

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

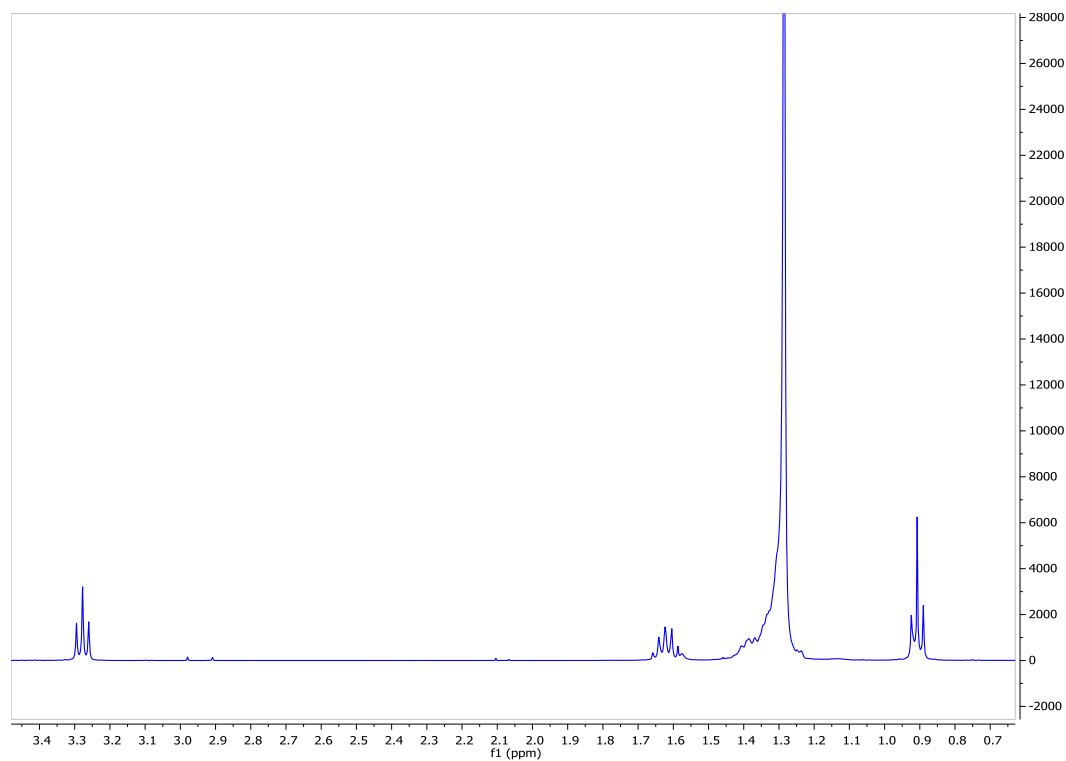


Figure S1. ^1H NMR spectra 400 MHz of 1-azidooctadecane (**8**) in CDCl_3

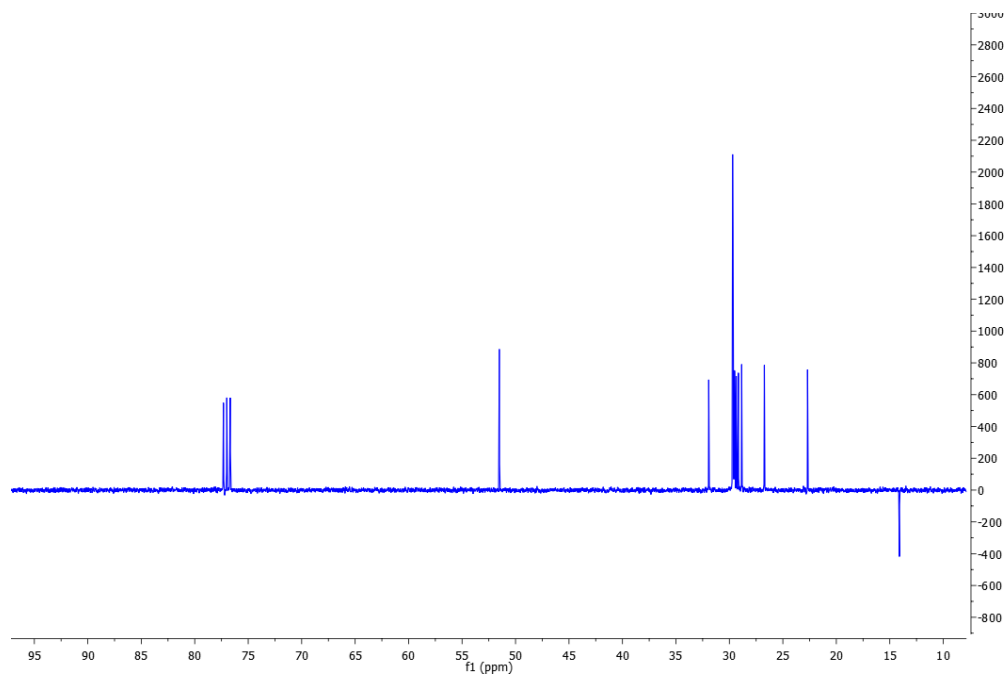


Figure S2. ^{13}C DEPT-Q NMR spectra 400 MHz of 1-azidooctadecane (**8**) in CDCl_3

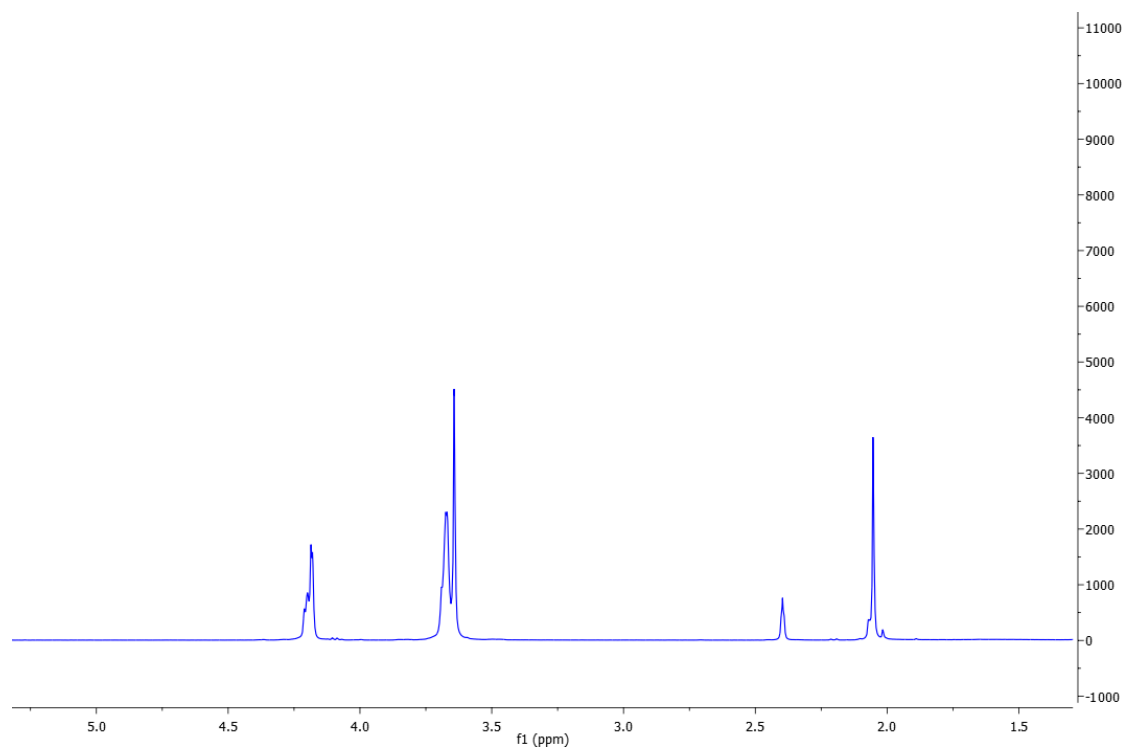


Figure S3. ^1H NMR spectra 400 MHz of 2-(2-propargylethoxy)ethyl acetate (**13**) in CDCl_3

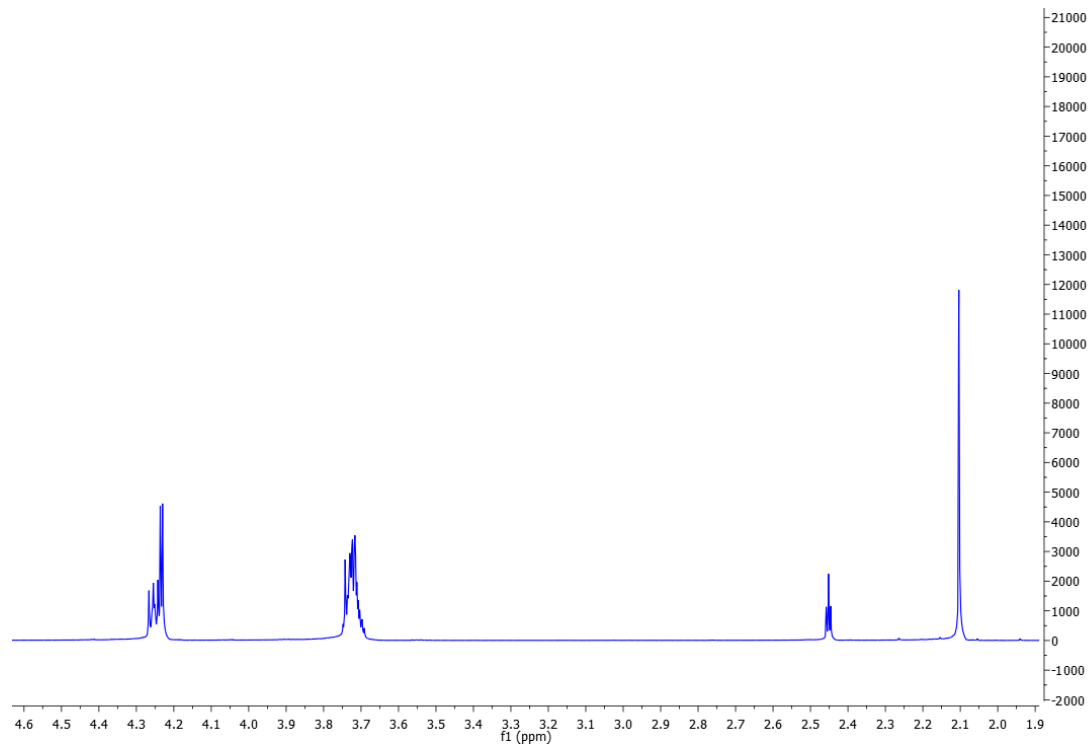


Figure S4. ^1H NMR spectra 400 MHz of (2-(2-(2-propargylethoxy)ethoxy)ethyl acetate (**14**) in CDCl_3

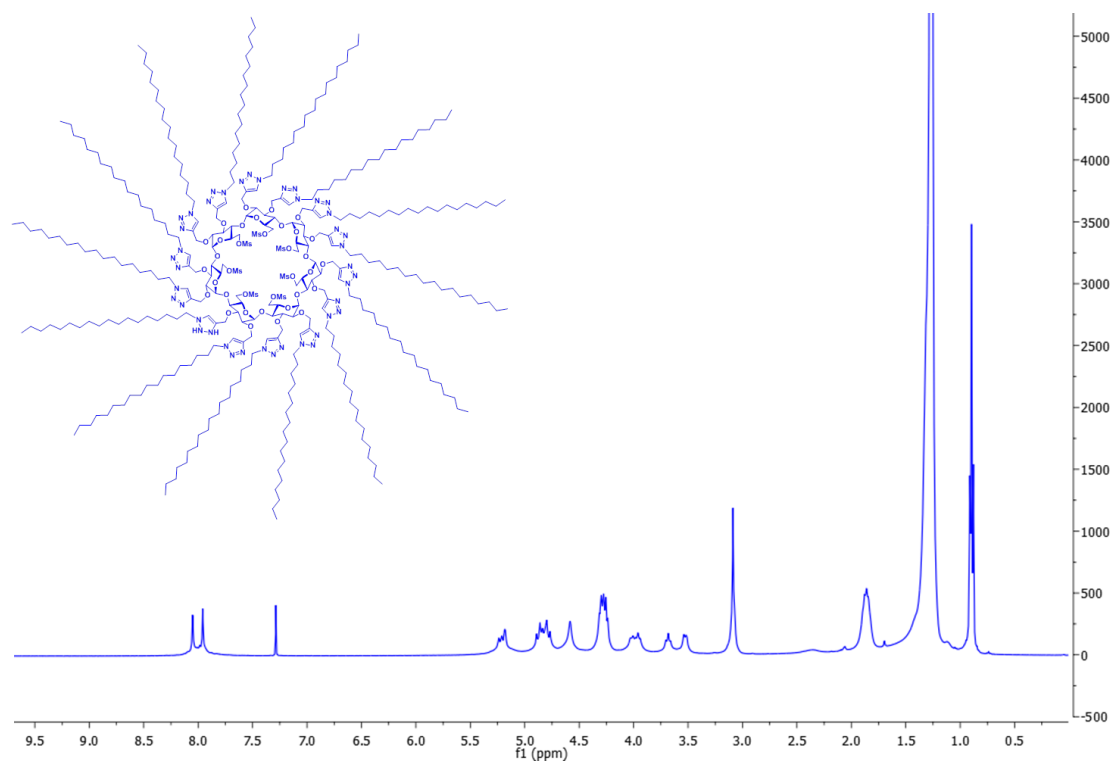


Figure S5. ^1H NMR spectra 400 MHz of per-2,3-di-O-(1-octadecyl-1H-1,2,3-triazol-4-yl)methyl-6-O-mesyl- β -cyclodextrin (**9**) in CDCl_3

