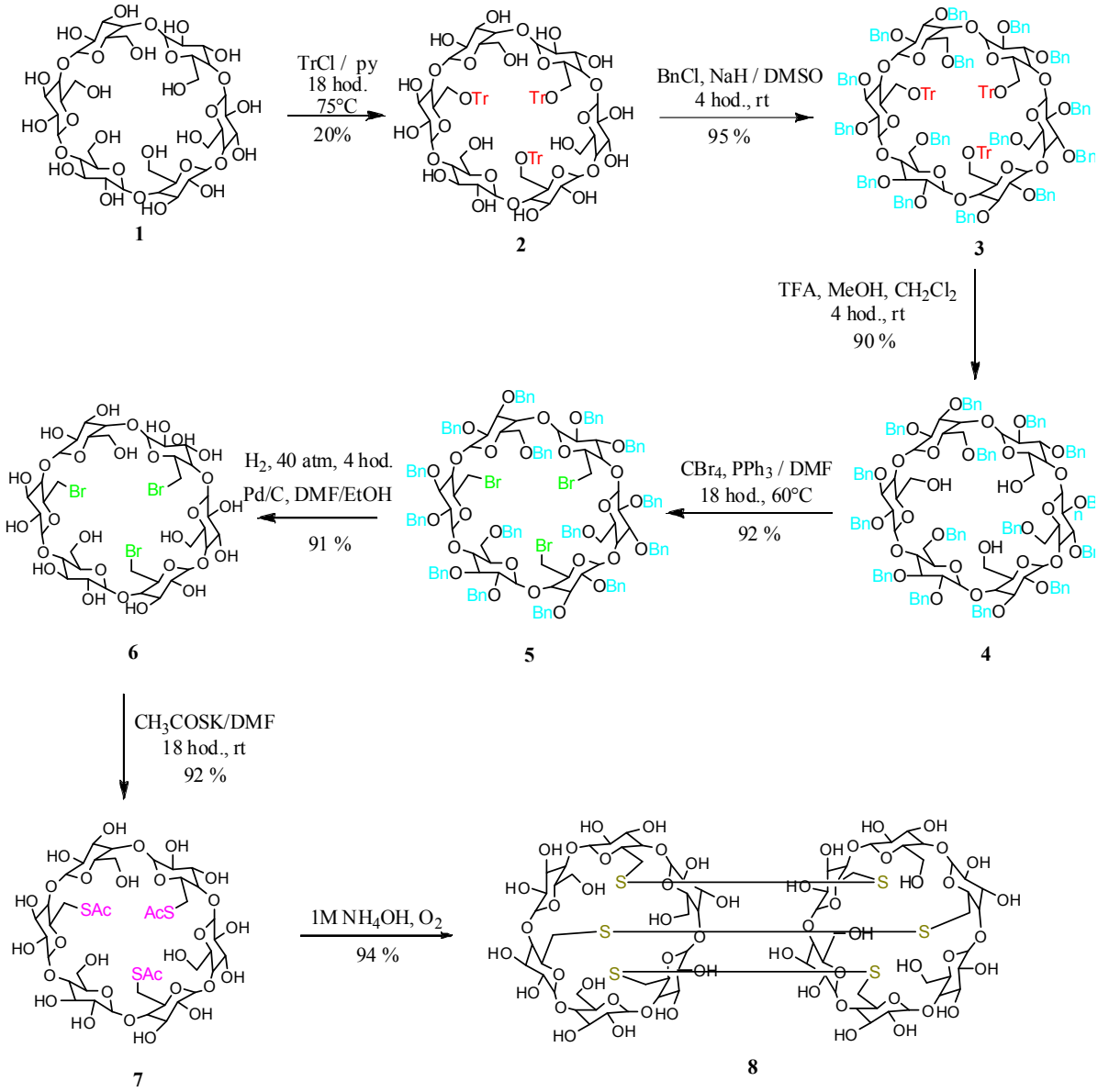
Lucie Krejčí,[†] Miloš Buděšínský,[†] Ivana Císařová[‡] and Tomáš Kraus[*,†]

[†]Institute of Organic Chemistry and Biochemistry AS CR, v.v.i. Flemingovo nám. 2, 166 10 Praha 6 Czech Republic, [‡]Department of Inorganic Chemistry, Charles University, Hlavova 2030, 128 40 Praha 2, Czech Republic

Contents:

1. Synthesis

1.1. Scheme 1 (structural formulas)



1.2. Experimental Procedures

General procedures

NMR spectra were acquired with spectrometers Bruker AVANCE 500 (^{1}H at 500.1 MHz and ^{13}C at 125.8 MHz) and AVANCE 600 (^{1}H at 600.1 MHz and ^{13}C at 150.9 MHz) in $CDCl_3$, CD_3SOCD_3 or D_2O at 300 K. Homonuclear 2D-NMR spectra (H,H-PFG-COSY, H,H-PFG-TOCSY and H,H-PFG-ROESY) and heteronuclear 2D-NMR spectra (H,C-PFG-HSQC a H,C-PFG-HMBC) were used for structural assignment of proton and carbon signals. Mass spectra were measured either using ES ionization in positive mode (Waters micromass ZQ) or MALDI-TOF (Reflex IV, Bruker Daltonics, nitrogen UV laser (337 nm). Optical rotations were recorded on AUTOPOL IV (Rudolph Research Analytical). Elemental analysis was carried out on Perkin Elmer 2400 II. CD spectra were recorded on JASCO J815 instrument. Preparative reversed-phase chromatography (RP) was carried out using medium pressure columns containing C-18 modified silica (Phenomenex Luna, 15 μm). Thin-layer (TLC) and reversed-phase thin-layer chromatography (RPTLC) were performed with precoated Silica Gel 60F and RP-18 F plates (E. Merck) resp., which were developed by spraying with an aqueous solution of phosphomolybdenic acid containing 5% of H_2SO_4 and heating. All chemicals used were commercially available. α-Cyclodextrin was dried under vacuum at temperature 80 °C for 24 hours prior use. Unless otherwise noted, samples were dried in a desiccator over P_2O_5 for 24 hours under diminished pressure. Satisfactory elemental analysis could not be obtained for the compound **8** unless water molecules were taken into account. Thus, calculations based on weights of compound **8** (molarity, yield, optical rotation) are related to the heptahydrated molecule.

Synthesis of compounds 2-8

6^I, 6^{III}, 6^V–tri–*O*–trityl–α–cyclodextrin (2). α-Cyclodextrin (7.45 g, 7.66 mmol) was dissolved in pyridine (190 mL) and trityl chloride (7.05 g, 25.28 mmol) was added to the stirred solution. The reaction mixture was heated to 75 °C under argon atmosphere for 18 hours. Then the reaction mixture was poured onto ice, and the yellow precipitate thus obtained was extracted with 600 mL of chloroform. Chloroform layer was washed with water (3×500 mL) and brine (500 mL). Then the chloroform solution was dried with sodium sulfate and concentrated on a rotatory evaporator. Crude product was subjected to column chromatography (reversed-phase column, gradient elution from methanol–water 8:2 to

methanol-water 9:1). Compound **2** (2.6 g, 20%) was isolated as a white powder. $[\alpha]^{D}_{20}$=+124.8 (*c*=0.08 in DMSO). ^{1}H NMR – see Table S1. ^{13}C NMR – see Table S2. MS (ES): Calcd for $C_{93}H_{102}O_{30}$ $[M + Na]^{+}$ *m/z* 1721.6; Found 1722.7. Elemental analysis (%): Calcd for $C_{93}H_{102}O_{30}$: C, 65.71; H, 6.05. Found C, 65.34; H, 6.21.

