Supporting Information for

Carbohydrate-functionalized catanionic surfactant vesicles: preparation and lectin-binding studies

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Glycoconjugates Synthesis. All reagents and solvents were purchased from commercial suppliers and used without further purification unless noted otherwise. Glassware used in the reactions was dried overnight in an oven at 120 ºC. The compounds prepared were characterized on the basis of one (^{1}H and ^{13}C) and two dimensional (COSY) NMR, IR, and MS spectroscopy.

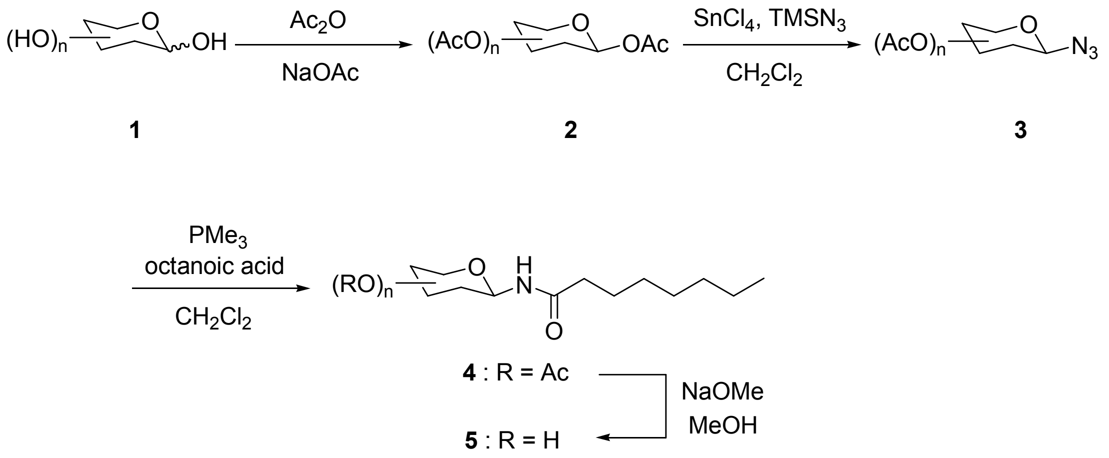

Figure S1. Synthetic route for the preparation of glycoconjugates.

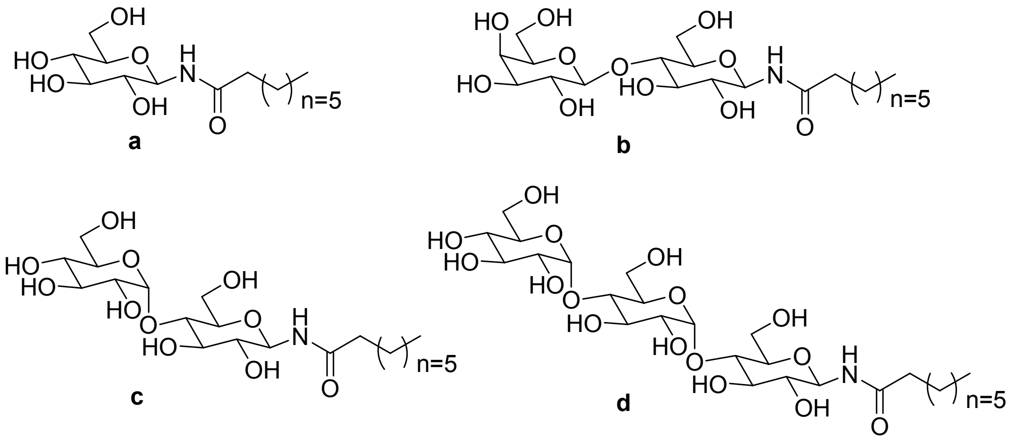

Figure S2. Structures of N-linked glycoconjugates for the surface functionalization of surfactant vesicles.

General procedure for the synthesis of glycosyl peracetate 2.

To a refluxing suspension of anhydrous NaOAc (4.0 equiv) in acetic anhydride (20 equiv) was added carbohydrate (1.0 equiv). The reaction mixture was refluxed for 3 h and cooled to 100 °C, then immediately transferred into ice-water mixture and stirred vigorously until a gum formed. After decanting the water, the gum was dissolved in CH_2Cl_2 and then washed with sat. aq. $NaHCO_3$, H_2O, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography to give β-glycosyl peracetate **2**.

