Electronic Supplementary Information

Dendritic polyglycerol cyclodextrin amphiphiles and their self-assembled architectures to transport hydrophobic guest molecules

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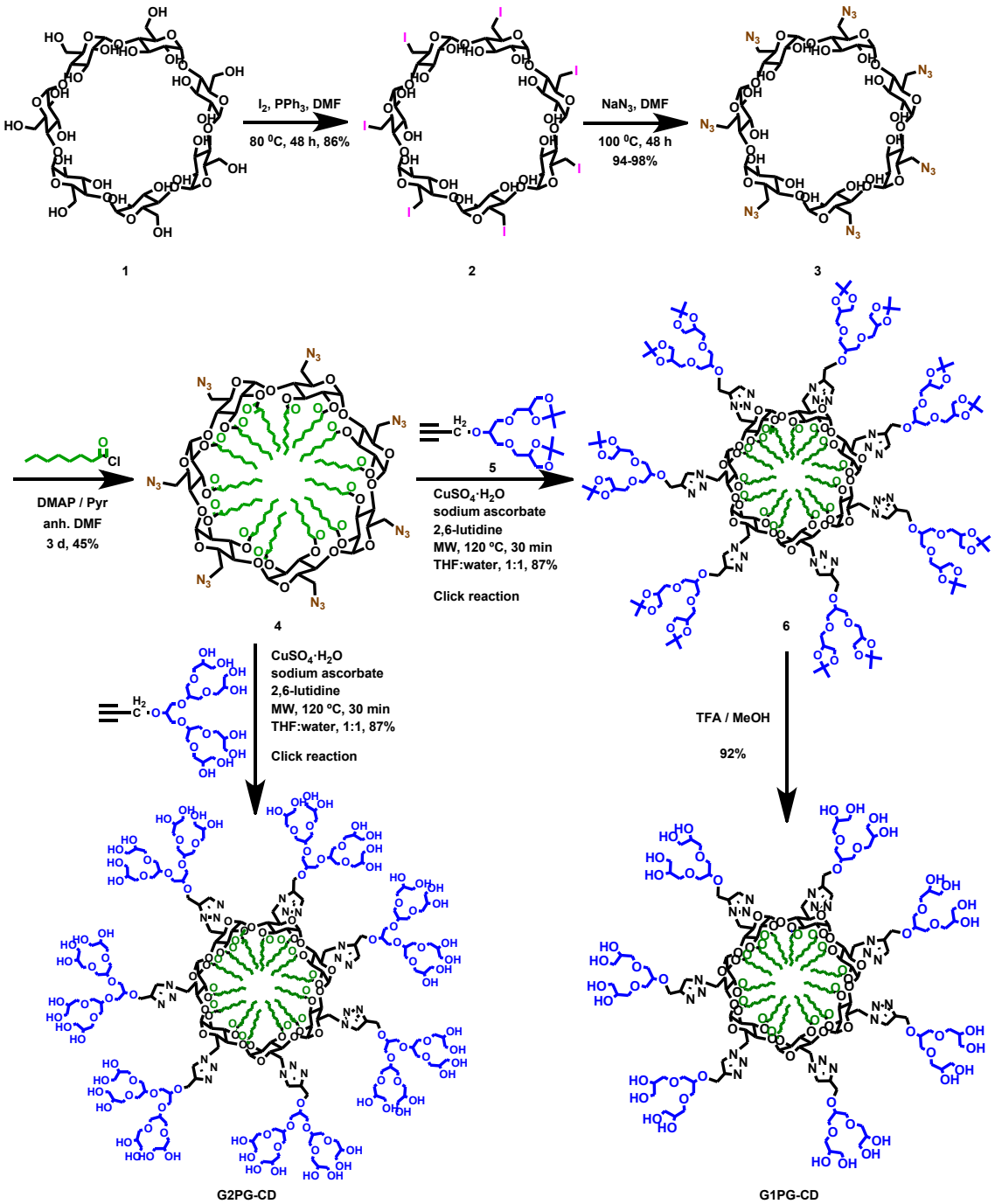
1. **Scheme S1**. Schematic representation of the synthesis of cyclodextrin-polyglycerol (CD-PG) amphiphilic dendrimers.



2. Experimental details of novel synthesized compounds

a. General Procedures.

Materials. Air and moisture sensitive reactions were carried out in flame-dried glass ware under argon atmosphere. Anhydrous solvents were either commercially purchased from Acros Organics in septum-sealed bottles or chemically dried using a MBRAUN SPS 800 solvent purification system.
All other chemicals were of reagent grade quality and used without further purification from the suppliers Acros Organics, Fluka, Sigma-Aldrich, Roth, Invitrogen, and Merck. All reactions were performed in standard glassware or microwave reactor vials purchased from Biotage. Microwave reactions were carried out in on a Biotage Initiator™ microwave synthesizer.

Characterization. *Chromatography and Spectroscopy*. Thin layer chromatography (TLC) analysis was carried out on silica coated aluminum plates from Merck either using silica gel 60, F254, or silica gel 60 RP-18 F254s when performing reversed phase (RP) analysis. Preparative column chromatography was conducted on silica gel 60 (0.040−0.063 mm, 230−400 mesh ASTM). Detection was accomplished by UV irradiation (254 nm; 366 nm) and different staining solutions such as potassium permanganate, cerium molybdate, ninhydrin, bromocresol green, and Dragendorff reagent.
NMR spectra were recorded on a Bruker ECX 400 (^{1}H: 400 MHz, ^{13}C: 100.5 MHz), a Jeol Eclipse (^{1}H: 500 MHz, ^{13}C: 125.8 MHz), or on a Bruker Biospin (^{1}H: 700 MHz, ^{13}C: 176.1 MHz) spectrometer at 25 °C and calibrated against residual solvent peaks as internal standard. All ^{13}C NMR spectra were recorded with ^{1}H broadband decoupling. Chemical shifts δ are given in ppm according to calibration to the corresponding solvents $CDCl_3$ (^{1}H: 7.26 ppm, ^{13}C: 77.00 ppm) and CD_3OD (^{1}H: 3.31 ppm, ^{13}C: 49.05 ppm).
Mass spectral data were obtained on an Agilent 6210 ESI-TOF (Agilent Technologies, Santa Clara, CA, USA) spectrometer at flow rates of 4 µl/min and spray voltage of 4 kV or a Bruker Ultraflex II (MALDI-TOF) instrument using α-hydroxycinnamic acid (HCCA) as matrix material. UV−vis studies were performed with SCINCO (S-3100) spectrometer (Jasco Co.) in $CHCl_3$.

Cryo-Transmission Electron Microscopy (cryo-TEM)

For all sample preparations, aqueous amphiphile solutions were used at a concentration of 4.5 x 10^{-3} M. Droplets of the corresponding sample solution (5 µl) were applied to perforated (1 µm hole diameter) carbon film covered 200 mesh copper grids (R1/4batch of Quantifoil Micro Tools GmbH, Jena,

Germany), which had been hydrophilized prior to use by 60 s plasma treatment at 8 W in a BALTEC MED 020 device. The supernatant fluid was removed with a filter paper until an ultra-thin layer spanning the holes of the carbon film was obtained. The samples were immediately vitrified by propelling the grids into liquid ethane at its freezing point (90 K) and by operating a guillotine-like plunging device. The vitrified samples were transferred under liquid nitrogen cooling into a Tecnai F20 FEG transmission electron microscope (FEI Company, Oregon, USA) using the Gatan (Gatan Inc., California, USA) cryoholder and -stage (Model 626). Microscopy was carried out at 94 K sample temperature using the microscope's low dose protocol at a calibrated primary magnification of 50,000 and an accelerating voltage of 160 kV (FEG-illumination). Images were recorded using an EAGLE 4k-CCD camera (FEI Company, Oregon, USA) operated with binning factor 2 (2048 by 2048 pixel). The defocus was chosen in all cases to be 2µ. It is important to note that although the determined diameter measurements were prone to error due to the very small size of the assemblies, more reliable diameter values could be derived from sample areas where micelles were densely packed. Fourier transforms of corresponding images revealed a diffraction pattern which indicates repetitive distances which can be said to correlate with the diameter of the micelles.

Dynamic Light Scattering (DLS)

DLS measurements were conducted at 25 °C using a Zetasizer Nano ZS analyzer with integrated 4 mW He−Ne laser, λ = 633 nm (Malvern Instruments Ltd., U.K.). The amphiphiles and host-guest complex were measured in water. The solutions were measure after mixing and incubation overnight. All measurements were carried out using folded capillary cells (DTS 1060) in five replicate measurements.

Encapsulations studies

Encapsulation Procedure and Determination of Weight Percentage Loading with Respect to Host Molecule.

The aqueous solution of host molecule (3mg) was prepared at (0.5 mg/mL for G1-PG-CD and 1 mg/mL for G2-PG-CD) concentration. The guest molecule (6 mg) was added to the aqueous solution of host molecule and stirred overnight at room temperature. The resultant suspension was filtered through a 0.45 µm size syringe filter to filter nonincorporated guest molecules. The filtrate of host−guest complex was freeze-dried for further analysis. All the encapsulations were performed by same procedure. The percentage of encapsulation of guest molecules was determined by molar extinction coefficient (ε max)

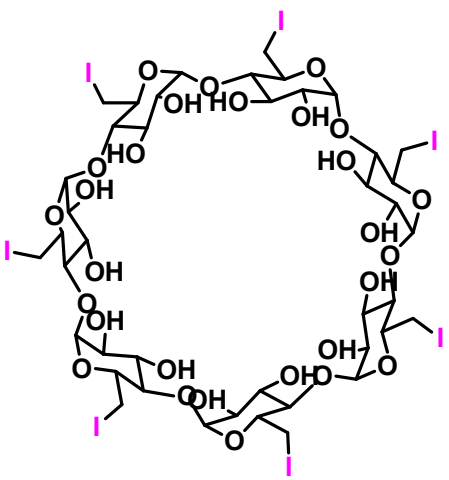
which was calculated from the calibration curve of guest molecule at its absorbance maxima in chloroform.

MTT Assay

A549 cells were seeded in 96 well plates at a density of 1x104 cells/ml in 100 µl/well DMEM medium containing 10% (v/v) fetal bovine serum and 1% (v/v) Penicillin/Streptomycin (Biochrom AG, Berlin, Germany) and incubated over night at 37 °C and 5% CO_2. The next day, the medium was removed and replaced with 50 µl fresh medium and 50µl of the test compounds diluted in medium in triplicate with a maximum final concentration of 25% (v/v). Each plate contained wells with untreated cells which were used as 100% viability reference and wells without cells serving as a background control. 48 h after the addition of the compounds, the cell culture supernatant was removed and cells were washed 3 times with 200µl PBS/well. 100µl fresh medium and 10µl MTT (5 mg/ml in PBS, Sigma-Aldrich) per well was added and incubated for 4h at 37°C and 5% CO_2. After the incubation time the solution was removed and 100µl/well Isopropanol with 0,04M HCl was added to dissolve the dye. Absorbance was measured at 570nm in a microplate reader (TECAN Infinite 200 Pro). Triplicate values were averaged and divided by the values of the untreated cells (100% viability) to obtain relative viability values. Each experiment was repeated 3 times independently and the data was plotted as mean relative viabilities +/- SEM over concentration.

b. Experimental details and spectroscopic characterization data for compounds **2, 3, 4, 6, G1PG-CD and G2PG-CD**.

Synthesis of per-iodo-β-cyclodextrin (2)

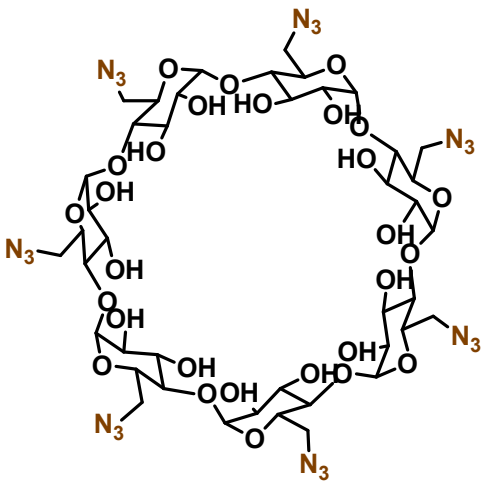


2

According to the procedure of Gadelle and Defaye (1991), to a mixture of triphenylphosphane (21 g, 80 mmol) and iodine (20.2 g, 80 mmol) in DMF (40 mL) was added β-cyclodextrin (4.32 g, 26.6 mmol equiv). The mixture was stirred at 80 ºC for 18 h and it was then concentrated under vacuum to half volume. The pH was adjusted to 9–10 by addition of sodium methoxide in methanol (3 M, 30 ml), with simultaneous cooling. The solution was kept at room temperature to destroy the formate esters formed in the reaction, after 1 h it was precipitated into methanol. The precipitate was collected by filtration to give per-iodo-β-cyclodextrin with 86% yield.