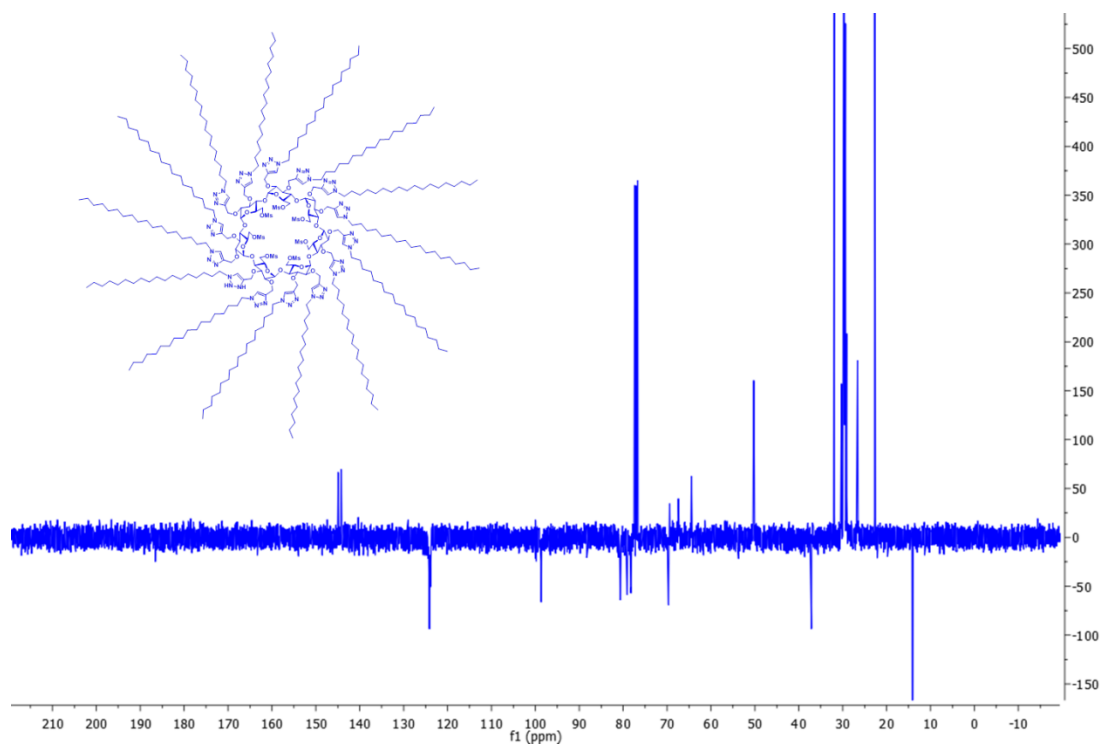


Figure S6. ^{13}C DEPT-Q NMR 101 MHz spectra of per-2,3-di-O-(1-octadecyl-1H-1,2,3-triazol-4-yl)methyl-6-O-mesyl- β -cyclodextrin (**9**) in CDCl_3

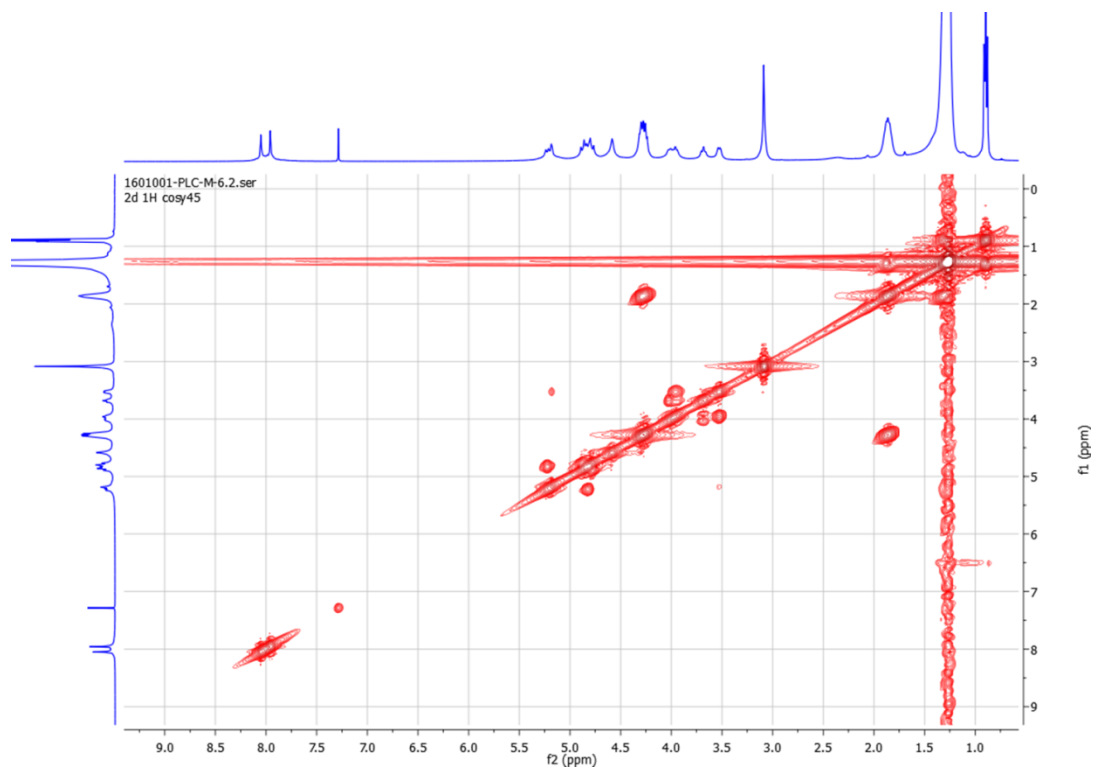


Figure S7. ^1H ^1H 2D COSY NMR spectra of per-2,3-di-O-(1-octadecyl-1*H*-1,2,3-triazol-4-yl)methyl-6-*O*-mesyl- β -cyclodextrin (**9**) 400 MHz in CDCl_3

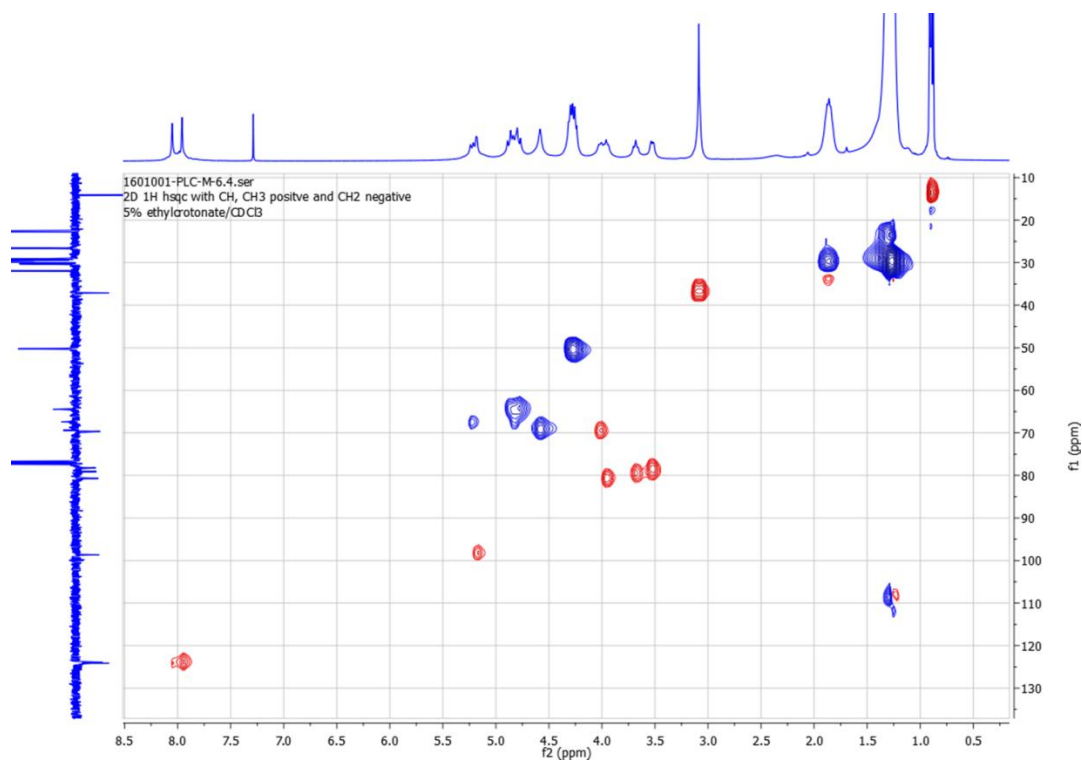


Figure S8. ^1H ^{13}C 2D HSQC 400 MHz NMR spectra of per-2,3-di-O-(1-octadecyl-1*H*-1,2,3-triazol-4-yl)methyl-6-*O*-mesyl- β -cyclodextrin (**9**) 400 MHz in CDCl_3

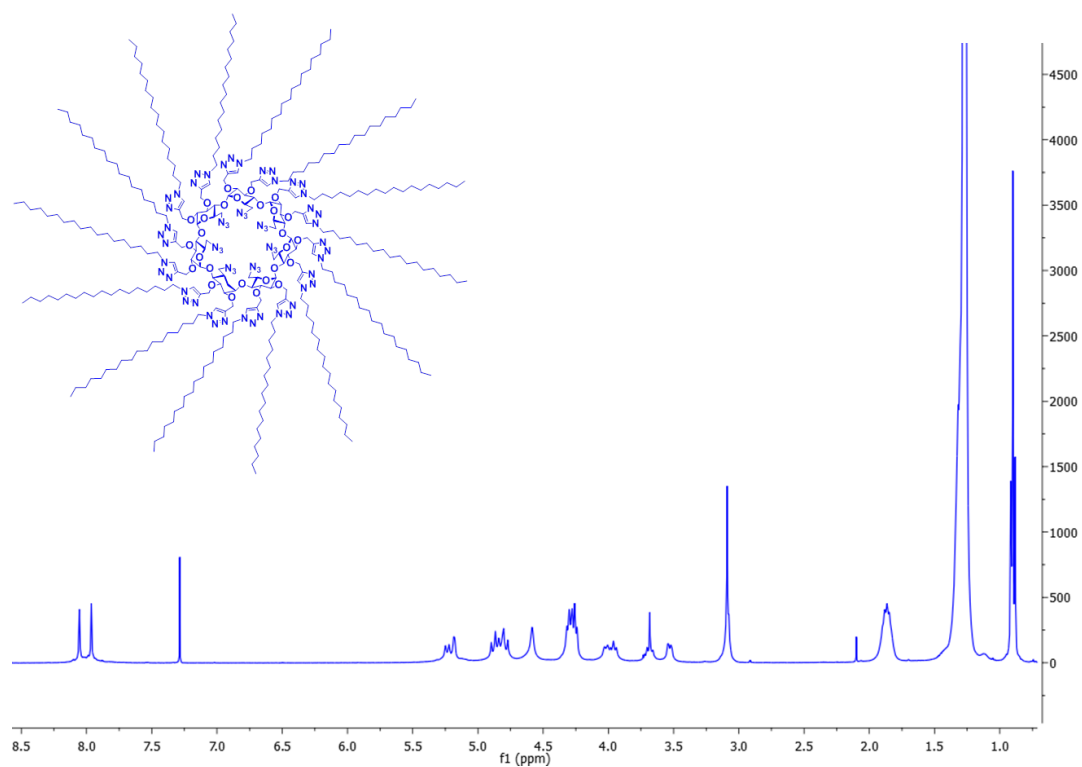


Figure S9. ^1H NMR spectra 400 MHz of per-6-azido-6-deoxy-2,3-di-*O*-(1-octadecyl-1*H*-1,2,3-triazol-4-yl)methyl- β -cyclodextrin (**10**) in CDCl_3

