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Supporting Information of:

Tuning Glyconanomaterial Shape and Size for Selective Bacterial Cell Agglutination

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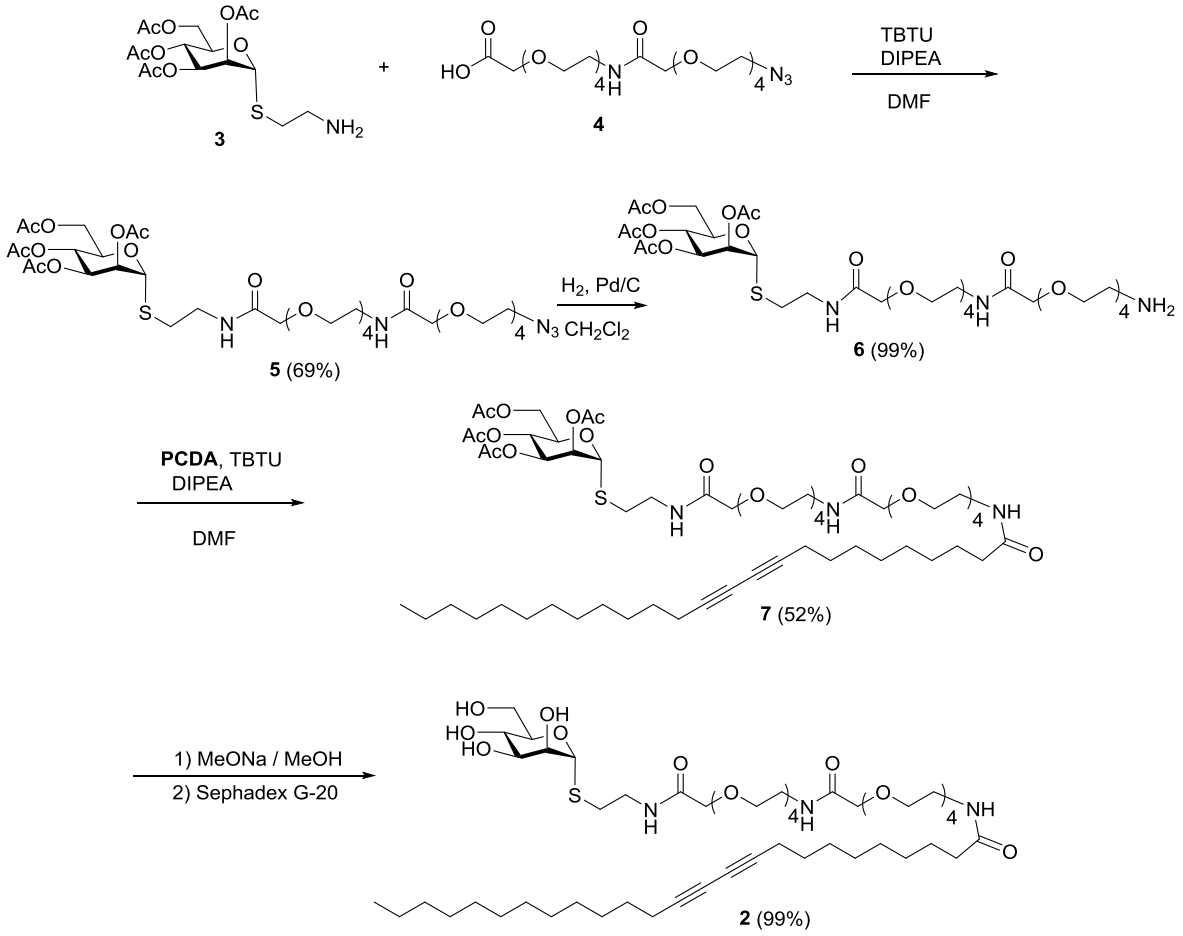
General methods.

