Electronic Supporting Information of the paper: Tailoring Carbon Nanotube Surface with Glycanorings: New Bionanomaterials with Specific Lectin Affinity

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General Methods.

All reactions were run under an atmosphere of dry argon using oven-dried glassware and freshly distilled and dried solvents. THF and diethyl ether were distilled from sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride. TLC was performed on Silica Gel GF254 (Merck) with detection by charring with phosphomolybdic acid/EtOH and sulphuric acid/EtOH. Reagents were obtained from commercial suppliers and used without further purification. For flash chromatography, silica Gel (Merck 230-400 mesh) was used. 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 AMX500 (1H, 500 MHz) and Bruker Avance DRX500 (1H, 500 MHz) spectrometers. Chemical shifts are reported in ppm, and coupling constants are reported in Hz. Routine spectra were referenced to the residual proton or carbon signals of the solvent. High-resolution mass spectra were recorded on a Kratos MS-80RFA 241-MC apparatus. Optical rotations were determined with a Perkin-Elmer 341 polarimeter. Elemental analyses were recorded on a leco CHNS-932 apparatus. The organic extracts were dried over anhydrous sodium sulfate and concentrated under vacuum.

A) Synthesis of the neoglycolipids used in this study

The synthesis of (2'-ethylamino) per-O-acetylated-1-thio-glycosides 1, 2 and 3 was done in a one step manner from the corresponding peracetylated sugars and will be reported in due course. The 10,12-Pentacosadiynoic acid 4 was purchased from Aldrich and used as received. The hydrophilic spacers 5 and 6 were obtained from tetraethylene glycol in three steps using the scheme A. The photopolymerizable glycolipids Lac-8 and Cellob-9 were obtained according to scheme B, while photopolymerizable glycolipid Man-11 with a more hydrophilic spacer was obtained according to scheme C.

![Scheme A](image-url)
Scheme B

Lac-8a: X = OAc, Y = H
Cellob-9a: X = H, Y = OAc

Lac-8c: X = OAc, Y = H
Cellob-9c: X = H, Y = OAc

Scheme C

Man-11a

Man-11c

Man-11
Synthesis of the spacer 5 (See scheme A),

To a solution of tetraethylene glycol (22.7 mL, 140 mmol), Et₃N (15 mL) and THF (100 mL) was cooled to 0°C. To this was added dropwise methanesulfonyl chloride solution (10.8 mL, 140 mmol). The reaction mixture was then allowed to warm to room temperature and stirred vigorously overnight. The solution was diluted with CH₂Cl₂ (250 mL) and washed with saturated NH₄Cl (50 mL) and brine (20 mL). The organic solution was dried over Na₂SO₄ and concentrated in vacuum to give the crude product. The oily residue was purified by flash column chromatography, eluting with dichloromethane/methanol (20:1) to give 12.9 g of the mesylated compound 5a as an oil (37% yield): Rf = 0.5 in dichloromethane/methanol (9:1); ¹H NMR (400 MHz, CDCl₃) δ: 4.41- 4.35 (m, 2H), 3.81-3.60 (m, 14H), 3.09 (s, 3H), 2.97 (s, 1H); ¹³C NMR (100.6 MHz, CDCl₃) δ: 72.5, 70.4, 70.3, 70.1, 69.4, 69.3, 69.0, 61.6, 37.6; HRMS (FAB) calcd. for C₉H₂₀O₇SNa [M+Na]+: m/z 273.1008. Found: 273.0997.

To a mixture of mesylated compound 5a (9.1 g, 33.4 mmol) and sodium azide (2.4 g, 36.8 mmol) in ethanol (50 mL) was heated at reflux overnight, cooled to room temperature and concentrated in vacuo. The residue was diluted with ether (250 mL), washed with brine (50 mL), and dried over Na₂SO₄. Solvent was removed under vacuum to yield the crude product, which was purified by flash column chromatography, eluting with a gradient of hexane/ethyl acetate (1:1) to give 6.4 g of the azide 5b as an oil (97% yield): Rf = 0.18 in hexane/ethyl acetate (1:1); ¹H NMR (500 MHz, CDCl₃) δ: 3.58 (t, 2H, J = 4.8 Hz), 3.55-3.51 (m, 10H), 3.46 (t, 2H, J = 4.8 Hz), 3.26 (t, 2H, J = 4.8 Hz), 3.10 (brs, 1H); ¹³C NMR (125.7 MHz, CDCl₃) δ: 72.5, 70.6, 70.5, 70.4, 70.2, 69.9, 61.5, 50.5; HRMS (FAB) calcd for C₈H₁₇N₃O₄Na [M+Na]+: m/z 220.1297. Found: 220.1288.

To a solution of azido alcohol 5b (2.4 g, 10 mmol) in acetone (100 mL) was cooled to 0°C. To this was added freshly prepared Jones reagent (44 mL). The reaction mixture was then allowed to warm to room temperature and stirred vigorously overnight. To the orange suspension was added dropwise propan-2-ol until the green colour was observed, then the reaction mixture was filtered over Celite® to remove chromium (IV) oxide and concentrated in vacuum to give the crude product. The oil residue was purified by flash column chromatography, eluting with dichloromethane/methanol (9:1) to give 1.8 g of 5 as an oil (75% yield): Rf = 0.4 in dichloromethane/methanol (9:1); ¹H NMR (500 MHz, CDCl₃) δ: 9.30 (brs, 1H), 4.15 (s, 2H), 3.80-3.60 (m, 10H), 3.29 (t, 2H, J = 4.5 Hz); ¹³C NMR (125.7 MHz, CDCl₃) δ: 173.5, 70.9, 70.4, 70.3, 70.2, 69.9, 68.3, 50.5; HRMS (FAB) calcd for C₈H₁₅N₃O₅Na [M+Na]+: m/z 234.1089. Found: 234.1085.