2^{I}, 2^{II}, 2^{III}, 2^{IV}, 2^{V}, 2^{VI}, 3^{I}, 3^{II}, 3^{III}, 3^{IV}, 3^{V}, 3^{VI}, 6^{II}, 6^{IV}, 6^{VI}–pentadeca–*O*– benzyl–6^{I}, 6^{III}, 6^{V}–tri–*O*–trityl–α–cyclodextrin (3). Solution of compound **2** (1.16 g, 0.68 mmol) in anhydrous DMSO (17.5 mL) and under argon atmosphere was added to sodium hydride (60 % w/w, 1.31 g , 32.7 mmol, washed 3× with anhydrous hexane) under stirring followed with benzyl chloride (2.83 mL, 24,5 mmol). After 4 hours the reaction was quenched by a slow addition of 100 mL of water at 0-5 °C. Then the mixture was extracted with diethyl ether (3x100 mL). Combined organic layers were washed with water (3x100 mL), dried with sodium sulfate, filtered, and concentrated on a rotatory evaporator. The crude product was purified by column chromatography (100 g silica gel, gradient elution from hexane–acetone 9:1 to hexane–acetone 6:4). Product was isolated as a white foam (1.97 g, 95%). $[\alpha]^{D}_{20}$=+56.5 (*c*=0.2 in chloroform). ^{1}H NMR – see Table S1. ^{13}C NMR – see Table S2. MS (MALDI-TOF): Calcd for $C_{198}H_{192}O_{30}$ $[M + Na]^{+}$ *m/z* 3072.3. Found 3072.3. Elemental analysis (%): Calcd for $C_{198}H_{192}O_{30}$: C, 77.93; H, 6.34. Found C, 78.06; H, 6.44.

2^{I}, 2^{II}, 2^{III}, 2^{IV}, 2^{V}, 2^{VI}, 3^{I}, 3^{II}, 3^{III}, 3^{IV}, 3^{V}, 3^{VI}, 6^{II}, 6^{IV}, 6^{VI}–pentadeca–*O*–benzyl–α–cyclodextrin (4). Compound **3** (1.30 g, 0.43 mmol) was dissolved in a mixture of dichloromethane (18 mL) and methanol (12 mL) in a Schlenk flask under argon atmosphere. To the stirred solution, trifluoroacetic acid (7.8 mL, 0.1 mol) was added dropwise. The mixture was allowed to react for 4 hours and then it was quenched by gradual addition of saturated solution of $NaHCO_3$ until the pH of the aqueous layer remained basic. The mixture was extracted with dichloromethane (3x100 mL). Collected dichloromethane layers were dried with sodium sulfate, filtered, and concentrated on rotatory evaporator. Crude product was purified by column chromatography (50 g of silica gel, gradient elution from mixture of toluene-acetone 95:5 to toluene-acetone 85:15). The product **4** was isolated as a white foam (0.91 g, 91%). $[\alpha]^{D}_{20}$=+41.9 (*c*=0.2 in chloroform). ^{1}H NMR – see Table S1. ^{13}C NMR – see Table S2. MS (ES): Calcd for $C_{141}H_{150}O_{30}$ $[M + Na]^{+}$ *m/z* 2346.0. Found 2346.0. Elemental analysis (%): Calcd for $C_{141}H_{150}O_{30}$: C, 72.85; H, 6.50. Found C, 72.66; H, 6.62.

2^{I}, 2^{II}, 2^{III}, 2^{IV}, 2^{V}, 2^{VI}, 3^{I}, 3^{II}, 3^{III}, 3^{IV}, 3^{V}, 3^{VI}, 6^{II}, 6^{IV}, 6^{VI}–pentadeca–*O*–benzyl–6^{I}, 6^{III}, 6^{V}–tribromo–6^{I}, 6^{III}, 6^{V}–trideoxy-α–cyclodextrin (5). Compound **4** (500 mg, 0.22 mmol) was dissolved in anhydrous DMF (2 mL) in a Schlenk flask under argon atmosphere, then triphenylphosphane (508 mg, 1.94 mmol) and tetrabromomethane (642 mg, 1.94 mmol) were added. The reaction mixture was stirred under argon atmosphere at 60 °C for 18 hours, and then it was diluted with toluene (100 mL). The toluene solution was washed with water (5x100 mL) and brine (100 mL), dried with sodium sulfate, and concentrated on rotatory evaporator. Compound **5** was isolated by column chromatography (30 g of silica gel, toluene-acetone 99:1) as a white foam (500 mg, 92 %) . $[\alpha]^{D}_{20}$ =+19.4 (*c*=0.2 in chloroform). ^{1}H NMR – see Table S1. ^{13}C NMR – see Table S2. MS (ES): Calcd for $C_{141}H_{147}Br_3O_{27}$ $[M + Na]^+$ *m/z* 2531.7. Found 2531.7. Elemental analysis (%): Calcd for $C_{141}H_{147}Br_3O_{27}$: C, 67.38; H, 5.90. Found C, 67.45; H, 5.81.

6^{I}, 6^{III}, 6^{V}–tribromo–6^{I}, 6^{III}, 6^{V}–trideoxy-α–cyclodextrin (6). Compound **5** (440 mg, 0.18 mmol) was dissolved in a mixture of ethanol-DMF (1:1, 20 mL). Then palladium on charcoal was added (10% w/w, 110 mg) and the reaction mixture was placed into an autoclave equipped with a magnetic stirring bar. The autoclave was flushed with argon and filled with hydrogen to the pressure of 40 bar. The reaction mixture was stirred for 4 hours at room temperature. Then the catalyst was separated by centrifugation and the solution was concentrated under reduced pressure. Compound **6** was isolated as an amorphous white solid (190 mg, 93%) after prolonged drying under vacuum over activated charcoal. $[\alpha]^{D}_{20}$ =+114.9 (c=0.1 in DMSO). ^{1}H NMR – see Table S1. ^{13}C NMR – see Table S2. MS (ES): Calcd for $C_{36}H_{57}Br_3O_{27}$ $[M + Na]^+$ *m/z* 1181.7. Found 1181.7. Elemental analysis (%): Calcd for $C_{36}H_{57}Br_3O_{27}$: C, 37.23; H, 4.95; Br, 20.64. Found C, 37.43; H, 5.23; Br, 21.01.

6^{I}, 6^{III}, 6^{V}–tris(acetylsulfanyl)–6^{I}, 6^{III}, 6^{V}–trideoxy–α–cyclodextrin (7). Compound **6** (200mg, 0.17 mmol) and potassium thioacetate (65 mg, 0.57 mmol) were dissolved in anhydrous DMF (3 mL) in a Schlenk flask under argon atmosphere. The reaction mixture was stirred for 18 hours at room temperature, and then it was added dropwise to acetone (50 mL). The fine precipitate was collected by centrifugation and dried under vacuum. The material was dissolved in of mixture of water-ethanol (9:1; 20 mL) and re-precipitated again by addition of acetone. Compound **7** was separated by centrifugation as white amorphous material (180 mg, 91%). $[\alpha]^{D}_{20}$ =+141.9 (*c*=0.2 in DMSO). ^{1}H NMR – see Table S1. ^{13}C

NMR – see Table S2. MS (ES): Calcd for $C_{42}H_{66}O_{30}S_3$ $[M + K]^+$ *m/z* 1185.2. Found 1185.2. Elemental analysis (%): Calcd for $C_{42}H_{66}O_{30}S_3$: C, 43.97; H, 5.80. Found C, 43.57; H, 5.56.

Duplex (8). Compound **7** (50 mg, 0.044 mmol) was dissolved in 1M NH_4OH (5.1 mL) and the solution was stirred for 24 hours in open flask. Then the reaction mixture was concentrated under reduced pressure and dried in vacuo. The solid material was then dissolved in water (10 mL) and filtered through ion exchanger (0.5 mL, Dowex 50W X8, prepared in water in H^+ cycle). The filtrate was freeze-dried to obtain compound **8** (44 mg, 94%, calculated for heptahydrate) as a colorless solid. $[\alpha]^D_{20}$ =+283.8 (*c*=0.1 in DMSO). ^{1}H NMR – see Table S1. ^{13}C NMR – see Table S2. MS (MALDI): Calcd for $C_{72}H_{114}O_{54}S_6$ $[M + Na]^+$ *m/z* 2057.4. Found 2057.4. Elemental analysis (%): Calcd for $C_{72}H_{114}O_{54}S_6 \bullet 7H_2O$: C, 40.00; H, 5.97. Found C, 39.73; H, 5.71.