Lactose peracetate 2b: α-D-Lactose monohydrate (9.00 g, 25.0 mmol), NaOAc (8.20 g, 100 mmol) and acetic anhydride (47.0 mL, 500 mmol). Purification by column chromatography (hexane/EtOAc, 1/1) afforded 14.7 g (87%) of lactose peracetate **2b**: R_f = 0.21 (hexane/EtOAc, 1/1); IR (CCl_4, cm^{-1}) 2982 (w), 1759 (s), 1366 (m), 1235 (s), 1051 (s); ^1H NMR (400MHz, $CDCl_3$) δ 1.97 (s, 3H), 2.03 (s, 3H), 2.05 (s, 3H), 2.05 (s, 3H), 2.07 (s, 3H), 2.10 (s, 3H), 2.12 (s, 3H), 2.16 (s, 3H), 3.76 (ddd, *J*=9.3, 4.7, 1.9, 1H), 3.85 (t, *J*=9.3, 1H), 3.86-3.89 (m, 1H), 4.06-4.18 (m, 3H), 4.45 (dd, *J*=12.0, 1.9, 1H), 4.47 (d, *J*=7.9, 1H), 4.95 (dd, *J*=10.4, 3.4, 1H), 5.05 (dd, *J*=9.3, 8.3, 1H), 5.11 (dd, *J*=10.4, 7.9, 1H), 5.25 (t, *J*=9.3, 1H), 5.34 (dd, *J*=3.4, 0.8, 1H), 5.67 (d, *J*=8.3, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 20.6, 20.6, 20.6, 20.6, 20.7, 20.8, 20.8, 60.8, 61.7, 66.6, 69.0, 70.5, 70.7, 70.9, 72.6, 73.5, 75.6, 91.5, 100.9, 168.8, 169.0, 169.5, 169.6, 170.0, 170.1, 170.3, 170.3; HRMS (FAB) cacld for $C_{28}H_{38}O_{19}Li$ $[M + Li]^+$ 685.2167, found 685.2191.

Maltose peracetate 2c: D-(+)-Maltose monohydrate (9.00 g, 25.0 mmol), NaOAc (8.20 g, 100 mmol) and acetic anhydride (47.0 mL, 500 mmol). Purification by column chromatography (hexane/EtOAc, 1/2) afforded 16.7 g (98%) of maltose peracetate **2c**: R_f = 0.61 (hexane/EtOAc, 1/2); IR (CCl_4, cm^{-1}) 2963 (w), 1754 (s), 1365 (m), 1230 (s), 1044 (s); ^1H NMR (400MHz, $CDCl_3$) δ 2.01 (s, 3H), 2.02 (s, 3H), 2.02 (s, 3H), 2.03 (s, 3H), 2.05 (s, 3H), 2.10 (s, 3H), 2.11 (s, 3H), 2.14 (s, 3H), 3.84 (ddd, *J*=9.2, 4.4, 2.4, 1H), 3.94 (ddd, *J*=9.6, 3.6, 2.4, 1H), 4.01-4.06 (m, 2H), 4.23 (dd, *J*=12.4, 4.4, 1H), 4.24 (dd, *J*=12.4, 3.6, 1H), 4.45 (dd, *J*=12.4, 2.4, 1H), 4.86 (dd, *J*=10.4, 4.0, 1H), 4.98 (dd, *J*=9.2, 8.4, 1H), 5.06 (t, *J*=9.6, 1H), 5.30 (t, *J*=9.2, 1H), 5.36 (dd, *J*=10.4, 9.6, 1H), 5.41 (d, *J*=4.0, 1H), 5.74 (d, *J*=8.4, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 20.6, 20.6, 20.6, 20.7, 20.8, 20.8, 20.9, 61.4, 62.5, 67.9, 68.6, 69.3, 70.0, 70.9, 72.4, 73.0, 75.2, 91.2, 95.7, 168.8, 169.4, 169.6, 169.6, 170.1, 170.4, 170.5, 170.6; HRMS (FAB) cacld for $C_{28}H_{38}O_{19}Li$ $[M + Li]^+$ 685.2167, found 685.2151.

