Supporting Information

for

Preparation of β-cyclodextrin-based dimers with selectively methylated rims and their use for solubilization of tetracene

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Synthetic procedures, characterization, $^1$H, $^{13}$C DEPT, 2D NMR, IR, UV–vis spectra of synthesized compounds; UV–vis spectra of tetracene solutions in DMSO; ITC thermograms
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I Synthesis and characterization
6-Azido-6-deoxy-β-cyclodextrin was prepared by two-step synthesis, starting with the
tosylation of β-cyclodextrin [1] and subsequent azidation [2]. Per-6-O-methyl-β-
cyclodextrin (18) and per-2,3-O-methyl-β-cyclodextrin (17) were prepared according to
the procedures described in [3]. Per-2,3,6-O-methyl-β-cyclodextrin (16) was synthesized
according to the method proposed by Zhou [4].

6A-Azido-6A-deoxy-hexakis-6B,C,D,E,F,G-O-tert-butyldimethylsilyl-β-cyclodextrin (1)
6A-Azido-6A-deoxy-β-CD (5.6 g, 4.828 mmol) was dried under vacuum at 85 °C for 3 h.
Then, imidazole (4.8 g, 63.7252 mmol) was added, and the mixture was dissolved in dry
DMF (100 mL). The reaction mixture was stirred under argon. A portion of tert-
butyldimethylsilyl chloride (4.8 g, 31.863 mmol), dissolved in THF (15 mL), was added
dropwise to the reaction mixture. The course of the reaction was followed by TLC
(EtOAc/EtOH/H2O 30/5/4) every 15 min after 1 h since the start of the reaction. The main
product has \( R_F = 0.6 \), while all spots with lower \( R_F \) represent undersilylated compounds
and all spots with higher \( R_F \) indicate oversilylated compounds. The reaction was allowed
to proceed for approximately 1.5 h until all undersilylated cyclodextrins had disappeared.
Then, the reaction mixture was poured into cold water, and the bulky precipitate was
filtered and washed several times on the frit with distilled water. The powder-like solid
was put into a Petri dish and moved to a desiccator for several days. The compound was
dried under a vacuum and dissolved in 50 mL of methanol under heating. Then the
compound was precipitated by the addition of 200 mL of acetonitrile. The compound was
filtered off, and the recrystallization process was repeated until all by-products had
disappeared. After drying, we obtained 3.32 g of pure product (79% yield).
$^1$H-NMR (400 MHz, CDCl$_3$) δ=6.57-6.83 (H-O$_2$, 7H); 5.2-5.33 (H-O$_3$, 7H); 4.88-4.98 (H-C$_1$, 7H); 4.01-4.09 (H-C$_4$; 3.35-4.09 H-C$_3$, H-C$_5$, H-C$_4$, H-C$_2$); 0.89 (t-butyl-Si, 54H); 0.06 (methyl-Si, 36H). $^{13}$C-NMR (100 MHz, CDCl$_3$) δ=101.64-102.32 (C$_1$); 81.16-83.16 (C$_2$); 70.44-73.86 (C$_3$, C$_4$, C$_5$); 61.38-62.62 (C$_{6B,C,D,E,F,G}$); 51.47 (C$_{6A}$); 25.78 (C-t-butyl-Si); 5 (C-methyl-Si); HRMS (ESI): \textit{m/z} calcd for C$_{78}$H$_{153}$N$_3$O$_{34}$Si$_6$Na$: 1866.88$ [M+Na$^+$]; found: 1866.88; [α]CHCl$_3$ = +114.3° (the data are consistent with the literature [5]).

\textbf{Fig. S1} $^1$H NMR spectrum of 1 in CDCl$_3$ at 25 °C.
Fig. S2 DEPT-\textsuperscript{13}C NMR spectrum of 1 in CDCl\textsubscript{3} at 25 °C.

6-azido-6-deoxy-6-TBS-b-CD.4.fid
Fig. S3 COSY spectrum of 1 in CDCl$_3$ at 25 °C.
Fig. S4 HSQC spectrum of 1 in CDCl₃ at 25 °C.
Fig. S5 IR spectrum of 1 in KBr pellet.