Synthesis of the spacer 6 (See scheme A),

To a solution of azido alcohol 5b (4.7 g, 0.022 mol) in dichloromethane (30 mL) was added triphenylphosphine (6.2 g, 0.024 mol). The reaction mixture was stirred 12 h and aqueous ammonium hydroxide solution (30% v/v) was added. The reaction was
stirred for 1h at room temperature. Solvents were removed under vacuum and the 
resulting crude product purified by flash chromatography, eluting with 
CH$_3$CN/H$_2$O/NH$_4$OH (30:2:1) $\rightarrow$ (10:1:1) to give 3.44 g of amine 5c as an oil (81% 
yield): R$_f$ = 0.16 CH$_3$CN/H$_2$O/NH$_4$OH (10:1:1); $^1$H NMR (400 MHz, CDCl$_3$): δ 3.70 (t, 
2H, $J$ = 4.8 Hz), 3.65-3.60 (m, 10H), 3.56 (t, 2H, $J$ = 4.8 Hz), 3.50 (t, 2H, $J$ = 4.8 Hz), 
2.83 (s, 2H), 2.27 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 73.0, 70.6, 70.3, 70.2, 
69.9, 61.5, 41.5; HRMS (FAB) calcd for C$_8$H$_{20}$NO$_4$ [M+H]$^+$: m/z 194.139844. Found: 
194.139233.

To a solution of 5 (1.02 g, 4.4 mmol) in DMF (10 mL) was added sequentially at 
room temperature o-Benzotriazol-1-yl-N,N,N',N´-tetramethyluronium tetrafluoroborate 
(TBTU) (1.4 g, 4.4 mmol) and N,N-diisopropylethylamine (DIPEA) (0.8 mL, 6.7 
mmol). The solution was stirred for 5 min before a solution of amine 5c (840.8 mg, 4.4 
mmol) and DIPEA (0.8 mL, 6.7 mmol) in DMF (1 mL) was added slowly. The solution 
was stirred for 2 h before the solvent was removed under vacuum. The residue 
was dissolved in CH$_2$Cl$_2$ (100 mL) and washed with 1M HCl (20 mL), saturated aqueous 
NaHCO$_3$ (40 mL) and brine (20 mL). After drying over Na$_2$SO$_4$ and removal of solvent, 
the crude product was purified by column chromatography eluting with 
dichloromethane/methanol 9:1 to give 1.08 g of an oil 6a (60% yield): R$_f$ = 0.48 
(CH$_2$Cl$_2$/MeOH 9:1); $^1$H NMR (500 MHz, CDCl$_3$): δ 7.38 (brs, 1H), 4.70 (brs, 1H), 
3.90 (s, 2H), 3.70-3.60 (m, 24H), 3.50-3.48 (m, 2H), 3.39 (t, 2H, $J$ = 4.8 Hz); $^{13}$C 
NMR (125.7 MHz, CDCl$_3$): δ 170.2, 170.8, 70.8, 70.7, 70.6, 70.3, 70.2, 69.8, 69.6, 61.4, 50.5, 
38.6; HRMS (FAB) calcd for C$_{16}$H$_{33}$N$_4$O$_9$ [M+H]$^+$: m/z 409.2280. Found: 409.2298.

To a solution of azido alcohol 6a (1.08 g, 2.6 mmol) in acetone (50 mL) at 0ºC was 
added freshly prepared Jones reagent (11 mL). The reaction mixture was then allowed 
to warm to room temperature and stirred vigorously overnight. To the orange 
suspension was added dropwise i-propanol until a green colour was observed, then the 
reaction mixture was filtered over Celite® to remove chromium (IV) oxide and 
concentrated in vacuum to give the crude product. The oil residue was purified by flash 
column chromatography, eluting with dicholoromethane/methanol 9:1 to give 987 mg 
of 6 as an oil (90% yield): R$_f$ = 0.2 in dichloromethane/methanol (9:1); $^1$H NMR (500 MHz, CDCl$_3$): δ 6.6 (brs, 2H), 4.14 (s, 2H), 4.00 (s, 2H), 3.74-3.56 (m, 20H), 3.39 (t, 2H, $J$ = 4.8 Hz); $^{13}$C 
NMR (125.7 MHz, CDCl$_3$): δ 172.7, 170.8, 70.8, 70.7, 70.6, 70.3, 70.2, 70.1, 70.0, 69.9, 69.0, 50.9, 39.0; HRMS (FAB) calcd for 
C$_{16}$H$_{31}$N$_4$O$_9$ [M+H]$^+$: m/z 423.2113. Found: 423.2091.