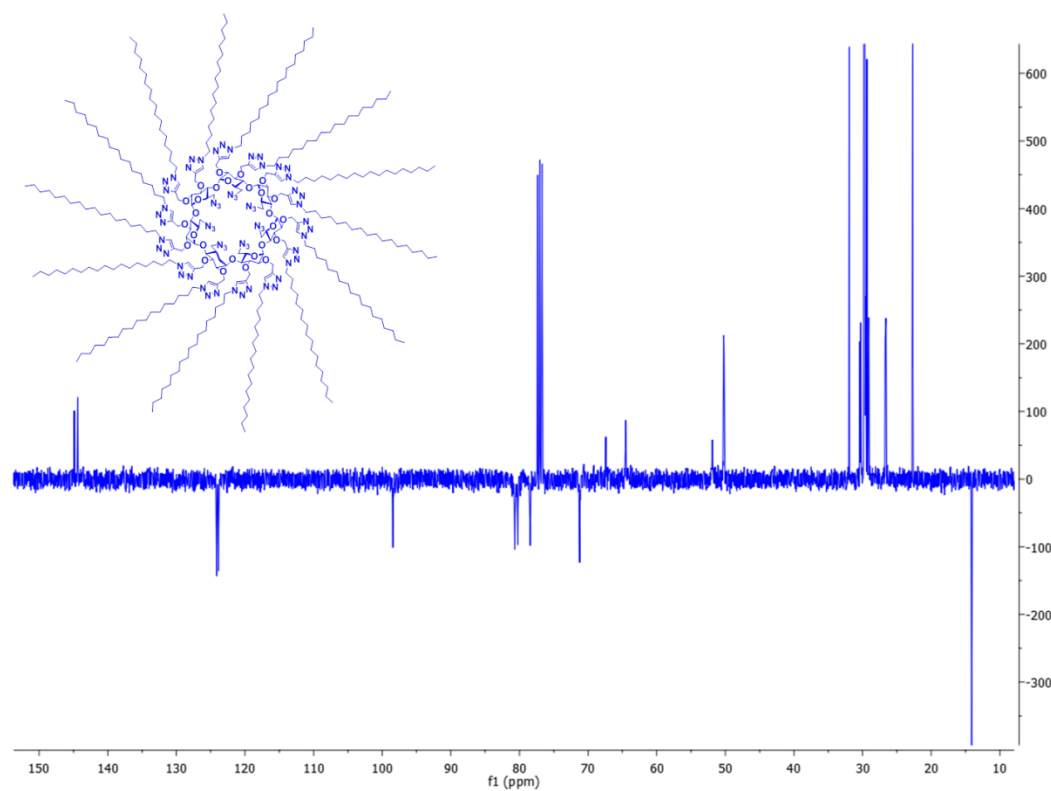


Figure S10. ^{13}C DEPT-Q NMR spectra 101 MHz of per-6-azido-6-deoxy-2,3-di-*O*-(1-octadecyl-1*H*-1,2,3-triazol-4-yl)methyl- β -cyclodextrin (**10**) in CDCl_3

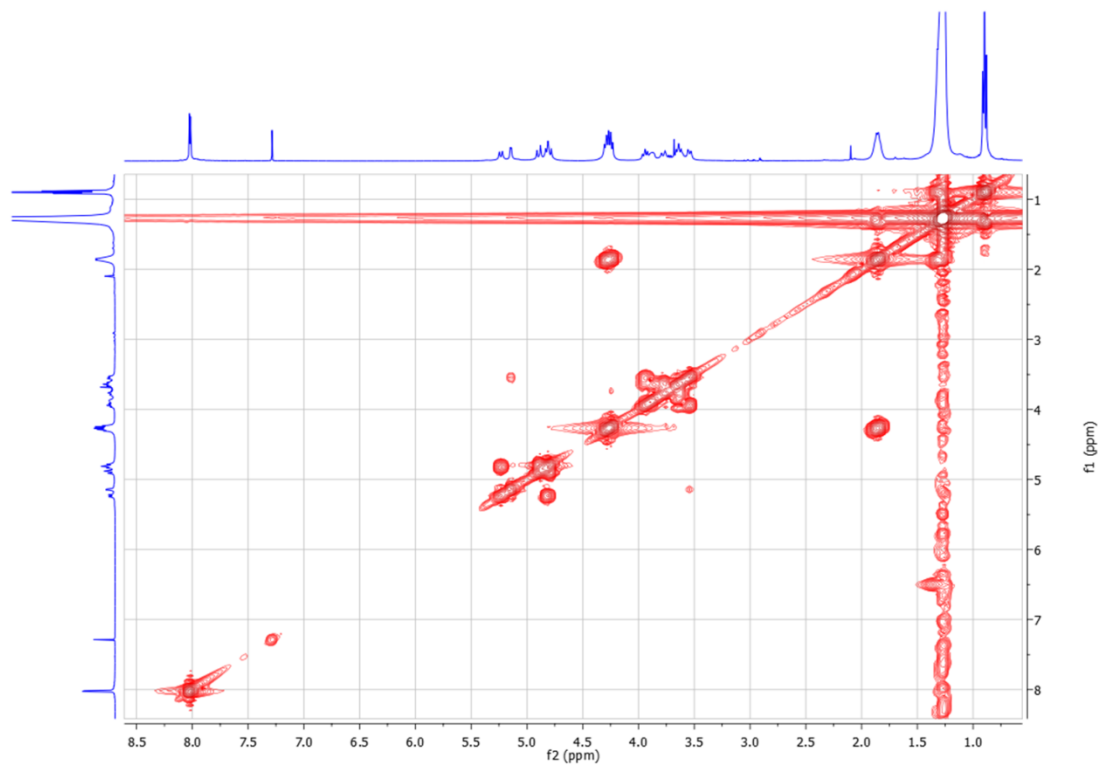


Figure S11. ^1H ^1H 2D COSY NMR spectra of per-6-azido-6-deoxy-2,3-di-*O*-(1-octadecyl-1*H*-1,2,3-triazol-4-yl)methyl- β -cyclodextrin (**10**) in CDCl_3

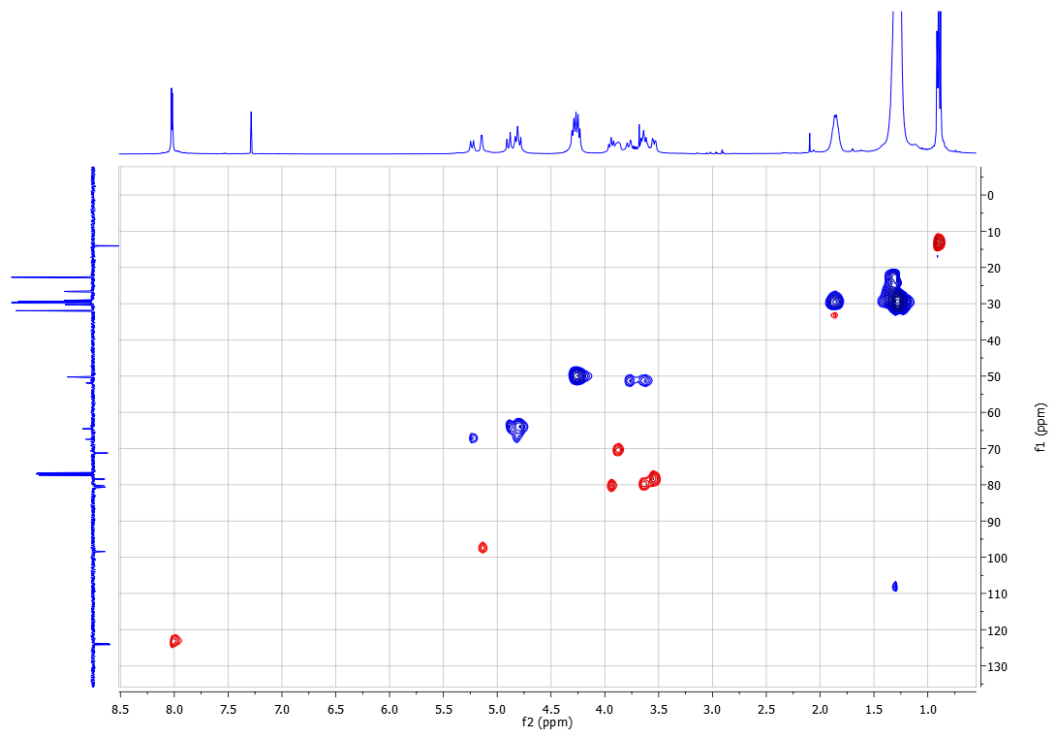


Figure S12. ^1H ^{13}C 2D HSQC 400 MHz NMR spectra of per-6-azido-6-deoxy-2,3-di-*O*-(1-octadecyl-1*H*-1,2,3-triazol-4-yl)methyl- β -cyclodextrin (**10**) in CDCl_3