Fig. S6 UV–vis spectrum of 1 in CHCl₃.
6A-Azido-6A-deoxy-hexakis-6B,C,D,E,F,G-O-tert-butyldimethylsilyl-per-2,3-O-methyl-β-cyclodextrin (2)

6A-Azido-6A-deoxy-hexakis-6B,C,D,E,F,G-O-tert-butyldimethylsilyl-β-cyclodextrin (1, 3.5 g, 1.9 mmol) together with methyltriphenylphosphine bromide (0.286 g, 0.8 mmol) and ground KOH (5.32 g, 95 mmol) were dissolved in THF (84 mL). The flask was set up in a magnetic stirrer and allowed to stir for 1 h. Then methyl iodide (6.55 mL, 46.2 mmol) was added dropwise. After 2 h, an ice bath was applied to the system, and a portion of NaH (60% suspension in oil, 2.12 g, 53.2 mmol) was added slowly to the reaction mixture. After 1 h, the ice bath was removed, and the reaction continued at room temperature overnight. A portion of methanol (2 mL) was added to quench the reaction, and then all solids were filtered off. The filtrate was dried and moved to a column (50 g silica gel). An elution started with a hexane/ethyl acetate 4/1 mixture and switched to a 5/2 mixture when TLC indicated the presence of the product. The extraction from the column gave 3.3 g of the product (85% yield).

1H-NMR (400 MHz, CDCl₃) δ=5.10-5.24 (H-C¹, 7H); 4.07-4.19 (H-C⁶B,C,D,E,F,G, 6H); 3.47-3.88 (H-C³,H-C⁴; H-C⁵, Me-O-C²; Me-O-C³, H-C⁶A); 3.05-3.20 (H-C², 7H); 0.91 (t-butyl-Si, 54H); 0.01 (methyl-Si, 36H; ¹³C-NMR (100 MHz, CDCl₃) δ=98.31-99.21 (C¹); 77.15-82.78 (C², C³, C⁴); 71.00, 72.43 (C⁵); 61.86-63.00 (C⁶B,C,D,E,F,G); 61.55 (Me-O-C²); 58.63 (MeO-C³); 51.88 (C⁶A); 68.00 (t-Bu-Si); -5.36 (Me-Si). HRMS (ESI): m/z calcd for C₉₁H₁₇₉N₃O₃₄Si₆+Na⁺: 2063.10 [M+Na⁺] found: 2063.10. [α]CHCl₃= +108.3° (the data are consistent with the literature [5]).
Fig. S7 $^1$H NMR spectrum of 2 in CDCl$_3$ at 25 °C.

6-azido-6-deoxy-6-TBS-2,3-permethyl-beta-CD.1.fid
Fig. S8 DEPT-\textsuperscript{13}C NMR spectrum of 2 in CDCl\textsubscript{3} at 25 \degree C.

6-azido-6-deoxy-6-TBS-2,3-permethyl-beta-CD.2.fid
Fig. S9 COSY spectrum of 2 in CDCl$_3$ at 25 °C.

6-azido-6-deoxy-6-TBS-2,3-permethyl-beta-CD.3.ser
Fig. S10 HSQC spectrum of 2 in CDCl$_3$ at 25 °C.
Fig. S11 IR spectrum of 2 in KBr pellet.

Fig. S12 UV–vis spectrum of 2 in CHCl₃.
6\(^{\text{A}}\)-Azido-6\(^{\text{A}}\)-deoxy-per-2,3-\(\text{O}\)-methyl-\(\beta\)-cyclodextrin (3)

6\(^{\text{A}}\)-Azido-6\(^{\text{A}}\)-deoxy-hexakis-6\(^{\text{B,C,D,E,F,G}}\)-O-tert-butyldimethylsilyl-per-2,3-\(\text{O}\)-methyl-\(\beta\)-cyclodextrin (2, 1.4 g, 0.686 mmol) together with NH\(_4\)F (1.37 g, 37 mmol) were dissolved in methanol (40 mL) in a small flask. The flask with the mixture was set in a magnetic stirrer and refluxed overnight. After, the compound was dried, dissolved in chloroform and moved to a silica gel column (50 g). The mixture of chloroform/methanol 8/1 was used to wash out the main product (0.81 g; 87% yield) from the column.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta=5.0-5.21\) (H-C\(^1\), 7H); 4.3-4.64 (HO-C\(^6\), 6H); 3.25-4.01 (H-C\(^6\), H-C\(^5\), Me-O-C\(^2\), H-C\(^4\), Me-O-C\(^3\), H-C\(^3\)); 3.15-3.23 (H-C\(^2\), 7H). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta=98.23-99.41\) (C\(^1\)); 78.93-82.36 (C\(^2\), C\(^3\), C\(^4\)); 71.00-72.48 (C\(^5\)); 61.75, 61.41, 61.22 (C\(^{6\text{B,C,D,E,F,G}}\)); 60.00-61.55 (Me-O-C\(^3\)); 58.31-59.19 (Me-O-C\(^2\)); 51.54 (C\(^{6\text{A}}\)). HRMS (ESI): \(m/z\) calcd for C\(_{55}\)H\(_{97}\)N\(_3\)O\(_{34}\)+H\(^+\): 1356.6 [M+H\(^+\)] found: 1356.60078. [\(\alpha\)]\(\text{CHCl}_3\) = +140.8° (the data are consistent with the literature [5]).
Fig. S13 $^1$H NMR spectrum of 3 in CDCl$_3$ at 25 °C.
Fig. S14 DEPT-\textsuperscript{13}C NMR spectrum of 3 in CDCl\textsubscript{3} at 25 °C.
Fig. S15 COSY spectrum of 3 in CDCl$_3$ at 25 °C.
Fig. S16 HSQC spectrum of 3 in CDCl$_3$ at 25 °C.
Fig. S17 IR spectrum of 3 in KBr pellet.