Synthesis of compound Lac-8a

To a solution of 5 (68 mg, 0.29 mmol) in DMF (0.5 mL) were added, sequentially at room temperature, TBTU (93 mg, 0.29 mmol) and DIPEA (70 μL, 0.43 
mmol). The solution was stirred for 5 min before a solution of (2' ethylamino)-hepta-O- 
acetyl-1-thio-$^E$-D-lactoside 1 (223 mg, 0.29 mmol) and DIPEA (70 μL, 0.43 mmol) in 
DMF (1 mL) was added slowly. The solution was stirred for 2 h before the solvent was 
removed under vacuum. The residue was dissolved in CH$_2$Cl$_2$ (100 mL) and washed 
with 1M HCl (20 mL), saturated aqueous NaHCO$_3$ (40 mL) and brine (20 mL). After
drying over Na$_2$SO$_4$ and removal of solvent, the crude product was purified by silica gel chromatography eluting with dichloromethane/methanol 20:1 to give 225 mg of a yellow oil **Lac-8a** (85% yield): \(R_f = 0.21\) (CH$_2$Cl$_2$/MeOH 20:1); \([\alpha]_D = -7.66\) (c 0.85, CHCl$_3$); \(^1\)H (500 MHz, CDC$_3$)$_3$: \(\delta = 7.25\) (t, 1H, \(J = 1.1\) Hz), 5.33 (d, 1H, \(J = 2.4\) Hz), 5.18 (t, 1H, \(J = 9.5\) Hz), 5.08 (dd, 1H, J = 10.0 Hz, \(J = 8.0\) Hz), 4.95-4.90 (m, 2H), 4.52-4.46 (m, 3H), 4.13-4.05 (m, 3H), 3.98 (s, 2H), 3.87-3.84 (m, 1H), 3.77 (t, 1H, \(J = 9.5\) Hz), 3.69-3.61 (m, 11H), 3.54-3.44 (m, 2H), 3.38 (t, 2H, \(J = 9.4\) Hz), 2.89-2.69 (m, 2H), 2.13 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.94 (s, 3H); \(^13\)C NMR (125.7 MHz, CDCl$_3$): \(\delta = 170.3, 170.1, 170.0, 169.6\) (2C), 169.0, 101.1, 83.7, 77.0, 76.8, 73.9, 71.0, 70.7, 70.6, 70.5, 70.4, 70.2, 70.0, 69.1, 66.6, 62.1, 60.8, 50.6, 38.9, 30.3, 20.8, 20.7, 20.6; HRMS (FAB) calcd for C$_{36}$H$_{54}$N$_4$O$_{21}$SNa [M+Na]$^+$: m/z 933.2898. Found: 933.2911.

**Synthesis of compound Cellob-9a**

![Chemical structure of Cellob-9a](image)

To a solution of **5** (102 mg, 0.44 mmol) in DMF (1.0 mL) were added, sequentially at room temperature, TBTU (140 mg, 0.44 mmol) and DIPEA (105 \(\mu\)L, 0.64 mmol). The solution was stirred for 5 min before a solution of (2’ ethylamino)-hepta-O-acetyl-1-thio-D-cellobioside **2** (334 mg, 0.44 mmol) and DIPEA (105 \(\mu\)L, 0.64 mmol) in DMF (1.0 mL) was added slowly. The solution was stirred for 2 h before the solvent was removed under vacuum. The residue was dissolved in CH$_2$Cl$_2$ (100 mL) and washed with 1M HCl (20 mL), saturated aqueous NaHCO$_3$ (40 mL) and brine (20 mL). After drying over Na$_2$SO$_4$ and removal of solvent, the crude product was purified by silica gel chromatography eluting with dichloromethane/methanol 20:1 to give 304 mg of a yellow oil **Cellob-9a** (76% yield): \(R_f = 0.2\) (CH$_2$Cl$_2$/MeOH 20:1); \([\alpha]_D = -2.4\) (c 0.96, CHCl$_3$); \(^1\)H NMR (500 MHz, CDCl$_3$): \(\delta = 7.23-7.21\) (m, 1H), 5.20-5.11 (m, 2H), 5.06 (t, 1H, \(J = 9.6\) Hz), 4.95-4.90 (m, 2H), 4.54-4.49 (m, 3H), 4.38 (dd, 1H, \(J = 12.4\) Hz, \(J = 4.3\) Hz), 4.09-4.02 (m, 2H), 3.98 (s, 2H), 3.78-3.61 (m, 13H), 3.55-3.37 (m, 4H), 2.90-2.70 (m, 2H), 2.11 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H); \(^13\)C NMR (125.7 MHz, CDCl$_3$): \(\delta = 170.4, 170.3, 170.1, 169.7, 169.6, 169.3, 169.1, 100.8, 83.7, 76.9, 76.4, 73.4, 72.9, 72.0, 71.6, 71.0, 70.7, 70.6, 70.2, 70.1, 68.9, 67.7, 67.2, 62.0, 61.5, 50.7, 38.9, 30.3, 20.8, 20.7, 20.6; HRMS (FAB) calcd for C$_{36}$H$_{54}$N$_4$O$_{21}$SNa [M+Na]$^+$: m/z 933.2898. Found: 933.2911.