Chemicals employed all over this work were purchased from Sigma Aldrich Chemical Co. Dry solvents were purchased from SDS in *HPLCs grade* and in addition dried in a solvent purification system (Pure Solv MD5, Innovative Technology)**.** The monitoring of the reactions was carried out by TLC, employing aluminum sheets coated with silica gel 60 F_{254} (normal phase) purchased from Merck, with detection by charring with phosphomolybdic acid/EtOH and sulphuric acid/EtOH. For flash chromatography, silica Gel (Merck 230-400 mesh) was used. The organic extracts were dried over anhydrous sodium sulfate and concentrated under vacuum. Columns were eluted with positive air pressure. Chromatographic eluents are given as volume to volume ratios (v/v). NMR spectra were recorded with a BRUKER AC-500 apparatus. Deuterated solvents are indicated in brackets. Chemical shift values (δ) are referred to tetramethylsilane (TMS), utilized as internal reference; then, the spectral signals were calibrated according to the non-deuterated residual peak of the solvent. Optical rotations $[\alpha]^{20}_{D}$ were determined with a Perkin-Elmer 341 polarimeter using a sodium lamp (λ = 589 nm) with a 10 cm cell length. UV/Vis spectra were recorded on a UV/vis Perkin Elmer Lambda 12, using quartz cuvettes. HR-MS were recorded on a Kratos MS-80RFA 241-MC apparatus. Transmission Electron Microscopy (TEM) images were taken by Philips CM 10 or CM 200 apparatuses with an accelerating voltage of 80 kV or 200 kV, respectively. Typically, a very small volume of the aqueous solutions (20 μL) was deposited over carbon-coated copper grids and uranyl acetate 2% as the negative stain. High resolution transmission electron microscopy (HRTEM) images were taken by a JEOL JEM-2200FS microscope, equipped with a field emission gun working at an accelerating voltage of 200 kV, a CEOS spherical aberration corrector and an Omega filter. Scanning electron microscopy (SEM) images were obtained on a JEOL JSM-5400 aparatus. Samples were prepared by depositing 15 μl of the suspension onto grids, allowing the grids to absorb for 2 minutes. Atomic force microscopy (AFM) images were taken by working on a tapping mode by a Pico Plus Molecular Imaging followed by a treatment with the WSxM 5.0 Develop 2.0 software. First, AFM samples were prepared by evaporation of the aqueous solutions previously deposited on a just exfoliated mica substrate (5 × 5 mm^2). Small angle X-ray scattering (SAXS) was performed on a *PANalytical X'Pert PRO*

Synthesis and characterization of neoglycolipid 2

The synthesis of compound **2** has been done starting from (2-aminoetil) 2,3,4,6-tetra-*O*-acetil-α-D-tiomanopyranoside **3**, and the new bi-functional spacer **4** following the method described in scheme S1, used for the synthesis of similar compounds.



Scheme S1

32-Azido-4,19-dioxo-6,9,12,15,21,24,27,30-octaoxa-3,18-diazadotriacontyl] 2,3,4,6-tetra-*O*-acetyl-α-D-thiomanopyranoside (5)

To a solution of the bifunctional spacer **4** (204 mg, 0.40 mmol) in DMF (2 mL) was added, sequentially at room temperature, TBTU (128 mg, 0.40 mmol) and DIPEA (98 µL, 0.4 mmol). The solution was stirred for 10 min before a solution of compound **3** (145 mg, 0.36 mmol) and DIPEA (98 µL, 0.4 mmol) in DMF (2 mL) was added slowly. The solution was stirred for 2 h before the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 (150 mL) and washed with 1M HCl (20 mL), saturated aqueous $NaHCO_3$ (60 mL) and brine (40 mL). After drying over Na_2SO_4 and removal of solvent, the crude product was purified by silica gel chromatography eluting with CH_2Cl_2/MeOH 20:1 to give 220mg (69%) of compound **5** as a yellowish oil.

5. R_f: 0.30 (CH_2Cl_2/MeOH 15:1). $[\alpha]^{20}_D$: +52.5 (c 0. 5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (t, 1H, J = 7.3 Hz, NHCO), 7.15 (sa, 1H, NHCO), 5.33-5.27 (m, 3H, H-1, H-4, H-2), 5.22 (dd, 1H, $J_{3,4}$ = 10.1 Hz, $J_{3,2}$ = 3.3 Hz, H-3), 4.38-4.34 (m, 1H, H-5), 4.29 (dd, 1H, $J_{6a,6b}$ = 12.4 Hz, $J_{6a,5}$ = 5.6 Hz, H-6a), 4.09 (dd, 1H, $J_{6b,6a}$ = 12.2 Hz, $J_{6b,5}$ = 2.2 Hz, H-6b), 3.98 (s, 4H, 2$COCH_2O$), 3.70-3.45 (m, 32H, 14CH_2O, 2C$\underline{H_2}$NH), 3.37 (t, 2H, J = 5.2 Hz, CH_2N_3), 2.86-2.73 (m, 2H, SCH_2), 2.15 (s, 3H, CH_3COO), 2.08 (s, 3H, CH_3COO), 2.04 (s, 3H, CH_3COO), 1.97 (s, 3H, CH_3COO). ^{13}C RNMR (125.7 MHz,$CDCl_3$): δ 170.6 (CO), 170.1 (CO), 170.0 (CO), 169.9 (CO), 169.8 (CO), 169.7 (CO), 82.5 (C1), 71.0, 70.9, 70.7 (C4), 70.6, 70.5, 70.4, 70.3, 70.2, 70.0, 69.8, 69.4 (C3), 69.1 (C5), 66.2 (C2), 62.4 (C6), 50.7 (CN_3), 38.6 (CH_2NH), 38.1 (CH_2NH), 31.1 (SCH_2), 20.9 (CH_3), 20.7 (CH_3), 20.6 (CH_3). HRMS (ESI, m/z): $[M + Na]^+$ calcd. for $C_{36}H_{61}N_5O_{19}SNa$ 922.3579 $[M+Na]^+$, found 922.3594.

[32-Amino-4,19-dioxo-6,9,12,15,21,24,27,30-octaoxa-3,18-diazadotriacontyl] 2,3,4,6-tetra-*O*-acetyl-α-D-thiomanopyranoside (6).

