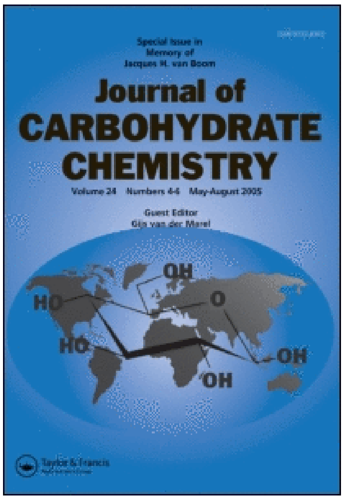

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DIRECT SYNTHESIS OF AMPHIPHILIC α-, β-, AND γ-CYCLODEXTRINS

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ABSTRACT

The clean one step synthesis of the amphiphilic α-, β-, and γ-cyclodextrins starting from per-(6-bromo-6-deoxy)-α-, -β-, and -γ-cyclodextrins is described. The role of the lipophilic tail is played by various aryl groups (phenyl, *p*-bromophenyl, *p*-*O*-butoxyphenyl, *p*-pentylphenyl, and *o*-, *m*-, and *p*-nitrophenyl) linked by a thioether bridge to the position C-6 of each glucopyranose unit. The yields of the S-alkylation reactions were very high (85-95%).

INTRODUCTION

The amphiphilic cyclodextrins are a special class of chemically modified cyclodextrins in which one of the two hydrophilic rims has been modified by introduction of lipophilic groups. Mainly long alkyl chains were used as hydrophobic tails joined to the primary or secondary face of cyclodextrins by thio,[1,2,3] thioxo,[4] amino[5,6,7] or amide[8] linkages. Secondary ester[9] and ether[10] derivatives were also used for the synthesis of the amphiphilic cyclodextrins.

In this paper we report the synthesis of amphiphilic cyclodextrins with aromatic functions grafted onto the primary positions by sulphur bridges. Usually, at least four carbon atoms[4] for each glucose unit in a cyclodextrin molecule, are needed for the alkyl group to be able to act as an amphiphile. In our case aromatic substituents had six or more carbon atoms, therefore we expected that these compounds would be able to behave as amphiphilic cyclodextrins forming stable films at the air-water interface.[11]

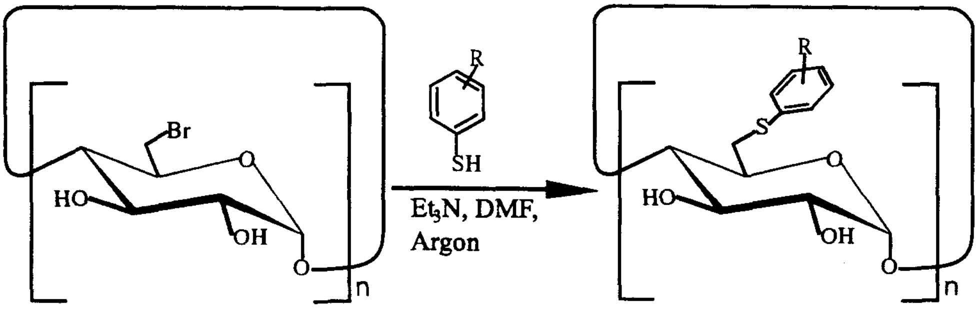
As it has been shown, per-(6-bromo-6-deoxy)-α-, β-, and γ-cyclodextrins (**1**, **2**, and **3**, respectively) are amphiphilic themselves[12] and are often used in preparation of the other amphiphilic systems. We used these compounds as starting materials in the direct synthesis of amphiphilic cyclodextrins bearing aromatic groups at C-6 positions.

RESULTS AND DISCUSSION

In our synthetic method per-(6-bromo-6-deoxy)-α-, β-, and γ-cyclodextrins (**1**, **2**, and **3**, respectively) dissolved in DMF were treated with an excess of various thiophenols in the presence of a base (triethylamine), under an argon atmosphere, affording amphiphilic derivatives in high yields (Figure 1).