**Synthesis of compound Man-11a**

![Chemical structure of Man-11a](image)

To a solution of **6** (685 mg, 1.70 mmol) in DMF (3.0 mL) were added, sequentially at room temperature, TBTU (540 mg, 1.70 mmol) and DIPEA (415 \(\mu\)L, 2.55 mmol). The
solution was stirred for 5 min before a solution of 3 (715 mg, 1.70 mmol) and DIPEA (415 μL, 2.55 mmol) in DMF (3.0 mL) was added slowly. The solution was stirred for 2 h before the solvent was removed under vacuum. The residue was dissolved in CH₂Cl₂ (100 mL) and washed with 1M HCl (20 mL), saturated aqueous NaHCO₃ (40 mL) and brine (20 mL). After drying over Na₂SO₄ and removal of solvent, the crude product was purified by silica gel chromatography eluting with dichloromethane/methanol 20:1 to give 726 mg of a yellow oil Man-11a (53% yield): R<sub>f</sub> = 0.18 (CH₂Cl₂/MeOH 9:1); [α]<sub>D</sub> = +57.2 (c 0.5, CHCl₃); <sup>1</sup>H NMR (500 MHz, CDCl₃): δ 7.27-7.26 (m, 1H), 7.16-7.15 (m, 1H), 5.32-5.26 (m, 3H), 5.21 (dd, 1H, J = 10.0 Hz, J = 3.2 Hz), 4.37-4.34 (m, 1H), 4.28 (dd, 1H, J = 12.2 Hz, J = 5.5 Hz), 4.09 (dd, 1H, J = 12.2 Hz, J = 1.7 Hz), 3.99 (s, 4H), 3.66-3.61 (m, 1H), 3.56-3.46 (m, 6H), 3.38 (t, 2H, J = 4.9 Hz), 2.84-2.74 (m, 2H), 2.14 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.96 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl₃): δ 170.6, 170.1, 170.0, 169.9, 169.8, 169.7, 82.5, 70.9 (2C), 70.8, 70.7, 70.6, 70.5 (2C), 70.4, 70.3, 70.2, 70.1, 69.8, 69.4, 69.1, 66.3, 62.4, 50.7, 38.6, 38.1, 31.1, 20.9, 20.7, 20.6; HRMS (FAB) calcd for C₃₂H₅₃N₅O₁₇SNa [M+Na]<sup>+</sup>: m/z 834.3054. Found: 834.3071.

Synthesis of compound Lac-8b

To a solution of Lac-8a (103 mg, 0.11 mmol) in dichloromethane (3.0 mL) was added triphenylphosphine (32 mg, 0.13 mmol). The reaction mixture was stirred 12 h and aqueous ammonium hydroxide solution (30% v/v) was added. The reaction was stirred for 1h at room temperature. Solvents were removed under vacuum and the resulting crude product purified by flash chromatography, eluting with CH₂Cl₂/MeOH 2:1 1% Et₃N to give 91 mg of Lac-8b as an oil (91% yield): R<sub>f</sub> = 0.40 (CH₂Cl₂/MeOH 9:1); [α]<sub>D</sub> = -6.4 (c 0.4, CHCl₃); <sup>1</sup>H NMR (500 MHz, CDCl₃): δ 7.40-7.39 (m, 1H), 5.31 (d, 1H, J = 2.7 Hz), 5.16 (t, 1H, J = 9.7 Hz), 5.05 (dd, 1H, J = 10.2 Hz, J = 8.1 Hz), 4.93 (dd, 1H, J = 10.2 Hz, J = 2.7 Hz), 4.88 (t, 1H, J = 9.7 Hz), 4.53-4.47 (m, 3H), 4.38 (brs, 2H), 4.10-4.05 (m, 3H), 3.98 (s, 2H), 3.87-3.85 (m, 1H), 3.77 (t, 1H, J = 9.7 Hz), 3.65-3.40 (m, 1H), 3.00-2.96 (m, 2H), 2.88-2.70 (m, 2H), 2.11 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 2.00 (s, 6H), 1.92 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl₃): δ 170.4, 170.3, 170.1, 170.0, 169.7, 169.1, 101.0, 83.6, 76.8, 76.1, 73.7, 71.0, 70.9, 70.7, 70.5, 70.3, 70.1, 70.0, 69.2, 66.7, 62.1, 60.8, 40.6, 38.9, 30.3, 20.8, 20.7, 20.6, 20.5, 20.4; HRMS (FAB) calcd for C₃₂H₅₃N₅O₂₁SNa [M+Na]<sup>+</sup>: m/z 907.2993. Found: 907.3008.