1.3. Table S1. Chemical shifts of ^{1}H NMR signals for compounds 2-8

Compound	Solvent	Residue 6-R	H-1 (d)	H-2 (dd)	H-3 (dd)	H-4 (dd)	H-5 (ddd)	H-6a (dd)	H-6b (dd)
2 [a]	DMSO	OTr	4.86	3.33	3.75	3.47	3.67	3.27	3.18
		OH	4.64	3.22	3.73	3.49	3.24	3.46	2.77
3 [b]	$CDCl_3$	OTr	5.65	3.70	4.25	4.56	3.85	3.82	3.53
		OBn	4.65	3.21	3.94	3.81	3.90	3.62	3.30
4 [c]	$CDCl_3$	OBn	5.12	3.47	4.10	3.90	3.96	3.92	3.66
		OH	4.94	3.40	4.07	3.72	3.89	3.82	3.78
5 [d]	$CDCl_3$	Br	4.91	3.38	4.06	3.68	4.01	3.73	3.69
		OBn	5.12	3.48	4.10	3.96	3.90	4.11	3.68
6	DMSO	Br	4.87	3.30	3.81	3.40	3.83	3.98	3.58
		OH	4.82	3.31	3.765	3.37	3.65	3.69	3.58
7 [e]	DMSO	$SCOCH_3$	4.88	3.29	3.75	3.23	3.69	3.55	2.88
		OH	4.75	3.30	3.81	3.50	3.67	3.85	3.62
8	DMSO	S-S	4.78	3.30	3.74	3.17	3.65	3.11	3.09
	(+TFA)	OH	4.89	3.31	3.85	3.64	3.45	4.18	3.79

Proton NMR data of substituents:
[a] **3xOTRT**: 7.33 m (18H); 7.21 m (18H); 7.10 m (9H).
[b] **15xOCH$_2$ (Bn)**: 5.315 d (3H) and 4.81 d (3H), *J*=9.9; 4.95 d (3H) and 4.465 d (3H), *J*=12.1; 4.71 d (3H) and 4.68 d (3H), *J*=12.4; 4.515 d (3H) and 4.29 d (3H), *J*=12.0; 3.97 d (3H) and 3.70 d (3H), *J*=12.4;
15xC$_6$H$_5$ (Bn) + 9xC$_6$H$_5$ (3xTr): 7.30 m (18H), 7.23 m (18H), 7.15-6.98 m (63H), 6.90 m (9H), 6.62 m (6H) and 6.77 m (6H).
[c] **15xOCH$_2$ (Bn)**: 5.13 d (3H) and 4.79 d (3H), *J*=10.8; 5.05 d (3H) and 4.82 d (3H), *J*=11.2, 4.56 d (3H) and 4.425 d (3H), *J*=12.1; 4.57 d (3H) and 4.43 d (3H), *J*=12.4; 4.51 d (3H) and 4.415 d (3H), *J*=12.3;
15xC$_6$H$_5$ (Bn): 7.10-7.30 m (75H).
[d] **15xOCH$_2$ (Bn)**: 5.16 d (3H) and 4.82 d (3H), *J*=10.9; 5.05 d (3H) and 4.80 d (3H), *J*=11.1, 4.57 d (3H) and 4.42 d (3H), *J*=12.0; 4.54 d (3H) and 4.40 d (3H), *J*=12.6; 4.42 d (3H) and 4.39 d (3H), *J*=12.5;
15xC$_6$H$_5$ (Bn): 7.10-7.30 m (75H).
[e] **3xOCSCH$_3$**: 2.28 s (9H).

1.4. Table S2. Chemical shifts of ^{13}C NMR signals for compounds 2-8

Compound	Solvent	Residue 6-R	C-1	C-2	C-3	C-4	C-5	C-6
2 [a]	DMSO	OTr	101.82	72.16	73.45	82.96	70.68	63.10
		OH	102.50	72.33	73.05	81.09	72.39	59.25
3 [b]	$CDCl_3$	OTr	98.94	78.27	81.79	78.78	70.69	62.75
		OBn	93.65	79.84	82.16	75.63	71.52	69.57
4 [c]	$CDCl_3$	OBn	98.43	78.47	80.74	79.29	71.70	69.32
		OH	97.61	79.09	80.96	79.02	72.24	62.15
5 [d]	$CDCl_3$	Br	98.15	79.11	80.43	82.15	70.75	34.70
		OBn	99.27	78.35	80.64	79.98	71.56	68.97
6	DMSO	Br	102.08	72.06	72.81	84.39	69.42	36.16
		OH	102.34	72.09	73.34	82.76	72.54	60.43
7 [e]	DMSO	$SCOCH_3$	102.49	72.11	73.24	86.26	69.77	30.84
		OH	101.47	72.14	73.09	81.67	72.30	59.59
8	DMSO (+TFA)	S-S	101.13	72.01	73.75	86.28	70.84	41.02
		OH	102.71	72.13	72.83	80.90	72.40	59.43

Carbon signals of substituents:

[a] **3xOTRT**: 86.15 (3C); 144.25 (9C), 128.55 (18C), 127.91 (18C), 127.02 (9C).

[b] **15xOCH_2 (Bn)**: 76.26 (3C), 74.41 (3C), 74.16 (3C), 73.62 (3C), 71.73 (3C);
15xC_6H_5 (Bn) + 9xC_6H_5 (3xTr): 143.92(9), 139.26(3), 138.86(6), 138.67(3) and 137.78(3) (>C=), 128.55, 128.21, 128.12, 128.08, 127.93, 127.78, 127.71, 127.65, 127.41, 126.89, 126.79, 126.72 and 126.35 (120 x –CH=), 85.94 (3C).

[c] **15xOCH_2 (Bn)**: 75.48 (3C), 75.26 (3C), 73.51 (3C), 72.90 (3C), 72.86 (3C);
15xC_6H_5 (Bn): 139.22(3), 139.14(3), 138.26(3), 138.17(3) and 137.75(3) (15x C_{ipso}); 128.32 (6), 128.23(6), 128.14(6), 128.03(6), 128.01(6), 127.98(6), 127.84(6), 127.61(6), 127.41(6) and 127.08(6) (30x C_{ortho} + 30x C_{meta}); 127.69(3), 127.55(3), 127.40(3), 127.04(3) and 126.94(3) (15x C_{para}).

[d] **15xOCH_2 (Bn)**: 75.58 (3C), 75.30 (3C), 73.45 (3C), 72.98 (3C), 72.69 (3C);
15xC_6H_5 (Bn): 139.14(6), 138.22(3), 138.04(3), 137.79(3) (15x C_{ipso}); 128.37 (6), 128.21(6), 128.14(6), 128.07(6), 127.98(6), 127.97(6), 127.76(6), 127.59(6), 127.31(6) and 126.94(6) (30x C_{ortho} + 30x C_{meta}); 127.72(3), 127.54(3), 127.42(3), 126.98(3) and 126.94(3) (15x C_{para}).

[e] **3x$OCSCH_3$:** 194.93(3) and 30.66(3).

2. Isothermal titration calorimetry

2.1. General procedures

All solutions for the titration experiments were prepared using ultra-pure water (Milli-Q Synthesis, total organic carbon content ≤ 5 ppb). Samples were prepared in bottles made of clear Duran borosilicate glass, which had been cleaned with peroxysulfuric and dried thoroughly prior to use. Calculations of the concentration of commercially available α,ω-alkanediols and 1-undecanol were based on the guaranteed content of compound as obtained from Batch Analysis Certificates supplied by manufacturers (Aldrich, Fluka) for each compound. Content of the prepared[1] 1,11-undecanediol and 1,13-tridecanediol in the samples is based elemental analysis and quantitative ^{1}H-NMR spectra. Due to hygroscopic nature of dimer **8**, its actual concentration in the prepared samples was determined by quantitative NMR measurements (in DMSO + 20 μL of CF_3COOD) of the lyophilized samples using acetanilide (sublimed, 99.99%) as an internal standard.

Titrations of solutions at the concentrations below 10^{-5} M required presaturation of the flasks containing sample solutions with the solutions of that particular compound prior the preparation of the final sample.

The titrations were carried out with MicroCal VP ITC system, model 2007. In a typical run, clean cell was washed twice with the sample solution and titrated with the solution of the titrant (11 additions). The added injected volumes varied from 5 to14 μL, except for the first throw-away injection which was 2 μL in all cases. The titrations were done in three-replicate series using the same stock solutions to ensure reproducibility of the results. The recorded thermograms were – after manual baseline corrections – analysed using Origine 7 based software supplied by Microcal. In all cases, one-site binding model gave the best fit. Each titration was evaluated independently (see detailed reports in pages SX-SX, experiments 1-3 in each table) to check for outlying experiments. However, the estimates of K and $\Delta H°$ given in Table 1 in the main text were achieved by fitting *pre-averaged* values of heats of all three experiments. Thus, the mean values of raw heats for the series of five n-th additions were calculated and fitted to the one-site model. As expected, the reported chi-square values (and, consequently the reported standard error estimates) were usually significantly lower then for individual titrations.