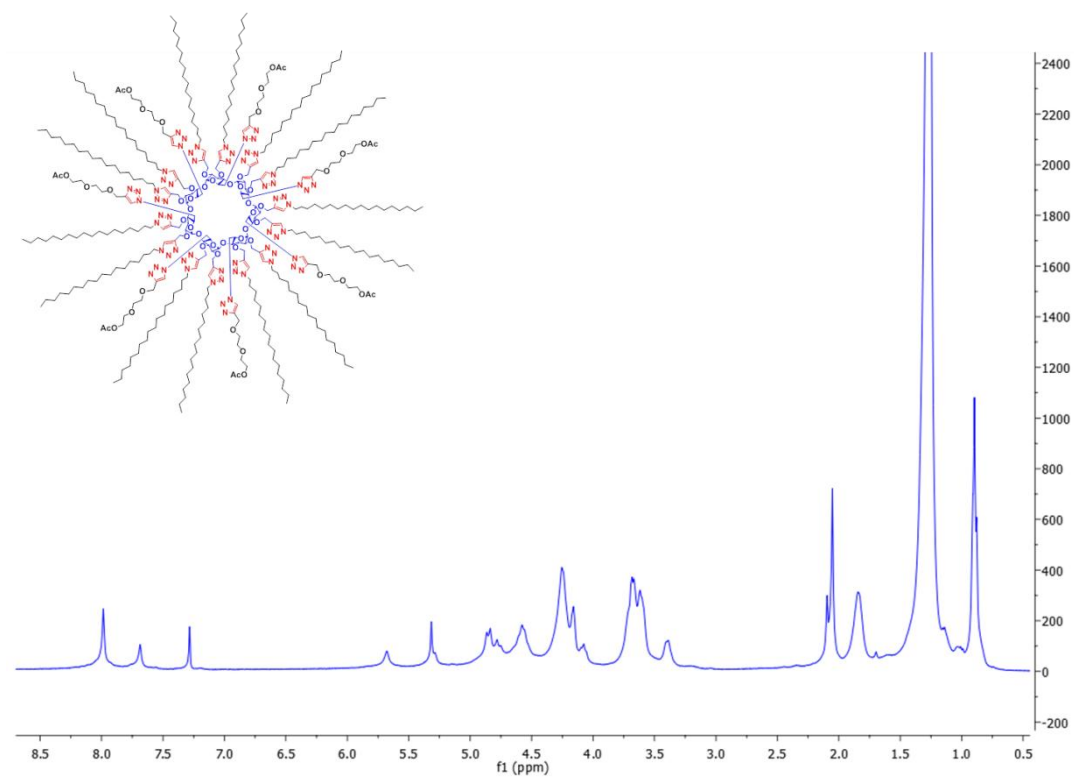


Figure S13. ^1H NMR spectra 400 MHz of compound **(4)** in CDCl_3

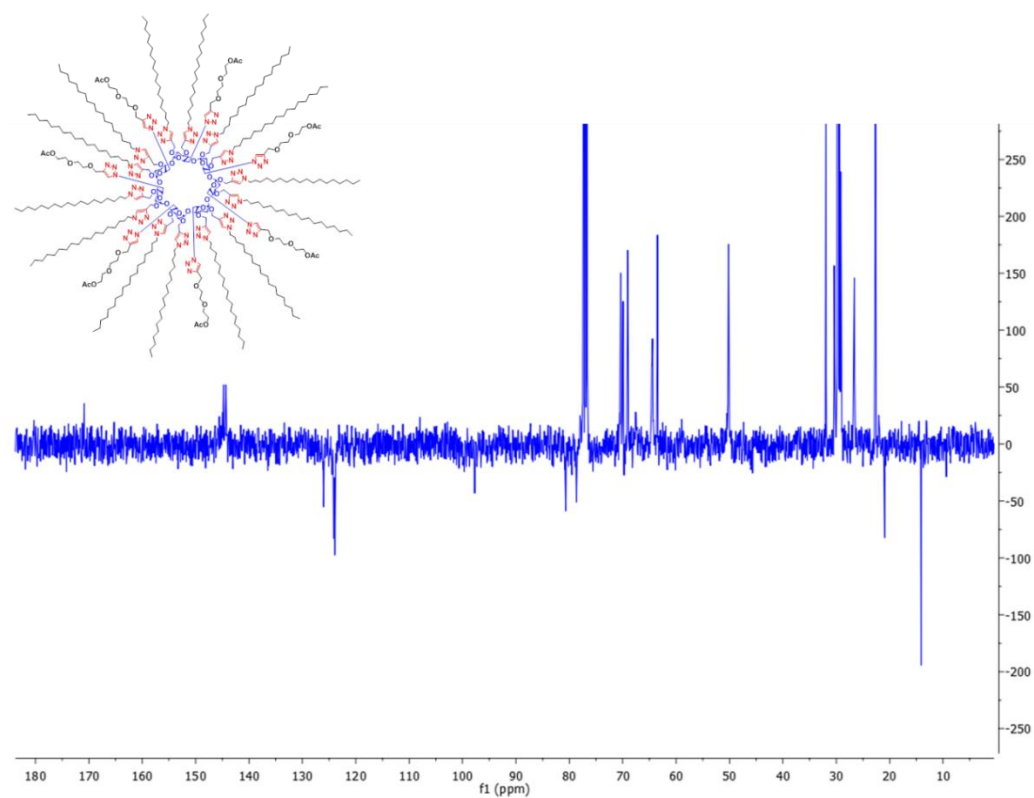


Figure S14. ^{13}C NMR DEPT-Q spectra 101 MHz of compound **(4)** in CDCl_3

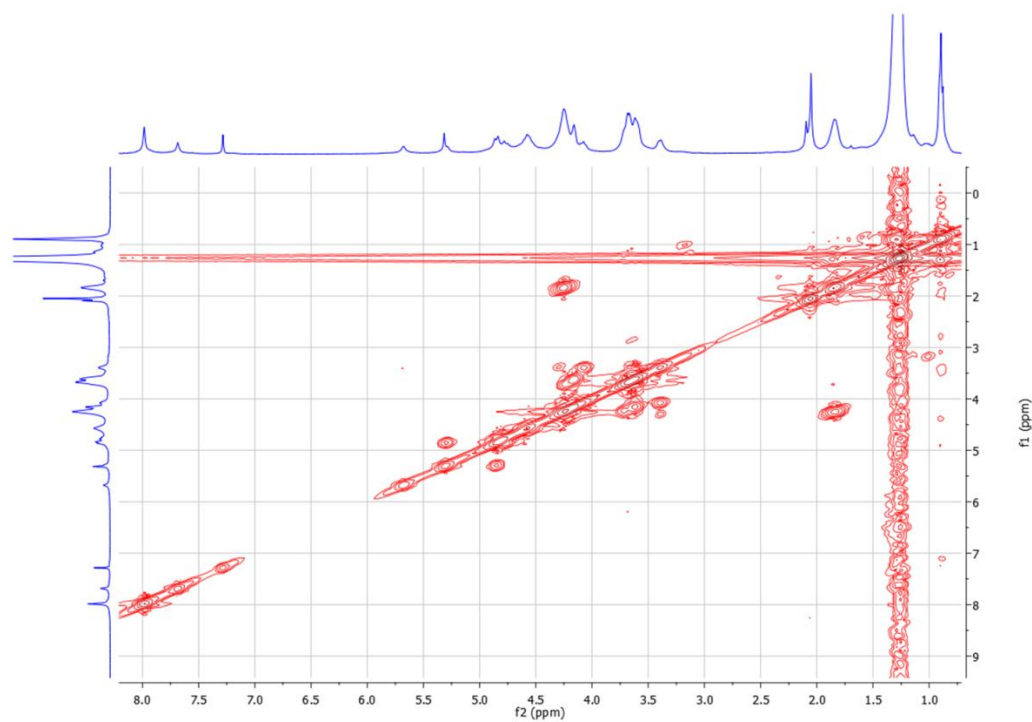


Figure S15. ^1H ^1H 2D COSY NMR spectra of compound **(4)** in CDCl_3

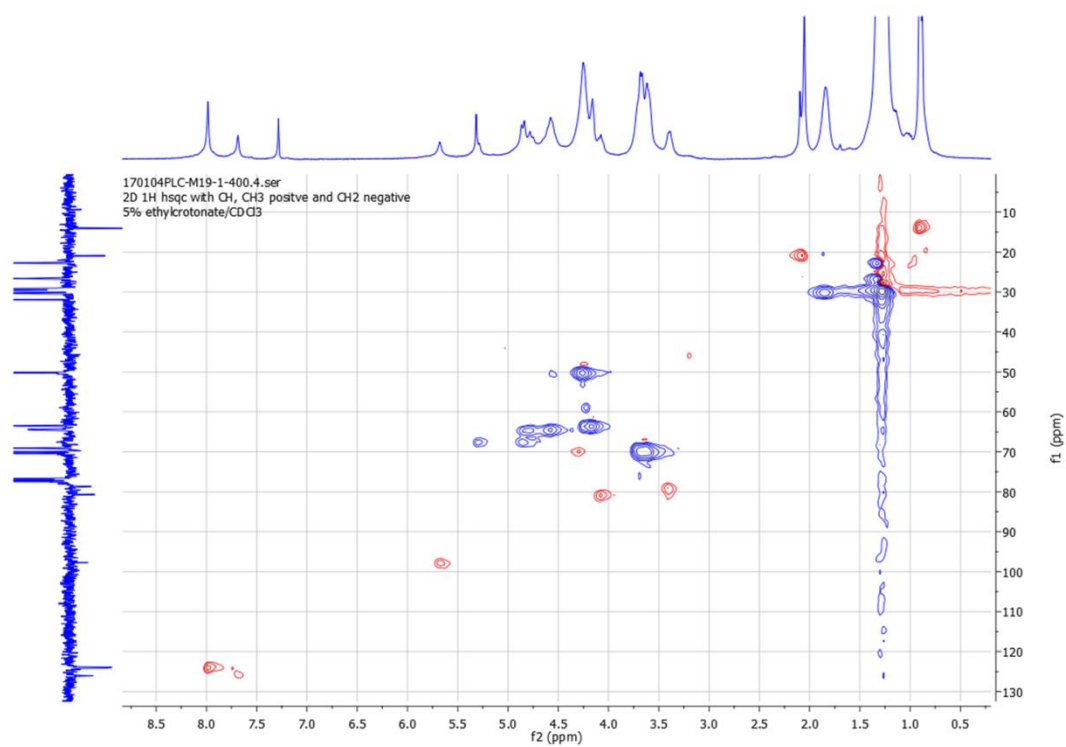


Figure S16. ^1H ^{13}C 2D HSQC 400 MHz NMR spectra of compound **(4)** in CDCl_3

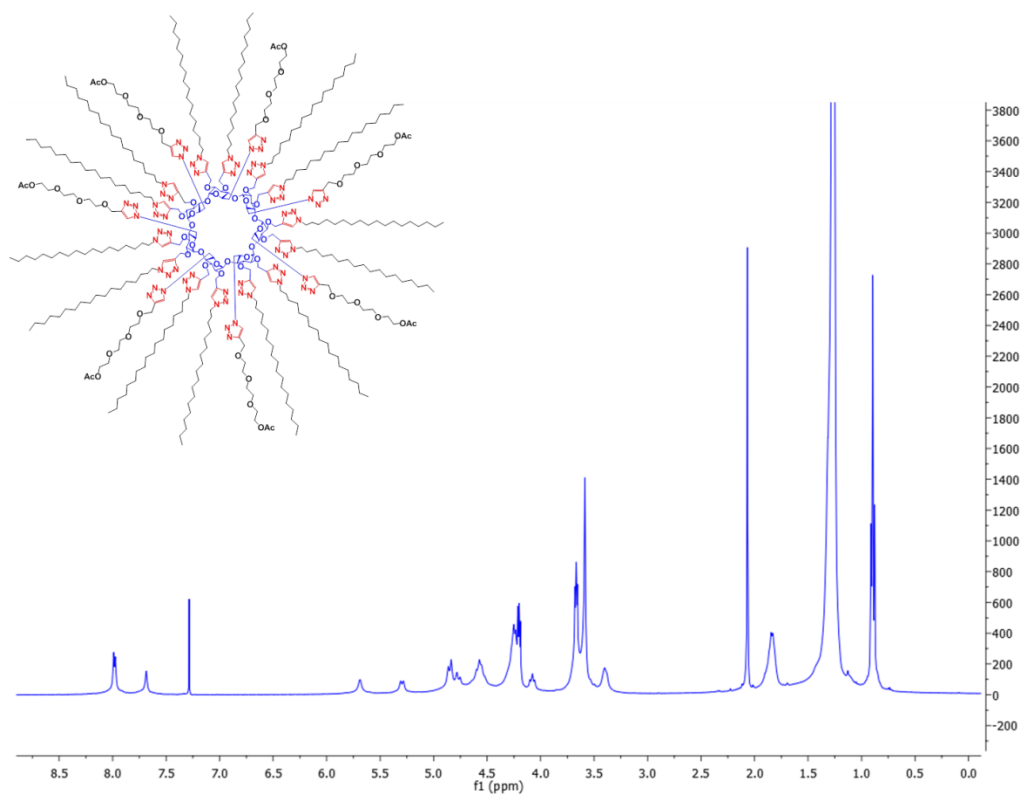


Figure S17. ^1H NMR spectra 400 MHz of compound (5) in CDCl_3

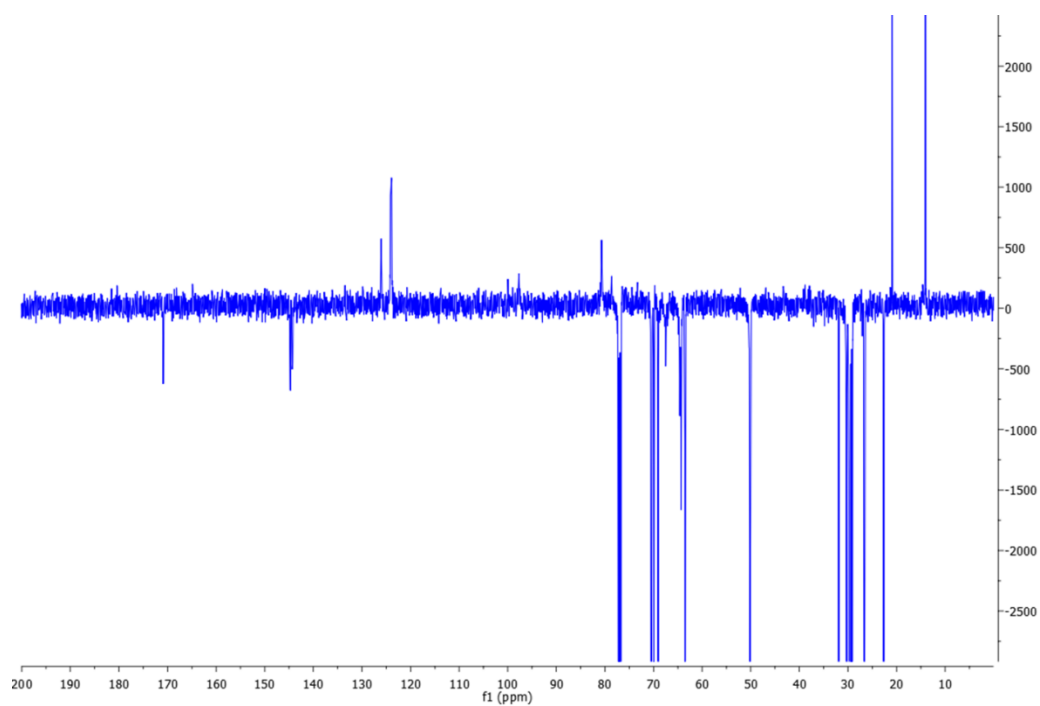


Figure S18. ^{13}C DEPT-Q NMR spectra 101 MHz of compound (4) in CDCl_3

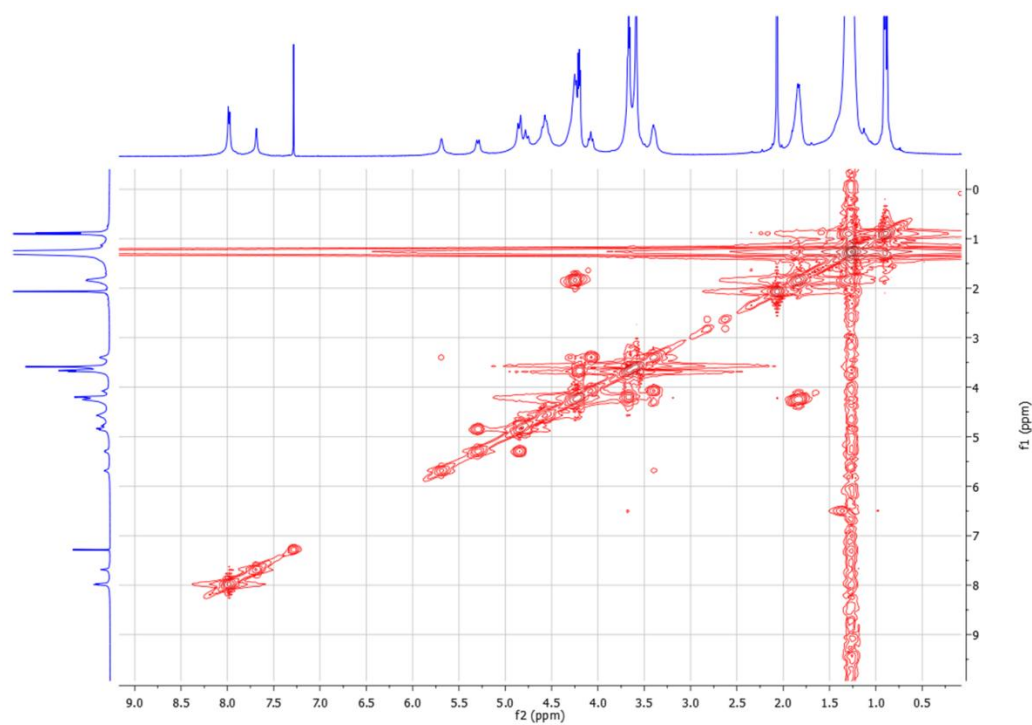


Figure S19. ^1H ^1H 2D COSY NMR spectra of compound (**5**) in CDCl_3

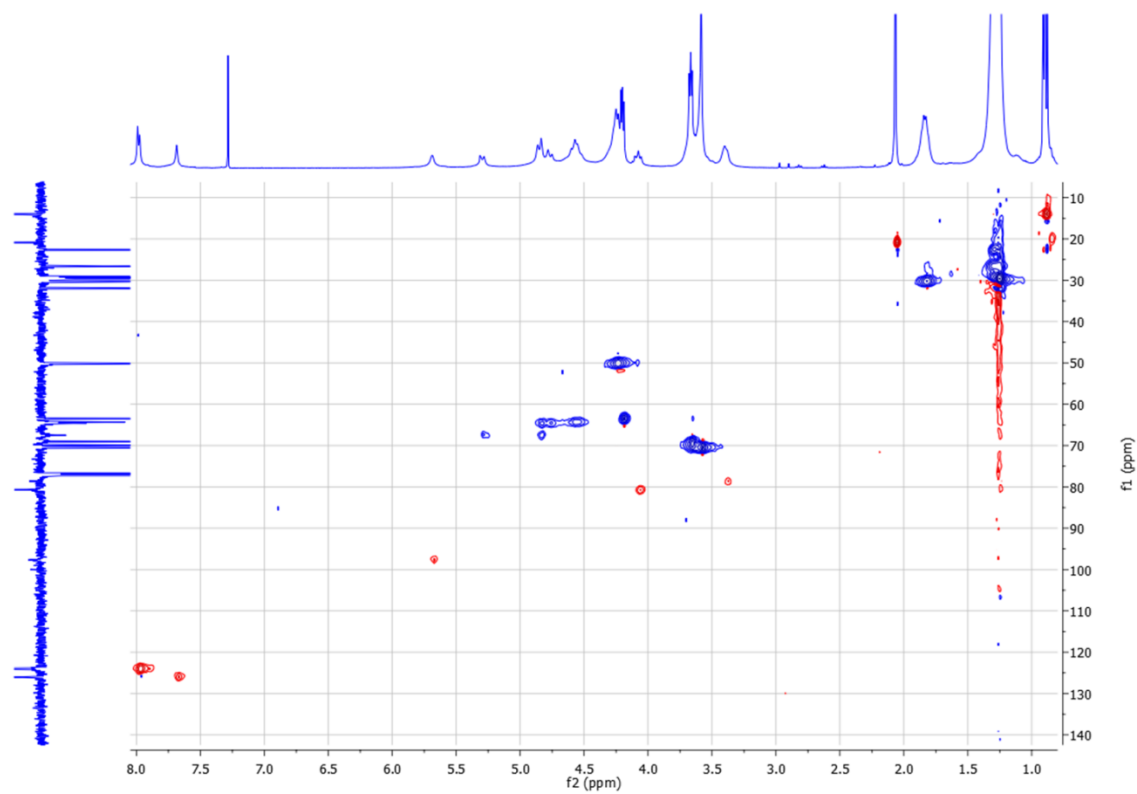


Figure S20. ^1H ^{13}C 2D HSQC 400 MHz NMR spectra of compound (**5**) in CDCl_3

B: Thermogravimetric Analysis

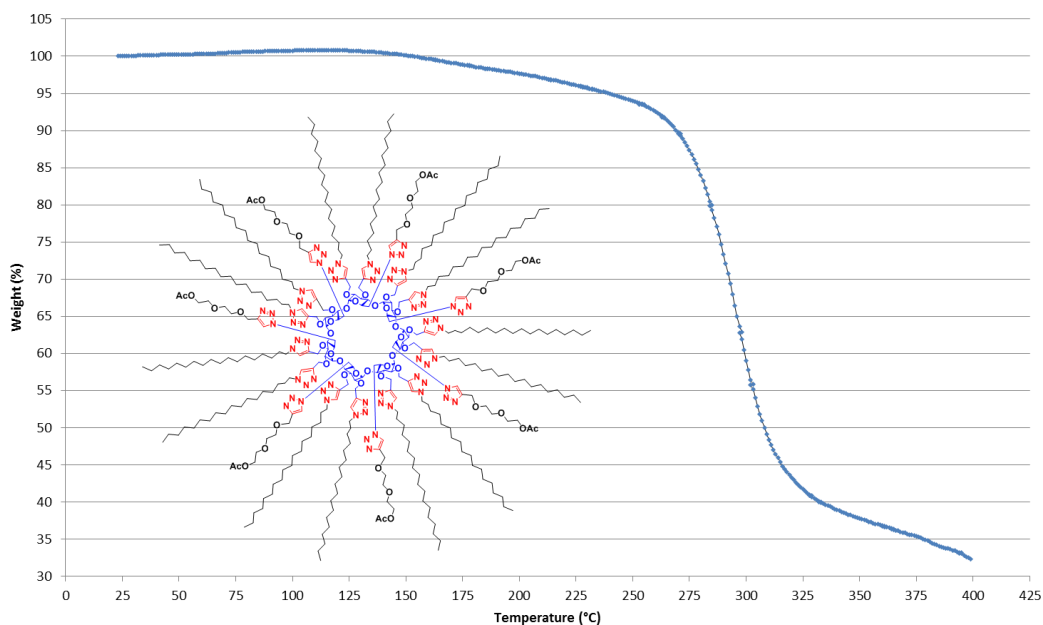


Figure S21. Thermogravimetric analysis of compound 4 (2°C/min)

Sample: PLC-M-14-2
Size: 3.2120 mg
Method: Ramp