Synthesis of compound Cellob-9b
To a solution of compound **Cellob-9a** (200 mg, 0.22 mmol) in dichloromethane (3.0 mL) was added triphenylphosphine (32 mg, 0.13 mmol). The reaction mixture was stirred 12 h and aqueous ammonium hydroxide solution (30% v/v) was added. The reaction was stirred for 1 h at room temperature. Solvents were removed under vacuum and the resulting crude product purified by flash chromatography, eluting with CH$_2$Cl$_2$/MeOH 2:1 1% Et$_3$N to give 86 mg of **Cellob-9b** as an oil (43% yield): R$_f$ = 0.40 (CH$_2$Cl$_2$/MeOH 2:1 1% Et$_3$N; $\alpha$$_D$ = +23.2 (c 0.9, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.21-7.18 (m, 1H), 5.16-5.08 (m, 2H), 5.06 (t, 1H, $J$ = 9.6 Hz), 4.92-4.85 (m, 2H), 4.50-4.47 (m, 3H), 4.35-4.31 (m, 1H), 4.05-3.95 (m, 4H), 3.75-3.56 (m, 1H), 3.53-3.47 (m, 2H), 2.90-2.60 (m, 4H), 2.07 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H), 1.93 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 170.4, 170.3, 170.1, 169.9, 169.7, 169.6, 169.3, 169.0, 100.8, 83.6, 76.7, 76.3, 73.4, 72.9, 72.0, 71.6, 71.0, 70.7, 70.5, 70.2, 70.1, 67.7, 61.9, 61.5, 41.5, 38.9, 30.2, 20.8, 20.7, 20.6, 20.5; HRMS (FAB) calcd for C$_{36}$H$_{56}$N$_2$O$_{21}$SNa [M+Na]$^+$: m/z 907.2993. Found: 907.2983.

Synthesis of compound **Man-11b**

To a solution of **Man-11a** (23 mg, 0.028 mmol) in dichloromethane (1.0 mL) was added triphenylphosphine (32 mg, 0.13 mmol). The reaction mixture was stirred 12 h and aqueous ammonium hydroxide solution (30% v/v) was added. The reaction was stirred for 1 h at room temperature. Solvents were removed under vacuum and the resulting crude product purified by flash chromatography, eluting with CH$_2$Cl$_2$/MeOH 2:1 1% Et$_3$N to give 16 mg of **Man-11b** as an oil (99% yield): R$_f$ = 0.40 (CH$_2$Cl$_2$/MeOH 2:1 1% Et$_3$N; $\alpha$$_D$ = +54.1 (c 0.8, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.40-7.20 (m, 2H), 5.32-5.27 (m, 3H), 5.21 (dd, 1H, $J$ = 10.0 Hz, $J$ = 3.2 Hz), 4.38-4.34 (m, 1H), 4.28 (dd, 1H, $J$ = 12.2 Hz, $J$ = 5.5 Hz), 4.09 (dd, 1H, $J$ = 12.2 Hz, $J$ = 1.7 Hz), 3.99 (s, 4H), 3.67-3.47 (m, 24H), 2.86-2.65 (m, 4H), 2.28 (brs, 2H), 2.15 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 1.96 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 170.6, 170.1, 169.9, 169.8, 169.7, 82.5, 70.9, 70.6, 70.5, 70.3, 70.2, 69.7, 69.4, 69.1, 66.3, 62.4, 41.6, 38.6, 38.1, 31.1, 20.9, 20.7, 20.6. HRMS (FAB) calcd for C$_{32}$H$_{55}$N$_3$O$_{17}$SNa [M+Na]$^+$: m/z 806.2993. Found: 806.3010.

Synthesis of compound **Lac-8c**

To a solution of **4** (42.4 mg, 0.12 mmol) in DMF (0.5 mL) were added, sequentially at room temperature in the dark, TBTU (38 mg, 0.12 mmol) and DIPEA (20 μL, 0.12 mmol). The solution was stirred for 5 min before a solution of **Lac-8b** (100 mg, 0.12
mmol) and DIPEA (20 μL, 0.12 mmol) in DMF (1 mL) was added slowly. The solution was stirred for 2 h before the solvent was removed under vacuum. The residue was dissolved in CH₂Cl₂ (50 mL) and washed with 1M HCl (20 mL), saturated aqueous NaHCO₃ (40 mL) and brine (20 mL). After drying over Na₂SO₄ and removal of solvent, the crude product was purified by silica gel chromatography eluting with dichloromethane/methanol 20:1 to give 98 mg of an amorphous solid Lac-8c (70% yield): R<sub>f</sub> = 0.24 (CH₂Cl₂/MeOH 20:1); [α]<sub>D</sub> = -5.6 (c 0.4, CHCl₃); <sup>1</sup>H NMR (500 MHz, CDCl₃): δ 7.24-7.23 (m, 1H), 6.26-6.24 (m, 1H), 5.33 (d, 1H, J = 3.2 Hz), 5.19 (t, 1H, J = 9.2 Hz), 5.08 (dd, 1H, J = 10.2 Hz, J = 8.0 Hz), 4.95 (dd, 1H, J = 10.2 Hz, J = 3.2 Hz), 4.91 (t, 1H, J = 9.2 Hz), 4.52-4.47 (m, 3H), 4.12-3.98 (m, 5H), 3.88-3.85 (m, 1H), 3.77 (t, 1H, J = 9.2 Hz), 3.70-3.61 (m, 11H), 3.55 (t, 2H, J = 6.9 Hz), 2.88-2.71 (m, 2H), 2.22 (t, 4H, J = 6.9 Hz), 2.18-2.13 (m, 5H), 2.09 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 6H), 1.95 (s, 3H), 1.62-1.59 (m, 2H), 1.51-1.40 (m, 4H), 1.35-1.24 (m, 26H), 0.86 (t, 3H, J = 6.5 Hz); <sup>13</sup>C NMR (125.7 MHz, CDCl₃): δ 173.5, 170.4, 170.3, 170.2, 170.1, 170.0, 169.7, 169.6, 169.1, 101.1, 83.6, 77.6, 77.4, 76.9, 76.1, 73.7, 71.0, 70.8, 70.7, 70.6, 70.5, 70.4, 70.2, 70.1, 70.0, 69.1, 66.6, 65.3, 65.2, 62.1, 60.8, 39.1, 38.9, 36.5, 33.8, 31.9, 30.4, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 29.0, 28.9, 28.8, 28.7, 28.4, 28.3, 25.7, 24.7, 22.7, 20.8, 20.6, 20.5, 19.2, 14.1; HRMS (FAB) calcd for C₆₁H₉₆N₂O₂₂SNa [M+Na]<sup>+</sup>: m/z 1263.6073. Found: 1263.6096.