Fig. S18 UV–vis spectrum of 3 in CHCl₃.
Bis-1,3-[1-(6A-deoxy-2,3-per-O-methyl-β-cyclodextrin-6A-C-yl)-1,2,3-triazol-4-yl]methoxymethylene (4)

6A-Azido-6A-deoxy-per-2,3-O-methyl-β-cyclodextrin (3, 1.00 g; 0.7377 mmol) was dissolved in DMF (25 mL), and the solution was bubbled by argon for 30 minutes. Then, portions of 0.5 M propargyl ether solution in DMF (0.664 mL; 0.332 mmol), copper sulfate hydrate (0.184 g; 0.7377 mmol), and sodium ascorbate (0.142 g; 0.7377 mmol) were added to the reaction mixture, and the reaction was allowed at the room temperature overnight. The solvent was removed in vacuo at 90 °C, and a column chromatography (30 g silica gel) with acetonitrile/water/conc. aq. NH₃ 12/1/1 gave 0.78 g of the desirable product (84% yield).

1H-NMR (400 MHz, D₂O) δ=8.0 (s, H-triazole 2H); 5.09-5.35 (H-C¹, 14H); 5.04, 4.57 (H-C⁶A, 4H); 4.67 (s, –CH₂-triazole, 4H); 4.20 (H-C⁵A, 2H); 2.97-3.97 (H-C⁶B,C,D,E,F,G; H-C⁵B,C,D,E,F,G; Me-O-C²; H-C⁴; Me-O-C³; H-C³; H-C²). 13C-NMR (100 MHz, D₂O) δ=126.85 (C-triazole); 96.77-97.66 (C¹); 70.24-81.44 (C², C³, C⁴, C⁵); 63.97, 60.53 (C⁶B,C,D,E,F,G); 62.84 (–CH₂-triazole); 51.71 (C⁶A). HRMS (ESI): m/z calcd for C₁₁₈H₂₀₀N₆O₇₉+2H⁺: 1404.13 [M+2H⁺] found: 1404.12527. [α]CHCl₃= +159.4°.
Fig. S19 $^1$H-NMR spectrum of 4 in D$_2$O at 25 °C.

KL_189_b.1.fid
Fig. S20 DEPT-\textsuperscript{13}C-NMR spectrum of 4 in D\textsubscript{2}O at 25 °C.

KL_189_b/carbon_13
Fig. S21 COSY spectrum of 4 in D$_2$O at 25 °C.
Fig. S22 HSQC spectrum of 4 in D$_2$O at 25 °C.
Fig. S23 NOESY spectrum of 4 in D$_2$O at 25 °C.
Fig. S24 IR spectrum of 4 in KBr pellet.

Fig. S25 UV–vis of 4 in CHCl₃.
**N,N’- Bis(6α-deoxy-2,3-per-O-methyl-β-cyclodextrin-6α-C-yl)urea (5).**

6α-Azido-6α-deoxy-per-2,3-O-methyl-β-cyclodextrin (3, 0.91 g; 0.67 mmol) together with triphenylphosphine (0.265 g; 1.01 mmol) were dissolved in dry DMF (19 mL). The reaction mixture was bubbled with dry CO₂ overnight. Then all solvent was distilled off under vacuum, and the residue was purified by column chromatography with acetonitrile/water/conc. aq NH₃ 12/1/1 (0.49 g; 54% yield).