Maltotriose peracetate 2d: Maltotriose hydrate (1.00 g, 1.98 mmol), NaOAc (0.810 g, 9.90 mmol) and acetic anhydride (4.70 mL, 49.5 mmol). Purification by column chromatography (hexane/EtOAc, 1/3) afforded 1.83 g (96%) of maltotriose peracetate **2d**: R_f = 0.34 (hexane/EtOAc, 1/2); IR (CCl_4, cm^{-1}) 2959 (w), 1760 (s), 1368 (m), 1232 (s), 1037 (s); ^{1}H NMR (400MHz, $CDCl_3$) δ 1.97 (s, 3H), 1.97 (s, 3H), 1.97 (s, 3H), 1.98 (s, 3H), 1.99 (s, 3H), 2.00 (s, 3H), 2.03 (s, 3H), 2.07 (s, 3H), 2.07 (s, 3H), 2.12 (s, 3H), 2.14 (s, 3H), 3.83-4.09 (m, 6H), 4.13 (dd, *J*=12.4, 2.4, 1H), 4.22 (dd, *J*=12.4, 3.4, 1H), 4.27 (dd, *J*=12.4, 4.2, 1H), 4.40-4.46 (m, 2H), 4.71 (dd, *J*=10.4, 4.0, 1H), 4.82 (dd, *J*=10.4, 4.4, 1H), 4.93 (dd, *J*=9.2, 8.1, 1H), 5.04 (t, *J*=10.4, 1H), 5.24 (d, *J*=4.0, 1H), 5.27-5.41 (m, 3H), 5.38 (d, *J*=4.4, 1H), 5.71 (d, *J*=8.1, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 20.5, 20.6, 20.6, 20.6, 20.7, 20.8, 20.8, 20.8, 20.8, 20.9, 61.3, 62.2, 62.6, 67.8, 68.5, 69.0, 69.3, 70.0, 70.4, 70.9, 71.6, 72.4, 72.9, 73.4, 75.1, 91.2, 95.6, 95.9, 168.8, 169.4, 169.6, 169.8, 169.8, 170.0, 170.3, 170.5, 170.5, 170.6, 170.6; HRMS (ESI) cacld for $C_{40}H_{54}O_{27}Na$ $[M + Na]^+$ 989.2750, found 989.2765.

General procedure for the synthesis of glycosyl azide 3.

To a solution of glycosyl peracetate **2** (1.0 equiv) in anhydrous CH_2Cl_2 was added trimethylsilyl azide (1.3 equiv), followed by 1.0 M solution of $SnCl_4$ (0.5 equiv). The resulting solution was stirred at room temperature for 24 h under a nitrogen atmosphere. The reaction mixture was diluted with CH_2Cl_2, washed with sat. aq. $NaHCO_3$, H_2O, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by either column chromatography or recrystallization to give β-glycosyl azide **3**.

Glucose azide 3a: β-D-Glucose pentaacetate (10.0 g, 25.6 mmol), trimethylsilyl azide (4.40 mL, 33.3 mmol), and $SnCl_4$ (12.8 mL, 12.8 mmol). Purification by recrystallization (hexane/CH_2Cl_2) afforded 9.10 g (95%) of glucose azide **3a**: R_f = 0.14 (hexane/ether, 1/1); IR (CCl_4, cm^{-1}) 2961 (w), 2119 (s), 1757 (s), 1543 (s), 1223 (s); ^{1}H NMR (400MHz,

$CDCl_3$) δ 2.01 (s, 3H), 2.04 (s, 3H), 2.08 (s, 3H), 2.11 (s, 3H), 3.80 (ddd, *J*=9.0, 4.8, 2.4, 1H), 4.18 (dd, *J*=12.4, 2.4, 1H), 4.28 (dd, *J*=12.4, 4.8, 1H), 4.65 (d, *J*=9.0, 1H), 4.96 (t, *J*=9.0, 1H), 5.11 (t, *J*=9.0, 1H), 5.22 (t, *J*=9.0, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 20.5, 20.5, 20.7, 61.6, 67.8, 70.6, 72.5, 73.6, 87.9, 169.2, 169.3, 170.1, 170.6.

Lactose azide 3b: Lactose peracetate **2b** (3.00 g, 4.42 mmol), trimethylsilyl azide (0.700 mL, 5.31 mmol), and $SnCl_4$ (2.21 mL, 2.21 mmol). Purification by column chromatography (hexane/EtOAc, 1/1) afforded 2.36 g (81%) of lactose azide **3b**: R_f = 0.34 (hexane/ EtOAc, 1/1); IR (CCl_4, cm^{-1}) 2963 (w), 2119 (s), 1764 (s), 1366 (s), 1231 (s), 1051 (s); ^1H NMR (400MHz, $CDCl_3$) δ 1.94 (s, 3H), 2.03 (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H), 2.05 (s, 3H), 2.12 (s, 3H), 2.13 (s, 3H), 3.67 (ddd, *J*=9.0, 5.2, 2.0, 1H), 3.79 (t, *J*=9.0, 1H), 3.82-3.87 (m, 1H), 4.03-4.13 (m, 3H), 4.45 (d, *J*=8.0, 1H), 4.49 (dd, *J*=12.4, 2.0, 1H), 4.60 (d, *J*=9.0, 1H), 4.84 (t, *J*=9.0, 1H), 4.93 (dd, *J*=10.4, 3.6, 1H), 5.08 (dd, *J*=10.4, 8.0, 1H), 5.19 (t, *J*=9.0, 1H), 5.32 (dd, *J*=3.6, 0.6, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 20.6, 20.6, 20.6, 20.6, 20.7, 20.8, 60.7, 61.7, 66.5, 69.0, 70.7, 70.9, 71.0, 72.5, 74.8, 75.8, 87.7, 101.1, 169.1, 169.5, 169.6, 170.0, 170.1, 170.3, 170.3; HRMS (FAB) cacld for $C_{26}H_{35}O_{17}N_3Li$ $[M + Li]^+$ 668.2127, found 668.2094.