^{13}C NMR (75 MHz, DMSO-*d6*) δ: 102.4, 86.2, 72.5, 72.2, 71.29, 9.8.

Synthesis of azido-β-cyclodextrin (3)

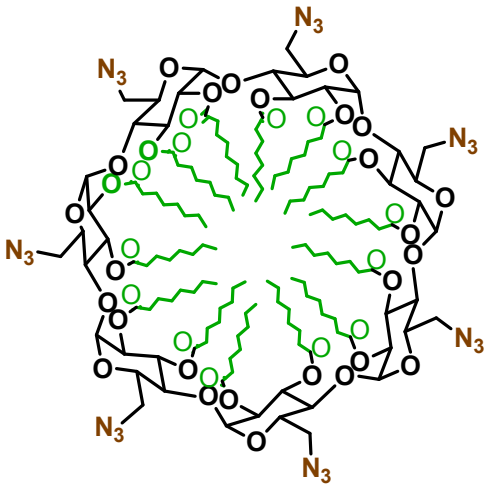


3

Per-azido-β-cyclodextrin **3** was obtained from reaction of the iodo-β-cyclodextrin with sodium azide (l.3 m eq. / hydroxyl group) in DMF at 65°C for 24 hr. Solvent was evaporated and the residue added to water. The precipitate was filtered and washed with acetone to give product in 94–98% yield.

^{13}C NMR (100 MHz, D_20) δ: 102.03, 83.18, 72.58, 71.99, 70.32, 51.32.

Synthesis of azido-CD-octanoyl (4)



4

The esterification was performed by the addition of azido-β-cyclodextrin (300 mg, 0.23 mmol) in anhydrous DMF (12 ml) in the presence of 3 equivalents of dimethylaminopyridine (DMAP) (84.30 mg, 0.69 mmol) and few drops of dry pyridine (180 µl) to a solution of octanoyl choride (3.3 ml, 19.66 mmol) in anhydrous DMF (8 ml) at 0 ºC under a nitrogen atmosphere. The solution was warmed to 60 ºC and held at this temperature during three days. The DMF was then removed *in vacuo* at 60 ºC and the residue taken up in $CHCl_3$ (20 ml). The solution was washed with H_2O (2 x 10 ml), dried over $NaSO_4$ and the solvent was evaporated *in vacuo* to leave the crude product. The crude product was purified by flash chromatography (alumina neutral, eluant hexane/AcOEt, 3:1) affording the desired product as a colourless solid (283 mg, 40%).

^{1}H NMR (700MHz, $CDCl_3$) δ: 5.33 (t, *J*=7.0 Hz, 7 x CH_2N$_3$, 7H); 5.08 (s, 7x CD*H*, 7H); 4.81 (d, *J*=7.0 Hz, 7 x CH_2N$_3$, 7H); 4.02 (broad s, 7 x CD*H*, 7H), 3.74 (q, 14 x CD*H*, 14H); 3.64 (d, *J*=7.0 Hz, 7 x CD*H*, 7H); 2.40-2.36 (m, CH_2COO, 14H), 2.30-2.25 (m, CH_2COO, 7H), 2.22-2.18 (m, CH_2COO, 7H), 1.66-1.54 (m, 14 x CH_2CH$_2$COO, 28H), 1.37-1.25 (m, 14 x CH$_3$(CH_2)$_4$, 112H), 0.91 (dt, *J*= Hz, 2.1, 14 x CH_3(CH$_2$)$_4$, 42H).

^{13}C NMR and DEPT ($CDCl_3$, 100MHz) δ: 173.23 (*C*=O), 171.74 (*C*=O), 96.38 (OCDO), 76.68 (OCHCHCH$_2$N)), 70.78 (CDH), 70.20 (CDH), 70.13 (CDH), 51.59 (*C*H$_2$N$_3$), 34.12 (*C*H$_2$), 33.87 (*C*H$_2$), 31.76 (*C*H$_2$), 29.15 (*C*H$_2$), 24.80 (*C*H$_2$), 22.67 (*C*H$_2$), 14.04 (*C*H$_3$).

ESI-MS: Calcd. [M+H]$^+$ ($C_{155}H_{262}N_{21}O_{28}$) *m/z* = 3089.89. Found. [M+H]$^+$ *m/z* = 3099.87.

ν_{max} (cm^{-1}): 2924*s* (C-H), 2103*s* (N$_3$), 1744*s*, 1590*w*, 1465*m*, 1157*m*, 1039*s*.