Synthesis of compound Cellob-9c

To a solution of 4 (22 mg, 0.058 mmol) in DMF (0.5 mL) were added, sequentially at room temperature in the dark, TBTU (19 mg., 0.058 mmol) and DIPEA (10 μL, 0.058 mmol). The solution was stirred for 5 min before a solution of Cellob-9b (51 mg, 0.058 mmol) and DIPEA (10 μL, 0.058 mmol) in DMF (1 mL) was added slowly. The solution was stirred for 2 h before the solvent was removed under vacuum. The residue was dissolved in CH₂Cl₂ (20 mL) and washed with 1M HCl (10 mL), saturated aqueous NaHCO₃ (20 mL) and brine (10 mL). After drying over Na₂SO₄ and removal of solvent, the crude product was purified by silica gel chromatography eluting with dichloromethane/methanol 20:1 to give 44 mg of an amorphous solid Cellob-9c (62% yield): R<sub>f</sub> = 0.24 (CH₂Cl₂/MeOH 20:1); [α]<sub>D</sub> = +14.3 (c 0.8, CHCl₃); <sup>1</sup>H NMR (500 MHz, CDCl₃): δ 7.25-7.23 (m, 1H), 6.27-6.26 (m, 1H), 5.16-5.12 (m, 2H), 5.08-5.06 (m, 1H), 4.94-4.90 (m, 2H), 4.53-4.51 (m, 3H), 4.38-4.35 (m, 1H), 4.06-3.95 (m, 4H), 3.70-3.60 (m, 13H), 3.58-3.42 (m, 4H), 2.88-2.70 (m, 2H), 2.23 (t, 4H, J = 6.9 Hz), 2.15 (t, 2H, J = 7.6 Hz), 2.11 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H), 1.63-1.57 (m, 2H), 1.52-1.47 (m, 4H), 1.37-1.24 (m, 26H), 0.86 (t, 3H, J = 6.5 Hz); <sup>13</sup>C NMR (125.7 MHz, CDCl₃): δ 173.3, 170.4, 170.3, 170.2, 170.1, 169.7, 169.6, 169.1, 100.8, 83.6, 77.6, 77.4, 76.7, 76.3, 73.4, 72.9, 72.0, 71.6, 70.9, 70.8, 70.7, 70.5, 70.2, 69.8, 67.7, 65.3, 65.2, 62.0, 61.5, 39.1, 38.9, 36.5, 31.9, 30.4, 29.6, 29.5, 29.3, 29.2, 29.1, 29.0, 28.9, 28.8, 28.7, 28.4, 28.3, 25.5, 24.7, 22.7, 20.8, 20.6, 20.5, 19.2, 14.1; HRMS (FAB) calcd for C₆₁H₉₆N₂O₂₂SNa [M+Na]<sup>+</sup>: m/z 1263.6079. Found: 1263.6096.
Synthesis of compound **Man-11c**

To a solution of **4** (31 mg, 0.084 mmol) in DMF (0.5 mL) were added, sequentially at room temperature in the dark, TBTU (27 mg, 0.084 mmol) and DIPEA (14 μL, 0.084 mmol). The solution was stirred for 5 min before a solution of **Man-11b** (66 mg, 0.084 mmol) and DIPEA (14 μL, 0.084 mmol) in DMF (1 mL) was added slowly. The solution was stirred for 2 h before the solvent was removed under vacuum. The residue was dissolved in CH$_2$Cl$_2$ (20 mL) and washed with 1M HCl (10 mL), saturated aqueous NaHCO$_3$ (20 mL) and brine (10 mL). After drying over Na$_2$SO$_4$ and removal of solvent, the crude product was purified by silica gel chromatography eluting with dichloromethane/methanol 9:1 to give 70 mg of an amorphous solid **Man-11c** (73% yield): $R_f$ = 0.33 (CH$_2$Cl$_2$/MeOH 9:1); $[\alpha]_D$ = +37.8 (c 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$): δ 7.30-7.28 (m, 1H), 7.21-7.19 (m, 1H), 6.47-6.46 (m, 1H), 5.32-5.25 (m, 3H), 5.21 (dd, 1H, $J$ = 10.0 Hz, $J$ = 3.2 Hz), 4.35-4.32 (m, 1H), 4.28 (dd, 1H, $J$ = 12.2 Hz, $J$ = 5.5 Hz), 4.09 (dd, 1H, $J$ = 12.2 Hz, $J$ = 1.7 Hz), 4.01 (s, 2H), 3.99 (s, 2H), 3.66-3.38 (m, 26H), 2.84-2.71 (m, 2H), 2.21 (t, 4H, $J$ = 6.9 Hz), 2.15 (t, 2H, $J$ = 7.6 Hz), 2.13 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.96 (s, 3H), 1.58-1.56 (m, 2H), 1.51-1.48 (m, 4H), 1.33-1.25 (m, 26H), 0.86 (t, 3H, $J$ = 6.5 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 173.6, 170.6, 170.3, 170.2, 170.0, 169.9, 169.8, 169.7, 82.4, 77.6, 77.4, 70.9, 70.6, 70.5, 70.4, 70.3, 70.2, 70.1, 69.9, 69.8, 69.4, 69.1, 66.2, 65.3, 65.2, 62.4, 39.2, 38.6, 38.1, 36.5, 31.9, 31.1, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 29.0, 28.9, 28.8, 28.4, 28.3, 25.7, 22.7, 20.9, 20.7, 20.6, 19.2, 14.1; HRMS (FAB) calcd for C$_{57}$H$_{95}$N$_3$O$_{18}$SNa [M+Na]$^+$/m/z 1164.6229. Found: 1164.6276.