Compounds **1**, **2**, and **3** were prepared according to the procedure published by Defaye and coworkers[13] with some important remarks. We found that the starting materials for the synthesis of these cyclodextrin derivatives have to be purified and completely dried. Otherwise the yields became lower and the presence of not completely substituted derivatives was detected by both SIMS and HPLC. Thus protection of the secondary positions was necessary in order to isolate symmetrical hepta-substituted products in the case of the β-cyclodextrin. Previously,[14] we separated heptakis(6-iodo-6-deoxy-2,3-di-*O*-acetyl)- and heptakis(6-bromo-6-deoxy-2,3-di-*O*-acetyl)-β-cyclodextrins by column chromatography and they were then treated with an excess of various thiophenols in the presence of a base. Deprotection of the secondary hydroxy functions then delivered the desired amphiphile.

In a simple modification of the previous synthesis, the following requirements were needed to obtain the pure fully brominated derivatives **1**, **2**, and **3** in reasonable yields:



n	Compound
6	**1**
7	**2**
8	**3**

R	Compound		
	n=6	n=7	n=8
H	**4**	**5**	**6**
p-Br	**7**	**8**	**9**
p-*O*-butyl	**10**	**11**	**12**
p-pentyl	**13**	**14**	**15**
p-nitro	**16**	**17**	**18**
o-nitro		**19**	
m-nitro		**20**	

Figure 1. The synthesis of the amphiphilic cyclodextrins

i) Starting cyclodextrins were twice crystallised from water and dried *in vacuo* at 110 °C for 48 hours. They were stored under those conditions until directly before use.

ii) Triphenylphosphine was twice crystallised from anhydrous ethanol and dried at 60 °C *in vacuo* for 4 hours.

iii) Dimethylformamide (DMF) was distilled over calcium hydride under nitrogen atmosphere before use.

If the reaction was carried out non-stop over a period of 17 hours at 80 °C and the mixture was protected against moisture, we were able to prepare in good yields the starting cyclodextrins **1**, **2**, and **3**. After typical workup, we used them in subsequent reactions without further purification, see also refs. 10 and 12.

The *S*-alkylation reaction carried out in DMF under mild conditions, afforded easily the pure amphiphilic derivatives in one step. What is important is that the protection-deprotection sequence is not required for the secondary face .

For the series of isomeric heptakis[6-thio(nitrophenyl)-6-deoxy]-β-cyclodextrins **17**, **19**, and **20**, Langmuir isotherms were measured.[15] These compounds form stable monolayers at the air-water interface.

EXPERIMENTAL

General methods. Melting points were determined using a Kofler-block apparatus and are not corrected. Optical rotations were measured with a JASCO DIP360 digital polarimeter at 25 °C. ^{1}H (200 MHz) and ^{13}C (50 MHz) NMR spectra were recorded in DMSO-d_6 with a Varian Gemini 200 spectrometer. Liquid matrix secondary ion mass spectrometry (SIMS) measurements were performed with an AMD604 Intectra spectrometer.

Preparation of hexakis(6-bromo-6-deoxy)-α- (1), heptakis(6-bromo-6-deoxy)-β- (2), and octakis(6-bromo-6-deoxy)-γ-cyclodextrin (3). Starting materials were synthesised according to the procedure published by Gadelle and Defaye,[13] with the neccessary modifications as discussed above. Bromine (3 equivalents) was slowly dropped into a solution of 3 equivalents of triphenylphosphine dissolved in freshly distilled DMF (1 mL for 1 mmol of triphenylphosphine). The reaction mixture was heated at 60 °C during 30 min, cooled to room temperature, and then the α–, β– or γ–cyclodextrin was added. The reaction mixture was stirred at 80 °C during 17 h. The solvent was evaporated to half of the initial volume, the solution was made basic using 3M sodium methoxide in methanol to pH ≈10, the mixture was stirred for an additional 30 min, poured onto vigorously stirred ice-water, and the precipitate was removed by filtration. Excess halogenating agents was removed by treatment with a large volume (2.5L) of methanol. The solid precipitate was further washed with several portions of methanol (5x1L), filtered, and dried *in vacuo*.

Hexakis(6-bromo-6-deoxy)-α-cyclodextrin (1). Yield: 85%; mp 253 °C (decomp.); {Lit.[16] mp 222 °C (decomp.)}; $[\alpha]_D^{25}$ +80.5° (*c* 0.2, DMSO); {Lit.[16] $[\alpha]_D^{25}$ +124° (*c* 1.5, DMF)}; ^{1}H NMR δ 5.81 (d, 1H, J=6.81 Hz, OH), 5.64 (d, 1H, J=1.91 Hz, OH), 4.96 (d, 1H, $J_{1,2}$=2.56 Hz, H-1), 4.0-3.65 (m, 4H), 3.5-3.3 (m, remaining H); ^{13}C

NMR δ 102.125 (C-1), 84.98 (C-4), 72.78, 71.92, 70.92 (C-2, C-3,C-5), 35.11 (C-6). SIMS(+) (GLY/TGL): *m/z* 1373.4 $(M+Na)^+$.