TGA

File: C:\...\PLC\Micheal\PLC-M-14-2.001
Operator: WZS
Run Date: 22-Dec-2016 16:17
Instrument: TGA Q50 V20.13 Build 39

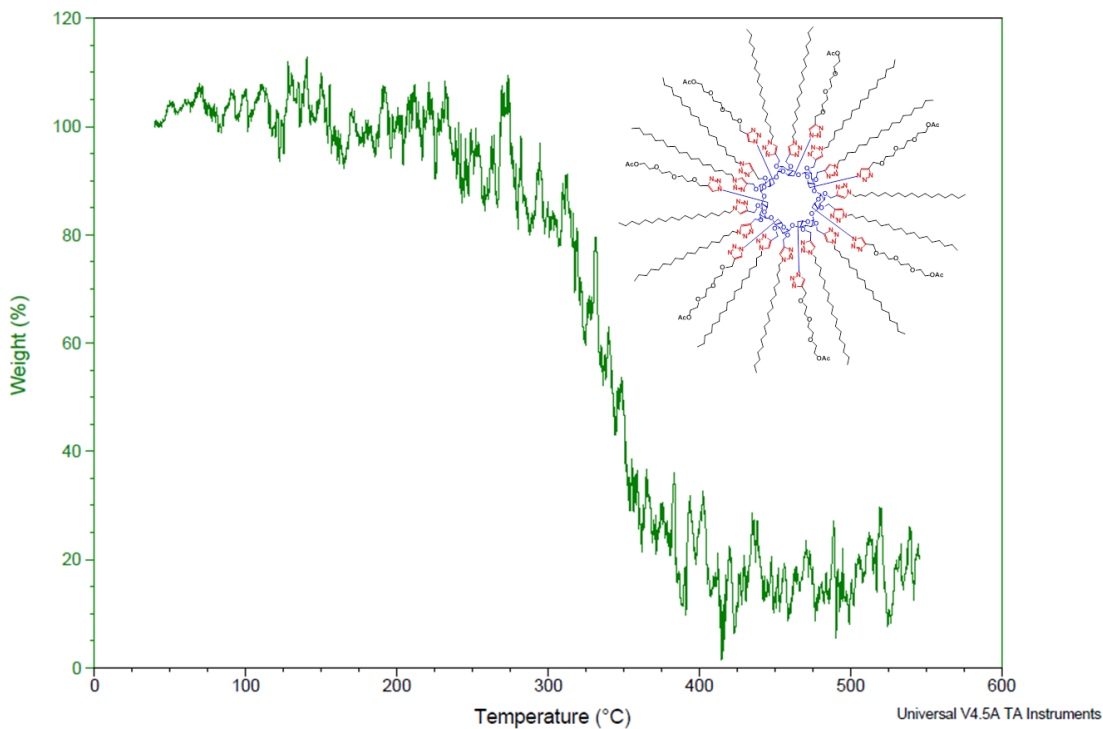


Figure S22. Thermogravimetric analysis of compound 5 (10°C/min)

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 $\frac{1}{d^2} = \frac{4}{3} \frac{(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2}$. PLC-M-14 is compound **4**; PLC-M-19 is compound **5**.

Compound	Temperature (°C)	Phase (a/Å)	d-spacing, observed (Å)	d-spacing, calculated (Å)	Miller indices
PLC-M-14	25	Col _h (66.6)	57.7	57.7	d ₁₀₀
			32.3	33.3	d ₁₁₀
			28.4	28.8	d ₂₀₀
			20.9	21.8	d ₂₁₀
			4.13		alkyl halo
	100	Col _h (61.7)	53.5	53.5	d ₁₀₀
			30.5	30.9	d ₁₁₀
			26.8	26.7	d ₂₀₀
			20.2	20.2	d ₂₁₀
			4.72		alkyl halo
	175	isotropic	48.7		--
			29.5		--
			4.79		alkyl halo
PLC-M-19	25	Col _h (62.5)	54.1	54.1	d ₁₀₀
			30.7	31.3	d ₁₁₀
			27.3	27.1	d ₂₀₀
			20.0	20.5	d ₂₁₀
			4.13		alkyl halo
	100	Col _h (58.9)	51.0	51.0	d ₁₀₀
			29.3	29.4	d ₁₁₀
			25.9	25.5	d ₂₀₀
			19.3	19.3	d ₂₁₀
			4.75		alkyl halo
	140	isotropic	48.2		--
			31.4		--
			4.76		alkyl halo