Synthesis of compound **Lac-8**

To a solution of **Lac-8c** (98 mg, 0.08 mmol) in dry methanol (1 mL) was added a NaOMe solution 1M (60 μL, 0.06 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 58 mg of a white solid **Lac-8** (75% yield) $R_f$ = 0.4 (CH$_3$CN/H$_2$O/NH$_4$OH 6:1:1); $[\alpha]_D$ = -2.38 (c 0.84, MeOH); $^1$H NMR (500 MHz,
MeOD): δ 4.43 (d, 1H, J = 9.8 Hz), 4.35 (d, 1H, J = 7.6 Hz), 4.00 (s, 2H), 3.92 (dd, 1H, J = 12.2 Hz, J = 2.2 Hz), 3.85-3.75 (m, 3H), 3.72-3.46 (m, 19H), 3.36 (t, 2H, J = 5.6 Hz), 3.30-3.26 (m, 1H), 2.93-2.75 (m, 2H), 2.25 (t, 4H, J = 6.9Hz), 2.15 (t, 2H, J = 7.6 Hz), 1.60 (t, 2H, J = 7.0 Hz), 1.53-1.47 (m, 4H), 1.39-1.32 (m, 26H), 0.90 (t, 3H, J = 6.5 Hz); 13C NMR (125.7 MHz, MeOD): δ 176.4, 172.8, 105.1, 87.0, 80.6, 80.4, 77.9, 77.1, 74.8, 74.1, 72.5, 72.0, 71.5, 71.4, 71.3, 71.2, 70.7, 70.3, 66.4, 62.5, 62.1, 40.5, 40.3, 37.1, 33.1, 30.7, 30.6, 30.5, 30.4, 30.3, 30.2, 30.1, 30.0, 29.9, 29.8, 29.6, 27.0, 23.7, 19.7, 14.4; HRMS (FAB) calcd for C47H82N2O15SNa [M+Na]+: m/z 969.5333. Found: 969.5306.

Synthesis of Compound Cellob-9

To a solution of Cellob-9c (60 mg, 0.048 mmol) in dry methanol (1 mL) was added NaOMe solution 1M (48 μL, 0.048 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 23 mg of a white solid Cellob-9 (51% yield) RF = 0.4 (CH3CN/H2O/NH4OH 6:1:1); [α]D = -10.4 (c 0.3, MeOH); 1H NMR (500 MHz, MeOD): δ 4.43 (d, 1H, J = 9.8Hz), 4.41 (d, 1H, J = 7.9Hz), 4.00 (s, 2H), 3.92-3.21 (m, 26H), 2.92-2.75 (m, 2H), 2.25 (t, 4H, J = 6.9Hz), 2.18 (t, 2H, J = 7.6Hz), 1.63-1.58 (m, 2H), 1.53-1.47 (m, 4H), 1.40-1.28 (m, 26H), 0.90 (t, 3H, J = 6.5Hz); 13C NMR (125.7 MHz, MeOD): δ 176.4, 172.8, 104.6, 86.9, 80.6, 80.4, 78.1, 77.9, 74.9, 74.1, 71.9, 71.5, 71.4, 71.3, 71.2, 70.6, 66.4, 62.5, 62.1, 40.5, 40.3, 37.1, 33.1, 30.7, 30.6, 30.5, 30.4, 30.3, 30.2, 30.1, 30.0, 29.9, 29.8, 29.5, 27.0, 23.7, 19.7, 14.5; HRMS (FAB) calcd for C47H82N2O15SNa [M+Na]+: m/z 969.5333. Found: 969.5349.