Heptakis(6-bromo-6-deoxy)-β-cyclodextrin (2). Yield: 78.8%; mp 232 °C (decomp.); {Lit.[16] mp 214 °C (decomp.)}; $[\alpha]_D^{25}$ +120.6° (*c* 0.2, DMSO); {Lit.[16] $[\alpha]_D^{25}$ +78.1 (*c* 1.76 DMF)}; ^{1}H NMR δ 6.03, 5.54 (s,d, 2H, J=7.0 Hz, 2xOH), 4.98 (d, 1H, $J_{1,2}$=3.04 Hz, H-1), 4.04 (d, 1H, J=10.3 Hz), 3.84 (t, 1H, J=8.5 Hz), 3.61 (bt, 2H) 3.5-3.0 (m, remaining H); ^{13}C NMR δ 101.98 (C-1), 84.54 (C-4), 72.2, 71.9, 71.14 (C-2, C-3, C-5), 34.01 (C-6). SIMS(+) (NBA): *m/z* 1598.5 $(M+Na)^+$.

Octakis(6-bromo-6-deoxy)-γ-cyclodextrin (3). Yield: 80%; mp 223 °C (decomp.); $[\alpha]_D^{25}$ +111.6° (*c* 0.2, DMSO); ^{1}H NMR δ 6.05, 6.01 (2s, 2H, 2xOH), 5.04 (bs, 1H, H-1), 4.1-3.2 (m, remaining H); ^{13}C NMR δ 101.97 (C-1), 83.99 (C-4), 72.16 broad line 70.96 (C-2, C-3, C-5), 34.35 (C-6). SIMS(+) (GLY/TGL): *m/z* 1823.1 $(M+Na)^+$.

Direct synthesis of amphiphilic derivatives 4-20. To a stirred solution of per-(6-bromo-6-deoxy)-cyclodextrin **1**, **2** or **3** in dry DMF, 1.5 equivalents (for each bromine atom) of the appropriate thiophenol were added. Then the reaction mixture was treated, under argon atmosphere, with 2 equivalents (for each thiol group) of dry triethylamine, and the reaction mixture was allowed to react overnight at room temperature. The resultant mixture was then concentrated to dryness, the solid residue was washed copiously with methanol, and the microcrystalline solid was filtered off. Finally, the solid was dried *in vacuo* at 60 °C for 4 h.

Hexakis(6-thiophenyl-6-deoxy)-α-cyclodextrin (4). Yield: 90%; mp 240-242 °C (decomp.); $[\alpha]_D^{25}$ +158° (*c* 0.1, DMSO); ^{1}H NMR δ 7.2-6.9 (m, 5H, phenyl), 5.74, 5.60 (s,d, 2H, J=7 Hz, 2x OH), 4.86 (d, 1H, $J_{1,2}$=2.3 Hz, H-1), 4.0 (bd, 1H), 3.84 (t, 1H), 3.6-3.2 (m, remaining H); ^{13}C NMR δ 136.7, 128.5, 127.9, 125.5 (phenyl), 101.9 (C-1), 85.06 (C-4), 72.8, 71.7, 69.8 (C-2, C-3, C-5), 34.79 (C-6). SIMS(+) (NBA): *m/z* 1574 $(M+Na)^+$.

Heptakis(6-thiophenyl-6-deoxy)-β-cyclodextrin (5). Yield: 92%; mp 277 °C (decomp.); {Lit.[16] mp 253-255 °C}; $[\alpha]_D^{25}$ +192° (*c* 0.2, DMSO); {Lit.[16] $[\alpha]_D^{25}$ +164° (*c* 1.5, pyridine)}; ^{1}H NMR δ 7.2-6.95 (m, 5H, phenyl), 5.99, 5.92 (2d, 2H, J=7 Hz, J=2 Hz, 2xOH), 4.95 (d, 1H, $J_{1,2}$=2.85 Hz, H-1), 3.88 (t, J=7 Hz, 1H), 3.64 (t, J=8 Hz, 1H), 3.4 (m, remaining H); ^{13}C NMR δ 136.65, 128.35, 127.96, 125.14 (phenyl), 101.7 (C-1), 84.4 (C-4), 72.22, 71.82, 69.83 (C-2, C-3, C-5), 34.66 (C-6). SIMS(+) (NBA): *m/z* 1802 $(M+Na)^+$.