1H-NMR (400 MHz, D₂O) δ=5.21 (H-C¹, 14H); 3.22-3.88 (H-C², H-C³, H-C⁴, H-C⁵, H-C⁶); 3.53 (s, Me-O-C²), 3.43 (s, Me-O-C³). 13C-NMR (100 MHz, D₂O) δ=97.40 (C¹); 81.14 (C³); 77.34 (C⁴); 71.76 (C⁵); 60.04 (Me-O-C²); 60.62 (C⁶); 58.30 (Me-O-C³). HRMS (ESI): m/z calcd for C₁₁₃H₁₉₆N₂O₆₉⁺2H⁺: 1344.10 [M+2H⁺] found: 1344.096; [α]CHCl₃ = +155.4°.

**Fig. S26** 1H-NMR spectrum of 5 in D₂O at 25 °C.
Fig. S27 DEPT-\textsuperscript{13}C-NMR spectrum of 5 in D\textsubscript{2}O at 25 °C.

KL_222_2_D2O.4.fid
Fig. S28 COSY spectrum of 5 in D$_2$O at 25 °C.
Fig. S29 HSQC spectrum of 5 in D$_2$O at 25 °C.
Fig. S30 IR spectrum of 5 in KBr pellet.

Fig. S31 UV–vis spectrum of 5 in CHCl₃.
6\textsuperscript{A}-Azido-6\textsuperscript{A}-deoxy-hexakis-6\textsuperscript{B,C,D,E,F,G}-O -tert-butyl-dimethylsilyl-per-2,3-O-acetyl-\textbeta- cyclodextrin (6)

6\textsuperscript{A}-Azido-6\textsuperscript{A}-deoxy-hexakis-6\textsuperscript{B,C,D,E,F,G}-O-tert-butyldimethylsilyl-\textbeta-cyclodextrin (1, 1.27 g, 0.6887 mmol) was dissolved in pyridine/acetic anhydride 2/1 mixture (25 mL). The reaction mixture was allowed to stir at 80 °C overnight. After this, the reaction mixture was diluted by chloroform and washed in a dropping funnel successively with 1 M hydrochloric acid, saturated NaHCO\textsubscript{3} solution, and brine (all 50 mL). Drying of the organic part gave the pure compound (1.64 g; 97% yield).

\textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) δ=5.27-5.45 (H-C\textsubscript{3}, 7H); 5.11-5.21 (H-C\textsubscript{1}, 7H), 3.50-4.27 (H-C\textsubscript{2}; H-C\textsubscript{6}; H-C\textsubscript{4}; H-C\textsubscript{5}); 2.0-2.13 (Me-C(O), 42H); 0.84-0.94 (t-Bu-Si, 54H); 0.04-0.09 (Me-Si, 36H). \textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}) δ=95.96-97.36 (C\textsuperscript{1}); 74.9-77.12 (C\textsuperscript{4}); 70.33-72.31 (C\textsuperscript{3}, C\textsuperscript{2}, C\textsuperscript{5}); 61.42-62.18 (C\textsuperscript{6B,C,D,E,F,G}); 51.49 (C\textsuperscript{6A}); 25.87 (t-Bu-Si); 20.91 (Me-C(O)); -5.67 (Me-Si). HRMS (ESI): m/z calcd for C\textsubscript{106}H\textsubscript{181}N\textsubscript{3}O\textsubscript{48}Si\textsubscript{6}+Na\textsuperscript{+}: 2455.03 [M+Na\textsuperscript{+}]; found: 2455.04. [\textalpha]CHCl\textsubscript{3}= +90°.
Fig. S32 ¹H-NMR spectrum of 6 in CDCl₃ at 25 °C.

6-azido-6-deoxy-6-TBS-2,3-peracetyl-b-CD.1.fid
Fig. S33 DEPT-13C-NMR spectrum of 6 in CDCl₃ at 25 °C.

KL_289_dried.2.fid
Fig. S34 COSY spectrum of 6 in CDCl₃ at 25 °C.
Fig. S35 HSQC spectrum of 6 in CDCl₃ at 25 °C.
Fig. S36 IR spectrum of 6 in KBr pellet.