Maltose azide 3c: Maltose peracetate **2c** (1.67 g, 2.46 mmol), trimethylsilyl azide (0.430 mL, 3.20 mmol), and $SnCl_4$ (1.23 mL, 1.23 mmol). Purification by column chromatography (hexane/EtOAc, 1/1) afforded 1.50 g (92%) of maltose azide **3c**: R_f = 0.73 (hexane/ EtOAc, 1/2); IR (CCl_4, cm^{-1}) 2958 (w), 2117 (s), 1754 (s), 1370 (s), 1232 (s); ^1H NMR (400MHz, $CDCl_3$) δ 2.01 (s, 3H), 2.02 (s, 3H), 2.03 (s, 3H), 2.05 (s, 3H), 2.06 (s, 3H), 2.11 (s, 3H), 2.17 (s, 3H), 3.79 (ddd, *J*=9.0, 4.4, 2.4, 1H), 3.96 (ddd, *J*=10.0, 3.6, 2.4, 1H), 4.02 (t, *J*=9.0, 1H), 4.05 (dd, *J*=12.4, 2.4, 1H), 4.24 (dd, *J*=12.4, 4.4, 1H), 4.25 (dd, *J*=12.4, 3.6, 1H), 4.51 (dd, *J*=12.4, 2.4, 1H), 4.71 (d, *J*=9.0, 1H), 4.79 (t, *J*=9.0, 1H), 4.86 (dd, *J*=10.8, 4.0, 1H), 5.06 (t, *J*=10.0, 1H), 5.26 (t, *J*=9.0, 1H), 5.36 (dd, *J*=10.8, 10.0, 1H), 5.41 (d, *J*=4.0, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 20.5, 20.6, 20.6, 20.7, 20.8, 20.8, 60.4, 62.5, 67.9, 68.6, 69.2, 70.0, 71.4, 72.3, 74.2, 75.1, 87.5, 95.7, 169.4, 169.5, 169.9, 170.1, 170.4, 170.5, 170.5; HRMS (FAB) cacld for $C_{26}H_{35}O_{17}N_3Li$ $[M + Li]^+$ 668.2127, found 668.2150.

Maltotriose azide 3d: Maltotriose peracetate **2d** (1.54 g, 1.59 mmol), trimethylsilyl azide (0.250 mL, 1.91 mmol), and $SnCl_4$ (0.800 mL, 0.800 mmol). Without further purification, 1.40 g (93%) of maltotriose azide **3d** was obtained: R_f = 0.49 (hexane/ EtOAc, 1/2); IR (CCl_4, cm^{-1}) 2959 (w), 2119 (m), 1760 (s), 1369 (m), 1232 (s); ^1H NMR (400MHz, $CDCl_3$) δ 1.97 (s, 3H), 1.98 (s, 3H), 1.98 (s, 3H), 1.99 (s, 3H), 2.01 (s, 3H), 2.03 (s, 3H), 2.03 (s, 3H), 2.08 (s, 3H), 2.14 (s, 3H), 2.16 (s, 3H), 3.89 (ddd, *J*=9.0, 4.0, 2.8, 1H), 3.89-3.99 (m, 4H), 4.03 (dd, *J*=12.4, 2.4, 1H), 4.15 (dd, *J*=12.4, 3.2, 1H), 4.22 (dd, *J*=12.4, 3.6, 1H), 4.30 (dd, *J*=12.0, 4.0, 1H), 4.44 (dd, *J*=12.4, 2.0, 1H), 4.48 (dd, *J*=12.0, 2.8, 1H), 4.69 (d, *J*=9.0, 1H), 4.72 (dd, *J*=9.6, 4.0, 1H), 4.76 (t, *J*=9.0, 1H), 4.83 (dd, *J*=10.4, 4.0, 1H), 5.05 (t, *J*=9.6, 1H), 5.24 (t, *J*=9.0, 1H), 5.25 (d, *J*=4.0, 1H), 5.31-5.37 (m, 2H), 5.39 (d, *J*=4.0, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 20.5, 20.6, 20.6, 20.6, 20.7, 20.8, 20.8, 20.8, 20.9, 61.3, 62.3, 62.6, 67.8, 68.5, 69.0, 69.3, 70.1, 70.4, 71.5, 71.7, 72.4, 73.4, 74.1, 74.9, 87.4, 95.6, 95.9, 169.4, 169.5, 169.7, 169.8, 169.9, 170.3, 170.4, 170.5, 170.6, 170.6; HRMS (ESI) cacld for $C_{38}H_{51}O_{25}N_3Na$ $[M + Na]^+$ 972.2709, found 972.2706.