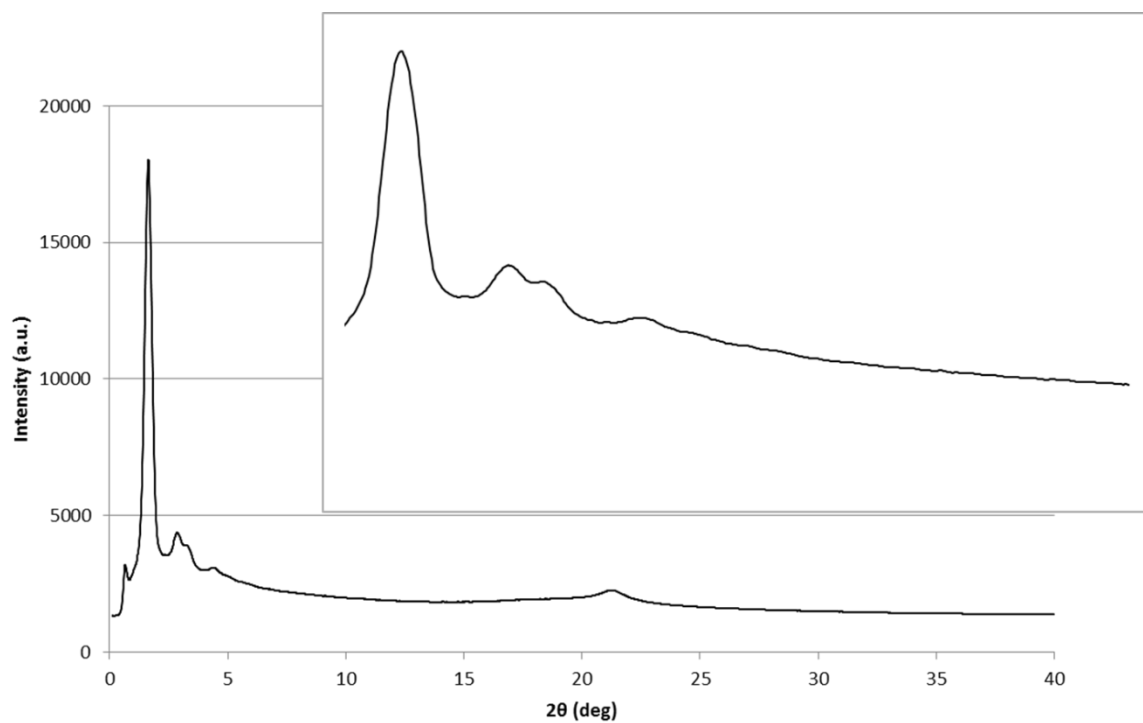


Figure S23. XRD spectra of β -CD-4 at 25°C

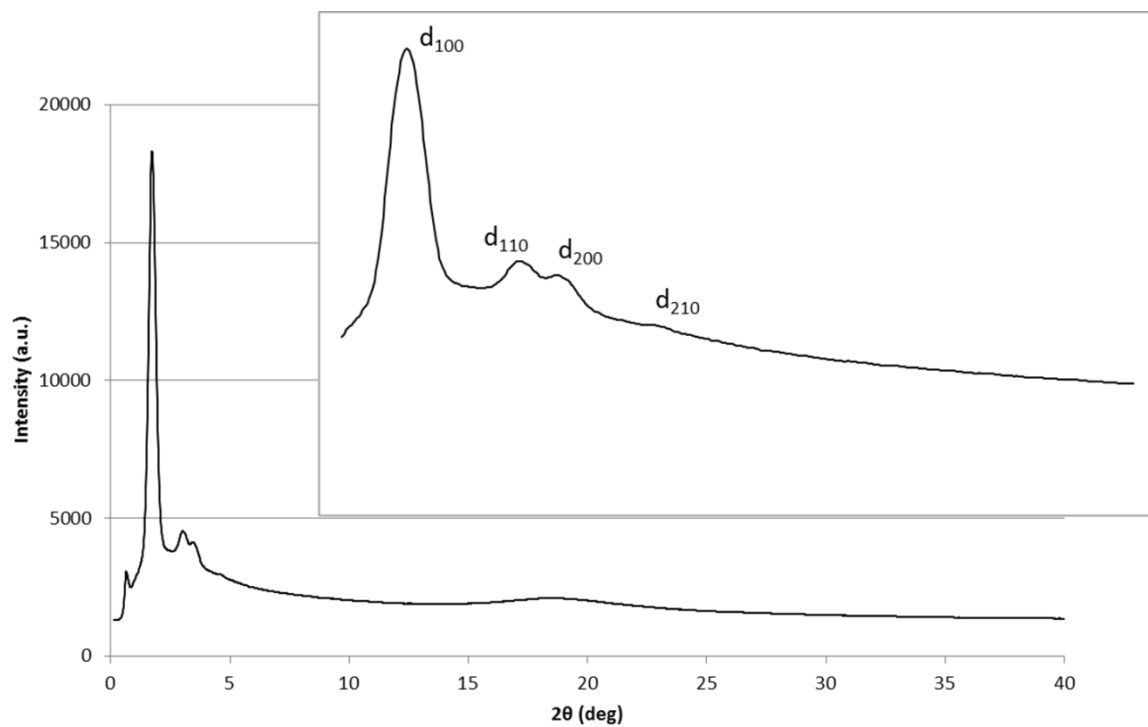


Figure S24. XRD spectra of β -CD-4 at 100°C

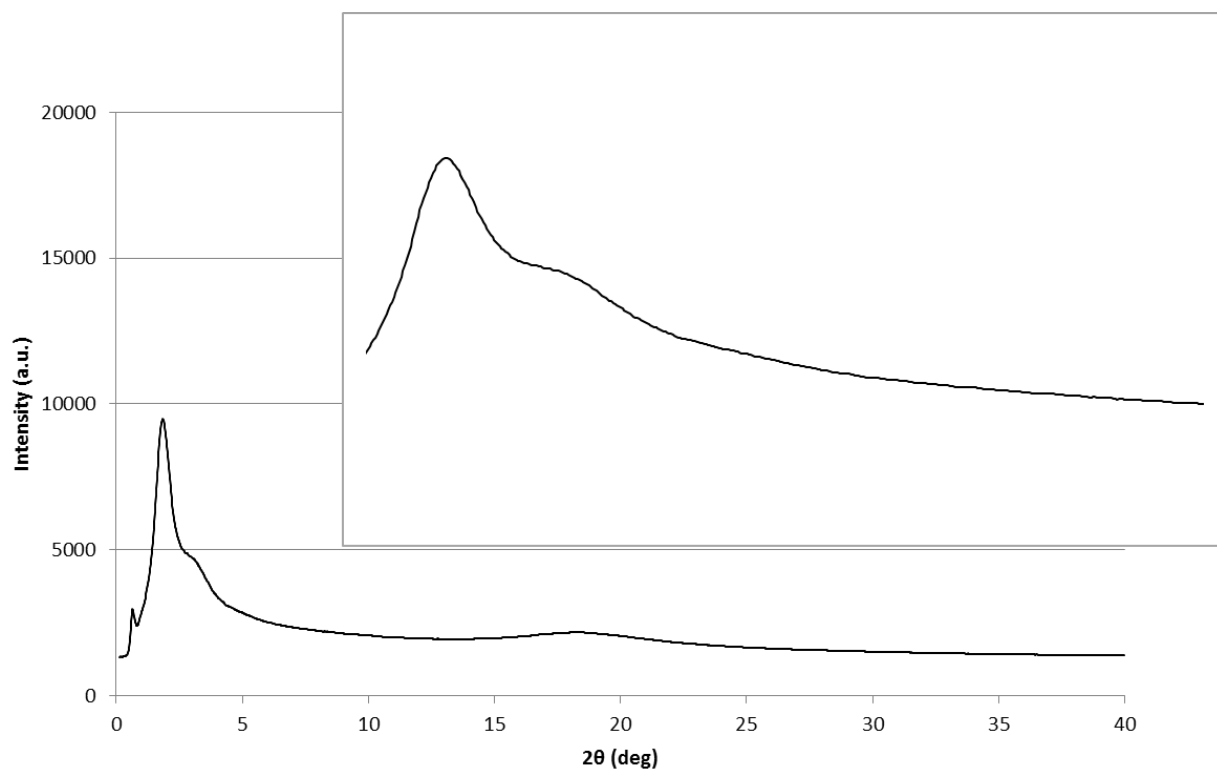


Figure S25. XRD spectra of β -CD-4 at 140°C

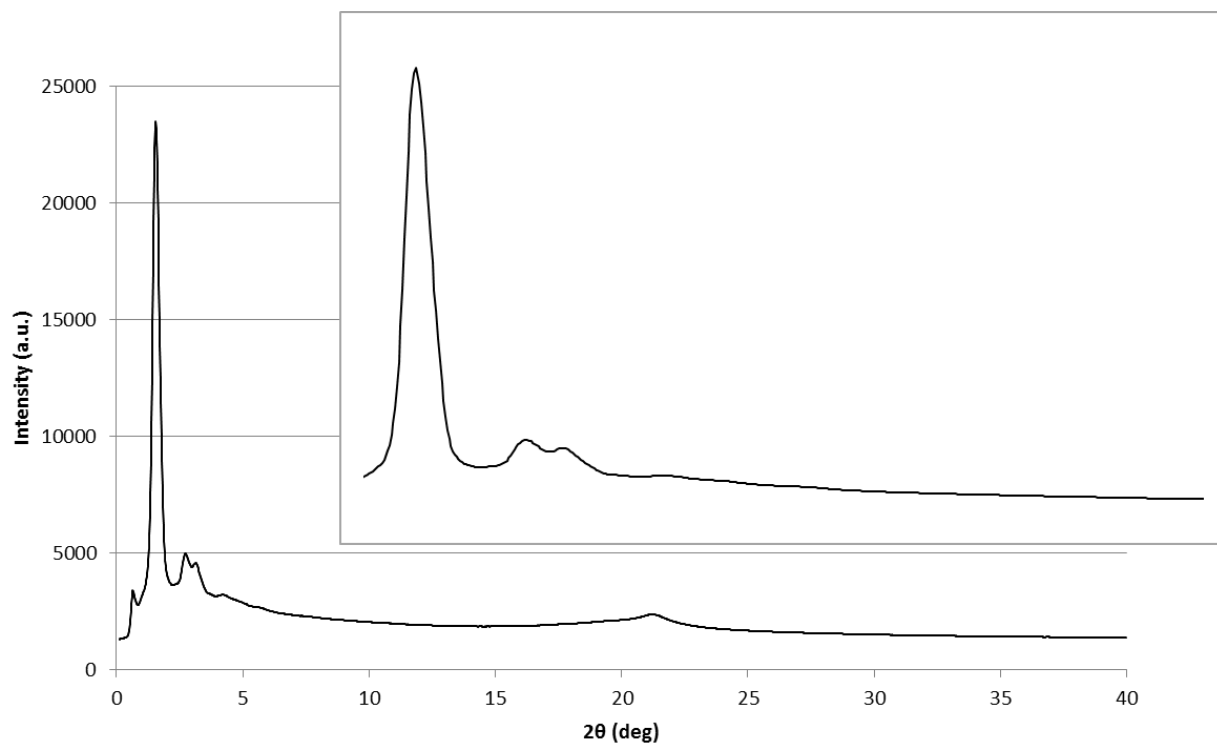


Figure S26. XRD spectra of β -CD-5 at 25°C

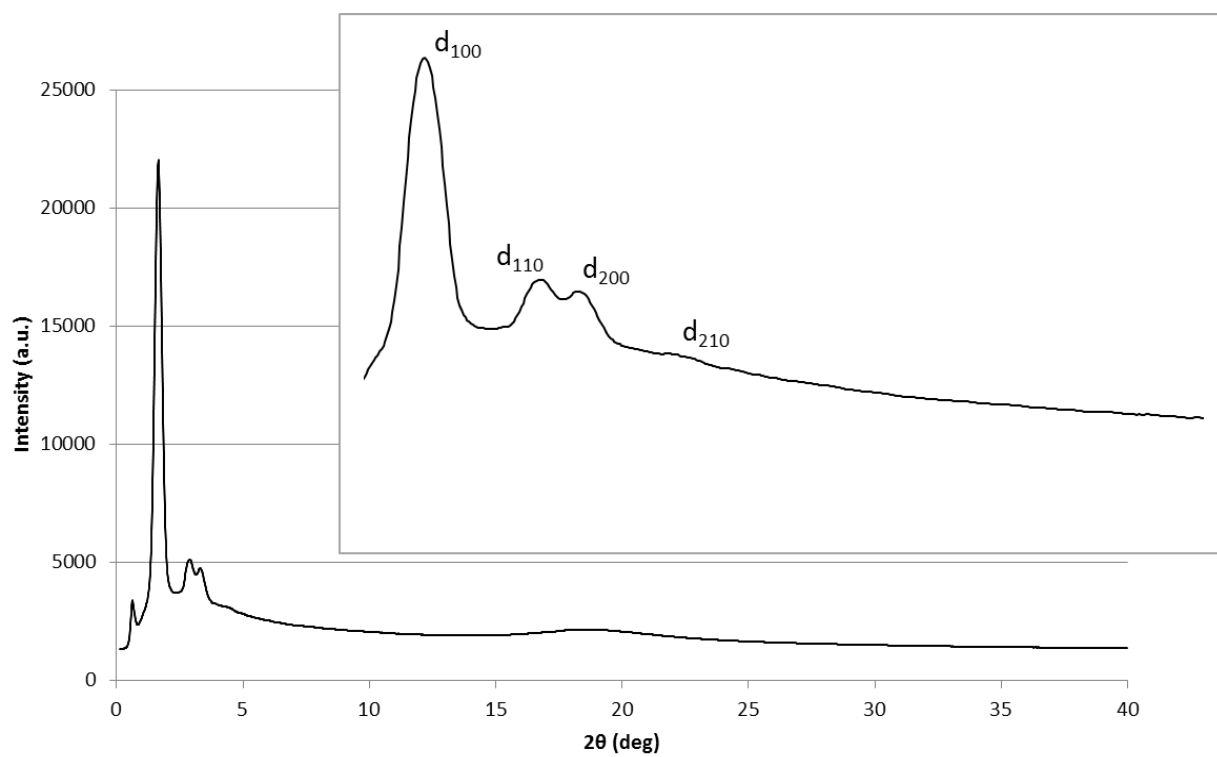


Figure S27. XRD spectra of β -CD-5 at 100°C

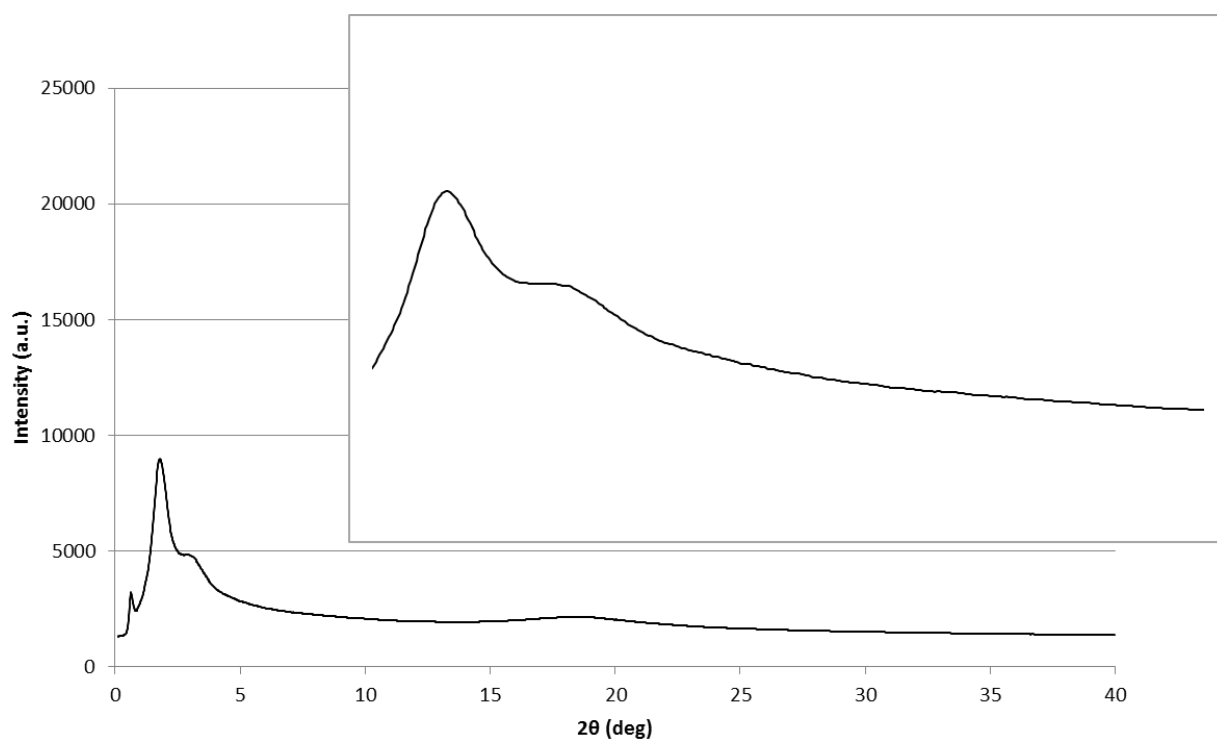


Figure S28. XRD spectra of β -CD-5 at 275°C

D: Differential Scanning Calorimetry Analysis

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

Compound	1 st Phase Transition, heating/cooling	2 nd Phase Transition, heating/cooling
PLC-M-14	51.0 °C (30.6 J/g)/ 38.1 °C (28.0 J/g)	141.9 °C (0.72 J/g)/ 138.9 °C (0.77 J/g)