The estimates of standard free energies $\Delta G°$ and entropic terms $T\Delta S°$ were calculated using Equations S-1 and S-2, respectively.

$$\Delta G° = -RTlnK \quad \text{(S1)}$$

$$T\Delta S° = \Delta H° - \Delta G° \quad \text{(S2)}$$

For the calculation of error propagation in values $\Delta G°$ and $T\Delta S°$, Equations S3 and S4 were derived in our previous work,[2] where $\sigma_{\Delta G°}$ and σ_K stand for the standard error estimates of $\Delta G°$ and K, respectively where $\sigma_{\Delta H°}$ and σ_K stand for the standard errors estimates of $\Delta H°$ and K, respectively, and $\rho_{K,H°}$ is the correlation coefficient for $\Delta H°$ and K calculated from variance-covariance matrix.

$$\sigma_{\Delta G°} = \sqrt{\left(\frac{-RT}{K}\right)^2 \sigma_K^2} \quad \text{(S3)}$$

$$\sigma_{T\Delta S°} = \sqrt{\sigma_{H°}^2 + \left(\frac{RT}{K}\right)^2 \sigma_K^2 + 2\left(\frac{RT}{K}\right)\rho_{K,H°}\sigma_{H°}\sigma_K} \quad \text{(S4)}$$

In addition, 2% concentration error was added by simulation of the least-square fitting for the lower (-1%) and higher (+1%) concentration: the error interval obtained in this way was, in general, unsymmetrical and so the larger σ value was used and implemented in the final resultant estimates. The analysis of the data of competitive titration required calculation for all eight possible combinations of error intervals: similarly to above, the largest error interval is reported.

2.2. Results of ITC Experiments

Determination of *K, ΔG°, ΔH°, TΔS°* of reaction of dimer **8** and 1,11-undecanediol in water at 25 °C.

Figure S1

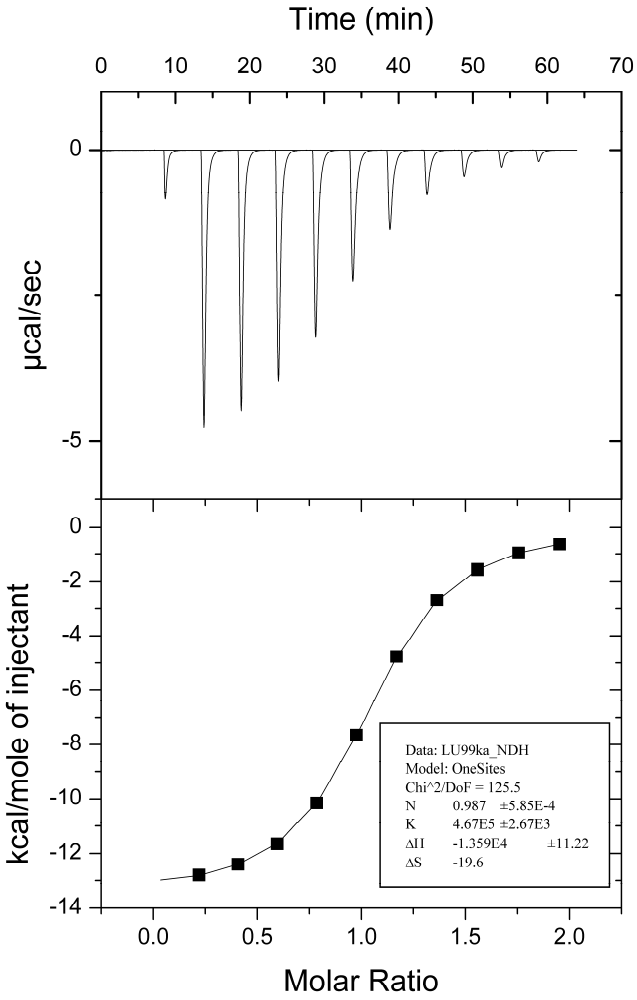


Table S3

exp. Nr.	Conc. of the diol in the cell (mM)	*K* (M^{-1})	Std. error[a] *K*(±M^{-1})	*ΔH* (cal)	Std. error[a] ΔH (±cal)	N	*T*ΔS* (cal)	Std. error[b] T*ΔS (±cal)	*ΔG* (cal)	Std. error[b] *ΔG* (±cal)	Reduced χ^2
1	0.047931	4.67E5	2.7E3	-13590	11	0.99	-5856	14	-7734	3	126
2	0.047931	5.12E5	4.9E3	-13330	21	1.04	-5542	25	-7788	6	292
3	0.047931	5.15E5	1.3E4	-13280	44	1.01	-5488	56	-7792	14	2195
Mean		4.98E5		-13400		1.01	-5629		-7771		
Fit of the mean raw heat		4.88E5	3.4E3	-13451	13	1.01	-5691	16	-7760	4	183
Propagation of ±1% concentration error		4.88E5	9.2E3	-13451	150	1.01	-5691	159	-7760	11	

[a] Standard error estimates obtained from covariance matrix after non-linear least-square fitting procedure.
[b] Calculated standard error by K and ΔH error propagation ($\rho_{K,H}$=0.74).

Determination of *K, ΔG°, ΔH°, TΔS°* of reaction of dimer **8** and 1,12-dodecanediol in water at 25 °C.

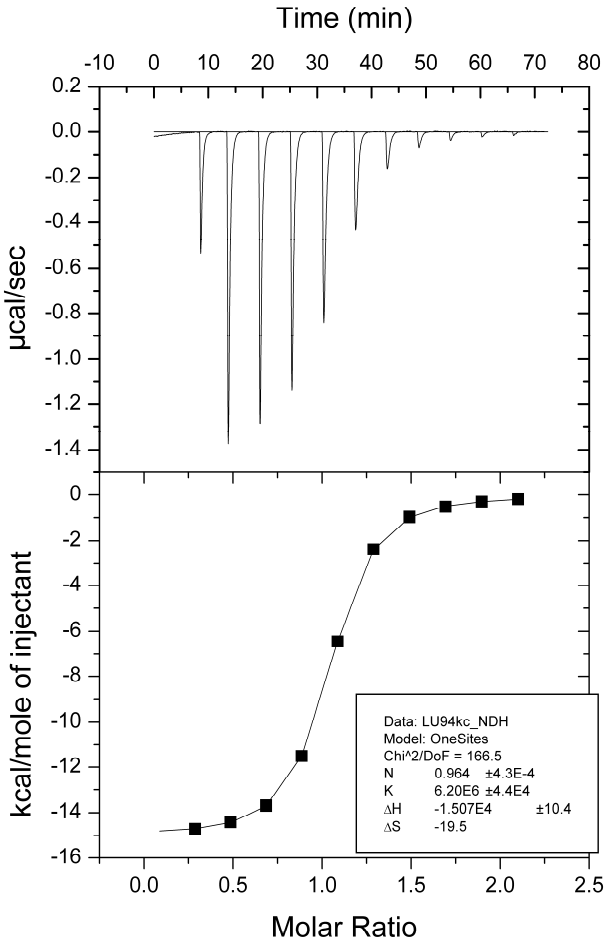


Figure S2

Table S4

exp. Nr.	Conc. of the diol in the cell (mM)	K (M^{-1})	Std. error[a] K(±M^{-1})	ΔH (cal)	Std. error[a] ΔH (±cal)	N	$T^*\Delta S$ (cal)	Std. error[b] T*ΔS (±cal)	ΔG (cal)	Std. error[b] ΔG (±cal)	Reduced χ^2
1	0.01041	6.20E+6	4.4E+4	-15070	10	0.96	-5804	14	-9266	4	167
2	0.01041	6.27E+6	1.2E+5	-15160	27	0.98	-5888	35	-9272	11	1155
3	0.01041	6.14E+6	9.8E+4	-15340	24	0.98	-6049	31	-9291	9	888
Mean		6.20E+6		-15190		0.97	-5914		-9276		
Fit of the mean raw heat		6.13E+6	7.4E+4	-15220	18	0.97	-5961	23	-9259	7	502
Propagation of ±1% concentration error		6.13E+6	1.4E+5	-15220	168	0.97	-5961	177	-9259	13	

[a] Standard error estimates obtained from covariance matrix after non-linear least-square fitting procedure.
[b] Calculated standard error by K and ΔH error propagation ($\rho_{K,H}$=0.66).