Fig. S37 UV–vis spectrum of 6 in CHCl₃.
6\textsuperscript{A}-Azido-6\textsuperscript{A}-deoxy-per-2,3-O-acetyl-\textbeta-cyclodextrin (7)

6\textsuperscript{A}-Azido-6\textsuperscript{A}-deoxy-hexakis-6\textsuperscript{B,C,D,E,F,G}-O-tert-butyl-dimethylsilyl-per-2,3-O-acetyl-\textbeta-cyclodextrin (6, 1.64 g, 0.676 mmol) was dissolved in DCM (24 mL). The flask with the reaction mixture was set up in a magnetic stirrer at room temperature, and boron trifluoride etherate (1.6 mL, 12.96 mmol) was added dropwise to the reaction mixture. After 3 h, the reaction mixture was washed with ice-cold NaHCO\textsubscript{3} solution in a dropping funnel, concentrated on rotavap. The product was isolated by chromatography on a silica gel column (100 g). The main product was eluted with chloroform/methanol mixture 9/1 in the 88% yield (1.03 g).

\textsuperscript{1}H-NMR (400 MHz, [d\textsubscript{4}] MeOH) \(\delta=5.38-5.48\) (H-C\textsuperscript{3}, 7H); 5.13-5.24 (H-C\textsuperscript{1}, 7H); 4.75-4.82 (H-C\textsuperscript{2}, 7H); 3.68-4.15 (H-C\textsuperscript{4}, H-C\textsuperscript{5}, H-C\textsuperscript{6}); 2.05-2.15 (Me-C(O), 42H). \textsuperscript{13}C-NMR (100 MHz, [d\textsubscript{4}] MeOH) \(\delta=96.17-96.78\) (C\textsuperscript{1}; 75.43-76.93 (C\textsuperscript{4}; 72.38 (C\textsuperscript{5}; 70.43-71.32 (C\textsuperscript{2}, C\textsuperscript{3}; 60.37 (C\textsuperscript{6}\textsuperscript{B,C,D,E,F,G}; 51.25 (C\textsuperscript{6\textsuperscript{A}}; 19.62 (Me-C(O)). HRMS (ESI): \(m/z\) calcd for C\textsubscript{70}H\textsubscript{97}N\textsubscript{3}O\textsubscript{48}+Na+: 1770.51 [M+Na\textsuperscript{+}]; found 1770.51; [\alpha]CHCl\textsubscript{3}= +118.5°.
Fig. S38 $^1$H-NMR spectrum of 7 in [d$_4$]-MeOH at 25 °C.
Fig. S39 DEPT-$^{13}$C-NMR spectrum of 7 in [d$_4$]-MeOH at 25 °C.
Fig. S40 COSY spectrum of 7 in [d₄]-MeOH at 25 °C.
Fig. S41 HSQC spectrum of 7 in [d₄]-MeOH at 25 °C.
Fig. S42 IR spectrum of 7 in KBr pellet.

Fig. S43 UV–vis spectrum of 7 in CHCl₃.
6^A-Azido-6^A-deoxy-hexakis-6^B,C,D,E,F,G-O-methyl-per-2,3-O-acetyl-β-cyclodextrin (8)

6^A-Azido-6^A-deoxy-per-2,3-O-acetyl-β-cyclodextrin (7, 2.64 g, 1.51 mmol) was dissolved in purified methyl p-toluenesulfonate (26 mL, 177 mmol) in a 100 mL flask. The flask was set in a magnetic stirrer at room temperature under the argon flow. After this, a portion of N,N-diisopropylethylamine (6.5 mL, 38 mmol) was slowly added to the reaction mixture. Then the process was allowed to proceed at 100 °C. Every two hours, the pH of the reaction mixture was checked by an indicator paper, and small portions of N,N-diisopropylethylamine (0.5 mL, 2.9 mmol) were added to maintain the basicity. The reaction mixture was finally left overnight when the pH of the mixture had stopped decreasing. After this, the reaction mixture was diluted by chloroform and washed successively with 9/1 ethanol/water solution of NaI, 1 M HCl, saturated solution of NaHCO₃, saturated solution of Na₂S₂O₃, and brine (all 50 mL). The organic layer was concentrated and applied to a silica gel column (40 g of silica gel). The product (2.25 g; 81% yield) was eluted with chloroform/methanol 75/1 mixture.