General procedure for the synthesis of acetylated glycoconjugate 4.

To a solution of glycosyl azide **3** (1.0 equiv) in anhydrous CH_2Cl_2 was added diisopropylethylamine (2.0 equiv), followed by 1.0 M solution of PMe_3 (1.2 equiv). The reaction mixture was stirred at room temperature for 30 min under a nitrogen atmosphere and then added octanoic acid (2.0 equiv). After being stirred 24 h, the reaction mixture was diluted with CH_2Cl_2 and washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography to give acetylated β-glycoconjugate **4**.

Acetylated glucose conjugate 4a: Glucose azide **3a** (0.520 g, 1.39 mmol), diisopropylethylamine (0.360 g, 2.79 mmol), PMe_3 (1.67 mL, 1.67 mmol), and octanoic acid (0.400 g, 2.79 mmol). Purification by column chromatography (hexane/EtOAc, 2/1) afforded 0.376 g (57%) of acetylated glucose conjugate **4a**: R_f = 0.48 (hexane/ EtOAc, 1/1); IR (CCl_4, cm^{-1}) 3434 (w), 2957 (m), 1759 (s), 1708 (m), 1507 (m), 1228 (s); ^1H NMR (400MHz, $CDCl_3$) δ 0.85 (t, *J*=7.2, 3H), 1.23 (br s, 8H), 1.54-1.57 (m, 2H), 1.99 (s, 3H), 2.01 (s, 3H), 2.02 (s, 3H), 2.05 (s, 3H), 2.11-2.18 (m, 2H), 3.80 (ddd, *J*=9.6, 4.0, 2.0, 1H), 4.05 (dd, *J*=12.4, 2.0, 1H), 4.29 (dd, *J*=12.4, 4.0, 1H), 4.89 (t, *J*=9.6, 1H), 5.04 (t, *J*=9.6, 1H), 5.23 (t, *J*=9.6, 1H), 5.28 (t, *J*=9.6, 1H), 6.15 (d, *J*=9.6, 1H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 14.0, 20.6, 20.6, 20.6, 20.7, 22.6, 25.1, 28.9, 29.0, 31.6, 36.7, 61.6, 68.1, 70.6, 72.7, 73.5, 78.1, 169.6, 169.9, 170.6, 171.0, 173.4; HRMS (FAB) cacld for $C_{22}H_{36}O_{10}N$ $[M + H]^+$ 474.2339, found 474.2340.

Acetylated lactose conjugate 4b: Lactose azide **3b** (0.480 g, 0.726 mmol), diisopropylethylamine (0.187 g, 1.45 mmol), PMe_3 (0.871 mL, 0.871 mmol), and octanoic acid (0.210 g, 1.45 mmol). Purification by column chromatography (hexane/EtOAc, 1/2) afforded 0.230 g (42%) of acetylated lactose conjugate **4b**: R_f = 0.45 (hexane/ EtOAc, 1/2); IR (CCl_4, cm^{-1}) 3309 (w), 2957 (m), 1756 (s), 1707 (m), 1369 (s), 1221 (s), 1050 (s); ^1H NMR (400MHz, $CDCl_3$) δ 0.81 (t, J=7.2, 3H), 1.20 (br s, 8H), 1.49-1.53 (m, 2H), 1.91 (s, 3H), 1.98 (s, 3H), 1.99 (s, 3H), 2.00 (s, 3H), 2.01 (s, 3H), 2.06 (s, 3H), 2.10 (s, 3H), 2.05-2.17 (m, 2H), 3.66-3.75 (m, 2H), 3.81-3.84 (m, 1H), 3.99-4.12 (m, 3H), 4.37 (dd, J=12.0, 1.2, 1H), 4.41 (d, J=8.0, 1H), 4.77 (t, J=9.2, 1H), 4.89 (dd, J=10.2, 3.2, 1H), 5.05 (dd, J=10.0, 8.0, 1H), 5.16 (t, J=9.2, 1H), 5.24 (t, J=9.2, 1H), 5.30 (d, J=3.2, 1H), 6.12 (d, J=9.2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 20.4, 20.5, 20.6, 20.6, 20.6, 20.6, 20.7, 20.8, 22.5, 25.1, 28.8, 28.9, 31.5, 36.5, 60.8, 61.9, 66.5, 68.9, 70.6, 70.8, 70.9, 72.2, 74.3, 75.9, 77.8, 100.8, 168.9, 169.2, 169.9, 170.1, 170.2, 170.3, 171.1, 173.2; HRMS (FAB) cacld for $C_{34}H_{51}O_{18}NCs$ $[M + Cs]^+$ 894.2160, found 894.2137.