Octakis(6-thiophenyl-6-deoxy)-γ-cyclodextrin (6). Yield: 90%; mp 282 °C; $[\alpha]_D^{25}$ +280° (*c* 0.1, DMSO); ^{1}H NMR δ 7.2-6.9 (m, 5H, phenyl), 5.95, 5.92 (2s, 2H, 2xOH), 5.00 (d, 1H, $J_{1,2}$=1.93 Hz, H-1), 3.86 (t, J=7 Hz, 1H), 3.65 (t, 1H, J=9 Hz), 3.5-3.2 (m, remaining H); ^{13}C NMR δ 136.76, 128.59, 128.09, 125.26, (phenyl), 101.73 (C-1), 83.89 (C-4), 72.36 broad line, 70.34 (C-2, C-3, C-5), 34.69 (C-6). SIMS(+) (GLY/TGL): *m/z* 2056 $(M+Na)^+$.

Hexakis[6-thio(4'-bromophenyl)-6-deoxy]-α-cyclodextrin (7). Yield: 95%; mp 270-273 °C; $[\alpha]_D^{25}$ +210° (*c* 0.2, DMSO); ^{1}H NMR δ 7.22 (d, 2H, J=8.5 Hz, phenyl), 6.93 (d, 2H, J=8.7 Hz, phenyl), 5.74 (d, 1H, J=6.8 Hz, OH), 5.56 (d, 1H, J=1.97 Hz, OH), 4.89 (d, 1H, $J_{1,2}$=2.87 Hz, H-1), 4.05 (bt, 1H), 3.8 (t, J=8.4., 1H); ^{13}C NMR δ 136.62, 131.4, 129.5, 118.17 (phenyl), 102.08 (C-1), 85.38 (C-4), 72.84, 71.77, 69.72 (C-2, C-3, C-5), 34.88 (C-6). SIMS(+) (NBA): *m/z* 2021 $(M+Na)^+$.

Heptakis[6-thio(4'-bromophenyl)-6-deoxy]-β-cyclodextrin (8). Yield: 95%; mp 270 °C (decomp.); $[\alpha]_D^{25}$ +229.8° (*c* 0.2, DMSO); ^{1}H NMR δ 7.23 (d, 2H, J=8.5 Hz, phenyl), 6.99 (d, 2H, J=8.54 Hz, phenyl), 6.03, 5.93 (bs,d, 2H, J=6.62 Hz, 2xOH), 4.95 (d, 1H, $J_{1,2}$=1.71 Hz, H-1), 3.86 (m, 1H), 3.64 (t, 1H, J=10 Hz); ^{13}C NMR δ 136.39, 131.35, 129.49, 118.22, (phenyl), 102.1 (C-1), 84.92 (C-4), 72.43, 72.09, 69.89 (C-2, C-3, C-5), 34.84 (C-6). SIMS(+) (NBA): *m/z* 2355 $(M+Na)^+$.

Octakis[6-thio(4'-bromophenyl)-6-deoxy]-γ-cyclodextrin (9). Yield: 95%; mp 273 °C (decomp.); $[\alpha]_D^{25}$ +176.75° (*c* 0.2, DMSO); ^{1}H NMR δ 7.22 (d, 2H, J=8.28 Hz, phenyl), 7.02 (d, 2H, J=8.57 Hz, phenyl), 5.96, 5.92 (2s, 2H, 2xOH), 5.01 (d, 1H, $J_{1,2}$=2.02 Hz, H-1), 3.82 (t, J=7.84, 1H), 3.65-3.15 (m, remaining H); ^{13}C NMR δ 136.28, 131.34, 129.4, 118.24 (phenyl), 101.86 (C-1), 84.18 (C-4), 72.36, 72.21, 70.19 (C-2, C-3, C-5), 34.41 (C-6). SIMS(+) (GLY/TGL): *m/z* 2688 $(M+Na)^+$.