^1H-NMR (400 MHz, CDCl₃) δ=5.28-5.43 (H-C³, 7H); 5.12-5.23 (H-C¹, 7H); 4.65-4.83 (H-C², 7H); 4.16-3.55 (H-C⁴, H-C⁵, H-C⁶, 28H); 3.42 (Me-O-C⁶, 18H); 2.02-2.12 (Me-C(O), 42H). ^13C-NMR (100 MHz, CDCl₃) δ=96.36 (C¹); 75.55-76.40 (C⁴); 69.80-72.01 (C², C³, C⁵, C⁶⁰,C,D,E,F,G); 59.41 (Me-O-C⁶); 51.98 (C⁶⁰A); 20.74 (Me-C(O)). HRMS (ESI): m/z calcd for C₇₆H₁₀₉N₃O₄₈+NH₄+: 1849.65 [M+NH₄⁺]; found: 1849.64870; [α]CHCl₃= +132.8°.
Fig. S44 $^1$H-NMR spectrum of 8 in CDCl$_3$ at 25 °C.
Fig. S45 DEPT-13C-NMR spectrum of 8 in CDCl3 at 25 °C.
KL_276.5.fid
Fig. S46 COSY spectrum of 8 in CDCl$_3$ at 25 °C.
Fig. S47 HSQC spectrum of 8 in CDCl₃ at 25 °C.
Fig. S48 IR spectrum of 8 in KBr pellet.

Fig. S49 UV–vis spectrum of 8 in CHCl₃.
Bis-1,3-[1-(6\(^\text{\text{A}}\)-deoxy-hexakis-6\(^\text{\text{B,C,D,E,F,G}}\)-O-methyl-per-2,3-O-acetyl-\(\beta\)-cyclodextrin-6\(^\text{\text{A}}\)-C-yl)-1,2,3-triazol-4-yl]methoxymethylene (9)

6\(^\text{\text{A}}\)-Azido-6\(^\text{\text{A}}\)-deoxy-hexakis-6\(^\text{\text{B,C,D,E,F,G}}\)-O-methyl-per-2,3-O-acetyl-\(\beta\)-cyclodextrin (8, 1 g; 0.546 mmol) was dissolved in DMF (25 mL), and the solution was bubbled by argon for 30 minutes. Then, portions of 0.5 M propargyl ether solution in DMF (0.49 mL; 0.2457 mmol), copper sulfate hydrate (0.136 g; 0.546 mmol), and sodium ascorbate (0.105 g; 0.546 mmol) were added to the reaction mixture, and the reaction mixture was allowed to stir at room temperature. After 72 hours, the temperature increased to 50 °C, and the reaction mixture was stirred for another 48h. After that, the solvent was removed in vacuo at 90 °C, and a column chromatography (30 g silica gel) with chloroform/methanol 50/1 to 25/1 mixture gave 0.6 g of the desirable product (60% yield).

\(^1\text{H-NMR}\) (400 MHz, CDCl\(_3\) \(\delta=7.68\) (s, H-triazole, 2H); 5.23-5.44 (H-C\(^3\), 14H); 5.05-5.2 (H-C\(^1\), 14H); 4.63-4.96 (H-C\(^2\), -CH\(_2\)-triazole, 18H); 3.27-4.37 (H-C\(^4\), H-C\(^5\), H-C\(^6\), Me-O-C\(^6\)); 2.02-2.12 (Me-C(O), 42H). \(^13\text{C-NMR}\) (100 MHz, CDCl\(_3\) \(\delta=125.63\) (C-triazole); 95.65-96-94 (C\(^1\)); 75.13-76.37 (C\(^4\)); 69.63-72.10 (C\(^3\), C\(^5\), C\(^2\), C\(^6\)); 63.77 (–CH\(_2\)-triazole); 20.51-20.90 (Me-C(O)). \(^1^\text{H-NMR}\) (400 MHz, CDCl\(_3\) \(\delta=7.68\) (s, H-triazole, 2H); 5.23-5.44 (H-C\(^3\), 14H); 5.05-5.2 (H-C\(^1\), 14H); 4.63-4.96 (H-C\(^2\), -CH\(_2\)-triazole, 18H); 3.27-4.37 (H-C\(^4\), H-C\(^5\), H-C\(^6\), Me-O-C\(^6\)); 2.02-2.12 (Me-C(O), 42H). \(^13\text{C-NMR}\) (100 MHz, CDCl\(_3\) \(\delta=125.63\) (C-triazole); 95.65-96-94 (C\(^1\)); 75.13-76.37 (C\(^4\)); 69.63-72.10 (C\(^3\), C\(^5\), C\(^2\), C\(^6\)); 63.77 (–CH\(_2\)-triazole); 20.51-20.90 (Me-C(O)). HRMS (ESI): \(m/z\) calcd for \(\text{C}_{158}\text{H}_{224}\text{N}_6\text{O}_{97}^+\text{H}^+\text{Na}^+\): 1889.15 [M+H\(^+\)+Na\(^+\)]; found 1889.15856.
Fig. S50 $^1$H-spectrum of 9 in CDCl$_3$ at 25 °C.