Fig. S1 ^{1}H NMR spectra (in $CDCl_3$) of compound **4**

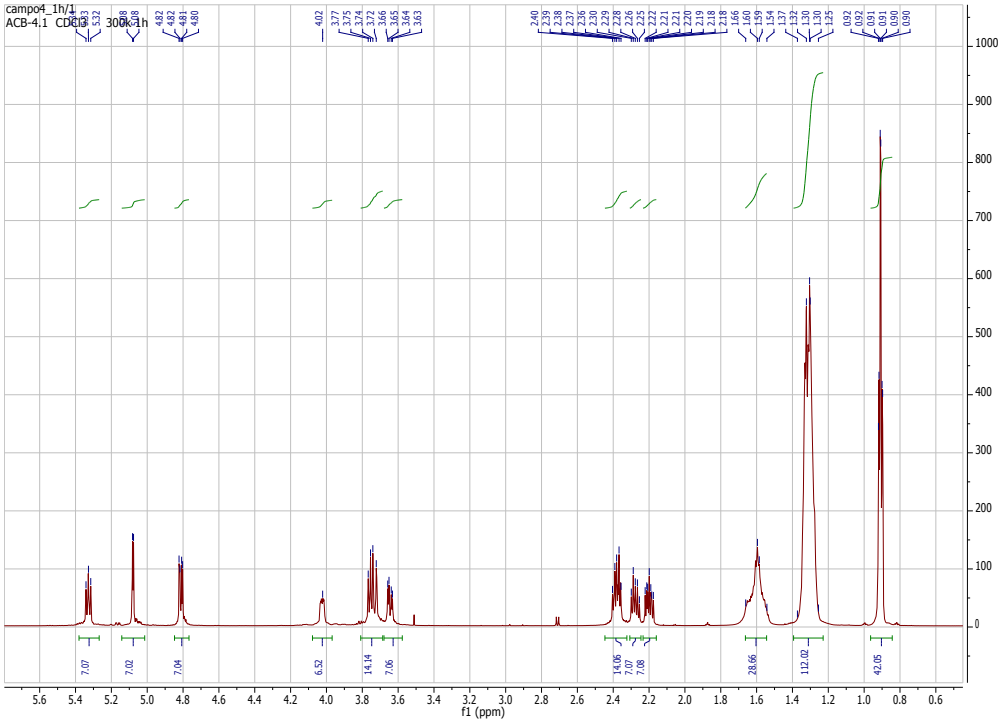


Fig. S2 ^{13}C NMR spectra (in $CDCl_3$) of compound **4**

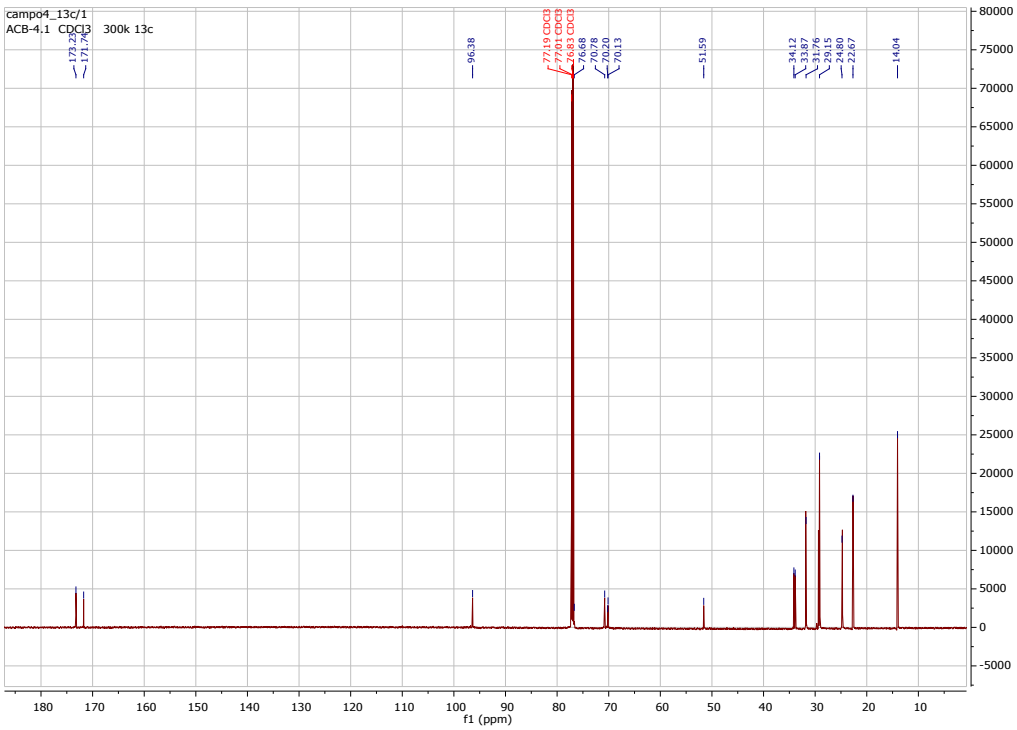


Fig. S3 DEPT spectra (in $CDCl_3$) of compound **4**

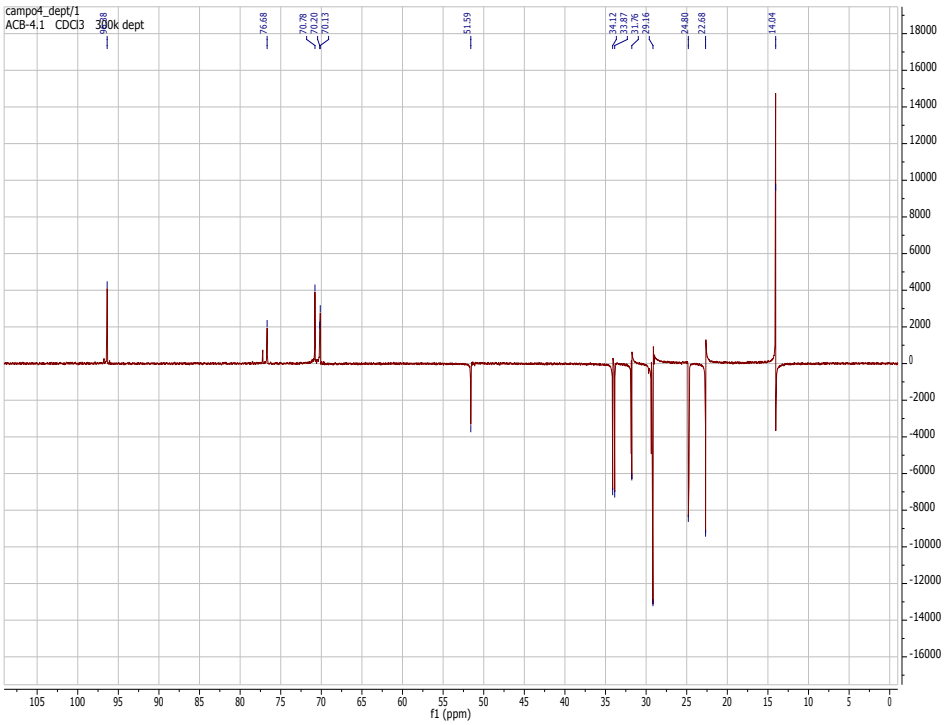


Fig. S4 ESI-MS spectra of compound **4**

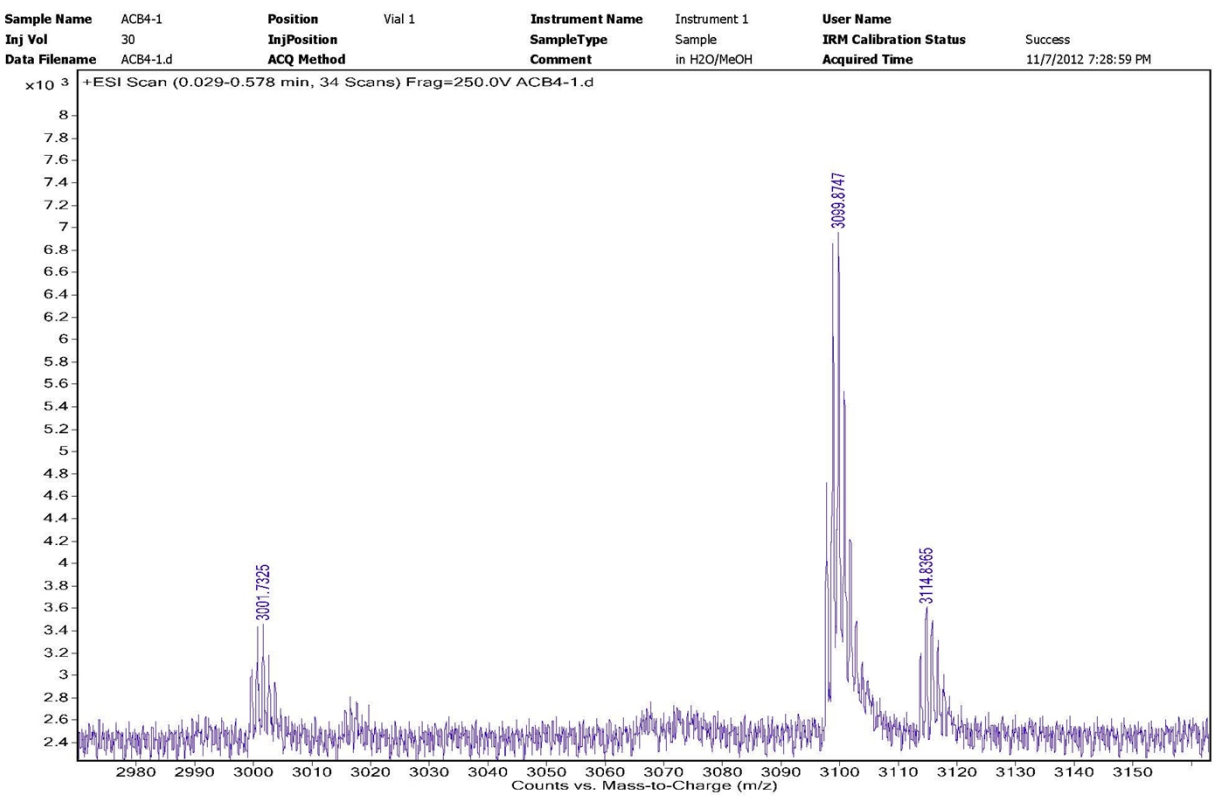
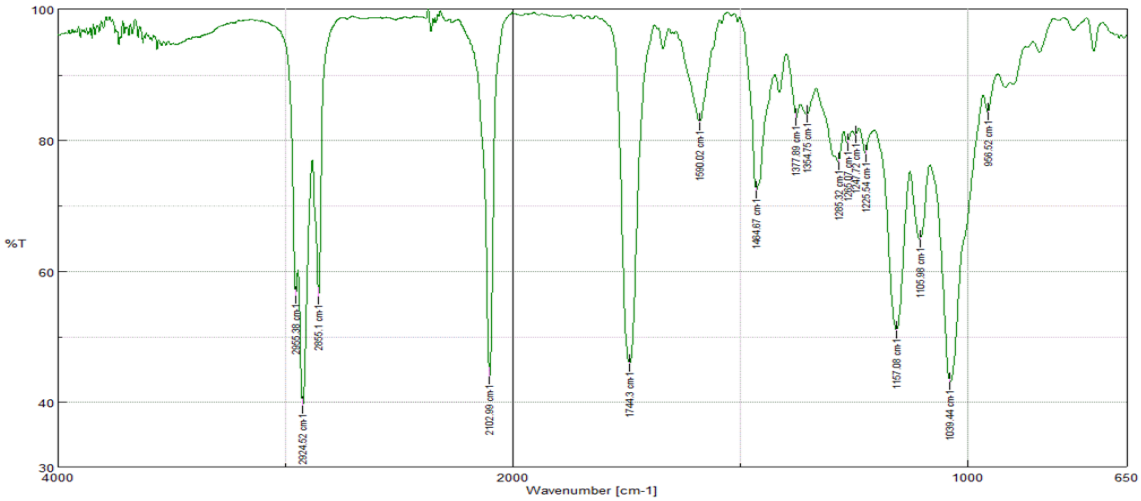
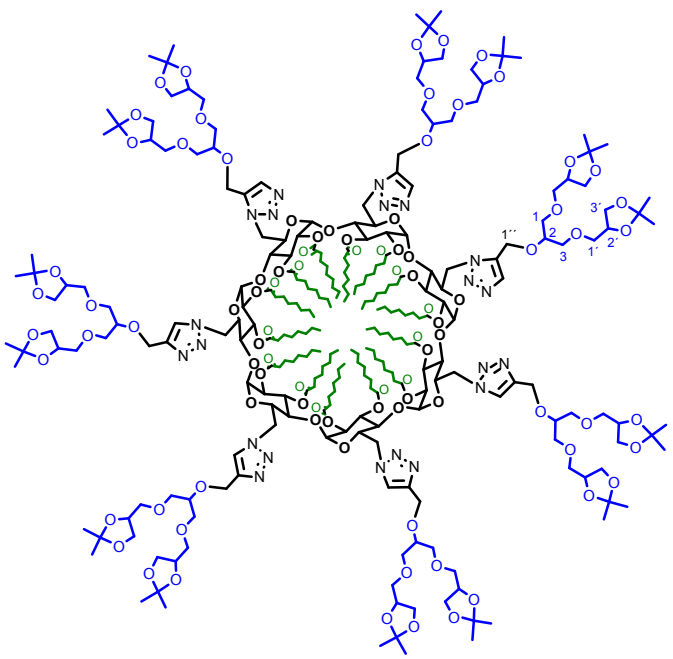


Fig. S5 IR spectra of compound **4**



Synthesis of compound 6



6

The reaction between azido-CD-octanoyl (79.5 mg, 0.026 mmol) and propargyl-G1 acetal PG dendron (70.9 mg, 0.198 mmol) was carried out in a 10 ml microwave reactor vial placed in a professional microwave oven. The reaction mixture containing $CuSO_4 \cdot 5H_2O$ (4.5 mg, 0.018 mmol), sodium ascorbate

(7.2 mg, 0.036 mmol) and 2,6-lutidine (6 µl, 0.052 mmol) suspended in THF/H_20 1:1 (4.8 ml) was heated at 120 ºC for 30 minutes. The THF was then removed *in vacuo* and the residue take up in $CHCl_3$ (30 ml). The solution was washed with water (2 x 10 ml), dried over $NaSO_4$ and the solvent was evaporated to yield the crude product as a yellow oil. The crude product was purified by flash chromatography (alumina neutral, $CHCl_3$; $CHCl_3$/MeOH; MeOH) to give the product as colourless sticky solid (122.9 mg, 0.020 mmol, 78%).

^{1}H NMR (700MHz, $CDCl_3$) δ: 7.77 (broad s, 7x C*H* triazole, 7H), 5.42 (br s, 7x CH_2N_3, 14H), 4.86-4.53 (m, 7x CDH_5, 35H), 4.33-4.19, 4.07-3.99, 3.80-3.70 & 3.63-3.40 (4 m , 7x C-1H, 7x C-2H, 7x C-3H, 7x C-1´H, 7x C-2´H, 7x C-3´H, and 7 x N_3CCH_2O, 119H) 2.47-2.14 (m, 7x CH_2COO, 28H), 1.92-1.55 (m, 14x CH_2CH_2COO, 28H), 1.43-1.38, 1.37-1.34, 1.30-1.24 (3m, 28x C(CH_3)$_2$, 14x CH_3(CH_2)$_4$, 198H), 0.89 (t, *J*= 7Hz, 14x CH_3(CH_2)$_4$, 42H).

^{13}C NMR and DEPT (176 MHz, $CDCl_3$) δ: 173.04 (*C*=O), 171.70 (*C*=O), 145.20 (*C* triazole), 125.80 (*C*H triazole), 109.30 (*C*(CH_3)$_2$), 96.44 (O*C*DO), 78,66 (O*C*HCHCH_2N), 77.62 (O*C*H(CH_2O-)$_2$), 74.62 (C-2´), 72.47 (C-1´), 71.65 (C-1/C-3), 71,51 (C-1/C-3), 70.77 (CDH), 69.64 (CDH), 69.45 (CDH), 66.76 (2x C-3´), 64.79 (C-1´´), 63.76 (C-1´´), 50.12 (O*C*H_2N), 34.04 (*C*H_2), 33.79 (*C*H_2), 31.74 (*C*H_2), 29.18 (*C*H_2), 26.79 (*C*H_2), 25.44 (C*C*H_3), 24.64 (C*C*H_3), 22.66 (*C*H_2), 14.03 (*C*H_3).

MALDI-TOF: Calcd. $[M+H]^+$ ($C_{281}H_{471}N_{21}O_{28}$) *m/z* = 5600.92 Found. $[M+H]^+$ *m/z* = 5601.58.

ν_{max} (cm^{-1}): 2924*s* (C-H), 1749*s*, 1457*w*, 1370*w*, 1252*m*, 1213*m*, 1151*m*, 1101*m*, 1044*m*, 843*w*.