Hexakis[6-thio(4'-butoxyphenyl)-6-deoxy]-α-cyclodextrin (10). Yield: 85%; mp 279 °C (decomp.); $[\alpha]_D^{25}$ +187° (*c* 0.2, DMSO); ^{1}H NMR δ 7.17 (d, 2H, J=8.61 Hz, phenyl), 6.64 (d, 2H, J=8.65 Hz, phenyl), 5.68, 5.53 (2d, 2H, J=6.82 Hz, J=2.02 Hz, 2xOH), 4.83 (d, 1H, $J_{1,2}$=2.38 Hz, H-1), 3.62-3.74 (m, 2H, $C_αH_2$ aliph.), 3.49 (t, 1H, J=9 Hz), 1.55 (m, 2H, $C_βH_2$ aliph.), 1.31 (m, 2H, $C_γH_2$ aliph.), 0.85 (t, 3H, CH_3); ^{13}C NMR δ 157.73, 132.20, 126.81, 115.08 (phenyl), 102.21 (C-1), 84.97 (C-4), 73.11, 72.07, 70.43 (C-2, C-3, C-5), 67.28 $(C_α)^{17}$, 37.35 (C-6), 30.89 ($C_β$), 18.93 ($C_γ$),13.89 (CH_3); DEPT 135° the same signals, except: 157.73 and 126.81 (C_{IV}); SIMS(+) (NBA): *m/z* 1981 $(M+Na)^+$.

Heptakis[6-thio(4'-butoxyphenyl)-6-deoxy]-β-cyclodextrin (11). Yield: 85%; mp 244 °C (decomp.); $[α]_D^{25}$ +180° (*c* 0.2, DMSO); ^1H NMR δ 7.19 (d, J=8.54 Hz, 2H, phenyl), 6.62 (d, 2H, J=8.38 Hz, phenyl), 5.92, 5.83 (s,d, 2H, J=6.24 Hz, 2xOH), 4.90 (d, 1H, $J_{1,2}$=2.18 Hz, H-1), 3.94 (bt, 1H), 3.64 (bt, 2H, $C_αH_2$ aliph.), 1.6-1.1 (m, 4H, $C_βH_2$+$C_γH_2$ aliph.), 0.83 (t, 3H, J=7.39 Hz, CH_3); ^{13}C NMR δ 157.57, 132.25, 126.25, 114.77 (phenyl), 102.04 (C-1), 84.31 (C-4), 72.73, 72.15, 70.19 (C-2, C-3, C-5), 67.07 ($C_α$), 37.22 (C-6), 30.62 ($C_β$), 18.63 ($C_γ$), 13.58 (CH_3); SIMS(+) (DTE/DTT): *m/z* 2285 $(M+Na)^+$.

Octakis[6-thio(4'-butoxyphenyl)-6-deoxy]-γ-cyclodextrin (12). Yield: 85%; mp 281-283 °C (decomp.); $[α]_D^{25}$ +175° (*c* 0.2, DMSO); ^1H NMR δ 7.2 (d, 2H, J=8 Hz, phenyl), 6.58 (d, 2H, J=8.29 Hz, phenyl), 5.93 (bs, 2H, 2xOH), 4.90 (d, 1H, $J_{1,2}$=0.83 Hz, H-1), 4-3 (compl.m , 8H, remaining sugar H +$C_αH_2$ aliph.), 1.7-1.2 (2m, 4H, $C_βH_2$+$C_γH_2$ aliph.), 0.86 (t, 3H, J=7.05 Hz, CH_3) ^{13}C NMR δ 157.50, 132.13, 126.03, 114.64 (phenyl), 101.83 (C-1), 84.02 (C-4), 72.36, 72.29, 70.22 (C-2, C-3, C-5), 66.89 ($C_α$), 37.03 (C-6), 30.56 ($C_β$), 18.60 ($C_γ$), 13.53 (CH_3); SIMS(+) (NBA): *m/z* 2634 $(M+Na)^+$.