KL_200_III_1.fid
Fig. S51 DEPT-13C-NMR spectrum of 9 in CDCl₃ at 25 °C.

KL_200_II.5.fid
Fig. S52 COSY spectrum of 9 in CDCl$_3$ at 25 °C.
Fig. S53 HSQC spectrum of 9 in CDCl₃ at 25 °C.
Fig. S54 NOESY spectrum of 9 in CDCl₃ at 25 °C.
Bis-1,3-[1-(6A-deoxy-hexakis-6B,C,D,E,F,G-O-methyl-β-cyclodextrin-6A-yl)-1,2,3-triazol-4-yl]methoxymethylene (10)

Bis-1,3-[1-(6A-deoxy-hexakis-6B,C,D,E,F,G-O-methyl-per-2,3-O-acetyl-β-cyclodextrin-6A-C-yl)-1,2,3-triazol-4-yl]methoxymethylene (9, 0.6 g; 0.165 mmol) was treated by 1 mL of 1 M solution of sodium methoxide in 20 mL of methanol for 1 h at room temperature. The solution was neutralized by 10 g of Amberlite 120 resin and dried to get the final product (0.38 g; 97% yield).

$^1$H-NMR (400 MHz, D$_2$O) $\delta=$8.04 (s, H-triazole, 2H); 4.88-5.1 (H-C$^1$, H-C$^6A$, 18H); 4.69 (–CH$_2$-triazole overlapped with H$_2$O); 4.48-4.56 (H-C$^6A$, 2H, diastereotopic); 4.17-4.23 (H-C$^5A$, 2H); 3.41-4.06 (H-C$^2$, H-C$^3$, H-C$^4$, H-C$^5$, H-C$^6$); 3.05-3.35 (Me-O-C$^6$, 18H); 2.64-2.98 (H-C$^6$ 4H). $^{13}$C-NMR (100 MHz, D$_2$O) $\delta=$126.48 (C-triazole); 101.34-102.13 (C$^1$); 80.44-83.27 (C$^2$); 69.08-73.04 (C$^3$, C$^4$, C$^5$, C$^6$); 62.78 (–CH$_2$-triazole, C$^6$); 58.43 (Me-C$^6$); 51.21 (C$^6A$). HRMS (ESI): $m/z$ calcd for C$_{102}$H$_{168}$N$_6$O$_{69}$+2H$^+$: 1291.99 [M+2H$^+$] found: 1291.99549; $[\alpha]$DMF=+106.3°.
Fig. S55 $^1$H-NMR spectrum of 10 in D$_2$O at 25 °C.
Fig. S56 DEPT-$^{13}$C-NMR spectrum of 10 in D$_2$O at 25 °C.

KL_200_deac/C13
Fig. S57 COSY spectrum of 10 in D$_2$O at 25 °C.
Fig. S58 HSQC spectrum of 10 in D$_2$O at 25 °C.
Fig. S59 NOESY spectrum of 10 in D$_2$O at 25 °C.
Fig. S60 IR spectrum of 10 in KBr pellet.

Fig. S61 UV–vis spectrum of 10 in H₂O.
6\(^{\text{A}}\)-Azido-6\(^{\text{A}}\)-deoxy-hexakis-6\(^{\text{B}},\text{C},\text{D},\text{E},\text{F},\text{G}\)-O-methyl-\(\beta\)-cyclodextrin (11)

6\(^{\text{A}}\)-Azido-6\(^{\text{A}}\)-deoxy-hexakis-6\(^{\text{B}},\text{C},\text{D},\text{E},\text{F},\text{G}\)-O-methyl-per-2,3-O-acetyl-\(\beta\)-cyclodextrin (8, 0.8 g; 0.643 mmol) was treated by 1 mL of 1 M solution of sodium methoxide in 20 mL of methanol for 1 h at room temperature. The solution was neutralized by 10 g of Amberlite 120 resin and dried to get the final product in the quantitative yield.