PLC-M-19	48.4 °C (26.8 J/g)/ 36.1 °C (23.5 J/g)	126.8 °C (0.34 J/g)/ 123.9 °C (0.20 J/g)

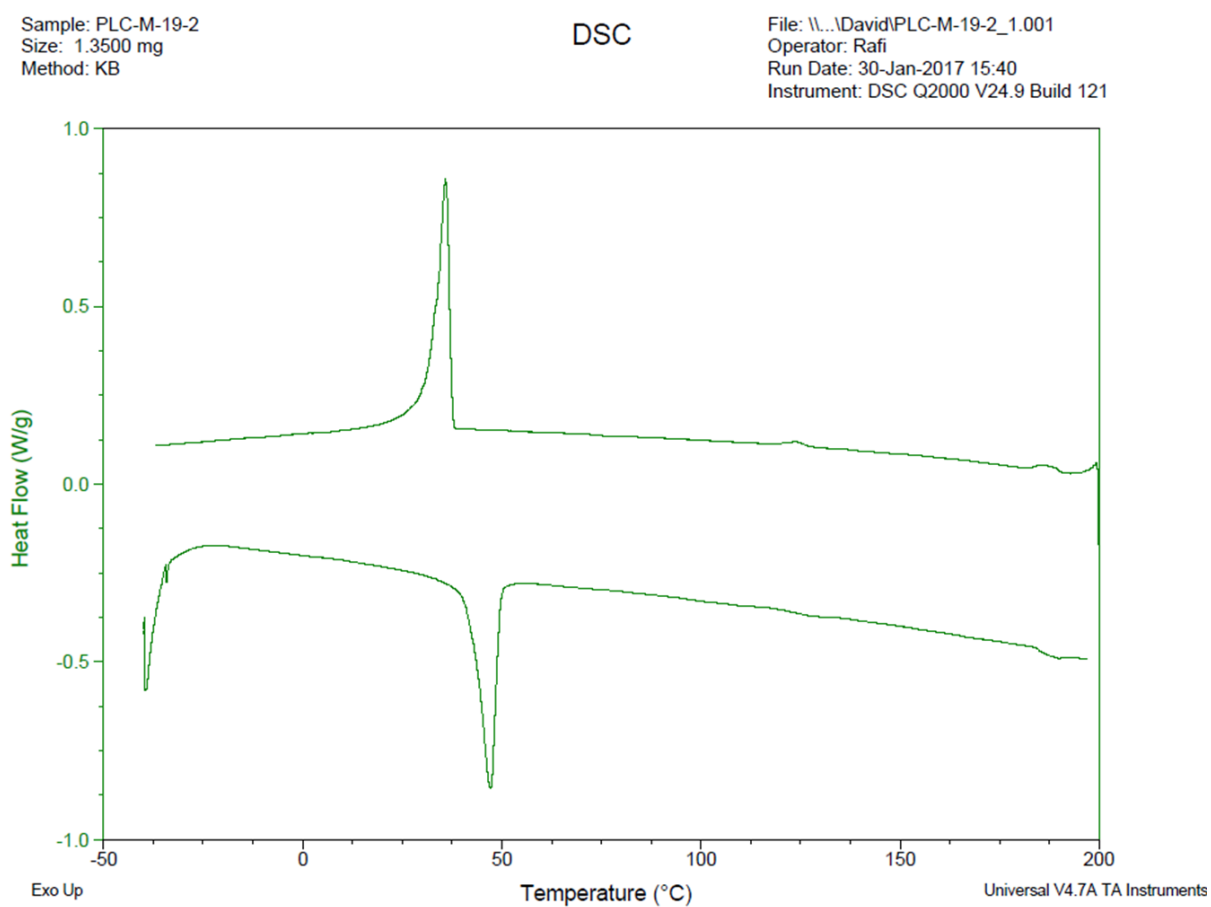


Figure S29. Differential scanning calorimetry thermogram of β -CD-4 (scan rate 10°C/min, with one minute isothermal at the end points of the temperature range).

Sample: PLC-M-14
Size: 2.2400 mg
Method: KB

DSC

File: \\...\\David\\PLC-M-14_1.001
Operator: Rafi
Run Date: 17-Jan-2017 15:07
Instrument: DSC Q2000 V24.9 Build 121

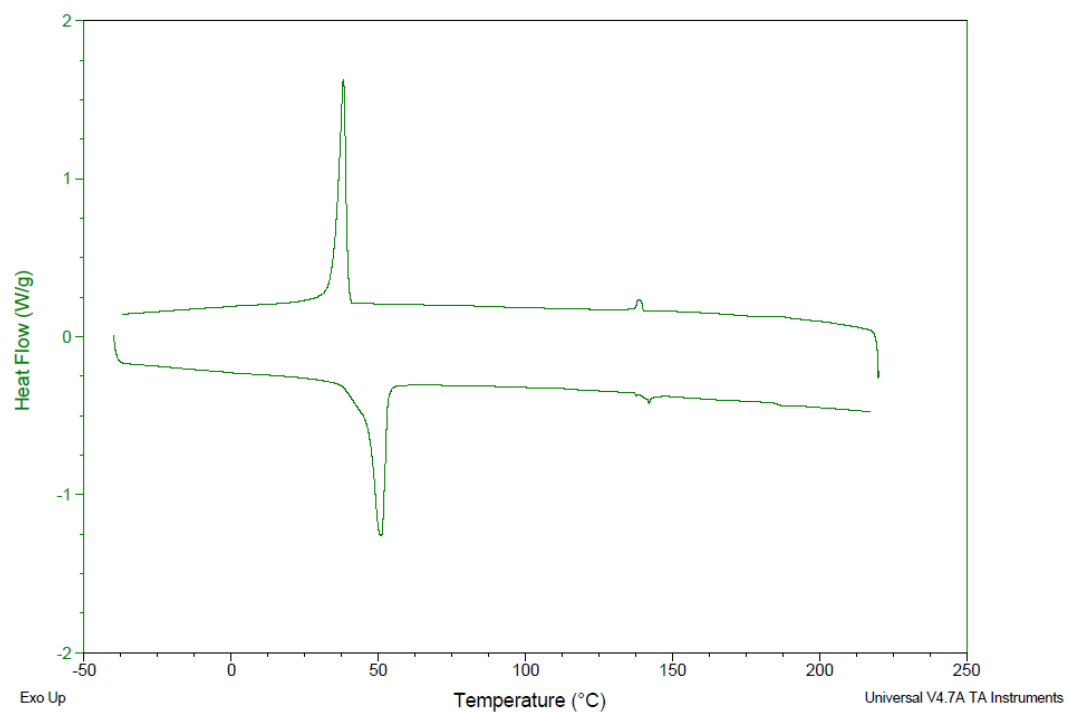


Figure S30. Differential scanning calorimetry thermogram of β -CD-5 (scan rate 10°C/min, with one minute isothermal at the end points of the temperature range).

E: Polarized Optical Microscope Pictures

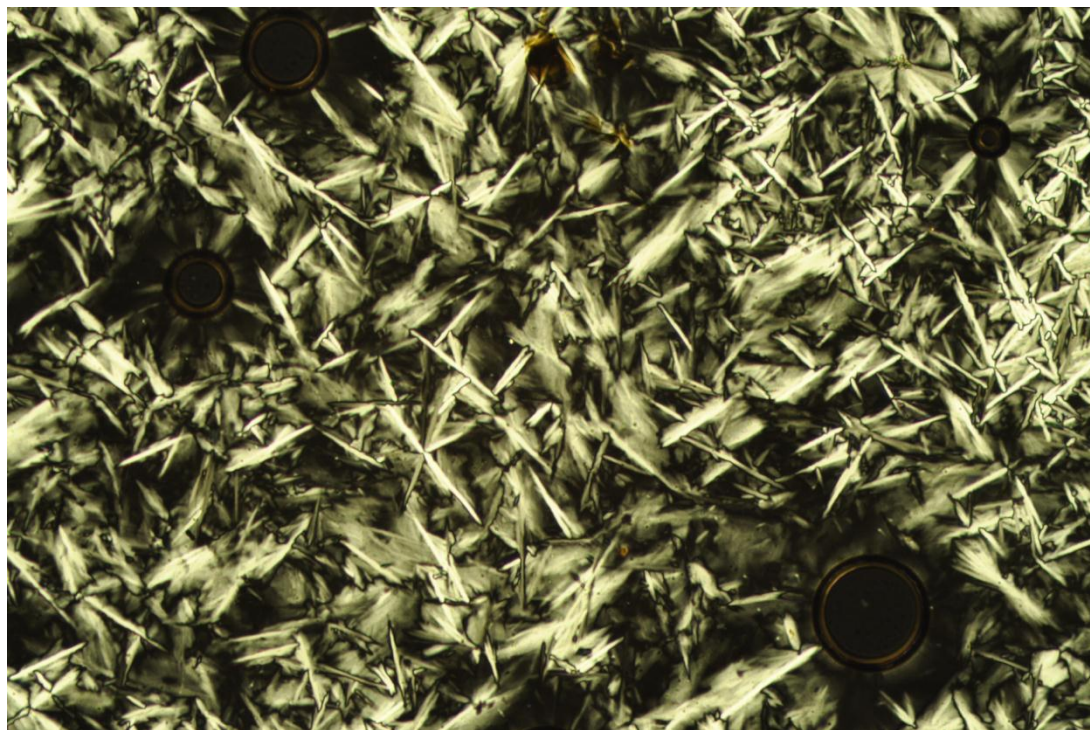


Figure S31.Polarized optical microscope image of β -CD-4.