To a solution of compound **5** (120 mg, 0.13 mmol) in CH_2Cl_2 (5 mL), in a Fisher-Porter, was added Pd/C (0.1 eq). The recipient was tightly sealed and stirred overnight under a positive H_2 pressure (4 bars). Subsequently, the mixture was filtered through a plug of celite® and the filtrate evaporated in vacuum. The compound was isolated from the crude by flash column chromatography, using CH_2Cl_2/MeOH (9:1) as eluent, to give compound **6** (112 mg, 96%) as a yellowish oil.

6. R_f: 0.20 (CH_2Cl_2/MeOH 9:1). $[\alpha]^{20}_D$: +52.3 (c 0.8, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (t, 1H, *J* = 5.9, NHCO), 7.44 (sa, 1H, NHCO), 5.27-5.22 (m, 3H, H-1, H-4, H-2), 5.16 (dd, 1H, $J_{3,4}$ = 10.1 Hz, $J_{3,2}$ = 2.8 Hz, H-3), 4.32-4.31 (m, 1H, H-5), 4.25 (dd, 1H, $J_{6a,6b}$ = 12.0 Hz, $J_{6a,5}$ = 5.5 Hz, H-6a), 4.05 (d, 1H, *J* = 12.7 Hz, H-6b), 3.99 (s, 2H, $COCH_2O$), 3.96 (s, 2H, $COCH_2O$), 3.83-3.39 (m, 34H, $14CH_2O$, $2C\underline{H_2}NH$, $C\underline{H_2}NH_2$), 3.01 (sa, 2H, NH_2), 2.82-2.72 (m, 2H, SCH_2), 2.11 (s, 3H, CH_3COO), 2.03 (s, 3H, CH_3COO), 2.00 (s, 3H, CH_3COO), 1.93 (s, 3H, CH_3COO). ^{13}C NMR (125.7 MHz,$CDCl_3$): δ 170.6 (CO), 170.3 (CO), 169.9 (CO), 169.8 (CO), 169.7 (CO), 157.5 (CO), 82.4 (C1), 70.8 (C4), 70.7, 70.3, 70.2, 70.1, 70.0, 69.8, 69.5, 69.4 (C3), 69.1 (C5), 66.2 (C2), 62.4 (C6), 41.8 (CNH_2), 38.6 (CH_2NH), 38.1 (CH_2NH), 30.9 (SCH_2), 20.8 (CH_3), 20.6 ($2CH_3$). HRMS (ESI, m/z): $[M + Na]^+$ calcd. for $C_{36}H_{63}N_3O_{19}SNa$ 896.3674 $[M+Na]^+$, found 896.3650.

(4,16,34-Trioxo-6,9,12,15,21,24,27,30-octaoxa-3,18,33-triaza-43,45-octapentacontadiinyl) 2,3,4,6-tetra-*O*-acetyl-α-D-thiomanopyranoside (7).

TBTU (42 mg, 0.20 mmol) and DIPEA (22 μL, 0.13 mmol) were added sequentially at room temperature and under an argon atmosphere to a solution of 10,12-pentacosadiyonic acid (**PCDA,** 62 mg, 0.17 mmol) in dry DMF (1 mL). The resulting solution was stirred for 5 min. and then, a solution of compound **6** (120 mg, 0.14 mmol) and DIPEA (43 μL, 0.25 mmol) in dry DMF (1 mL) was added slowly. The afforded mixture was stirred for 14 h. under an argon atmosphere before the solvent was removed under vacuum. The obtained residue was dissolved in CH_2Cl_2 (100 mL), washed with a 1 M HCl solution (20 mL) and neutralized with a saturated aqueous $NaHCO_3$ (30 mL), and finally with brine (20 mL). After drying over Na_2SO_4 and removal of solvent, the crude product was subjected to a chromatographic column with CH_2Cl_2/MeOH (20:1), affording compound **6** (90 mg, 52%) as a yellowish oil

7. R_f: 0.34 (CH_2Cl_2/MeOH 20:1). $[\alpha]^{20}_D$: +36.0 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (t, 1H, *J* = 6.3 Hz, NHCO), 7.16 (sa, 1H, NHCO), 6.30 (sa, 1H, NHCO), 5.32-5.27 (m, 3H, H-1, H-4, H-2), 5.22 (dd, 1H, $J_{3,4}$ = 9.5 Hz, $J_{3,2}$ = 3.1 Hz, H-3), 4.40-4.33 (m, 1H, H-5), 4.30 (dd, 1H, $J_{6a,6b}$ = 12.2 Hz, $J_{6a,5}$ = 5.5 Hz, H-6a), 4.10 (d, 1H, *J* = 12.4 Hz, H-6b), 4.00 (s, 2H, $COCH_2O$), 3.98 (s, 2H, $COCH_2O$), 3.73-3.42 (m, 34H, $14CH_2O$, $3C\underline{H_2}NH$), 2.84-2.75 (m, 2H, SCH_2), 2.22 (t, 4H, *J* = 7.1 Hz, 2 $C\underline{H_2}C{\equiv}C$), 2.15 (t, 5H, *J* =