Fig. S6 ^{1}H NMR spectra (in $CDCl_3$) of compound **6**

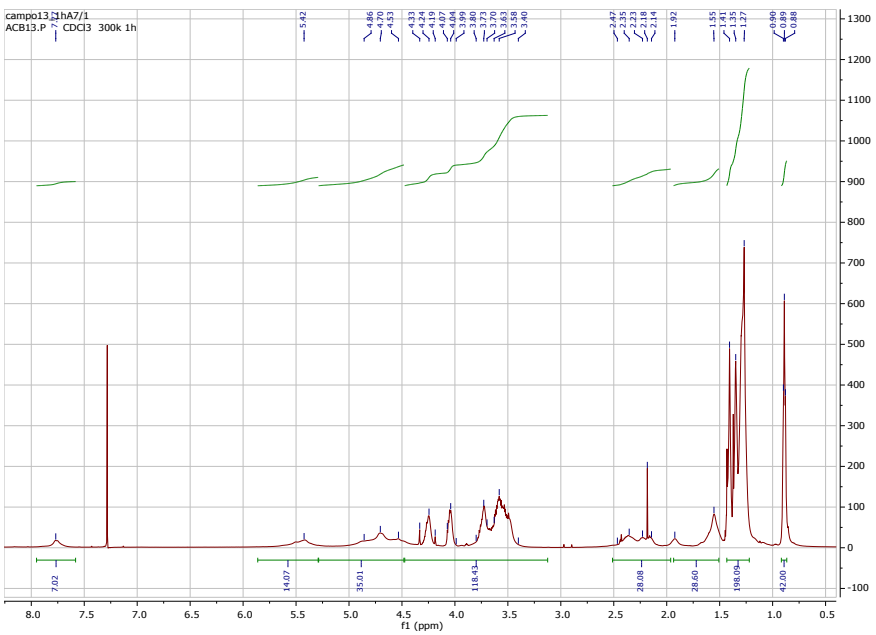


Fig. S7 ^{13}C-NMR spectra (in $CDCl_3$) of compound **6**

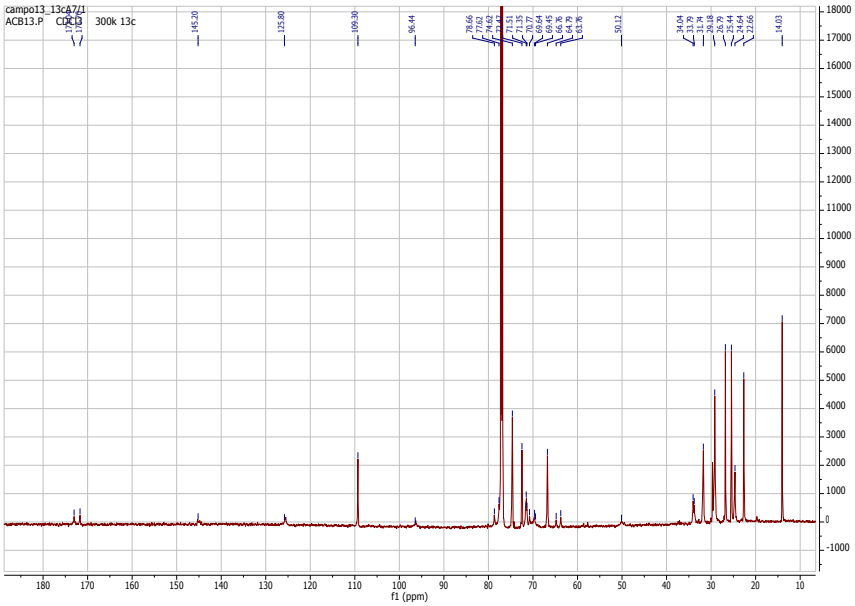


Fig. S8 DEPT spectra (in $CDCl_3$) of compound **6**

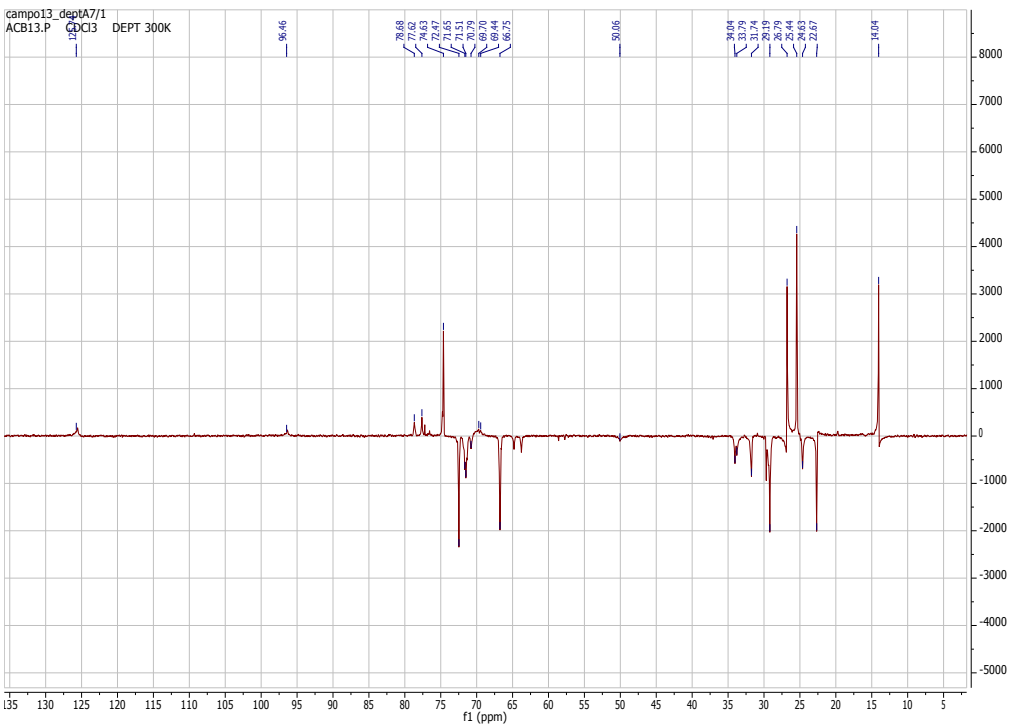


Fig. S9 IR spectra of compound **6**

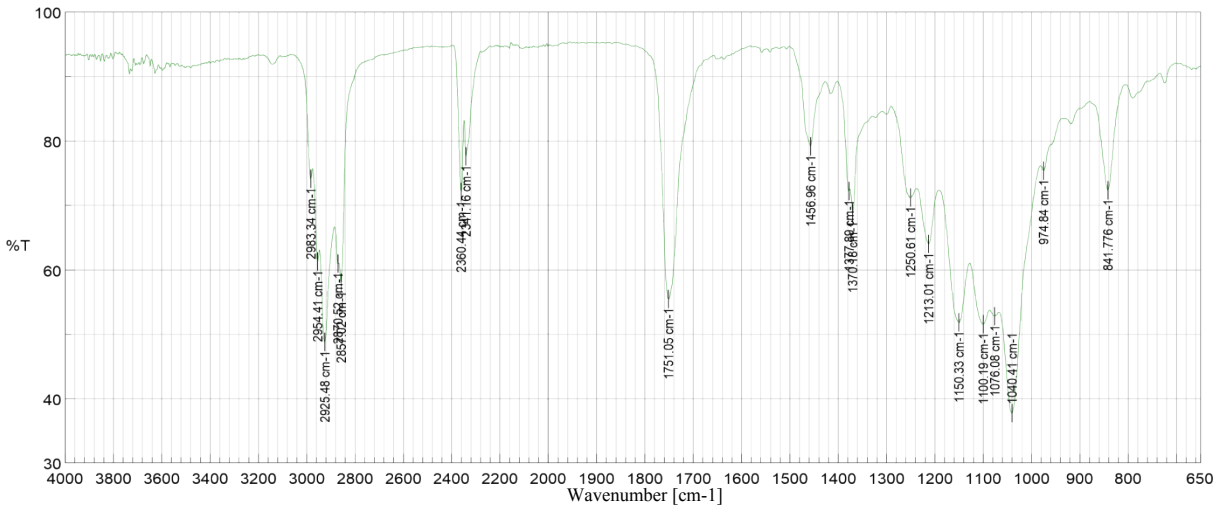
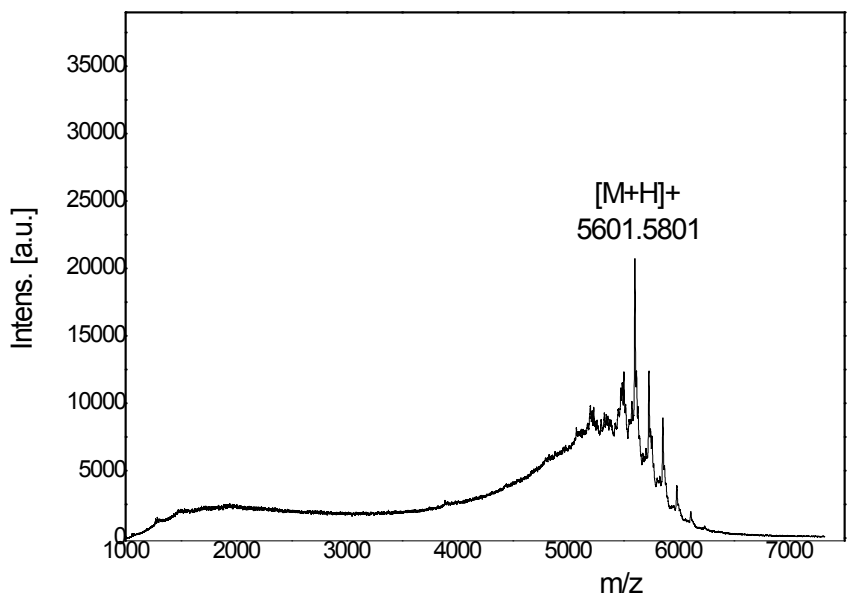
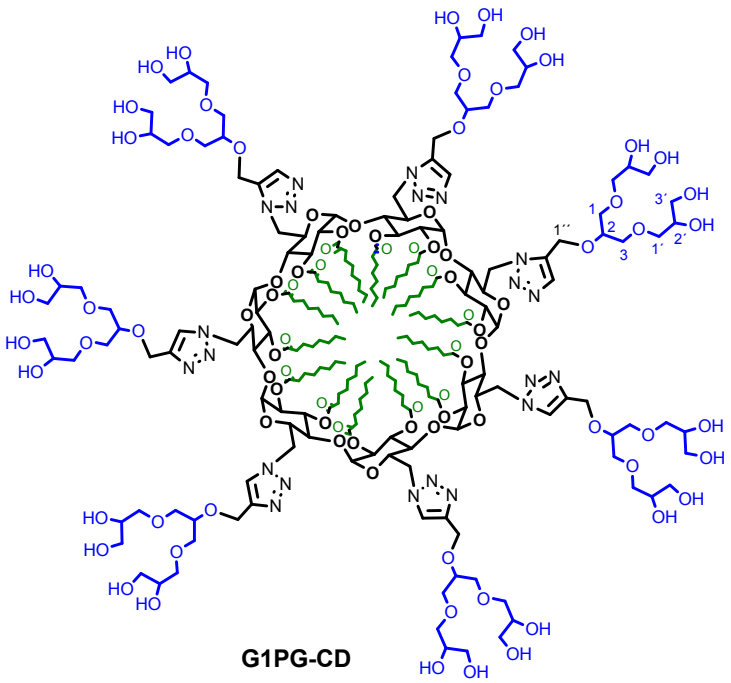


Fig. S10 MALDI-TOF spectra of compound **6**



Synthesis of G1PG-CD



G1PG-CD

The acetal protected dendrimer (47 mg) was treated with a mixture of TFA/MeOH (1:1, 6 ml) during 4 hours. The solvent was then removed in vacuo. The crude product was washed with hexane (3 x 1.5 ml) and diethyl ether (1.5 ml) to give the pure product as a colourless solid (40.1 mg, 0. 008 mmol, 95%).

^{1}H NMR (700MHz, CD_3OD) δ: 8.11 (broad s, 7x C*H* triazole, 7H), 5.53 (br s, 7x CH_2N_3, 14H), 4.72-4.20 (m, 7x CDH_5, 35H), 3.87-3.74, 3.66-3.47 (2 m , 7x C-1H, , 7x C-2H, 7x C-3H, 7x C-1´H, 7x C-2´H, 7x C-3´H and 7 x N_3CCH_2O, 119H), 2.60-2.13 (m, 7x CH_2COO, 28H), 1.80-1.51 (m, 14x CH_2CH_2COO, 28H), 1.35 (broad s, 14x CH_3(CH_2)$_4$, 112H), 0.93 (t, *J*= 6.3Hz, 14x CH_3(CH_2)$_4$, 42H).

^{13}C NMR and DEPT (176 MHz, CD_3OD) δ: 172.98 (*C*=O), 171.96 (*C*=O), 144.43 (*C* triazole), 126.60 (*C*H triazole), 96.40 (O*C*DO), 78.36 (O*C*HCHCH_2N), 77.57 (O*C*H(CH_2O-)$_2$), 72.59 (C-1´), 71.50 (C-1/C-3), 70.99 (C-1/C-3), 70.79 (C-2´), 70.16 (CDH), 69.29 (CDH), 68.99 (CDH), 63.90 (C-1´´), 63.05 (2x C-3´), 50.22 (O*C*H_2N), 33.75 (*C*H_2), 33.58 (*C*H_2), 31.65 (*C*H_2), 29.00 (*C*H_2), 24.61 (*C*H_2), 22.47 (*C*H_2), 13.16 (*C*H_3).

MALDI-TOF: Calcd. $[M+H]^+$ ($C_{239}H_{415}N_{21}O_{91}$) *m/z* = 5039,01 Found. $[M+H]^+$ *m/z* = 5040.81.

ν_{max} (cm^{-1}): 3370 (O-H), 2924 (C-H), 2857 (C-H), 1749*s*, 1675*w*, 1459*w*, 1147*s*, 1103*s*, 1039*s*.