Determination of *K, ΔG°, ΔH°, TΔS°* of reaction of dimer **8** and 1,13-tridecanediol in water at 25 °C.

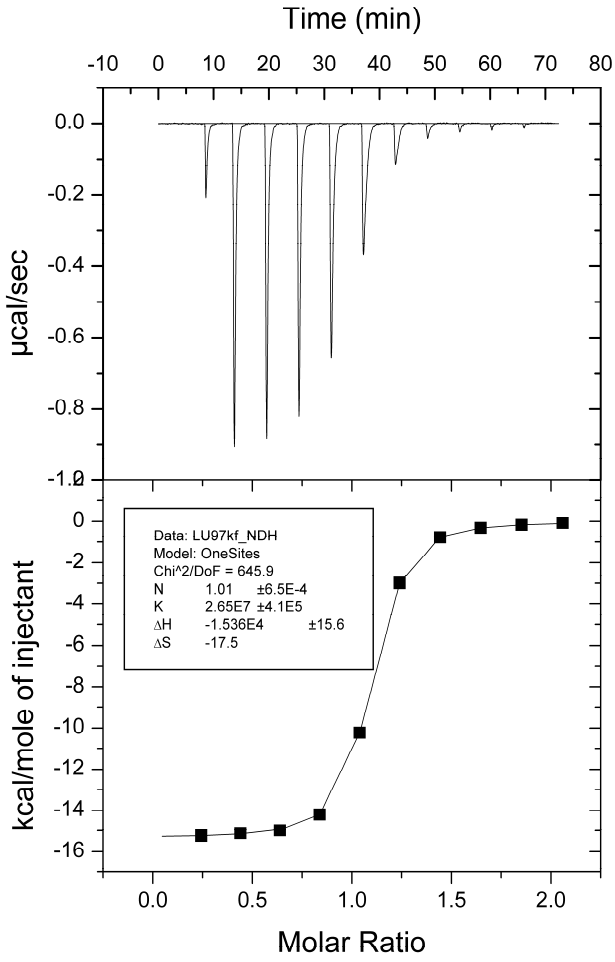


Figure S3

Table S5

exp. Nr.	Conc. of the diol in the cell (mM)	*K* (M^{-1})	Std. error[a] *K*(±M^{-1})	*ΔH* (cal)	Std. error[a] ΔH (±cal)	N	*T*ΔS* (cal)	Std. error[b] T*ΔS (±cal)	*ΔG* (cal)	Std. error[b] *ΔG* (±cal)	Reduced χ^2
1	Tridecanediol 0.006324	2.65E+07	4.1E+05	-15360	16	1.01	-5234	22	-10126	9	646
2	Tridecanediol 0.006324	2.21E+07	8.7E+05	-15420	41	0.98	-5402	58	-10018	23	4008
3	Tridecanediol 0.006324	1.81E+07	4.2E+05	-15460	31	0.98	-5598	42	-9862	16	2124
Mean		2.22E+07		-15413		0.99	-5411		-10002		
Fit of the mean raw heat		2.08E+07	3.2E+05	-15410	17	0.99	-5427	23	-9983	9	672
Propagation of ±1% concentration error		2.08E+07	5.4E+05	-15410	167	0.99	-5427	176	-9983	15	

[a] Standard error estimates obtained from covariance matrix after non-linear least-square fitting procedure.
[b] Calculated standard error by K and ΔH error propagation ($\rho_{K,H}$=0.56).

Determination of *K, ΔG°, ΔH°, TΔS°* of reaction of dimer **8** and 1-undecanol in water at 25 °C.

Figure S4

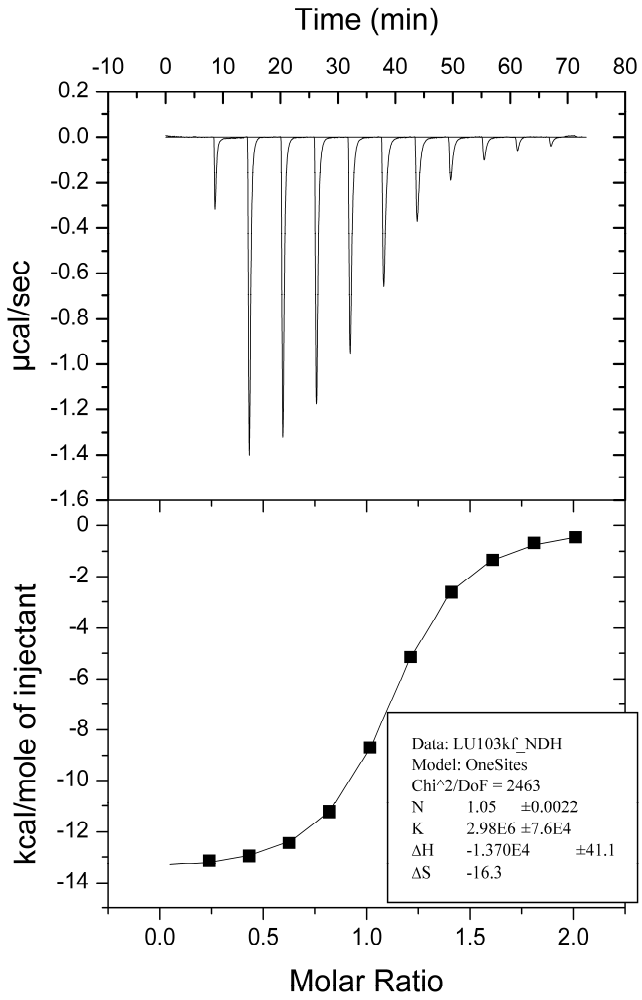
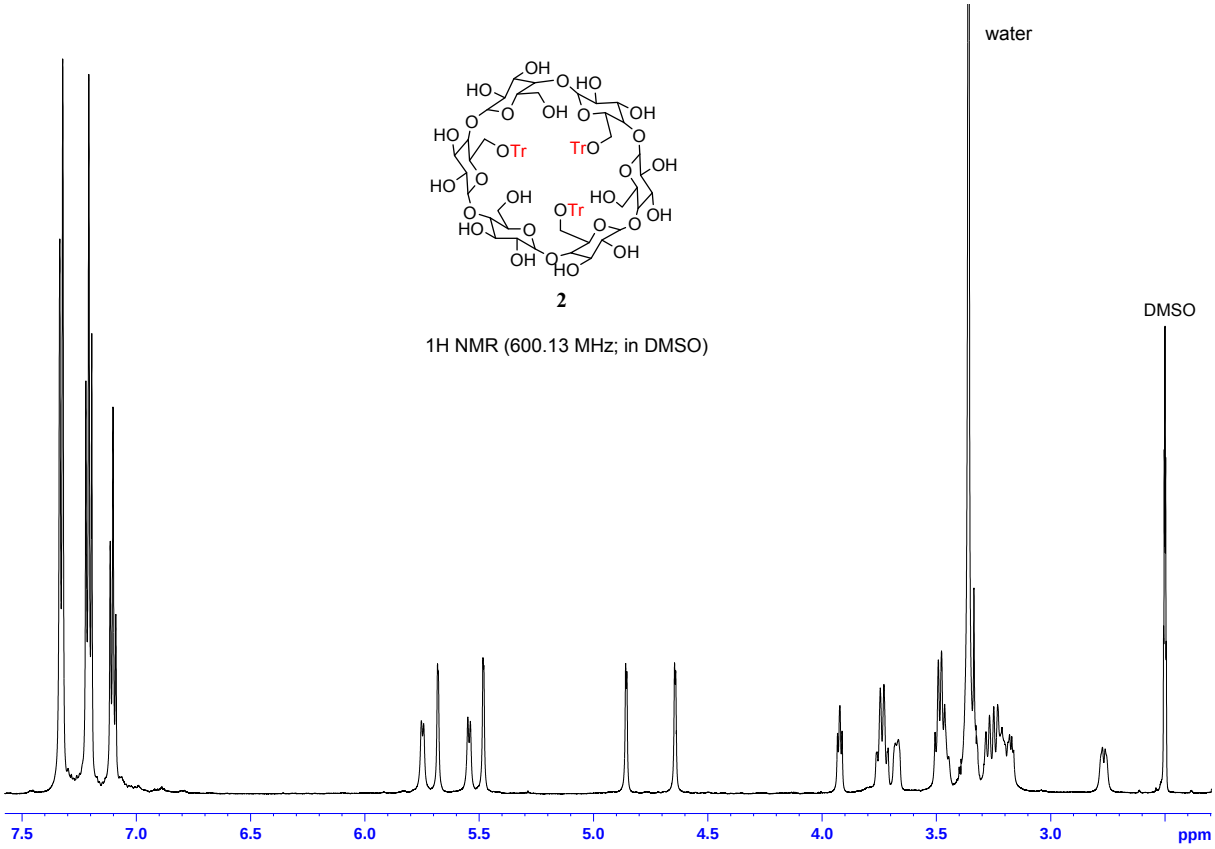