7.14 Hz, COC$\underline{H_2}$CH$_2$, CH$_3$COO), 2.08 (s, 3H, CH$_3$COO), 2.04 (s, 3H, CH$_3$COO), 1.97 (s, 3H, CH$_3$COO), 1.64-1.56 (m, 2H, COCH$_2$C$\underline{H_2}$), 1.53-1.45 (m, 4H, 2 C$\underline{H_2}$CH$_2$C≡C), 1.39-1.21 (m, 26H, 13 CH$_2$), 0.86 (t, 3H, *J* = 6.8 Hz, C$\underline{H_3}$CH$_2$). ^{13}C NMR (125.7 MHz,CDCl$_3$): δ 173.2 (CO), 170.6 (CO), 170.1 (CO), 170.0 (CO), 169.9 (CO), 169.8 (CO), 169.7 (CO), 82.5 (C1), 77.6 (CH$_2$C≡$\underline{C}$), 77.4 (CH$_2$C≡$\underline{C}$), 71.0, 70.9, 70.8, 70.6, 70.5, 70.4, 70.3, 70.2, 70.0, 69.8, 69.4 (C3), 69.2 (C5), 66.2 (C2), 65.3 (CH$_2$C≡$\underline{C}$), 65.2 (CH$_2$C≡$\underline{C}$), 62.4 (C6), 39.1 (CH$_2$NH), 38.6 (CH$_2$NH), 38.1 (SCH$_2$$\underline{C}H_2$), 36.6 (NHCO$\underline{C}H_2CH_2$), 31.9 ($\underline{C}H_2CH_2CH_3$), 31.1 (SCH$_2$), 29.6, 29.4, 29.3, 29.2, 29.1, 28.9, 28.8, 28.3, 25.7 (COCH$_2$$\underline{C}H_2CH_2$), 22.7 ($\underline{C}H_2CH_3$), 20.9 (CH$_3$), 20.7 (CH$_3$), 20.6 (CH$_3$), 19.2 (2 $\underline{C}$H$_2$C≡C), 14.1 ($\underline{C}$H$_3$CH$_2$). HRMS (ESI, m/z): [M + Na]$^+$ calcd. For $C_{61}H_{103}N_3O_{20}SNa$ 1252.6726 [M+Na]$^+$, found 1252.6753.

(4,16,34-Trioxo-6,9,12,15,21,24,27,30-octaoxa-3,18,33-triaza-43,45 octapentacontadiinyl) α-D-thiomanopyranoside (2).

To a solution of compound **7** (90 mg, 0.07 mmol) in dry methanol (2 mL) was added NaOMe solution 1M (100 µL, 0.1 mmol). The reaction was allowed to proceed at rt in the dark for 1 h at which time the reaction was judged complete by TLC analysis. The solution was neutralized with Amberlyst Ir-120 (plus) resin. The resin was removed by filtration and the solvent removed under vacuum. The crude product was purified by size-exclusion chromatography (sephadex G20) eluting with methanol. Lyophilization of the solvent gave the desired compound **2** with a 99% of yield (75 mg).

2. R$_f$: 0.13 (CH$_2$Cl$_2$/MeOH 9:1). [α]$^{20}_D$: +39.5 (c 1.0, MeOH). ^{1}H NMR (500 MHz, MeOD): δ 7.55 (t, 1H, *J* = 5.5 Hz, NHCO), 6.34 (t, 1H, *J* = 5.8 Hz, NHCO), 5.36 (s, 1H, H-1), 4.02 (s, 2H, COCH$_2$O), 4.00 (s, 2H, COCH$_2$O), 3.94-3.78 (m, 5H, H-4, H-2, H-3, H-5, H-6a), 3.76-3.40 (m, 35H, H-6b, 14 CH$_2$O ,3C$\underline{H_2}$NH), 2.87-2.65 (m, 2H, SCH$_2$), 2.23 (t, 4H, *J* = 7.1 Hz, 2 C$\underline{H_2}$C≡C), 2.17 (t, 2H, *J* = 7.4 Hz, COC$\underline{H_2}$CH$_2$), 1.65-1.57 (m, 2H, COCH$_2$C$\underline{H_2}$), 1.55-1.46 (m, 4H, 2 C$\underline{H_2}$CH$_2$C≡C), 1.41-1.22 (m, 26H, 13 CH$_2$), 0.88 (t, 3H, *J* = 6.6 Hz, CH$_3$). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ 173.5 (CO), 170.6 (CO), 170.4 (CO), 85.1 (C1), 77.6 (CH$_2$C≡$\underline{C}$), 77.4 (CH$_2$C≡$\underline{C}$), 73.3 (C4), 72.3 (C3), 72.1 (C5), 70.9, 70.8,