Fig. S11 ^{1}H NMR spectra (in CD_3OD) of **G1PG-CD**

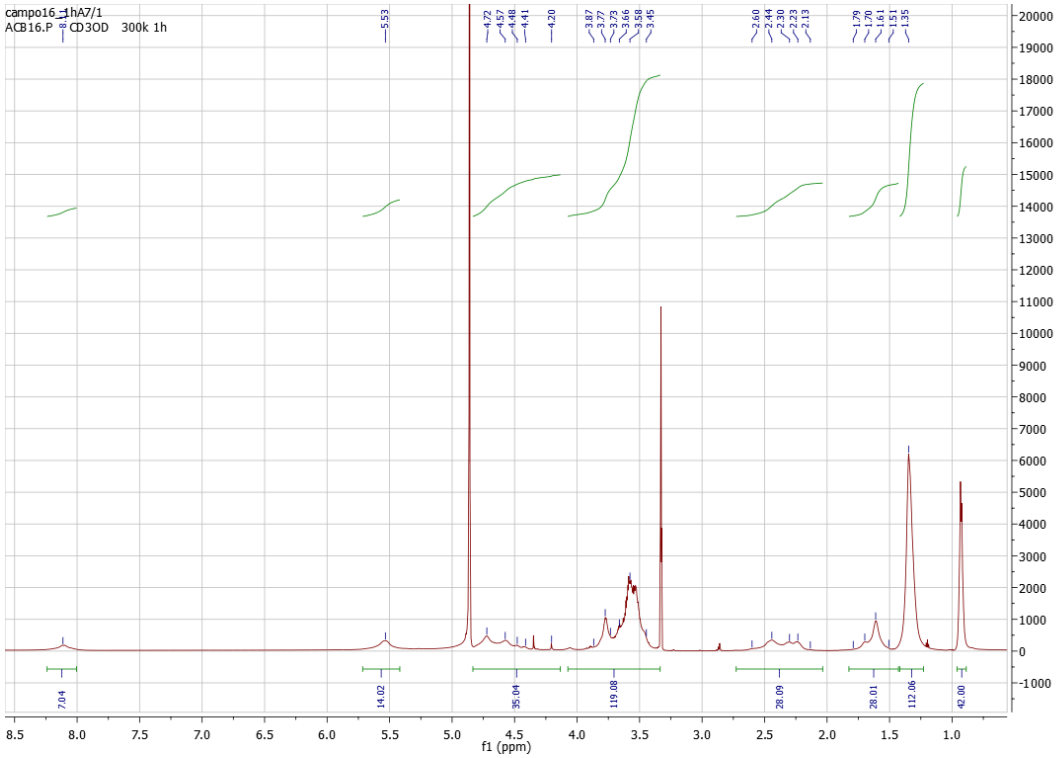


Fig. S12 ^{13}C-NMR spectra (in CD_3OD) of **G1PG-CD**

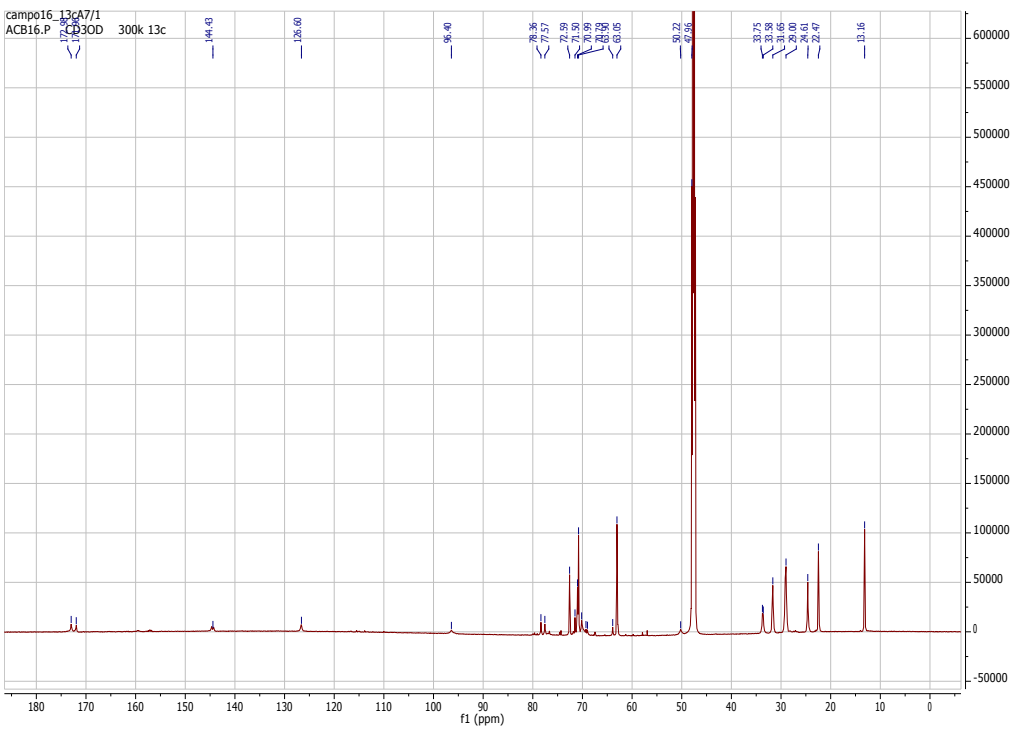


Fig. S13 DEPT spectra (in CD_3OD) of **G1PG-CD**

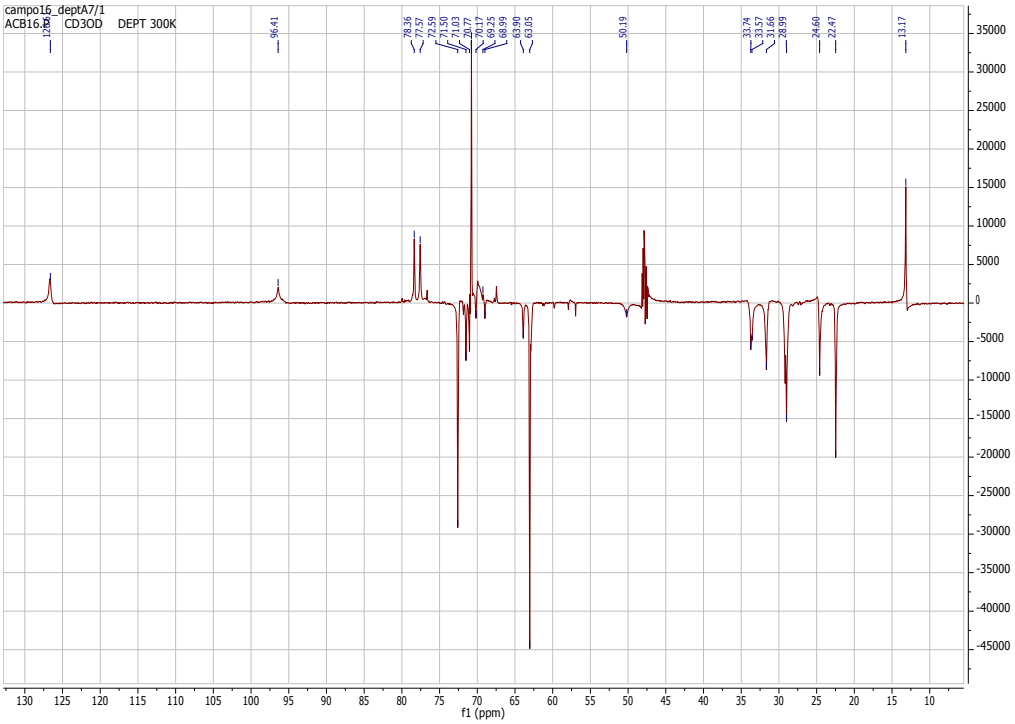


Fig. S14 MALDI-TOF spectra of **G1PG-CD**

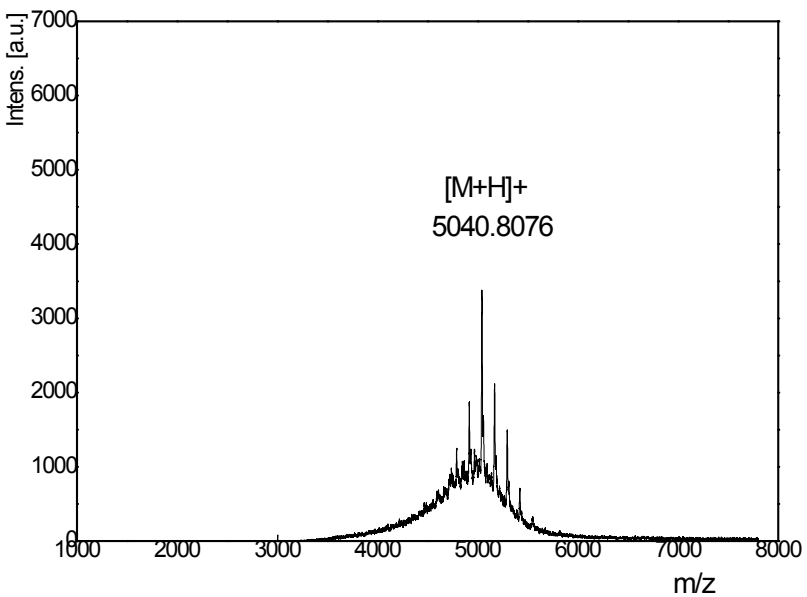
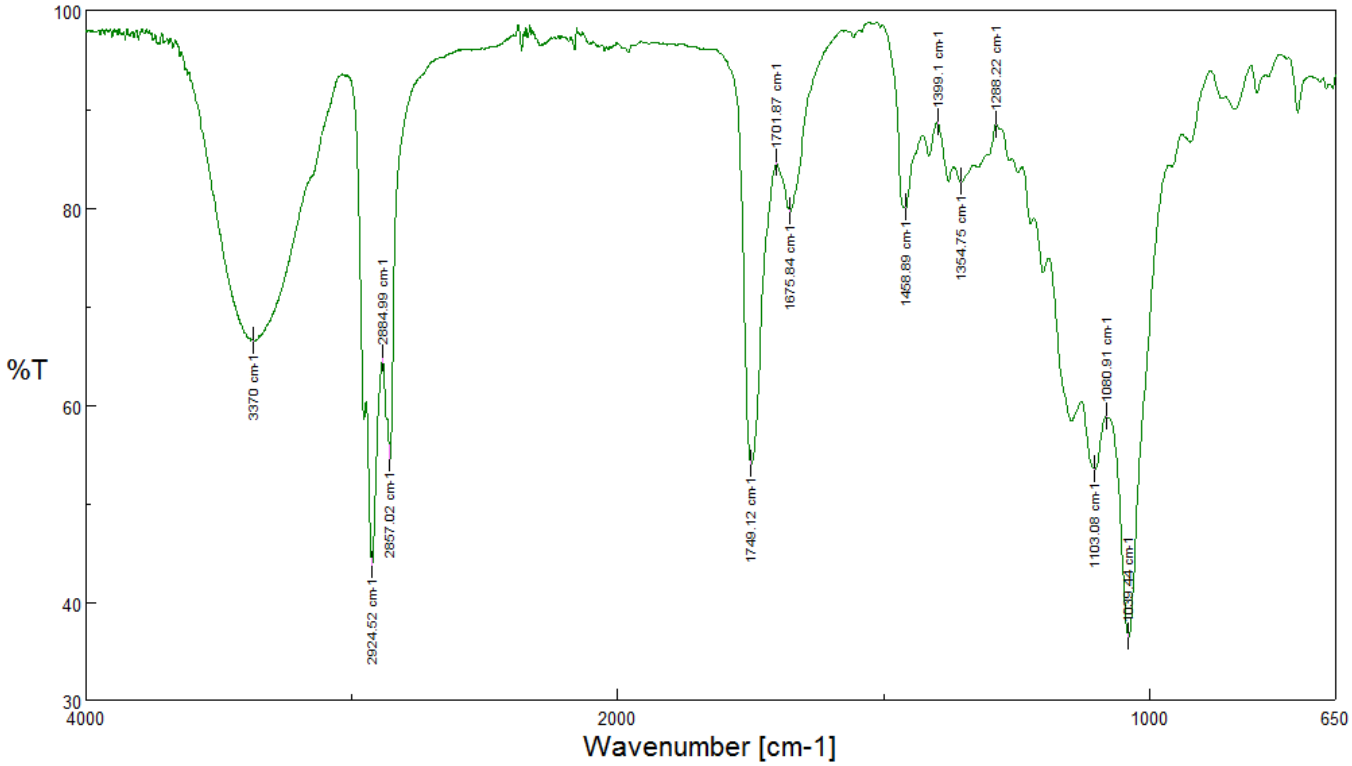
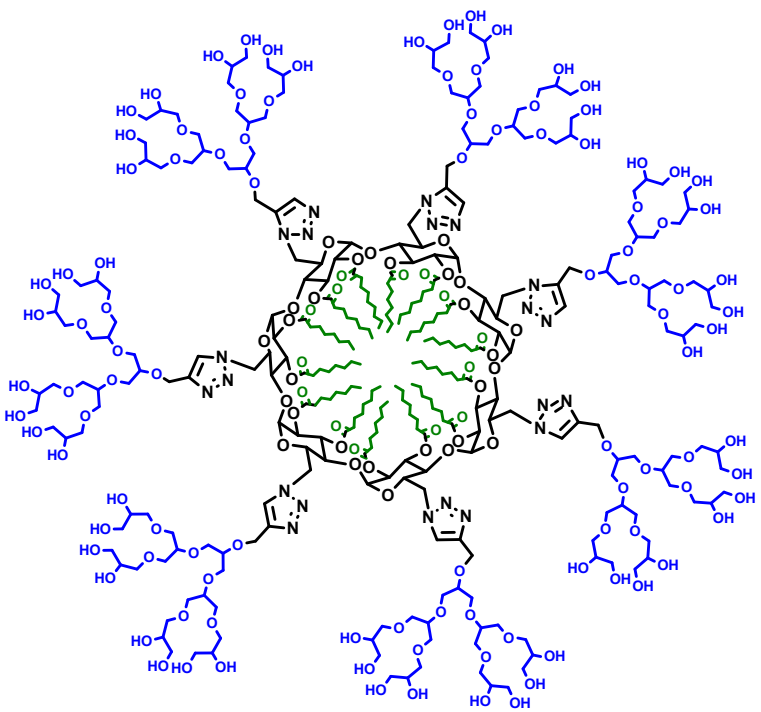