Synthesis of compound Man-11

To a solution of Man-11c (27 mg, 0.023 mmol) in dry methanol (1 mL) was added NaOMe solution 1M (10 μL, 0.01 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 24 mg of a white solid Man-11 (99% yield) R<sub>f</sub> = 0.16 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9:1); [α]<sub>D</sub> = +43.5 (c 1.2, MeOH); ¹H NMR (500 MHz,MeOD): δ 5.30 (s, 1H), 4.00 (m, 2H), 3.98 (m, 2H), 3.91-3.84 (m, 5H), 3.74-3.60 (m, 19H), 3.57 (t, 2H, J = 5.1 Hz), 3.55-3.52 (m, 2H), 3.47-3.44 (m, 2H), 3.37-3.44 (m, 2H), 2.88-2.72 (m, 2H), 2.21 (t, 4H, J = 6.9 Hz), 2.18 (t, 2H, J = 7.5 Hz), 1.62-1.58 (m, 2H), 1.52-1.47 (m, 4H), 1.41-1.27 (m, 26H), 0.90 (t, 3H, J = 6.9 Hz); ¹³C NMR (125 MHz, MeOD): δ 176.4, 172.9, 172.8, 86.6, 77.9, 77.8, 75.2, 73.6, 73.1, 72.0, 71.9, 71.6, 71.5, 71.4, 71.3, 71.2, 70.6, 70.5, 68.9, 66.4, 62.9, 40.3, 39.8, 39.7, 37.0, 33.0, 31.4, 30.7, 30.6, 30.5, 30.4, 30.3, 30.2, 30.1, 30.0, 29.9, 29.8, 29.5, 26.9, 23.7, 19.7, 14.4; HRMS (FAB) calcd for C₄₉H₈₇N₃O₁₄SNa [M+Na]+: m/z 996.5806. Found: 996.5823.

B) General procedure for the self-assembly of neoglycolipids I (8, 9 and 11) on carbon nanotube and photopolymerization.

SWNT’s were purchased from Mer Corporation company. In a typical experiment, 0.1 to 0.3 mg of neoglycolipid is dissolved in 1 ml of pure water. 1 mg of SWNT’s is then added to the homogenous solution. The mixture is then sonicated using a simple water-bath sonicator for 30 min. Insoluble material and impurities (amorphous carbon and catalyst) are then removed by low-speed centrifugation at 2000g for 5 min. The stable black aqueous suspension of functionalized SWNT-neoglycolipids is irradiated by a UV lamp at 254nm for 2h to initiate and complete the photopolymerization of the di-yne function to poldiacetylene. A second high-speed centrifugation at 14 000g for 30 min is then performed for the sedimentation of the stable polymerized functionalized SWNT-neoglycolipids, and the elimination of excess neoglycolipids I (micelles) which remains in the supernatant solution. If needed, the stable polymerized functionalized SWNT-neoglycolipids can be washed with pure water by resuspension, sonication and centrifugation, for the complete removal of unreacted glycolipids.

C) Control of stability of aggregates CNT-lipids.

After mixing the neutral lipid Lac-8 with SWCNTs in water, followed by sonication for 30 min, the obtained black solution remained stable for months before a sedimentation start (Figure 1, vial A). In contrast after photopolymerization, the black solution remained stable for the last 6 months (Figure 1, vial B). The stability of CNT-neoglycolipids aggregates at high temperature and in high ionic force buffer environment (Hepes 20mM, pH 7.5) was assessed by the following experiments: 1 mL of a stable aqueous suspension of CNT-Lac-8 aggregates was heated at 70°C for one week (Figure 1, vial C). On the other hand, 250 µL of Hepes buffer (20mM, pH 7.5) solution was added to 250 µL of a stable aqueous suspension of CNT-Lac-8 aggregates (Figure 1, vial D). In both cases, the SWCNT-Lac-8 aggregates remained remarkably stable. These results indicate that the nanoconstruct act as a single entity and rule out the dynamic nature of the association between SWCNT and Lac-8.
Figure 1. Stability of the aggregates: A) Aqueous solution of SWCNT-Lac-8 without polymerization after 6 months. B) Aqueous solution of Polymerized SWCNT-Lac-8 after 6 months. C) SWCNT-Lac-8 in water heated at 70°C during one week. D) SWCNT-Lac-8 in Hepes (20mM, pH 7.5) buffer.

D) Transmission Electron Microscopy Analysis
TEM images of SWNT-neoglycolipids were obtained on a Philips CM120 transmission electron microscope operating at 100 kV with a LaB6 filament. Areas covered with molecules of interest were recorded under low dose condition, at a magnification of x 60,000 on a Pelletier cooled CCD camera (Model 794, Gatan, Pleasanton, CA).

E) Lectin Arachis hypogaea Peanut agglutinin (PNA) binding assay.
A 100µl stable aqueous suspension of functionalized SWNT-neoglycolipids is incubated for 1h at room temperature in presence of a PNA lectine solution (20 mM Hepes aqueous buffer at pH=7.5) diluted to different final concentrations: 1µg/ml, 10µg/ml, 100µg/ml. The mixture is then briefly centrifuged at low speed. 10µl of the supernatant is deposited on an air glow-discharged carbon-coated grid. After 2 min adsorption the sample was negatively stained with a 2% (w/v) uranyl acetate solution and observed by TEM microscopy.
Figure 2: IR spectrum of compound Lac-8 alone (a) and SWCNT-Lac-8 nanohybrids (b).
Figure 3: $^1$HNMR (D$_2$O, 500MHz) spectra of Lac-8 (a), and SWCNT-Lac-8 aggregate.
Figure 4: Raman spectrum of Lac-8-SWCNT aggregate in solution excited by 568.2 nm laser. The absence of increase on D band (disorder mode at ≈ 1350 cm⁻¹) indicates the purity of the prepared aggregate without damaging the SWCNT surface.