70.5, 70.4, 70.3, 70.2, 70.1, 70.0, 69.7, 67.4 (C2), 65.3 ($CH_2C{\equiv}\underline{C}$), 65.2 ($CH_2C{\equiv}\underline{C}$), 61.5 (C6), 42.1 ($CH_2NH$), 39.2 ($CH_2NH$), 38.7 ($CH_2NH$), 36.6 ($NHCO\underline{C}H_2CH_2$), 31.9 ($\underline{C}H_2CH_2CH_3$), 30.8 ($SCH_2$), 29.6, 29.5, 29.3, 29.2, 29.1, 29.0, 28.9, 28.8, 28.4, 28.3, 23.5 ($COCH_2\underline{C}H_2$), 22.7 ($\underline{C}H_2CH_3$), 19.2 (2 $\underline{C}H_2C{\equiv}C$), 14.1 ($\underline{C}H_3CH_2$). HRMS (ESI, m/z): $[M + Na]^+$ calcd. For $C_{53}H_{94}N_3O_{16}SNa$ 1083.6253 $[M+Na]^+$, encontrado 1083.6238

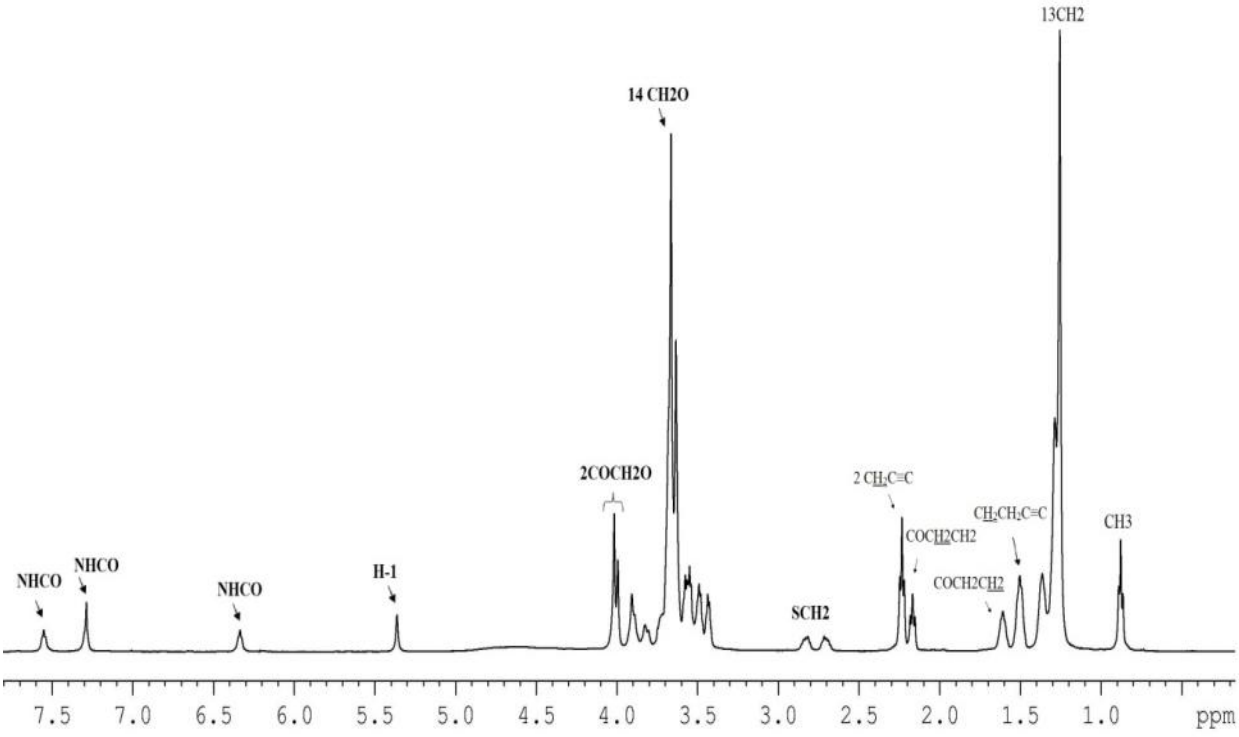


Figure S1: Assigned ^{1}HNMR spectrum of compound **2**

Fluorescence CMC Determination.

The CMC of micelles were determined using pyrene as an extrinsic fluorescence probe. The pyrene concentration was maintained constant (0.6 10^{-6}M in THF), and the concentration of **2** was varied from 1 x 10^{-3} M to 0.5 x 10^{-6}. Fluorescence measurements were carried out at 25 ºC using a Varian Cary Eclipse spectrofluorometer. At the fixed excitation wavelength of 334 nm, the emission spectras were scanned from 300 to 350 nm. The fluorescence intensity ratios of pyrene at 339 and 335 nm (I339/I335, I1/I3) were calculated and plotted against the concentration logarithm of the neoglycolipid **2.** The CMC value was determined from the intersection of the two tangent lines, Figure S2.