Fig. S15 IR spectra of **G1PG-CD**



Synthesis of G2PG-CD



G2PG-CD

The reaction between azido-CD-octanoyl (**4**) (20 mg, 0.0065 mmol) and propargyl-G2 glycerol PG dendron (28.6 mg, 0.049 mmol) was carried out in a 5 ml microwave reactor vial placed in a professional microwave oven. The reaction mixture containing $CuSO_4 \cdot 5H_2O$ (1.13 mg, 0.005 mmol), sodium ascorbate (1.79 mg, 0.009 mmol) and 2,6-lutidine (1.5 µl, 0.013 mmol) suspended in THF/$H_2$0 1:1 (2 ml) was heated at 120 ºC for 30 minutes. The THF was then removed *in vacuo* and the residue take up in $CHCl_3$ (20 ml). The solution was washed with water (2 x 10 ml). The organic phase contained only impurities and then, the aqueous phase was concentrated *in vacuo*. After dissolving the crude product in MeOH, it was then filtrated off (22.7 mg). The crude product was further purified by Sephadex in MeOH to yield the product as colourless sticky solid (20.6 mg, 0.003 mmol, 45%).

^{1}H NMR (500MHz, CD_3OD) δ: 8.10 (broad s, 7x C*H* triazole, 7H), 5.53 (br s, 7x CH_2N_3, 14H), 3.88-3.48 (m, 7x CDH_5, 7 x N_3CCH_2O, 7 x PG dendron, 35H), 2.56-2.32 (m, 7x CH_2COO, 28H), 2.10 (m, 14x CH_2CH_2COO, 28H), 1.84-1.47 (m, 14x CH_2CH_2COO, 28H), 1.31 (broad s, 14x $CH_3(CH_2)_4$, 112H), 0.91 (broad s, 14x $CH_3(CH_2)_4$, 112H).

^{13}C NMR (176 MHz, CD_3OD) δ: 172.88 (*C*=O), 144.75 (*C* triazole), 126.72 (*C*H triazole), 78.47 (O*C*HCHCH$_2$N), 77.11(O*C*H(CH$_2$O-)$_2$), 76.80, 74.37, 72.58, 71.54, 69.66, 63.08, 56.90, 47.59, 33.73 (*C*H$_2$), 31.68 (*C*H$_2$), 29.04 (*C*H$_2$), 24.64 (*C*H$_2$), 22.46 (*C*H$_2$), 13.18 (*C*H$_3$).

MALDI-TOF: Calcd. [M+H]+ ($C_{323}H_{583}N_{21}O_{147}$) m/z 7113.22 Found. [M+H]+ m/z = 7113.736.

νmax (cm-1): 3376 (O-H), 2924 (C-H), 2872 (C-H), 1752m, 1644w, 1457w, 1352w, 1039s, 927w.

Fig. S16 ^{1}H NMR spectra (in CD_3OD) of **G2PG-CD**

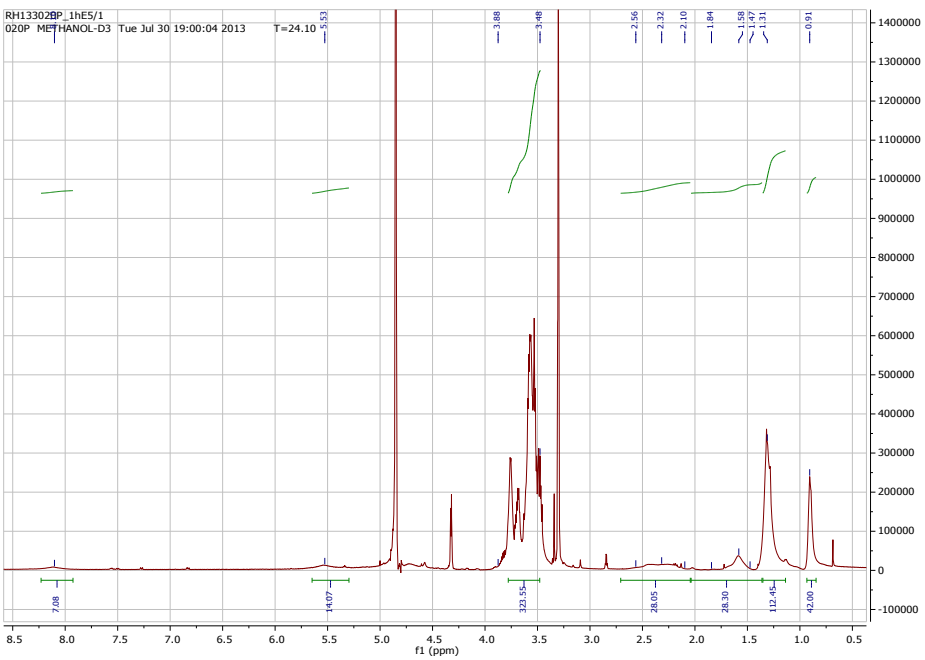


Fig. S17 ^{13}C-NMR spectra (in CD_3OD) of **G2PG-CD**

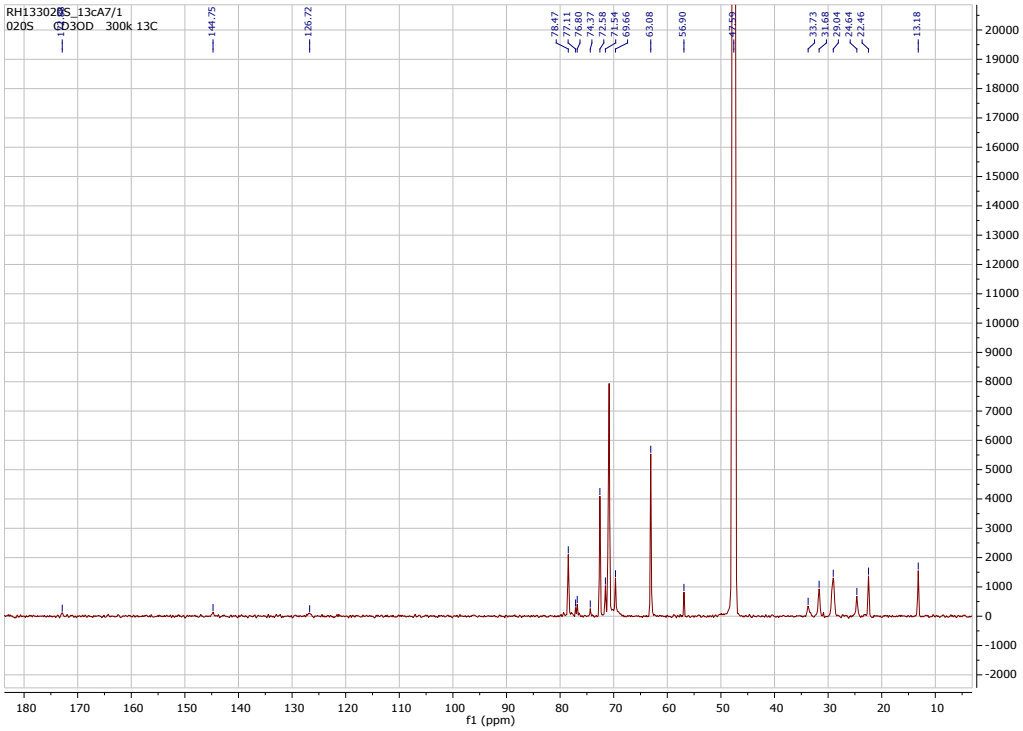


Fig. S18 MALDI-TOF spectra of G2PG-CD

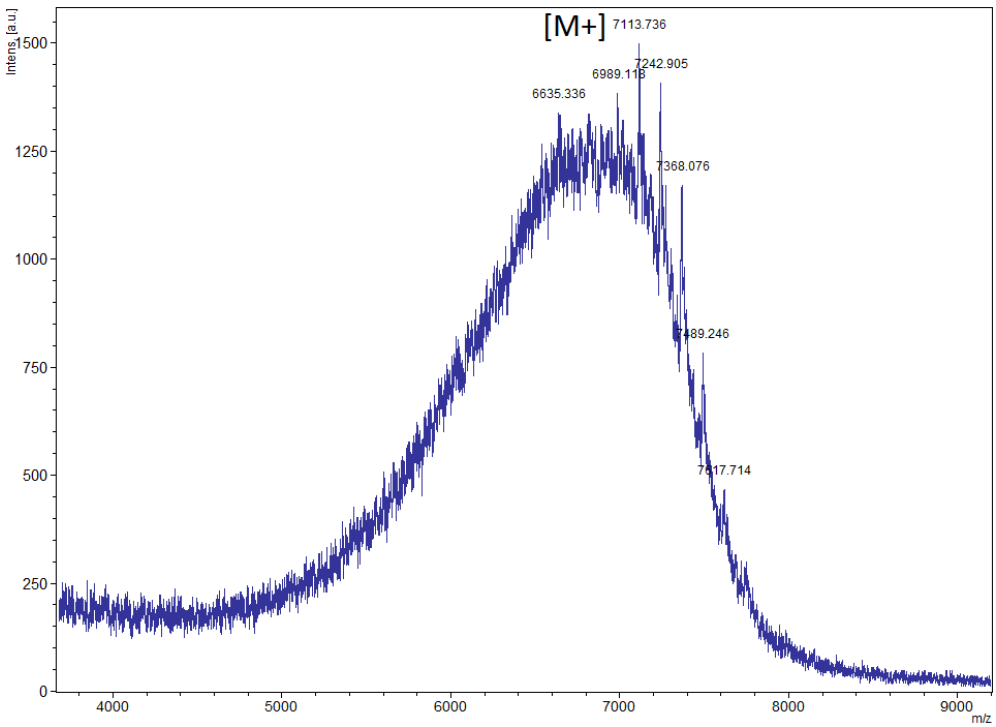
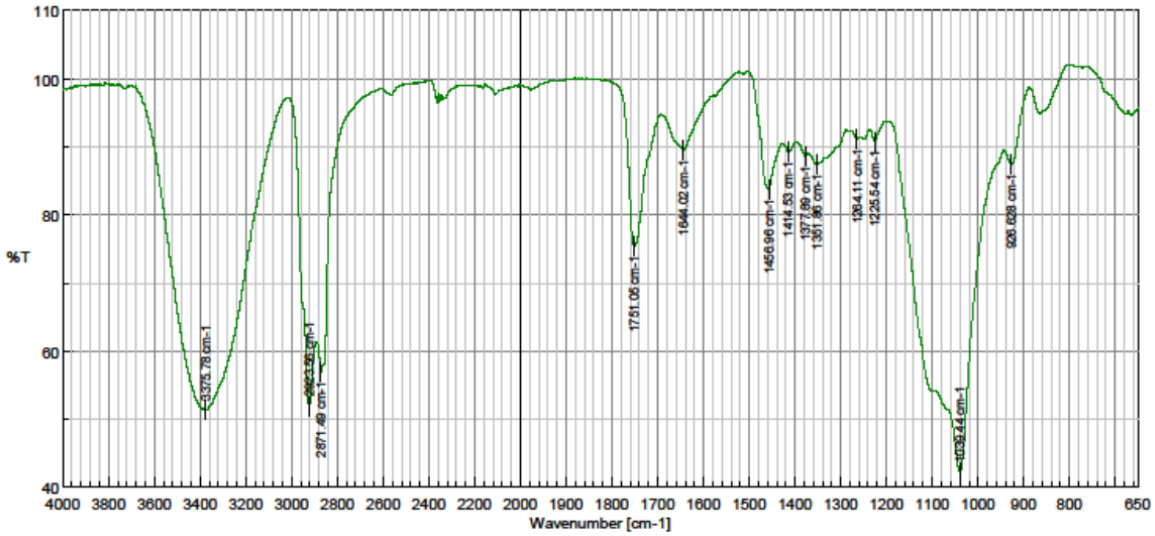


Fig. S19 IR spectra of **G2PG-CD**



3. Table S1. Hydrodynamic diameter of host molecules without and with guest molecules in water. [a]Size-distribution by DLS (by volume).