Table S6

exp. Nr.	Conc. of the diol in the cell (mM)	*K* (M^{-1})	Std. error[a] *K*(±M^{-1})	*ΔH* (cal)	Std. error[a] ΔH (±cal)	N	*T*ΔS* (cal)	Std. error[b] T*ΔS (±cal)	*ΔG* (cal)	Std. error[b] *ΔG* (±cal)	Reduced χ^2
1	Undecanol 0.01169	2.98E+6	7.63E4	-13697	41	1,05	-4865	53	-8832	15	2463
2	Undecanol 0.01169	3.02E+6	9.28E4	-13727	49	1,05	-4888	63	-8839	18	3556
3	Undecanol 0.01169	2.97E+6	9.14E4	-13743	50	1	-4883	64	-8860	18	3585
Mean		2.99E+6		-13722		1,03	-4879		-8843		
Fit of the mean raw heat		2.99E+6	7.41E4	-13730	40	1.04	-4897	51	-8833	15	2324
Propagation of ±1% concentration error		2.99E6	1.06E5	-13730	180	1.04	-4897	196	-8833	21	

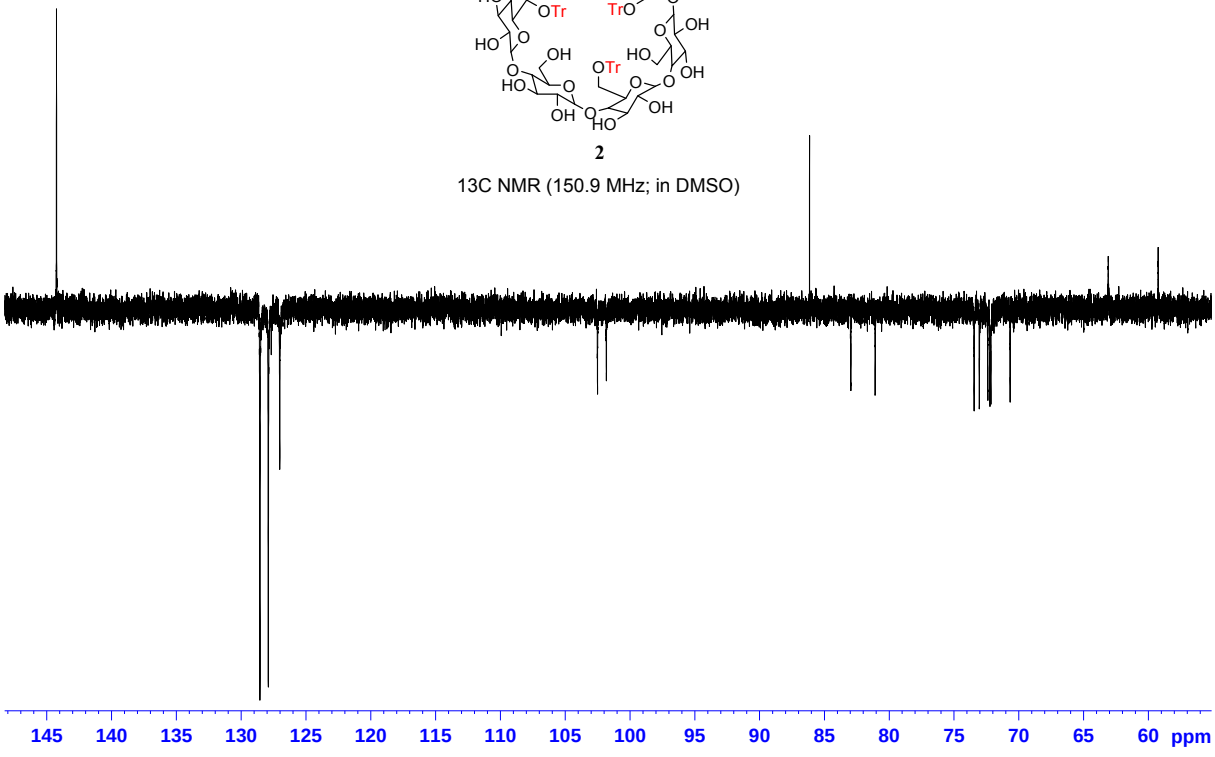
[a] Standard error estimates obtained from covariance matrix after non-linear least-square fitting procedure.
[b] Calculated standard error by K and ΔH error propagation ($\rho_{K,H}$=0.70).

3. Copies of ^{1}H NMR and ^{13}C NMR spectra of compounds 2-8



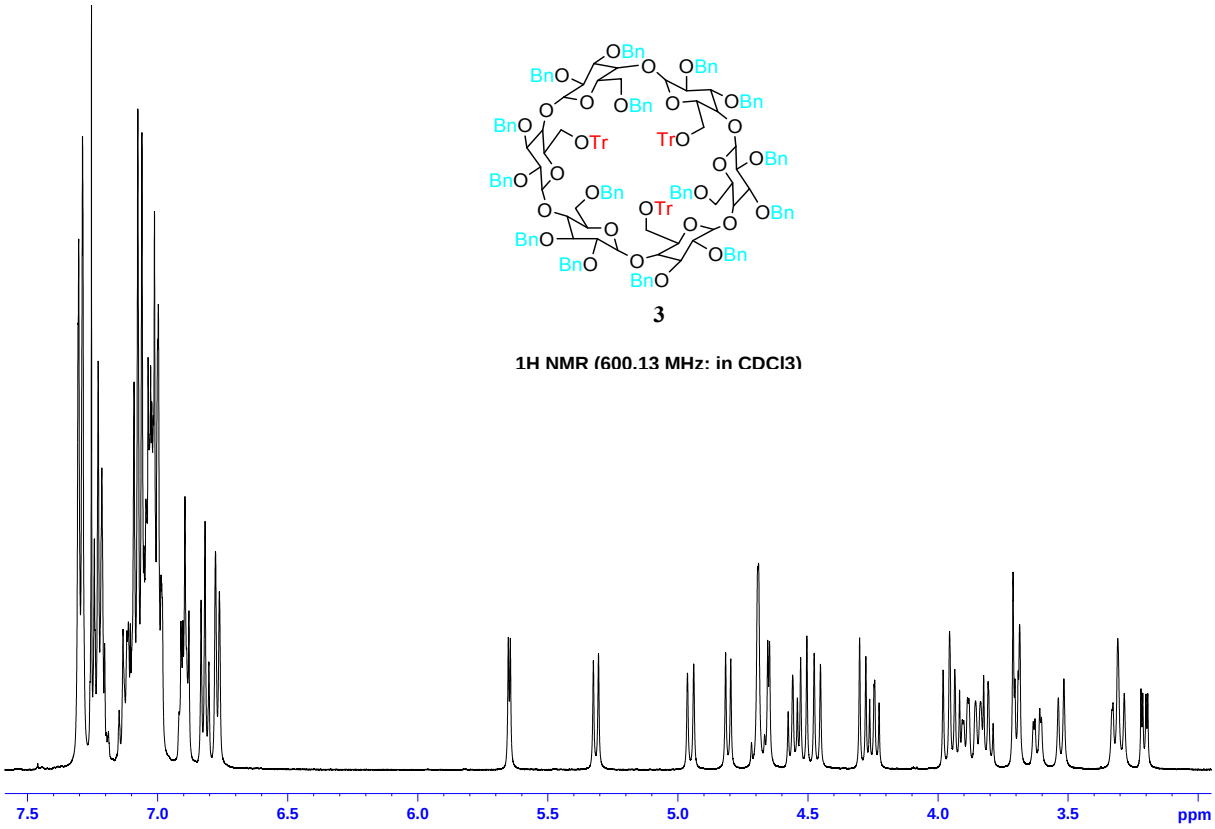
2

1H NMR (600.13 MHz; in DMSO)