Hexakis[6-thio(4'-pentylphenyl)-6-deoxy]-α-cyclodextrin (13). Yield: 90%; mp 275-276 °C (decomp.); $[α]_D^{25}$ +243° (*c* 0.2, DMSO); ^1H NMR δ 7.07 (d, 2H, J=8 Hz, phenyl), 6.85 (d, 2H, J=8.11 Hz, phenyl), 5.72, 5.58 (s,d, 2H, J=6.79 Hz, 2xOH), 4.88 (d, 1H, $J_{1,2}$=2.73 Hz, H-1), 4.02, 3.82 (s,t, 2H, J=8 Hz,), 3.6-3.1 (m, remaining H), 2.33 (t, 2H, J=7 Hz, $C_αH_2$ aliph.), 1.5-1.0 (2m, 6H,$C_βH_2$+$C_γH_2$+$C_δH_2$ aliph.), 0.79 (t, 3H, J=10 Hz, CH_3); ^{13}C NMR δ 139.74, 133.37, 128.75, 128.55 (phenyl), 102.05 (C-1), 85.03 (C-4), 72.84, 71.86, 70.04 (C-2, C-3, C-5), 35.79 (C-6), 34.88 ($C_α$), 31.13 ($C_β$), 30.77 ($C_γ$), 22.23 ($C_δ$), 14.09 (CH_3); DEPT 135° the same signals, except: 139.74, 133.37 (C_{IV}); SIMS(+) (NBA): *m/z* 1969 $(M+Na)^+$.

Heptakis[6-thio(4'-pentylphenyl)-6-deoxy]-β-cyclodextrin (14). Yield: 90%; mp 265-267 °C (decomp.); $[\alpha]_D^{25}$ +233° (*c* 0.2, DMSO); ^{1}H NMR δ 7.13 (d, 2H, J=7 Hz, phenyl), 6.86 (d, 2H, J=7 Hz, phenyl), 6.00, 5.9 (s,d, 2H, J=6.0 Hz, 2xOH), 4.92 (d, 1H, $J_{1,2}$=2.0 Hz, H-1), 3.93 (bs), 3.62 (bt), 4.0-3.0 (m, remaining H), 2.29 (m, 2H, $C_\alpha H_2$ aliph.), 1.4-1.0 (m, 6H,$C_\beta H_2$+$C_\gamma H_2$+$C_\delta H_2$ aliph.), 0.76 (t, 3H, CH_3); ^{13}C NMR δ 140.21, 133.34, 129.52, 128.79(phenyl), 102.41 (C-1), 84.87 (C-4), 72.79, 72.46, 70.26 (C-2, C-3, C-5), 36.07 (C-6), 34.86 (C_α), 31.04 (C_β), 30.69 (C_γ), 22.20 (C_δ) 14.06 (CH_3); DEPT 135° the same signals, except: 140.21 and 133.34 (C_{IV}); SIMS(+) (NBA): *m/z* 2270 $(M+Na)^+$.

Octakis[6-thio(4'-pentylphenyl)-6-deoxy]-γ-cyclodextrin (15). Yield: 90%; mp 265-266 °C (decomp.); $[\alpha]_D^{25}$ +210° (*c* 0.2, DMSO); ^{1}H NMR δ 7.12 (d, 2H, J=8 Hz, phenyl), 6.86 (d, 2H, J=8 Hz, phenyl), 5.96 (s, 2H, 2xOH), 4.99 (bs, 1H, H-1), 3.0-4.0 (m, remaining H), 2.31 (t, 2H, $C_\alpha H_2$ aliph.), 1.5-1.0 (2×m, 6H, $C_\beta H_2$+$C_\gamma H_2$ aliph.), 0.78 (t, J=7 Hz, 3H, CH_3); ^{13}C NMR δ 139.86, 132.99, 129.03, 125.54 (phenyl), 102.12 (C-1), 84.32 (C-4), 72.58, 72.49, 72.41 (C-2, C-3, C-5), 35.53 (C-6), 34.61 (C_α), 30.80 (C_β), 30.43 (C_γ), 21.95 (C_δ) 13.83 (CH_3); DEPT 135° the same signals, except: 139.86 and 132.99 (C_{IV}); SIMS(+) (NBA): *m/z* 2617 $(M+Na)^+$.

Hexakis[6-thio(4'-nitrophenyl)-6-deoxy]-α-cyclodextrin (16). Yield: 95%; mp 228-230 °C (decomp.); $[\alpha]_D^{25}$ +334° (*c* 0.1, DMSO); ^{1}H NMR δ 7.83 (d, 2H, J=8.9 Hz, phenyl), 7.08 (d, 2H, J=8.8 Hz, phenyl), 5.87, 5.65 (s,d, 2H, J=6.7 Hz, 2xOH), 5.01 (d, 1H, $J_{1,2}$= 2.3 Hz, H-1), 4.13 (bt), 3.88 (bt), 3.7-3.2(remaining H); ^{13}C NMR δ 147.66, 143.92, 125.68, 123.24 (phenyl), 101.99 (C-1), 85.72 (C-4), 72.61, 72.58, 69.62 (C-2, C-3, C-5), 35.55 (C-6). SIMS(+) (NBA): *m/z* 1818 $(M+Na)^+$.