Acetylated maltose conjugate 4c: Maltose azide **3c** (1.05 g, 1.58 mmol), diisopropylethylamine (0.410 g, 3.17 mmol), PMe_3 (2.06 mL, 2.06 mmol), and octanoic acid (0.460 g, 3.17 mmol). Purification by column chromatography (hexane/EtOAc, 1/2) afforded 0.730 g (61%) of acetylated maltose conjugate **4c**: R_f = 0.18 (hexane/ EtOAc, 1/1); IR (CCl_4, cm^{-1}) 3410 (w), 2952 (w), 1758 (s), 1708 (w), 1367 (w), 1230 (s), 1043 (m); ^1H NMR (400MHz, $CDCl_3$) δ 0.84 (t, J=7.0, 3H), 1.23 (br s, 8H), 1.53-1.64 (m, 2H), 1.97 (s, 3H), 1.98 (s, 3H), 2.00 (s, 3H), 2.00 (s, 3H), 2.04 (s, 3H), 2.07 (s, 3H), 2.11 (s, 3H), 2.09-2.18 (m, 2H), 3.77 (ddd, J=9.5, 4.0, 2.4, 1H), 3.89 (ddd, J=10.0, 3.8, 2.2, 1H), 3.94 (t, J=9.5, 1H), 4.01 (dd, J=12.4, 2.2, 1H), 4.20 (dd, J=12.4, 3.8, 1H), 4.21 (dd, J=12.3, 4.0, 1H), 4.39 (dd, J=12.3, 2.4, 1H), 4.73 (t, J=9.5, 1H), 4.83 (dd, J=10.0, 4.0, 1H), 5.03 (t, J=10.0, 1H), 5.25 (t, J=9.5, 1H), 5.30-5.38 (m, 3H), 6.02 (d, J=9.5, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 20.6, 20.6, 20.6, 20.6, 20.7, 20.8, 20.8, 22.5, 25.1, 28.9, 29.0, 31.6, 36.6, 61.4, 62.8, 67.9, 68.5, 69.2, 70.0, 71.3, 72.6, 73.9, 74.9, 77.6, 95.5, 169.5, 169.6, 169.8, 170.4, 170.5, 170.7, 171.1, 173.2; HRMS (ESI) cacld for $C_{34}H_{52}O_{18}N$ [*M* + H]$^+$ 762.3184, found 762.3192.