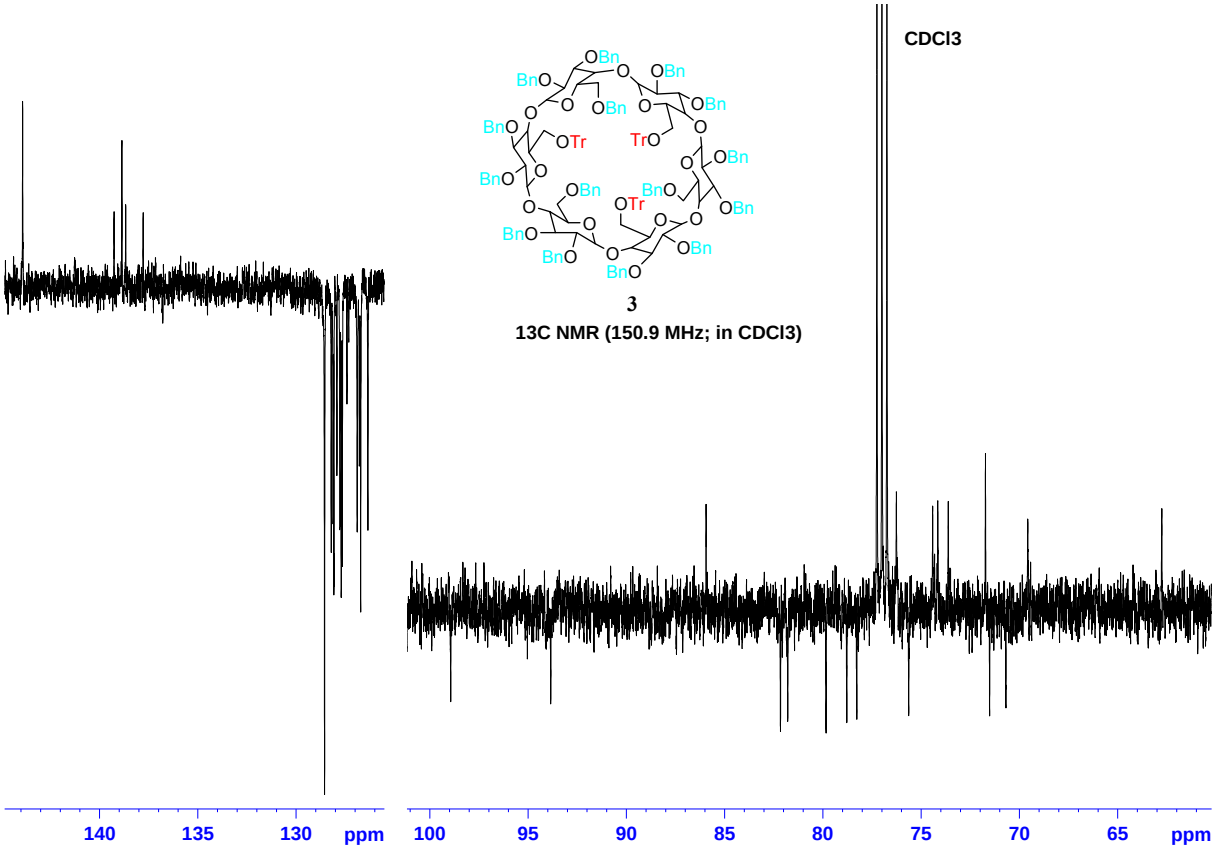
2

13C NMR (150.9 MHz; in DMSO)



3

1H NMR (600.13 MHz; in CDCl3)



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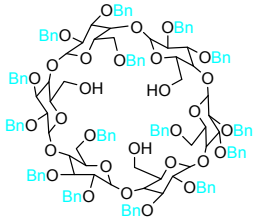
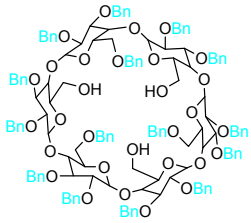
13C NMR (150.9 MHz; in CDCl3)



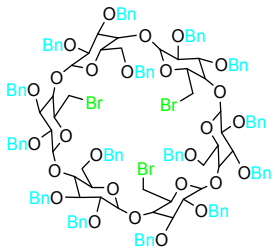
4

1H NMR (600.13 MHz; CDCl3)



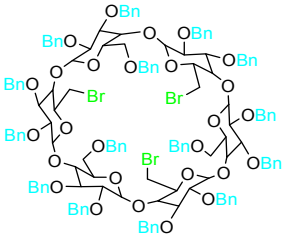
4

13C NMR (150.9 MHz; in CDCl3)



5

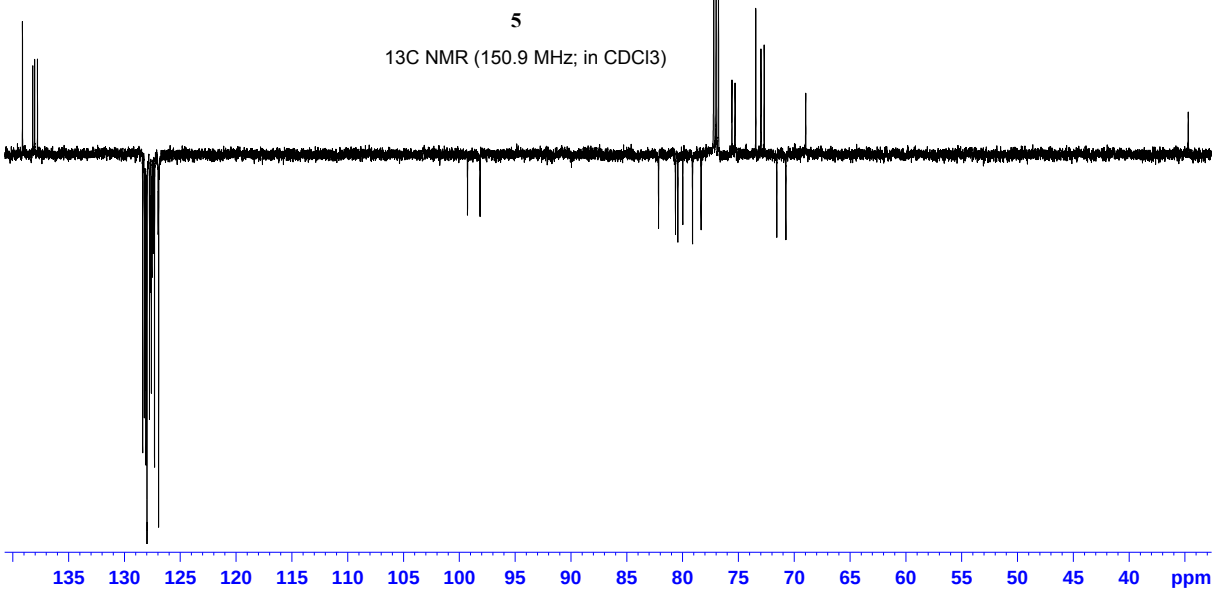
1H NMR (600.13 MHz; in CDCl3

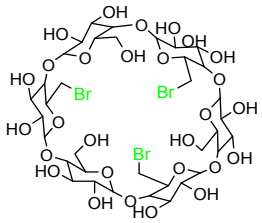


CDCl3

5

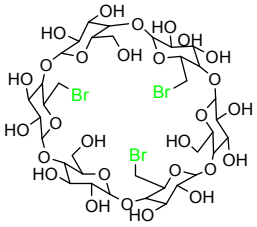
13C NMR (150.9 MHz; in CDCl3)





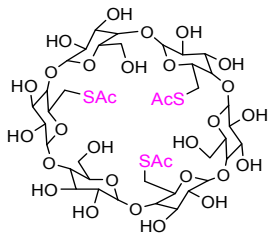
6

1H NMR (600.13 MHz; in DMSO)



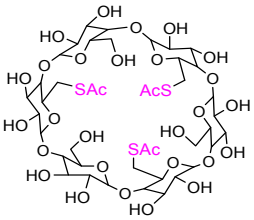
6

13C NMR (150.9 MHz; in DMSO)