Heptakis[6-thio(4'-nitrophenyl)-6-deoxy]-β-cyclodextrin (17). Yield: 94%; mp 220-225 °C (decomp.); $[\alpha]_D^{25}$ +185° (*c* 0.1, DMSO); ^{1}H NMR δ 7.8 (d, 2H, J=8.1 Hz, phenyl), 7.05 (d, 2H, J=8.7 Hz, phenyl), 6.03 (bs, 2H, 2xOH) 5.01 (bd, 1H, H-1), 4.0-3.2 (m, remaining H); ^{13}C NMR δ 148.25, 144.39, 125.85, 123.59 (phenyl), 102.55 (C-1), 85.63 (C-4), 72.75, 72.33, 69.82 (C-2, C-3, C-5), 33.60 (C-6). SIMS(-) (DTE/DTT): *m/z*$^{(-)}$ 2093 $(M)^-$.

Octakis[6-thio(4'-nitrophenyl)-6-deoxy]-γ-cyclodextrin (18). Yield: 95%; mp 260 °C (decomp.); $[\alpha]_D^{25}$ +415° (*c* 0.1, DMSO); ^{1}H NMR δ 7.8 (d, 2H, J=7.7 Hz, phenyl), 7.12 (d, 2H, J=8 Hz, phenyl), 6.08 (m, 2H, 2xOH), 5.03 (bd, 1H, $J_{1,2}$=0.9 Hz, H-1), 4.0-3.1 (m, remaining H); ^{13}C NMR δ 149.8, 147.7, 125.52, 123.35 (phenyl), 102.37 (C-1), 84.88 (C-4), 72.36, 72.15, 69.74 (C-2, C-3, C-5), 33.21 (C-6). SIMS(+) (NBA+DMSO): *m/z* 2417 $(M+Na)^+$.

Heptakis[6-thio(2'-nitrophenyl)-6-deoxy]-β-cyclodextrin (19). Yield: 90%; mp 240-245 °C (decomp.); $[\alpha]_D^{25}$ +223° (*c* 0.125, DMSO); ^{1}H NMR δ 7.9 (d, 1H, J=8 Hz, phenyl), 7.37 (d, 1H, J=7.7 Hz, phenyl), 7.25 (t, 1H, J=7 Hz, phenyl), 7.1 (t, 1H, J=7.5, phenyl), 6.03 (bs, 2H, 2×OH), 4.98 (d, 1H, $J_{1,2}$=2.0 Hz, H-1); ^{13}C NMR δ 145.84, 136.54, 133.73, 127.43, 125.78, 125.26 (phenyl), 102.63 (C-1), 84.87 (C-4), 72.69, 72.29, 69.77 (C-2, C-3, C-5), 34.36 (C-6). SIMS(+) (NBA): *m/z* 2118 $(M+Na)^+$.

Heptakis[6-thio(3'-nitrophenyl)-6-deoxy]-β-cyclodextrin (20). Yield: 92%; mp 240-242 °C (decomp.); $[\alpha]_D^{25}$ +158° (*c* 0.1, DMSO); ^{1}H NMR δ 7.7-7.15 (2m, 4H, phenyl), 6.06, 5.94 (s,d, 2H, J=6.5 Hz, 2xOH), 4.98 (d, 1H, $J_{1,2}$=1.8 Hz, H-1), 3.95(t), 3.68 (t, J=9 Hz), 4.0-3.2 (m, remaining H); ^{13}C NMR δ 147.55, 139.88, 132.82, 129.58, 120.48, 119.53 (phenyl), 102.22 (C-1), 85.38 (C-4), 72.51, 72.16, 69.85 (C-2, C-3, C-5), 34.18 (C-6). SIMS(+) (NBA): *m/z* 2116 $(M+Na)^+$.

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17. In ^{1}H NMR assignments greek characters denote the carbon atoms at the aliphatic chain attached to the thiophenyl subtituents. C_{IV} represents the non-hydrogen bearing aromatic carbon atoms.