Acetylated maltotriose conjugate 4d: Maltotriose azide **3d** (1.16 g, 1.22 mmol), diisopropylethylamine (0.320 g, 2.44 mmol), PMe_3 (1.59 mL, 1.59 mmol), and octanoic acid (0.350 g, 2.44 mmol). Purification by column chromatography (hexane/EtOAc, 1/2) afforded 0.540 g (42%) of acetylated maltotriose conjugate **4d**: R_f = 0.37 (hexane/ EtOAc, 1/2); IR (CCl_4, cm^{-1}) 3412 (w), 2958 (m), 1758 (s), 1709 (m), 1368 (m), 1233 (s), 1040 (s); ^{1}H NMR (400MHz, $CDCl_3$) δ 0.81-0.87 (m, 3), 1.24 (br s, 8H), 1.53-1.56 (m, 2H), 1.97 (s, 3H), 1.98 (s, 3H), 1.98 (s, 3H), 1.98 (s, 3H), 2.00 (s, 3H), 2.01 (s, 3H), 2.04 (s, 3H), 2.07 (s, 3H), 2.12 (s, 3H), 2.14 (s, 3H), 2.09-2.18 (m, 2H), 3.80 (ddd, *J*=9.4, 4.0, 2.6, 1H), 3.87-3.99 (m, 4H), 4.02 (dd, *J*=12.4, 2.2, 1H), 4.13 (dd, *J*=12.2, 2.7, 1H), 4.22 (dd, *J*=12.4, 3.5, 1H), 4.28 (dd, *J*=12.2, 4.0, 1H), 4.39 (dd, *J*=12.2, 2.6, 1H), 4.44 (dd, *J*=12.2, 1.5, 1H), 4.71 (dd, *J*=10.3, 4.1, 1H), 4.72 (t, *J*=9.4, 1H), 4.82 (dd, *J*=10.0, 4.0, 1H), 5.04 (t, *J*=10.0, 1H), 5.22 (d, *J*=4.1, 1H), 5.26 (t, *J*=9.4, 1H), 5.30-5.38 (m, 4H), 6.00 (d, *J*=9.4, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 20.6, 20.6, 20.6, 20.6, 20.6, 20.7, 20.8, 20.8, 20.9, 20.9, 22.6, 25.1, 28.9, 29.0, 31.6, 36.7, 61.3, 62.2, 62.9, 67.9, 68.5, 69.0, 69.3, 70.1, 70.4, 71.4, 71.6, 72.4, 73.7, 73.9, 74.8, 77.6, 95.6, 95.8, 169.5, 169.5, 169.6, 169.8, 170.3, 170.5, 170.5, 170.6, 170.7, 171.1, 173.2; HRMS (ESI) cacld for $C_{46}H_{68}O_{26}N$ [*M* + H]$^+$ 1050.4029, found 1050.3988.

General procedure for the synthesis of glycoconjugate 5.

To a solution of acetylated glycoconjugate **4** (1.0 equiv) in MeOH was added 0.2 M solution of sodium methoxide (given equiv) and then stirred at room temperature for 24 h under a nitrogen atmosphere. The reaction mixture was neutralized with Dowex MAC-3 resin (weakly acidic cation exchanger), filtered and concentrated *in vacuo*. The crude product was purified by column chromatography to give β-glycoconjugate **5**.

Glucose conjugate 5a: Acetylated glucose conjugate **4a** (0.320 g, 0.680 mmol) and NaOMe (6.80 mL, 1.35 mmol). Purification by column chromatography (CH_2Cl_2/MeOH, 6/1) afforded 0.177 g (85%) of glucose conjugate **5a**: R_f = 0.17 (CH_2Cl_2/MeOH, 6/1); IR (ATR, Ge window, cm^{-1}) 3430 (br), 2918 (w), 1628 (s), 1545 (s), 1077 (s); ^{1}H NMR (400MHz, DMSO) δ 0.85 (t, *J*=7.1, 3H), 1.23 (br s, 8H), 1.42-1.50 (m, 2H), 2.05-2.09 (m, 2H), 2.99-3.12 (m, 3H), 3.15 (t, *J*=9.0, 1H), 3.39 (br d, *J*=11.4, 1H), 4.61 (br d, *J*=11.4, 1H), 4.45 (br s, 1H), 4.68 (t, *J*=9.0, 1H), 4.87 (br s, 3H), 8.23 (d, *J*=9.0, 1H); ^{13}C NMR (100 MHz, DMSO) δ 14.0, 22.1, 24.9, 28.5, 28.7, 31.2, 35.4, 60.9, 70.0, 72.5, 77.6, 78.5, 79.4, 172.5; HRMS (FAB) cacld for $C_{14}H_{28}O_6N$ $[M + H]^+$ 306.1917, found 306.1927.

Lactose conjugate 5b: Acetylated lactose conjugate **4b** (0.230 g, 0.300 mmol) and NaOMe (10.6 mL, 2.11 mmol). Purification by column chromatography (CH_2Cl_2/MeOH, 2/1) afforded 0.100 g (71%) of lactose conjugate **5b**: $R_f = 0.28$ (CH_2Cl_2/MeOH, 3/1); IR (Drop casting on CaF_2, cm^{-1}) 3269 (br), 2919 (m), 1655 (m), 1548 (m), 1373 (w); ^{1}H NMR (400MHz, D_2O) δ 0.72 (t, *J*=6.8, 3H), 1.13-1.17 (m, 8H), 1.44-1.51 (m, 2H), 2.18 (t, *J*=7.2, 2H), 3.27-3.32 (m, 1H), 3.41 (dd, *J*=9.2, 7.6, 1H), 3.51-3.69 (m, 8H), 3.78-3.81 (m, 2H), 4.32 (d, *J*=8.0, 1H), 4.84 (d, *J*=9.2, 1H); ^{13}C NMR (100 MHz, D_2O) δ 13.2, 21.8, 24.9, 27.9, 28.0, 30.8, 35.7, 59.7, 60.9, 68.4, 70.8, 71.3, 72.4, 75.0, 75.2, 76.3, 77.6, 78.9, 102.7, 178.7; HRMS (FAB) cacld for $C_{20}H_{38}O_{11}N$ $[M + H]^+$ 468.2445, found 468.2465.