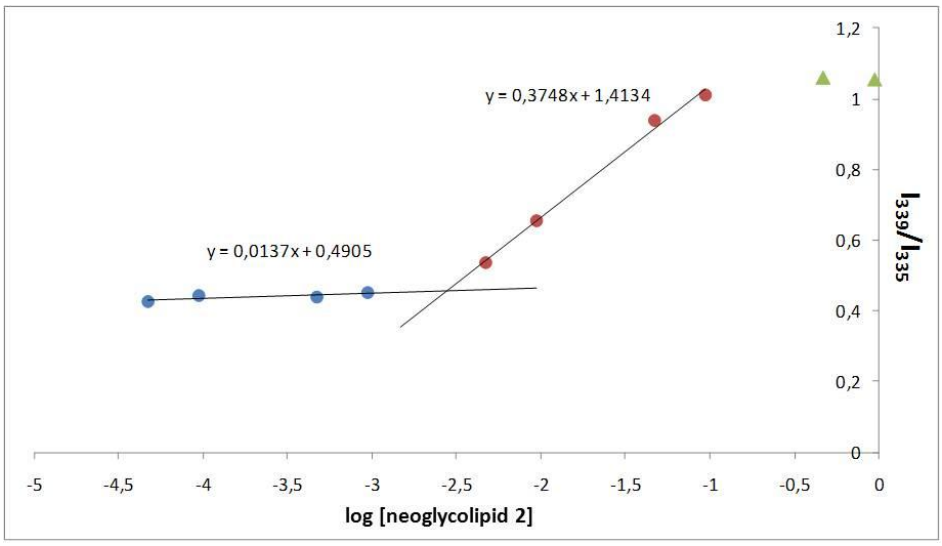
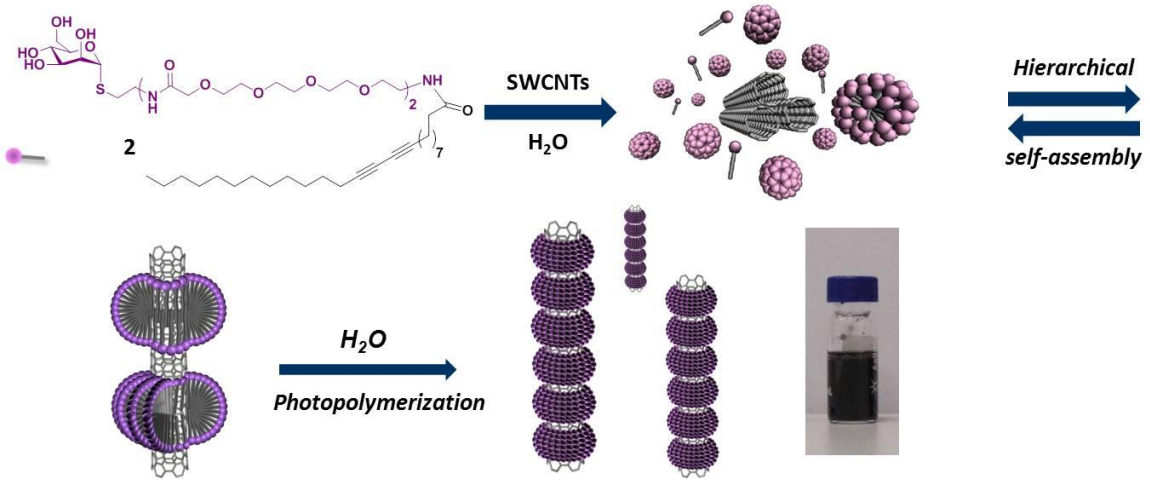


Figure S2. Fluorescence intensity ratios of pyrene excitation bands (I339 nm / I335 nm) as a function of the concentration of logarithm of neoglycolipid **2**. The inflection points of the curves were taken as the critical micelle concentrations (CMC).

Synthesis and characterization of NP3



Scheme S2: Synthesis of **NP3** by hierarchical self-assembly of neoglycolipid **2** on the carbon nanotube sidewalls followed by photopolymerization. Photograph of the vial showing the high dispersability of NP3 in water

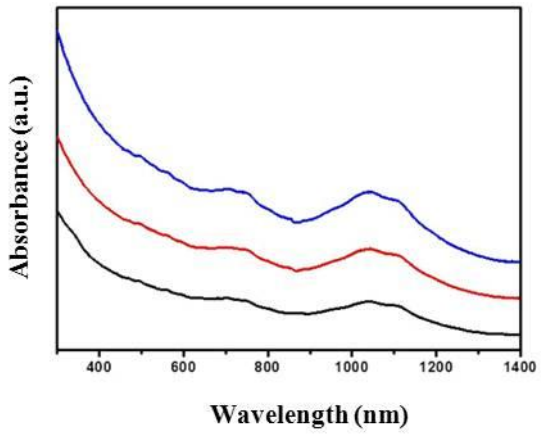


Figure S3: UV-Vis-NIR spectra of unfunctionalized SWCNT (black line), SWCNT-**1** (blue line) and **NP3** (red line).