Sample	**Size (Vol.)[a] (d.nm)**	**PDI**
G1PG-CD	43.77	0.29
G2PG-CD	19.07	0.35
G1PG-CD-Nimo	330.5; 44.53	0.59
G1PG-CD-NR	412.9; 52.5	0.44
G2PG-CD-Nimo	25.60	0.29
G2PG-CD-NR	27.48	0.35

4. DLS diagrams of host **G1PG-CD** & **G2PG-CD** without and with guest molecules.

Fig. S20 DLS diagram of host **G1CD-PG. (**concentration= 0.33 mg/ml)

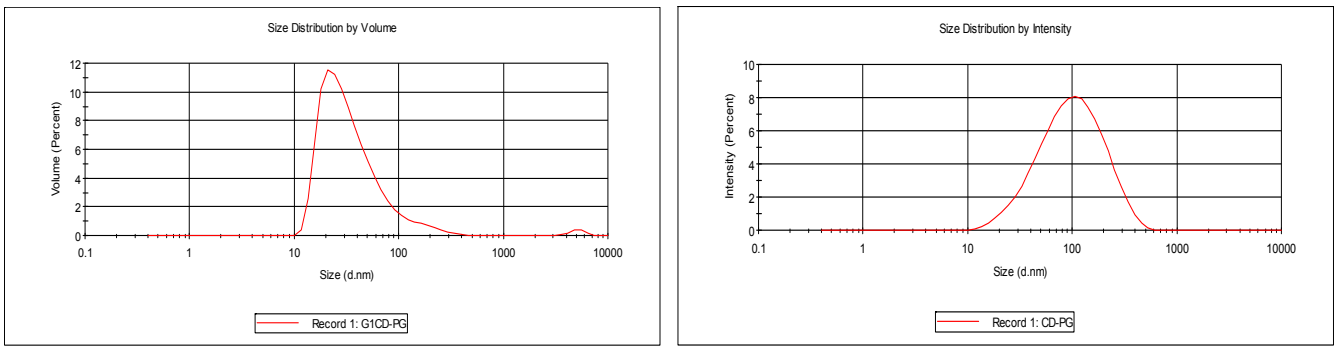


Fig. S21 DLS diagram of host **G2CD-PG. (**concentration= 0.33 mg/ml)

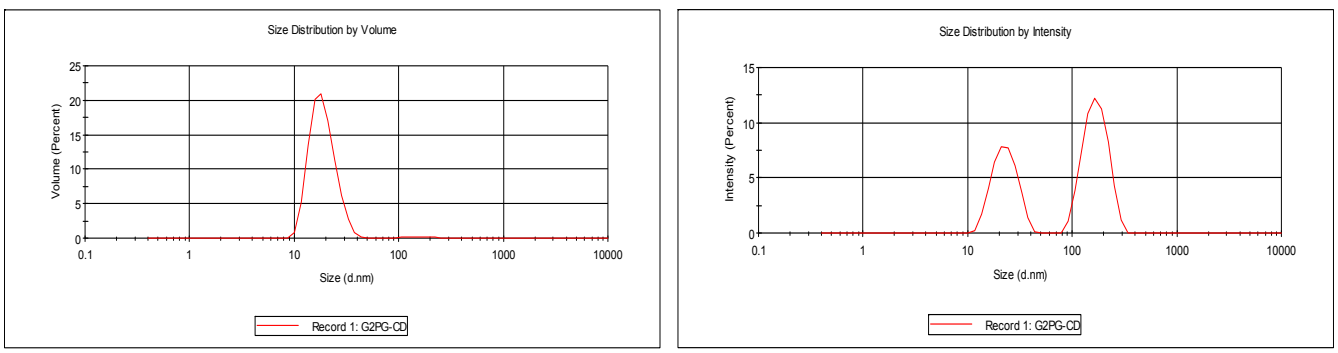


Fig. S22 Host-guest complex of **G1PG-CD** with Nimodipine

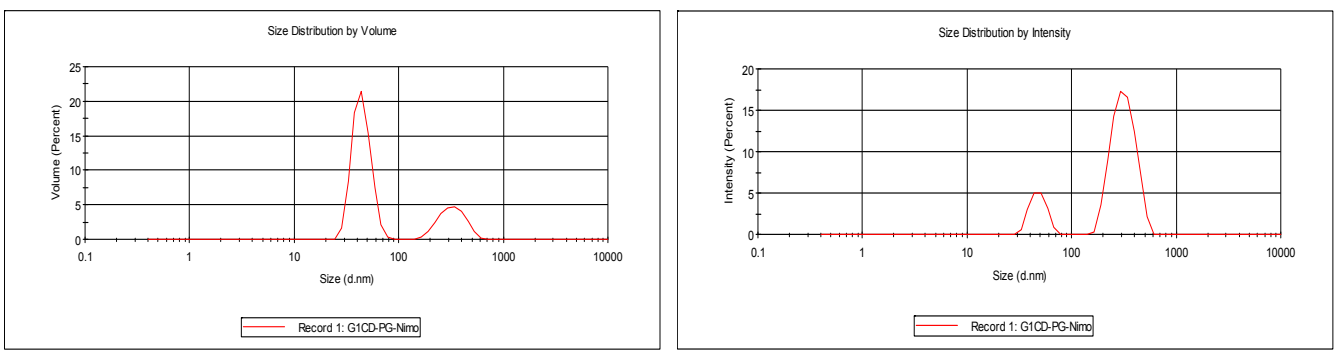


Fig. S23 Host-guest complex of **G1PG-CD** with Nile Red

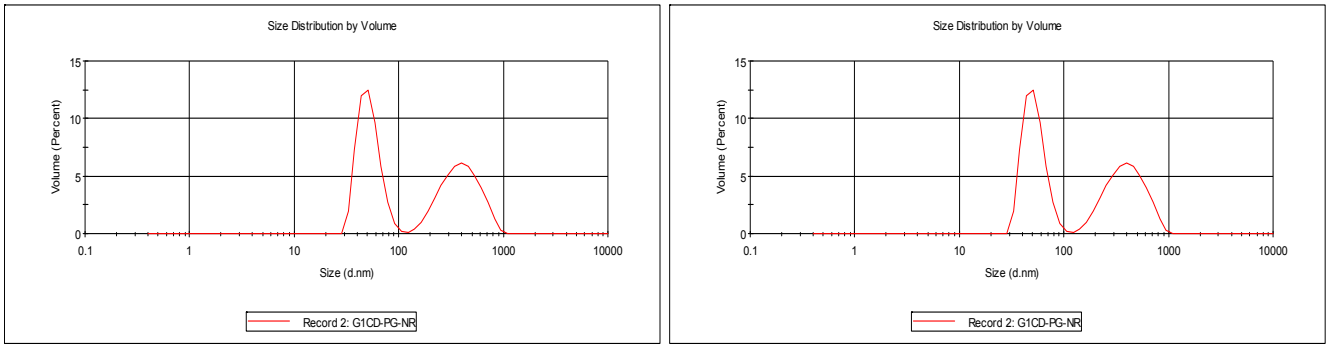


Fig. S24 Host-guest complex of **G2G-CD** with Nimodipine

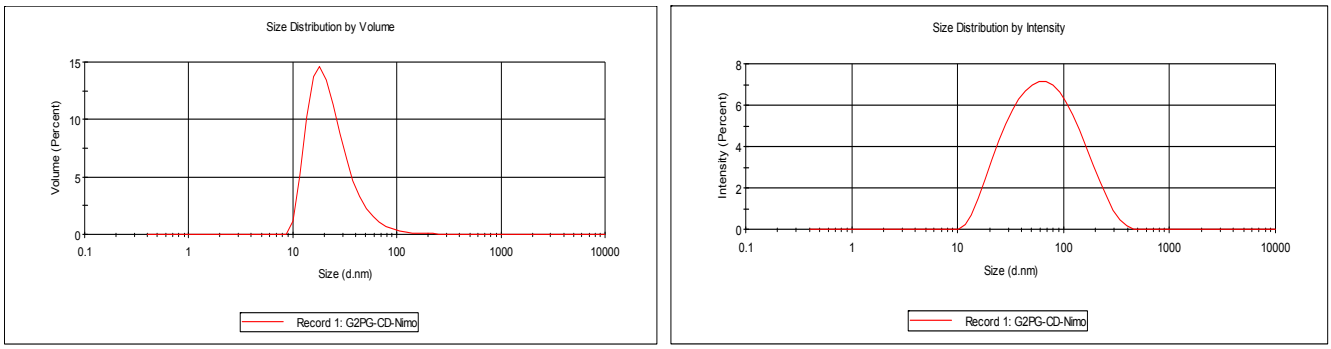
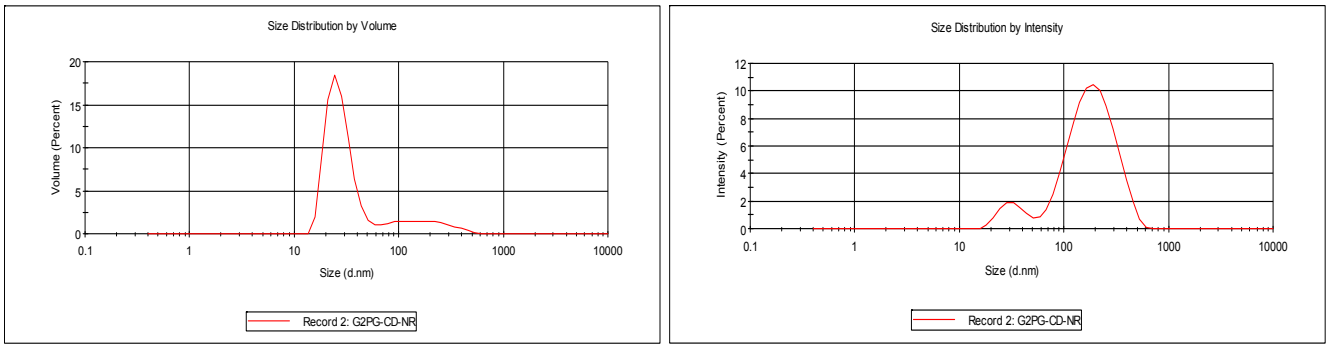