Maltose conjugate 5c: Acetylated maltose conjugate **4c** (0.37 g, 0.49 mmol) and NaOMe (17 mL, 3.4 mmol). Purification by column chromatography (CH_2Cl_2/MeOH, 3/1) afforded 0.17 g (74%) of maltose conjugate **5c**: $R_f = 0.38$ (CH_2Cl_2/MeOH, 3/1); IR (Drop casting on CaF_2, cm^{-1}) 3331 (br), 2926 (m), 1664 (m), 1546 (m), 1377 (w); ^{1}H NMR (400MHz, D_2O) δ 0.71 (t, *J*=7.9, 3H), 1.13-1.16 (m, 8H), 1.43-1.51 (m, 2H), 2.15-2.19 (m, 2H), 3.26 (t, *J*=9.3, 1H), 3.27 (t, *J*=9.3, 1H), 3.43 (dd, *J*=10.0, 3.9, 1H), 3.49-3.76 (m, 9H), 4.81 (d, *J*=9.3, 1H), 5.28 (d, *J*=3.9, 1H); ^{13}C NMR (100 MHz, D_2O) δ 13.2, 21.8, 24.9, 27.9, 28.0, 30.8, 35.7, 60.3, 60.4, 69.2, 71.5, 71.6, 72.5, 72.7, 75.9, 76.0, 76.9, 78.9, 99.4, 178.7; HRMS (ESI) cacld for $C_{20}H_{38}O_{11}N$ $[M + H]^+$ 468.2445, found 468.2445.

Maltotriose conjugate 5d: Acetylated maltotriose conjugate **4d** (0.43 g, 0.41 mmol) and NaOMe (21 mL, 4.1 mmol). Purification by column chromatography (CH_2Cl_2/MeOH, 2/1) afforded 0.15 g (58%) of maltotriose conjugate **5d**: $R_f = 0.17$ (CH_2Cl_2/MeOH, 3/1); IR (Drop casting on CaF_2, cm^{-1}) 3338 (br), 2927 (m), 1653 (m), 1544 (m), 1375 (w); ^{1}H NMR (400MHz, D_2O) δ 0.73 (t, *J*=6.8, 3H), 1.15-1.18 (m, 8H), 1.45-1.51 (m, 2H), 2.17-2.21 (m, 2H), 3.28 (t, *J*=9.2, 1H), 3.29 (t, *J*=9.2, 1H), 3.44-3.86 (m, 16H), 4.84 (d, *J*=9.2, 1H), 5.27 (d, *J*=4.0, 1H), 5.29 (d, *J*=3.6, 1H); ^{13}C NMR (100 MHz, D_2O) δ 13.2, 21.8, 24.9, 27.9, 28.0, 30.8, 35.7, 60.3, 60.3, 60.3, 69.2, 71.0, 71.4, 71.5, 71.6, 72.6, 72.7, 73.2, 75.9, 76.2, 76.5, 76.8, 78.9, 99.3, 99.6, 178.7; HRMS (FAB) cacld for $C_{26}H_{47}O_{16}NNa$ [M + Na]$^+$ 652.2793, found 652.2806.

Procedure for formation of bare vesicles

Bare vesicles with a total surfactant concentration of 1 wt% were prepared by adding 70 mg of SDBS and 30 mg of CTAT to 9.90 mL water (3:1 molar excess of SDBS). Samples were gently stirred for 30 min and then allowed to equilibrate for at least 48 h.

Procedure for formation of glycoconjugated vesicles

A 1 mM aqueous solution of the desired C_8-glycoconjugate was prepared. Vesicles with incorporated glycoconjugate and a total surfactant concentration of 1 wt% were prepared by adding 9.90 mL of the desired 1 mM glycoconjugate solution to 70 mg SDBS and 30 mg CTAT (3:1 molar excess of SDBS). Samples were gently stirred for 30 min and then allowed to equilibrate for at least 48 h. The vesicle preparation was subjected to size exclusion chromatography (see experimental section) to remove unincorporated glycoconjugate.