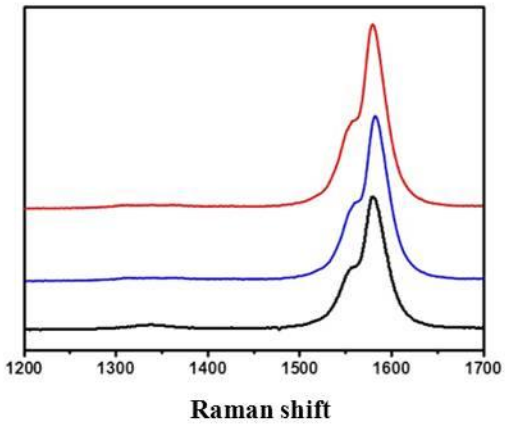


Figure S4: Raman spectra of unfunctionalized SWCNT (black line), SWCNT-**1** (blue line) and **NP3** (red line).

Determination of mannose quantity in NP3.

A)- Anthrone method.

A freshly prepared solution of anthrone (0.5 % w/v in concentrated H_2SO_4, 1 mL) was added to various solutions of D-mannose of known concentration (0.5 mL) under stirring in a water-bath. The mixtures were heated to 90ºC for 12 min and the resulting green bluish solutions were rapidly cooled down in an ice bath during further 10 min. Next, the absorbance of the solutions were measured at 620 nm and the data were plotted against D-mannose concentrations, obtaining the calibration curve, Figure S2.

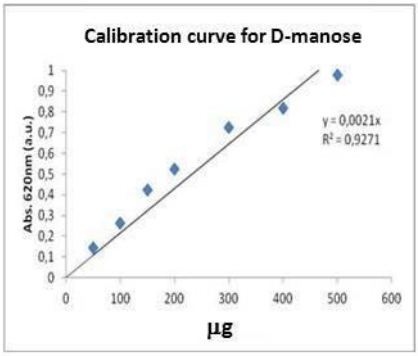


Figure S5: D-mannose calibration curve.

To calculate the quantity of mannose the nanoparticle, 1.15 mg of **NP3** were dissolved in 0.5 mL Milli-Q water, and then a freshly prepared solution of anthrone was added, following the same procedure described above.

B)- Thermogravimetric Analysis (TGA)

The spectra of the TGA, Figure S3, were recorded on a on TA intruments TGA Q600 thermal analyzer, between 25-600°C (under a stream of N_2 at a heating rate of 20°C / min).

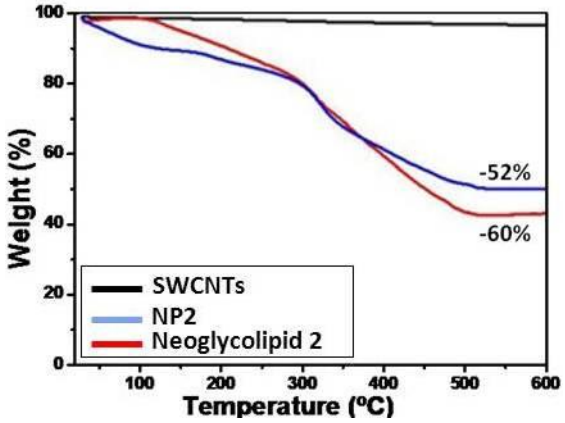


Figure S6: Thermogravimetric analysis of SWCNT (black line), **NP3** (blue line), and neoglycolipid **2** (red line).

Additional images for selective interaction of NP3 with Selective interaction of NP3 with *E.coli* strain ORN178.