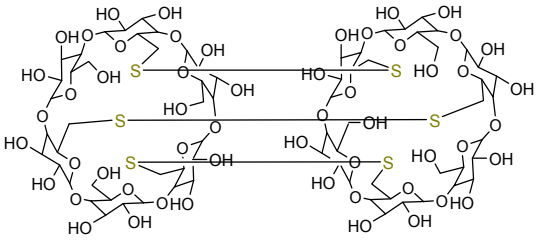
7

1H NMR (600.13 MHz; in DMSO)



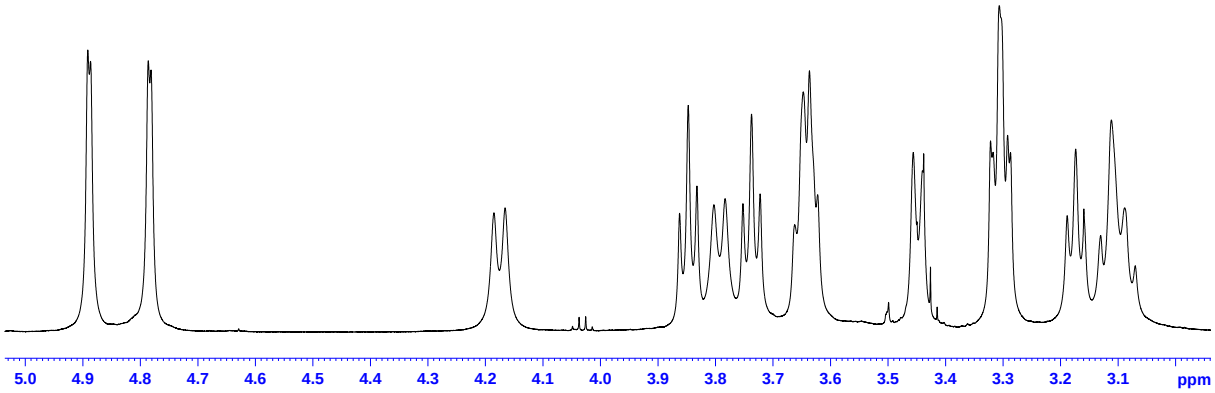
7

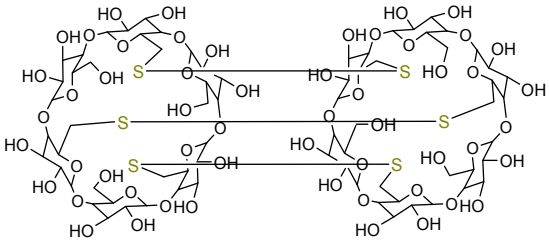
13C NMR (150.9 MHz; in DMSO)



8

1H NMR (600.13 MHz; in DMSO (+TFA))





8

13C NMR (150.9 MHz; in DMSO (+TFA))

4. X-ray: Experimental procedure

Crystal data for dimer **8**: $C_{72}H_{114}O_{54}S_6 \cdot (C_3H_6O) \cdot 11(H_2O)$ M=2292.25, triclinic, *P 1* (No 1), *a* = 13.7086(2) Å, *b* = 13.7560(2) Å, *c* = 16.0247(2) Å, α = 81.3890(10) °, β = 81.6130(10) °, γ = 61.0206(7) °, *V* = 2604.30(6) Å^3, Z = 1, D_x = 1.462 Mg m^{-3}. A colourless crystal of dimensions 0.4 × 0.3 × 0.1 mm was mounted on a Lindemann capillary and measured at Nonius KappaCCD diffractometer by monochromatized MoKα radiation (λ = 0.71073 Å) at 150 K. An absorption was neglected (μ = 0.23 mm^{-1}); a total of 73040 measured reflections in the range *h* = -16 to 16, *k* = –16 to 16, *l* = –19 to 19 (θ_{max}= 26˚), from which 20107 were unique (Rint=0.044) and 18257 observed according to the $I > 2\sigma(I)$ criterion. The structure was solved by direct methods (SIR92[3]) and refined by full-matrix least squares based on F^2 (SHELXL97[4]).

PLATON/ SQUEEZE[5] was used to correct the data of **8** for the presence of the disordered solvent. 117 electrons per unit cell worth of scattering were located in the voids, highest peak corresponds to electron density 9.33 e/A^3. As only one molecule of acetone could be clearly distinguished on difference Fourier map, the overall electron counts were divided into one molecule of acetone and eleven water molecule (acetone as well as water were used for crystallization), providing rough estimation of crystal composition. The SQUEEZE procedure improved the precision of the structure determination significantly (R-factor decreased from 0.081 to 0.056).

The positions of two oxygen atoms of cyclodextrine moiety were each split into two and refined with restricted bond distances and displacement factors.

As the positions of all hydrogen atoms could not be resolved from difference Fourier map, those on carbon atoms were fixed into idealised positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom). Hydrogen atoms of -C-O-H moieties were calculated into idealized position, with C-O-H angle tetrahedral, the torsion angle was chosen to maximize the electron density on difference Fourier map. The idealized geometry was preserved during refinement, only change of torsion angle due to rotation along C-O bond was allowed. The refinement converged (Δ/σ_{max}=0.001) to *R* = 0. 056 for observed reflections and $wR(F^2)$ = 0. 157, *GOF* = 1.05 for 1185 parameters and all 20107 reflections. The final difference map displayed peaks, which could be ascribed to positions of additional solvent molecules with, however, very low occupancy ($\Delta\rho_{max}$ = 1.25, $\Delta\rho_{min}$ = − 1.10 e.Å^{-3}).

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 723533. Copies of this information may be obtained

free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

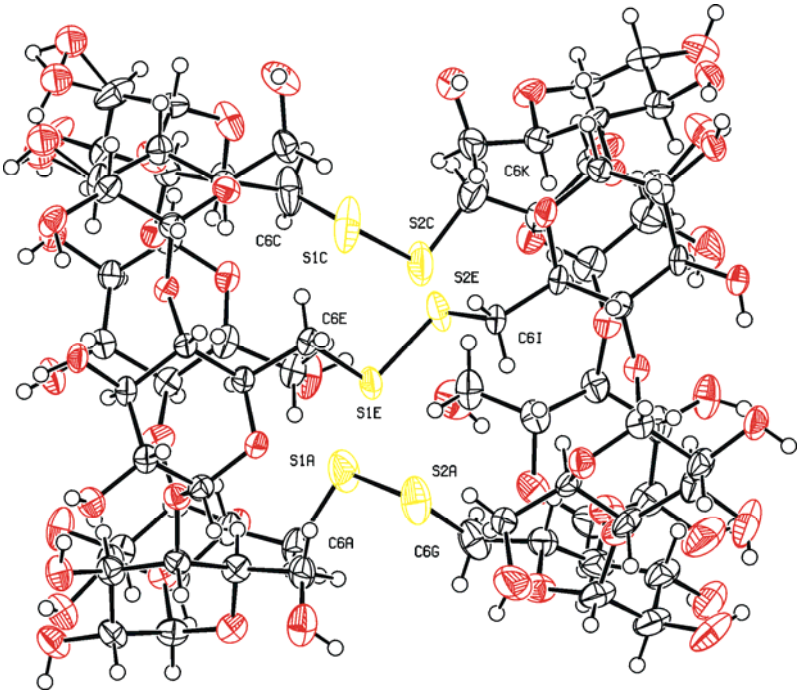


Fig. S5. View of the molecule of duplex **8**. The displacement ellipsoids are drawn on 50% probability level. Selected bond distances and angles. (Å,°): S(1A)—C(6A) 1.824(4), S(1A)—S(2A) 2.0278(15), S(2A)—C(6G) 1.811(5), S(1C)—C(6C) 1.824(5), S(1C)—S(2C) 2.0228(17), S(2C)—C(6K) 1.806(5), S(1E)—C(6E) 1.821(4), S(1E)—S(2E) 2.0214(13), S(2E)—C(6I) 1.822(4), C(6C)—S(1C)—S(2C) 103.51(15), C(6K)—S(2C)—S(1C) 103.01(16), C(6E)—S(1E)—S(2E) 102.95(12), C(6I)—S(2E)—S(1E) 104.06(12), C(6A)—S(1A)—S(2A) 102.94(13), C(6G)—S(2A)—S(1A) 101.79(14), C(6C)—S(1C)—S(2C) 103.51(15), C(6K)—S(2C)—S(1C) 103.01(16), C(6E)—S(1E)—S(2E) 102.95(12)

5. References for ESI

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[3] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst* .**1994**, *27*, 435-435.

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