Supporting information

Inverting Substitution Patterns on Amphiphilic Cyclodextrins
Induces Unprecedented Formation of Hexagonal Columnar Superstructures


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A: NMR spectra of synthesized compounds

Figure S1. $^1$H NMR spectra 400 MHz of 1-azidoctadecane (8) in CDCl$_3$

Figure S2. $^{13}$C DEPT-Q NMR spectra 400 MHz of 1-azidoctadecane (8) in CDCl$_3$
Figure S3. $^1$H NMR spectra 400 MHz of 2-(2-propargylethoxy)ethyl acetate (13) in CDCl$_3$

Figure S4. $^1$H NMR spectra 400 MHz of (2-(2-propargylethoxy)ethoxy)ethyl acetate (14) in CDCl$_3$
Figure S5. $^1$H NMR spectra 400 MHz of per-2,3-di-O-(1-octadecyl-1H-1,2,3-triazol-4-yl)methyl-6-O-mesy1-β-cyclodextrin (9) in CDCl$_3$.

Figure S6. $^{13}$C DEPT-Q NMR 101 MHz spectra of per-2,3-di-O-(1-octadecyl-1H-1,2,3-triazol-4-yl)methyl-6-O-mesy1-β-cyclodextrin (9) in CDCl$_3$. 
Figure S7. $^1$H $^1$H 2D COSY NMR spectra of per-2,3-di-O-(1-octadecyl-$^{1}H$-$1,2,3$-triazol-$4$-yl)methyl-$6$-O-mesyl-$\beta$-cyclodextrin (9) 400 MHZ in CDCl$_3$.

Figure S8. $^1$H $^{13}$C 2D HSQC 400 MHz NMR spectra of per-2,3-di-O-(1-octadecyl-$^{1}H$-$1,2,3$-triazol-$4$-yl)methyl-$6$-O-mesyl-$\beta$-cyclodextrin (9) 400 MHZ in CDCl$_3$. 
**Figure S9.** $^1$H NMR spectra 400 MHz of per-6-azido-6-deoxy-2,3-di-O-(1-octadecyl-1H-1,2,3-triazol-4-yl)methyl-β-cyclodextrin (10) in CDCl$_3$.

**Figure S10.** $^{13}$C DEPT-Q NMR spectra 101 MHz of per-6-azido-6-deoxy-2,3-di-O-(1-octadecyl-1H-1,2,3-triazol-4-yl)methyl-β-cyclodextrin (10) in CDCl$_3$.
Figure S11. $^1$H $^1$H 2D COSY NMR spectra of per-6-azido-6-deoxy-2,3-di-O-(1-octadecyl-1H-1,2,3-triazol-4-yl)methyl-β-cyclodextrin (10) in CDCl$_3$.

Figure S12. $^1$H $^13$C 2D HSQC 400 MHz NMR spectra of per-6-azido-6-deoxy-2,3-di-O-(1-octadecyl-1H-1,2,3-triazol-4-yl)methyl-β-cyclodextrin (10) in CDCl$_3$. 
Figure S13. $^1$H NMR spectra 400 MHz of compound (4) in CDCl$_3$.

Figure S14. $^{13}$C NMR DEPT-Q spectra 101 MHz of compound (4) in CDCl$_3$. 


Figure S15. $^1\text{H}$ $^1\text{H}$ 2D COSY NMR spectra of compound (4) in CDCl$_3$

Figure S16. $^1\text{H}$ $^{13}\text{C}$ 2D HSQC 400 MHz NMR spectra of compound (4) in CDCl$_3$
Figure S17. $^1$H NMR spectra 400 MHz of compound (5) in CDCl$_3$.

Figure S18. $^{13}$C DEPT-Q NMR spectra 101 MHz of compound (4) in CDCl$_3$. 
Figure S19. $^1$H $^1$H 2D COSY NMR spectra of compound (5) in CDCl$_3$

Figure S20. $^1$H $^{13}$C 2D HSQC 400 MHz NMR spectra of compound (5) in CDCl$_3$
B: Thermogravimetric Analysis

Figure S21. Thermogravimetric analysis of compound 4 (2°C/min)

Figure S22. Thermogravimetric analysis of compound 5 (10°C/min)
C: X-ray Diffraction Analysis

Table S1. XRD data for the compounds studied, including comparison of experimentally observed d-spacings and calculated values based on  \[ \frac{1}{d^2} = \frac{4(h^2+k^2+l^2)}{a^2} + \frac{l^2}{c^2} \]. PLC-M-14 is compound 4; PLC-M-19 is compound 5.

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Figure S23. XRD spectra of $\beta$-CD-4 at 25°C

Figure S24. XRD spectra of $\beta$-CD-4 at 100°C
Figure S25. XRD spectra of β-CD-4 at 140°C

Figure S26. XRD spectra of β-CD-5 at 25°C
Figure S27. XRD spectra of β-CD-5 at 100°C

Figure S28. XRD spectra of β-CD-5 at 275°C
D: Differential Scanning Calorimetry Analysis

Table S2. Phase transitions of β-CD-4 and 5 recorded by DSC

<table>
<thead>
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<th>Compound</th>
<th>1st Phase Transition, heating/cooling</th>
<th>2nd Phase Transition, heating/cooling</th>
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<tbody>
<tr>
<td>PLC-M-14</td>
<td>51.0 °C (30.6 J/g)/ 38.1 °C (28.0 J/g)</td>
<td>141.9 °C (0.72 J/g)/ 138.9 °C (0.77 J/g)</td>
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<tr>
<td>PLC-M-19</td>
<td>48.4 °C (26.8 J/g)/ 36.1 °C (23.5 J/g)</td>
<td>126.8 °C (0.34 J/g)/ 123.9 °C (0.20 J/g)</td>
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Figure S29. Differential scanning calorimetry thermogram of β-CD-4 (scan rate 10°C/min, with one minute isothermal at the end points of the temperature range).
Figure S30. Differential scanning calorimetry thermogram of β-CD-5 (scan rate 10°C/min, with one minute isothermal at the end points of the temperature range).
E: Polarized Optical Microscope Pictures

Figure S31. Polarized optical microscope image of β-CD-4.

Figure S32. Polarized optical microscope image of β-CD-4.
Figure S33. Polarized optical microscope image of β-CD-5.

Figure S34. Polarized optical microscope image of β-CD-5.
Figure S35. Polarized optical microscope image of β-CD-5.

Figure S36. Polarized optical microscope image of β-CD-5 after clearing point.
Figure S37. Structure of β-CD-4 before (a) and after (b) optimization.
Figure S38. Structure of β-CD-5 before (a) and after (b) optimization.