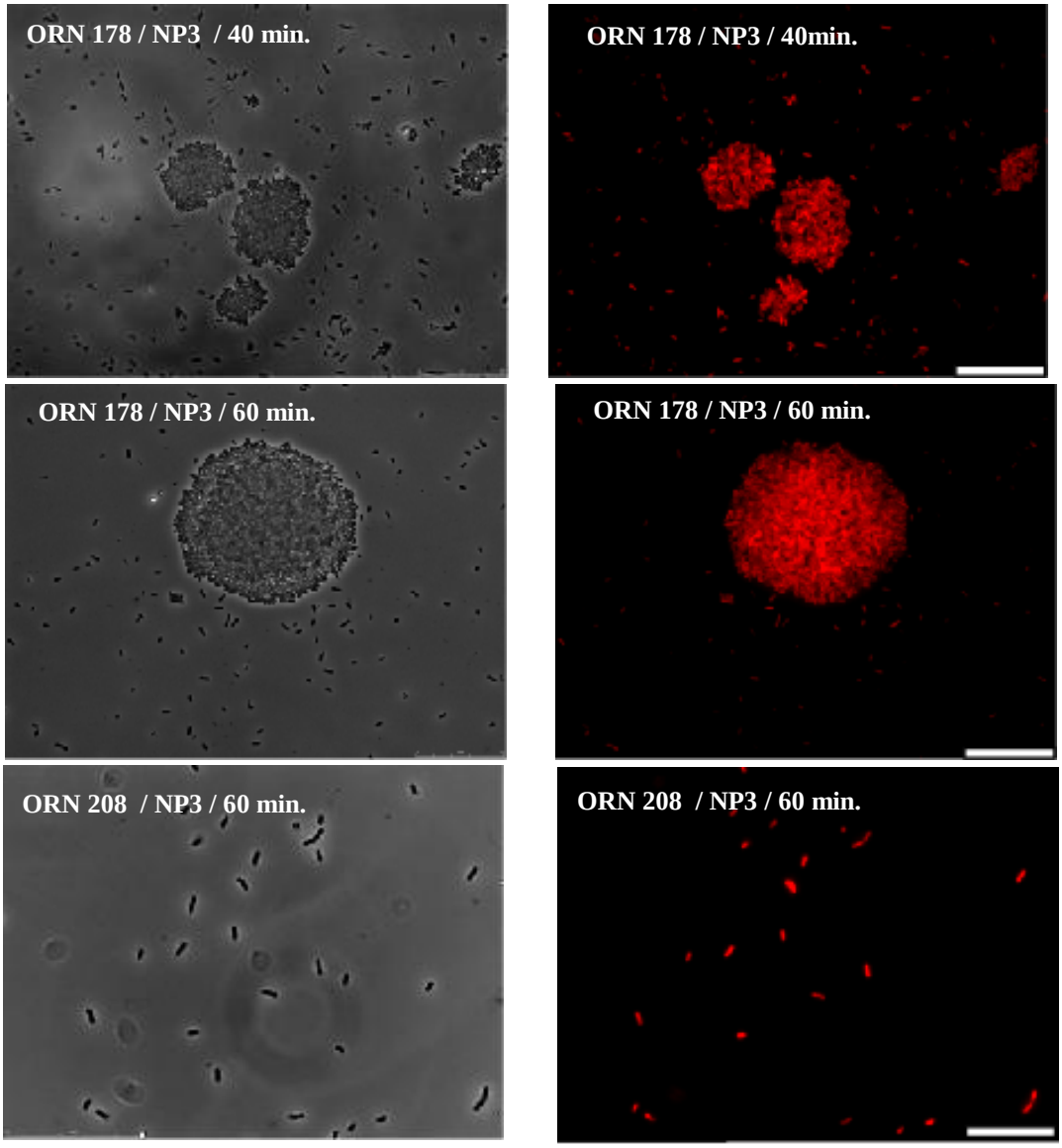


Figure S7. Representative phase contrast and fluorescence microscopy images of *E.coli* strains ORN178 and ORN 208 with **NP3** at different incubation times (Scale bars, 10µm).

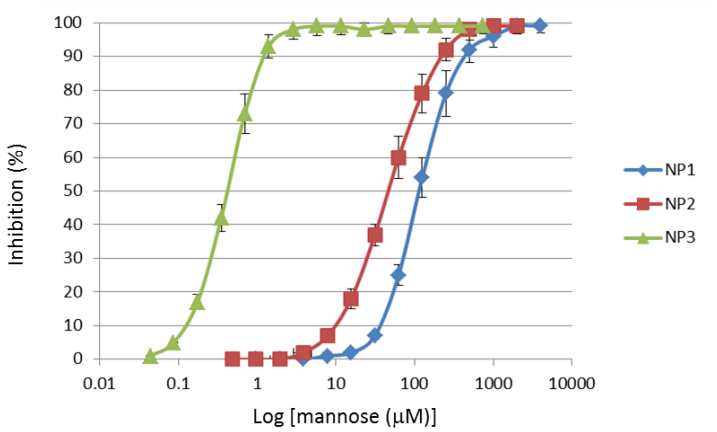
ELLA Raw Data

NP1		
conc. (μM)	Inh. (%)	SD (n = 3)
4000	99	2
2000	99	2.2
1000	96	3.2
500	92	3.9
250	79	6.8
125	54	5.9
62.5	25	3.1
31.25	7	1.1
15.62	2	0.3
7.81	1	0.2
3.9	0	0
1.95	0	0
0.97	0	0

NP2		
conc. (μM)	Inh. (%)	SD (n = 3)
2000	99	1.7
1000	99	2.1
500	98	3.2
250	92	3.3
125	79	5.8
62.5	60	6.2
31.25	37	3.2
15.62	18	3
7.81	7	0.8
3.9	2	0.2
1.95	0	0
0.97	0	0
0.48	0	0

NP3		
conc. (μM)	Inh. (%)	SD (n = 3)
2000	99	2.2
1000	99	2.1
500	99	1.5
250	99	2
125	99	2.2
62.5	98	1.9
31.25	99	2.7
15.6	99	2.9
7.81	98	3
3.9	93	3.5
1.95	73	5.9
0.97	42	4.1
0.48	17	2.2
0.24	5	0.2
0.12	1	0.1

Micelles formulated with lactose glycolipid 1 (negative control)		
conc. (μM)	Inh. (%)	SD (n = 3)
4000	4	1.6
2000	5	1.7
1000	3	1.4
500	4	1.5
250	4	1.5
125	2	0.8
62.5	2	1
31.25	3	1.3
15.62	1	0.5
7.81	0	0
3.9	0	0
1.95	0	0
0.97	0	0


Inhibition (%)
100
90
80
70
60
50
40
30
20
10
0
0.01
0.1
1
10
100
1000
10000
Log [mannose (μM)]
NP1
NP2
NP3