\(^1\)H-NMR (400 MHz, [d\(^6\)] DMSO) \(\delta= 6.08-6.47\) (HO-C\(^2\), HO-C\(^3\), 14H); 4.71-4.84 (H-C\(^1\), 7H); 3.15-3.79 (H-C\(^2\), H-C\(^3\), H-C\(^4\), H-C\(^5\), H-C\(^6\), Me-O-C\(^6\) (overlapped with H\(_2\)O). \(^{13}\)C-NMR (100 MHz, [d\(^6\)] DMSO) \(\delta= 103.28\) (C\(^1\)); 82.65-83.94 (C\(^2\)); 70.60-73.44 (C\(^3\), C\(^4\), C\(^5\), C\(^6\)); 69.51, 61.00 (C\(^6\)); 58.54 (Me-C\(^6\), C\(^{6\text{A}}\)). HRMS (ESI): \(m/z\) calcd for C\(_{48}\)H\(_{81}\)N\(_3\)O\(_{34}\)+NH\(_4^+\): 1261.50 [M+NH\(_4^+\)]; found: 1261.49846. \([\alpha]\)\(_{\text{DMF}}^\text{M}\)=+140.8°.

Fig. S62 \(^1\)H-NMR spectrum of 11 in [d\(^6\)]-DMSO at 25 °C.
Fig. S63 DEPT-\textsuperscript{13}C-NMR spectrum of \textbf{11} in [d\textsubscript{6}]-DMSO at 25 °C.

KL_142_deac_2.fid
Fig. S64 COSY spectrum of 11 in [d₆]-DMSO at 25 °C.
Fig. S65 HSQC spectrum of 11 in $[d_6]$-DMSO at 25 °C.
Fig. S66 IR spectrum of 11 in KBr pellet.

Fig. S67 UV–vis spectrum of 11 in DMSO.
N,N'-Bis(6A-deoxy-6B,C,D,F,G-O-hexakis-methyl-β-cyclodextrin-6A-C-yl)urea (12)

6A-Azido-6A-deoxy-hexakis-6B,C,D,E,F,G-O-methyl-β-cyclodextrin (11, 0.1 g; 0.0804 mmol) together with triphenylphosphine (0.05 g; 0.1907 mmol) and lithium iodide (0.023 g; 0.1717 mmol) were dissolved in dry DMF (19 mL). The reaction mixture was bubbled by dry CO₂ at 40 °C overnight. The solvent was distilled off, and column chromatography (10 g silica gel) with acetonitrile/water/ conc. aq. NH₃ 12/3/1 afforded 0.04 g of the desirable product (41% yield).

¹H-NMR (400 MHz, D₂O) δ=4.93-4.99 (H-C¹, 14H); 3.45-3.91 (H-C², H-C³, H-C⁴, H-C⁵, H-C⁶); 3.33 (Me-O-C⁶, 36H). ¹³C-NMR (100 MHz, D₂O) δ=101.92 (C¹); 81.47 (C²); 72.96 (C⁴); 72.15 (C⁵); 71.13 (C⁶); 70.38 (C⁷); 58.63 (Me-C⁶). HRMS (ESI): m/z calcd for C₉₇H₁₆₄N₂O₆₉+2H⁺: 1231.98 [M+2H⁺]; found: 1231.96992; [α]DMF=+115.4°.
Fig. S68 $^1$H-NMR spectrum of 12 in D$_2$O at 25 °C.
Fig. S69 DEPT-\textsuperscript{13}C-NMR spectrum of 12 in D\textsubscript{2}O at 25 °C.
KL_229.6.fid
Fig. S70 COSY spectrum of 12 in D₂O at 25 °C.
Fig. S71 HSQC spectrum of 12 in D$_2$O at 25 °C.
Fig. S72 IR spectrum of **12** in KBr pellet.

Fig. S73 UV–vis spectrum of **12** in DMSO.
II UV experiments with tetracene

Fig. S74 UV–vis spectrum of tetracene in DMSO at different concentrations.

Fig. S75 Concentration dependence of tetracene’s light absorbance in DMSO at 476 nm.
Fig. S76 UV–vis spectrum of 5-times diluted saturated tetracene solutions with the studied CDs and without any supramolecular host (O).

Fig. S77 UV–vis spectrum of 10-times diluted saturated tetracene solutions with the studied CDs and without any supramolecular host (O).
III ITC experiments

Fig. 78 ITC thermograms.

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a) DMSO to DMSO

b) DMSO to DMSO with 5% vol. water

c) DMSO to tetracene in DMSO
d) 13 dilution to DMSO

e) 13 to tetracene in DMSO

f) 16 to DMSO

g) 16 to tetracene in DMSO
h) 4 to DMSO

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i) 4 to tetracene in DMSO

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k) 5 to tetracene in DMSO

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g) 10 to DMSO

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h) 10 to tetracene in DMSO

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**IV References for SI**