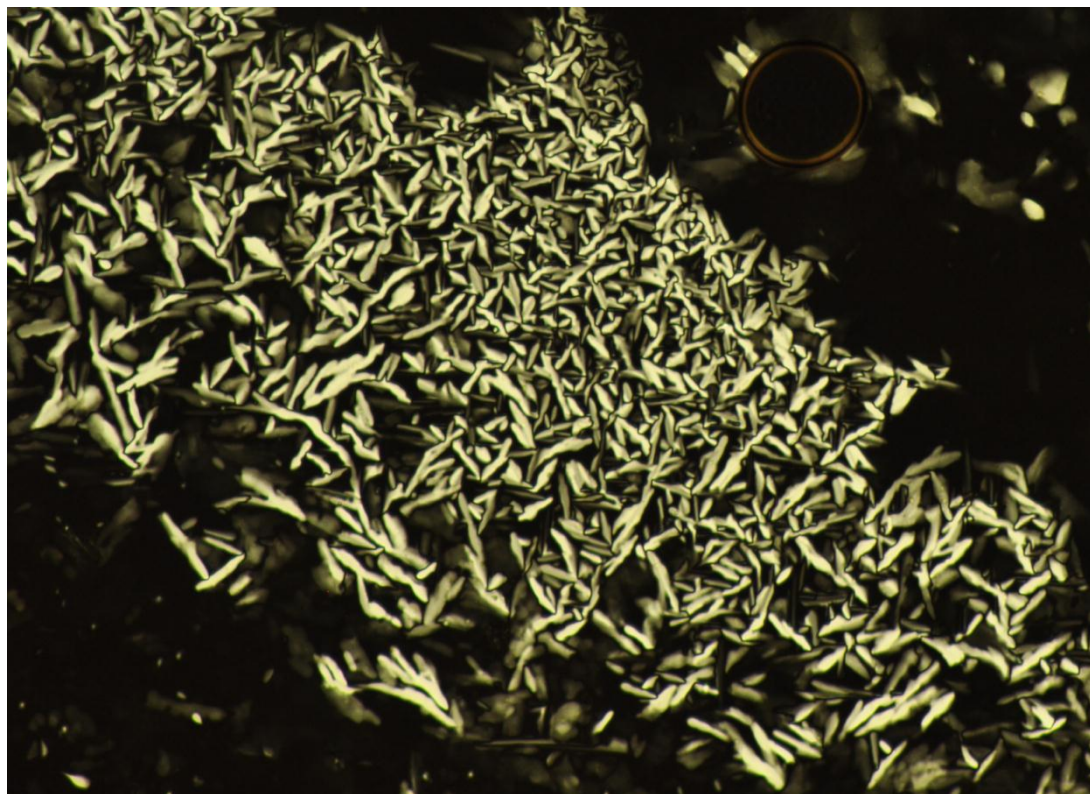


Figure S32.Polarized optical microscope image of β -CD-4.



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.

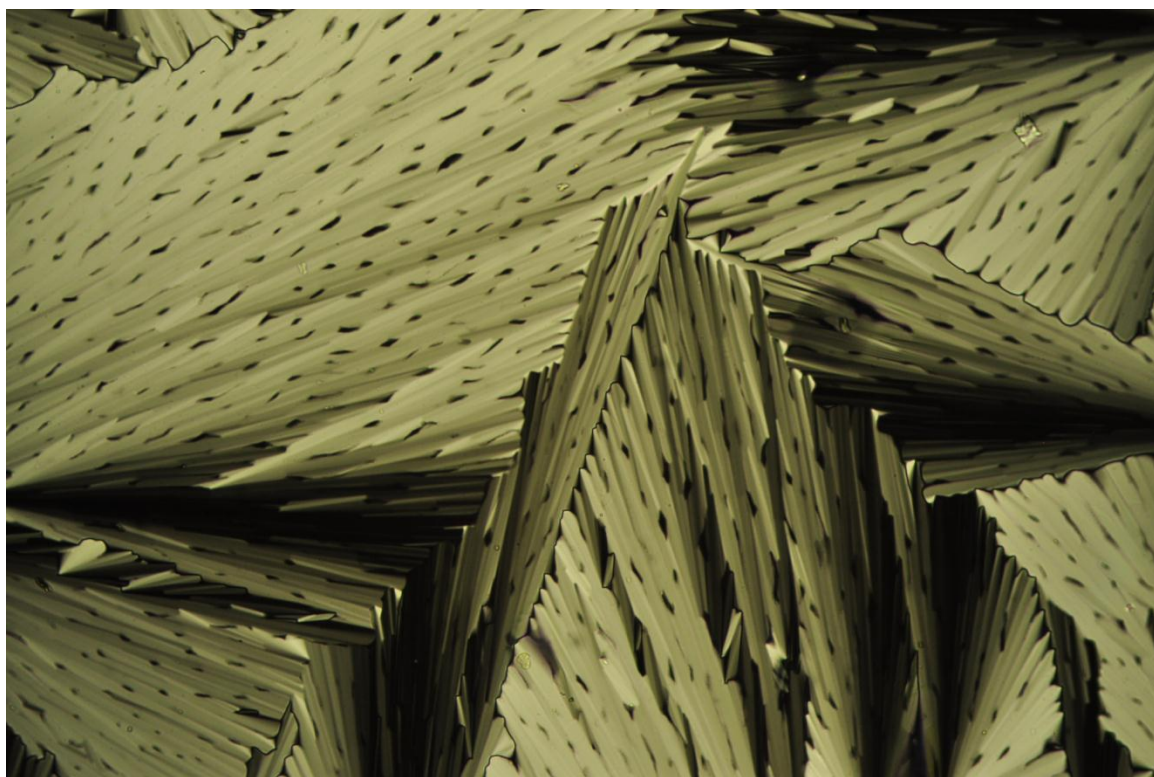
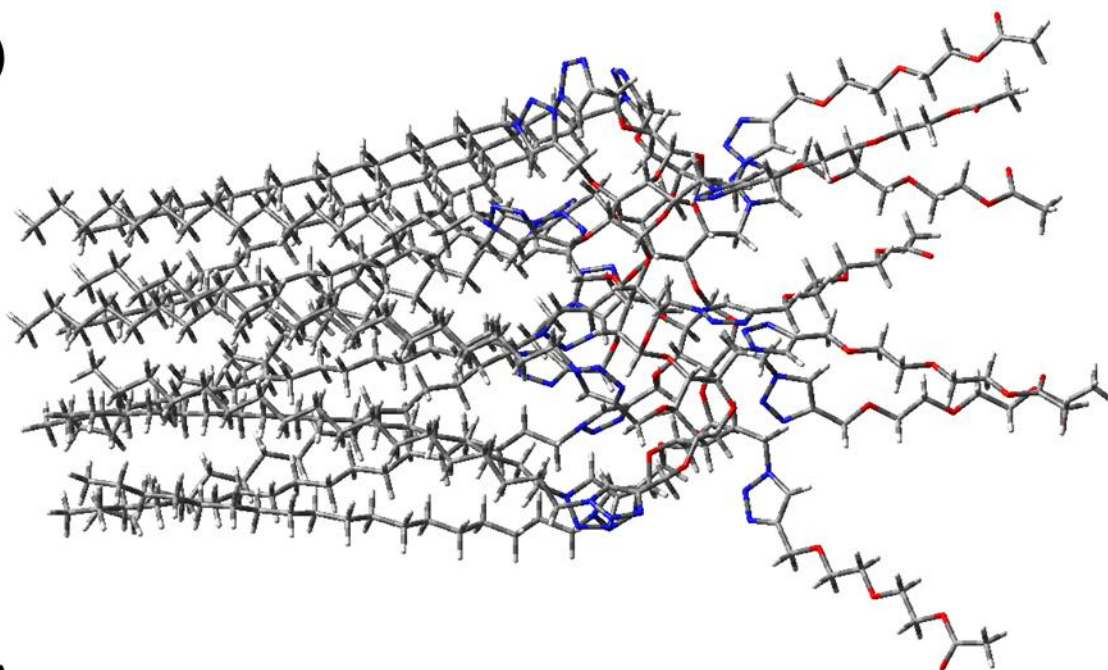


Figure S36. Polarized optical microscope image of β -CD-5 after clearing point.

F: Computational Studies

a)



b)

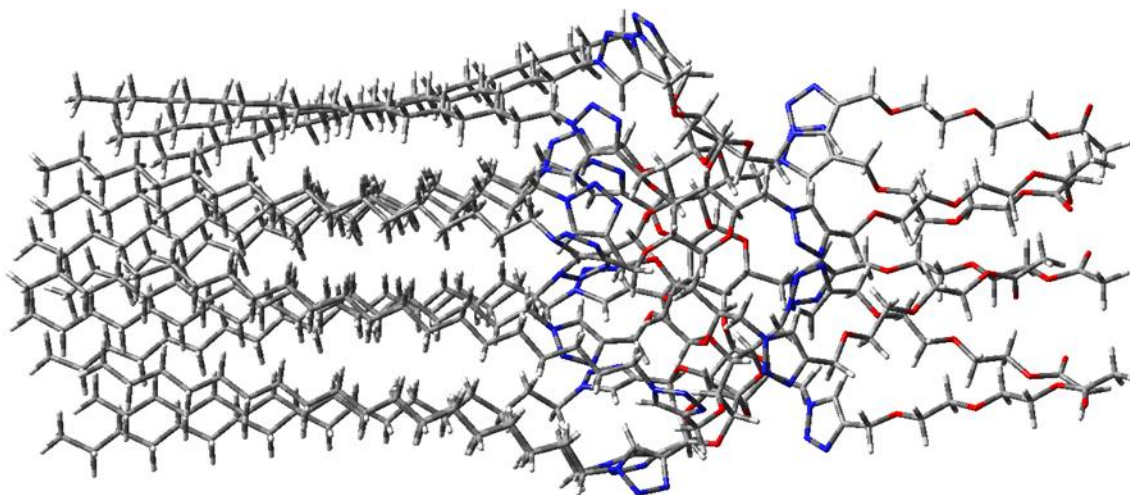


Figure S37. Structure of β -CD-4 before (a) and after (b) optimization..

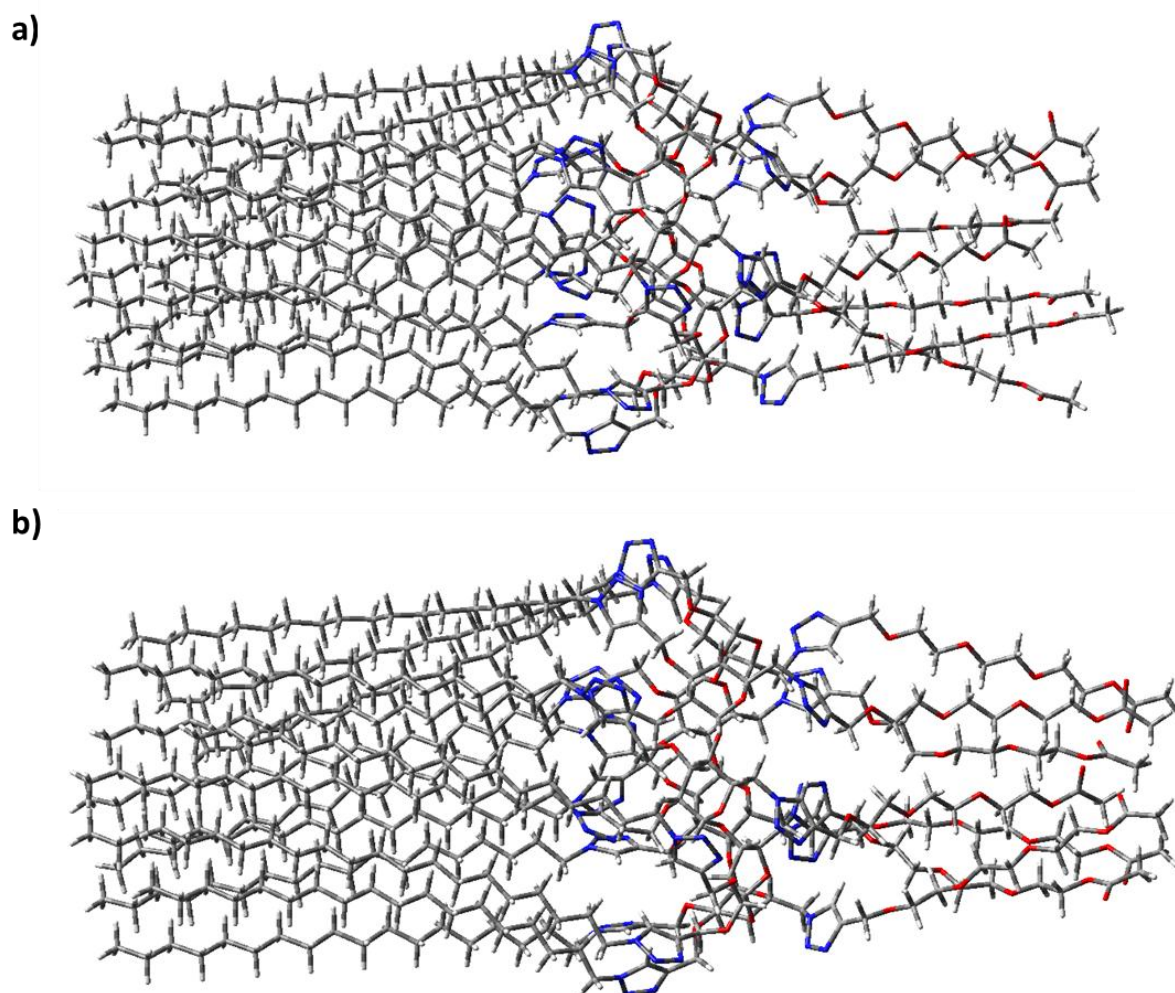


Figure S38. Structure of β -CD-5 before (a) and after (b) optimization.