Fig. S25 Host-guest complex of **G2PG-CD** with Nile Red

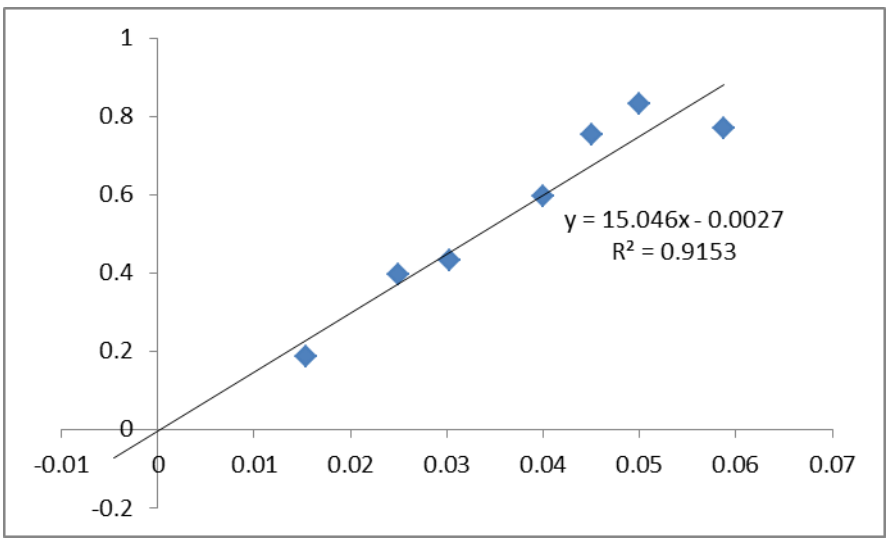


5. **Table S2.** Encapsulation percentage of nimodipine and nile red in host G1PG-CD and G2PG-CD

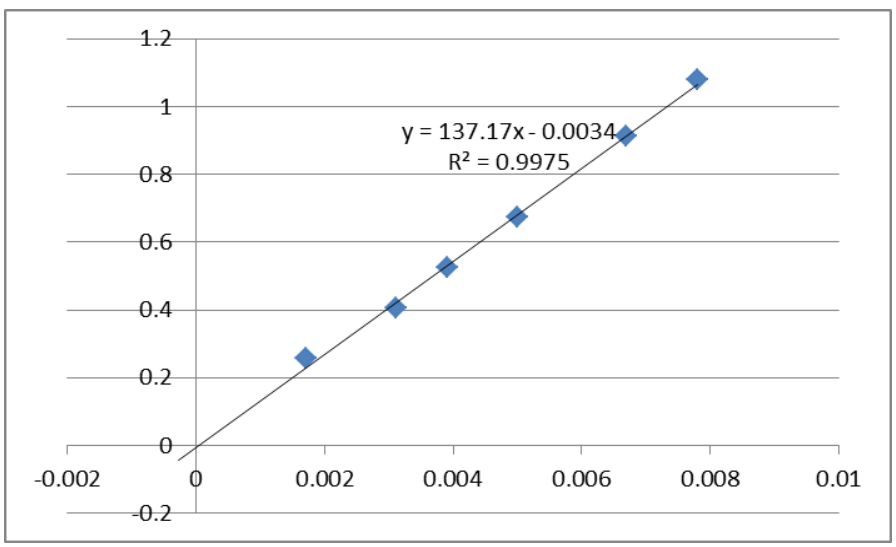
Host-Guest	% Encapsulation (weight %)	% Encapsulation (mole %)
G1PG-CD-Nimo	7.0	85
G1PG-CD-Nile Red	6.3	100
G2PG-CD-Nimo	1.3	50
G2PG-CD-Nile Red	3.1	15

6. Calibration curves of nimidipine and nile red and UV-*vis* spectrum of the complexes of guests with host G1PG-CD

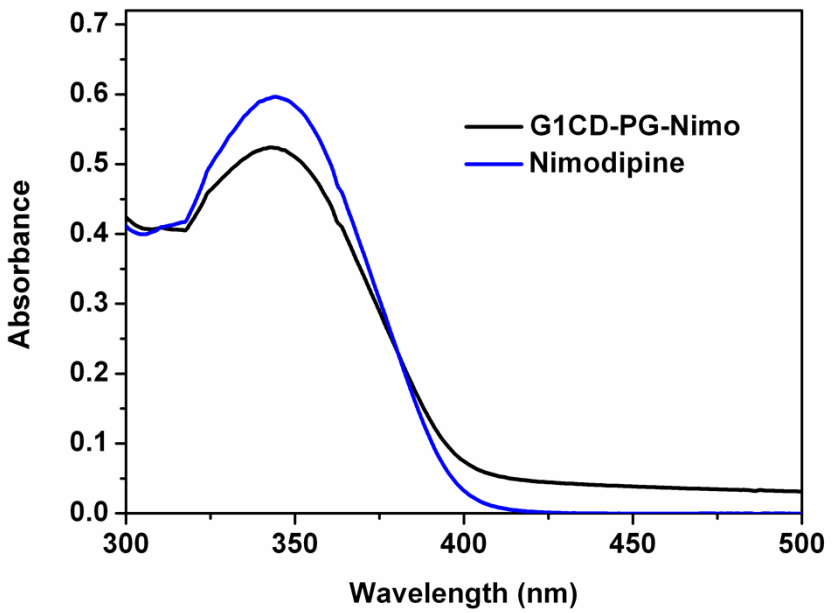
a. **Fig. S26** Calibration curve of nimodipine in $CHCl_3$.



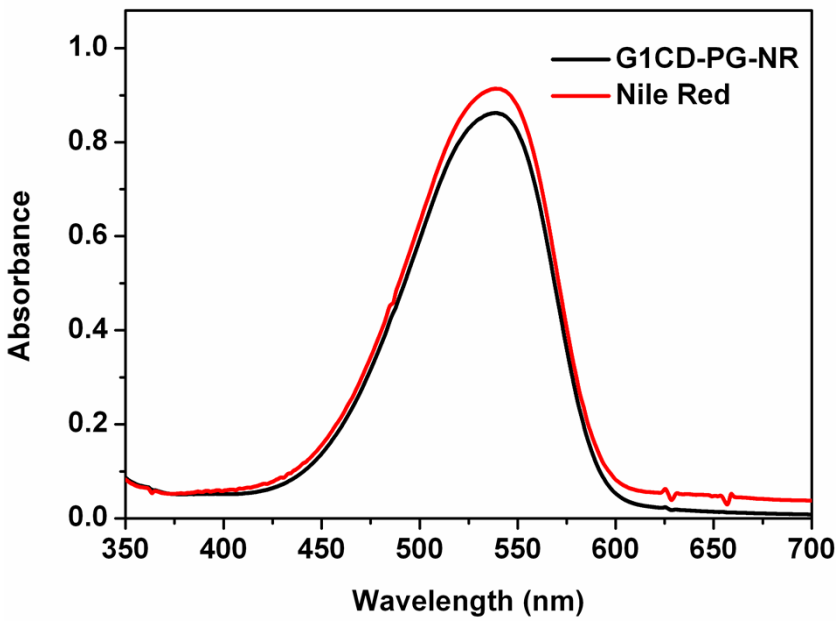
b. **Fig. S27** Calibration curve of nile red in $CHCl_3$.



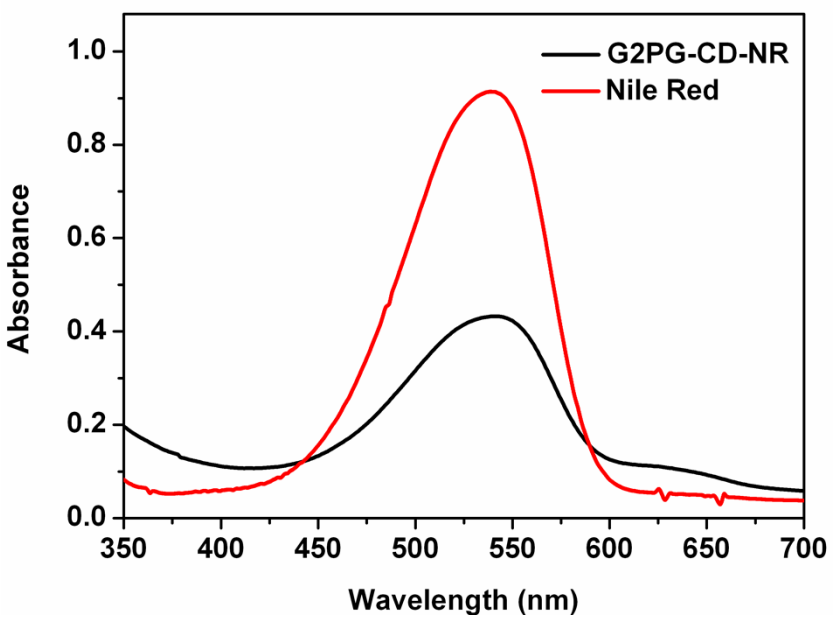
c. **Fig. S28** Overlay of UV-vis spectrum of the host-guest G1PG-CD-Nimodipine complex in $CHCl_3$.



d. **Fig. S29** Overlay of UV-vis spectrum of the host-guest G1PG-CD-Nile red complex in $CHCl_3$.

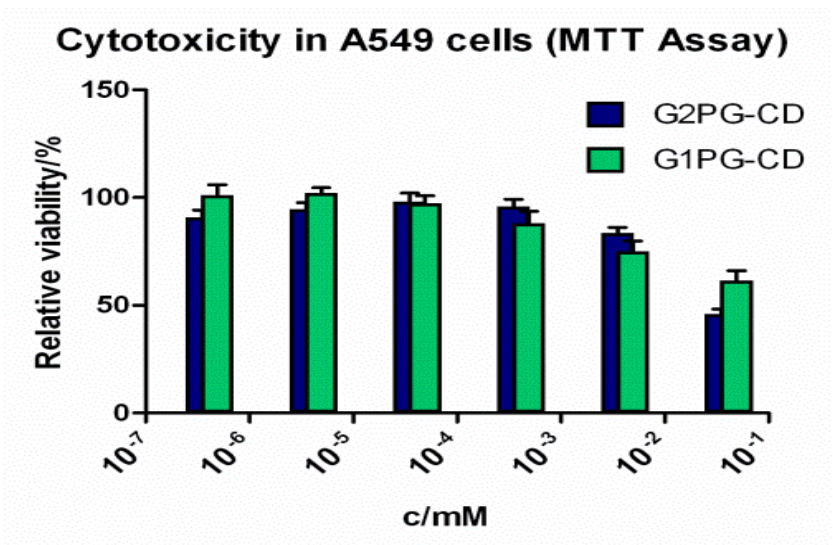


e. **Fig. S30** Overlay of UV-vis spectrum of the host-guest G2PG-CD-Nile red complex in $CHCl_3$



7. MTT assay for cyclodextrin-polyglycerol (CD-PG) amphiphilic dendrimers incubated with A549 cells**.**

Fig. 31 MTT assay for the evaluation of cytotoxicity of G1PG-CD & G2PG-CD



8. Determination of CMC of G1PG-CD by using DPH as a probe and different concentrations of amphiphile.

Fluorescence emission spectra were recorded with a Jasco FP-6500 spectrofluorimeter equipped with a thermostatted cell holder, a DC-powered 150 W xenon lamp, a Hamamatsu R928 photomultiplier, and a variable slit system. Both excitation and emission slits were set at 5 nm. In the present study, diphenyl-1,3,5-hexatriene (DPH) was used as a hydrophobic probe to determine the critical micelle concentrations (CMCs) of **G1PG-CD** in water solution. Fluorescence of DPH was recorded from 360 to 600 nm after excitation at 345 nm. In order to determine the CMCs, the fluorescence intensity of the most intensive peak at 430 nm was plotted against the amphiphile concentration. Independent linear regressions were performed on the data points above and below the putative CMC.

Prior to measurements, DPH stock solution of 0.5 µM in water was freshly prepared by dissolving the probe in acetonitrile. Different volumes of G1PG-CD solution in water were then added to DPH (0.5 µM) from a stock solution and fluorescence emission spectra were measured at different amphiphile concentrations. To ensure proper mixing and dissolution of the compounds all samples were stirred thoroughly by using a laboratory vortex shaker. The samples were then incubated for at least 12 h at room temperature. All measurements were carried out at 22 ± 2 °C and taken in triplicate and averaged. Data analysis was performed using SigmaPlot 8.0 software.

Fig. S32 Fluorescence spectra of DPH in the presence of different concentrations of G1PG-CD.