Experimental Section

General Techniques

NMR spectra were recorded on a JEOL Model ECP-400 (400 MHz for 1H, 100 MHz for 13C) instrument in the indicated solvent. Chemical shifts are reported in units per million (ppm) relative to the signal for internal tetramethylsilane (δ 0 ppm for 1H) for solutions in CDCl₃. NMR spectral data are reported as follows: chloroform-d (7.26 ppm for 1H), D₂O (HOD (4.8654 ppm at 285 K, 4.7015 ppm at 303 K, 4.6201 ppm at 311 K, 4.3560 ppm at 339 K as internal standard using 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt as external standard)) or (CD₃)₂CO (215.9 ppm for 13C) as internal standard for D₂O. Multiplicities are reported by using the following abbreviations: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, doublet of triplets; sep, septet; m, multiplet; br, broad; and , J, coupling constants in Hertz. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrophotometer. Only the strongest and/or structurally important absorption is reported as the IR data in cm⁻¹. All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254) with UV light, visualized by p-anisaldehyde solution, ceric sulfate or 0.5% ninhydrin n-butanol solution. Merck silica gel 60 (0.063 – 0.200 mm) was used for column chromatography. ESI TOF Mass spectra were measured with Waters LCT PremierTM XE. HRMS (ESI-TOF) were calibrated with leucine enkephalin (SIGMA) as an internal standard. Gel permeation chromatography (GPC) for quantitative analysis were performed on a Japan Analytical Industry Model LC 605 (recycling preparative HPLC), with a Japan Analytical Industry Model RI-5 refractive index detector and a Japan Analytical Industry Model 310 ultra violet detector with polystyrene gel column (JAIGEL- 1H, 20mm x 600mm) using chloroform as a solvent (3.5mL/min). Dry THF, dry CH₂Cl₂, dry MeCN, and dry toluene were obtained using a GlassContour solvent purification system.
Methyl (8-azidoctyl 5-amino-5-N,4-O-carbonyl-3,5-dideoxy-8-O-(methyl 5-amino-9-O-benzyl-5N,4O-carbonyl-3,5-dideoxy-7,8-O-isopropylidene-D-glycero-α-D-galacto-2-nonulopyranosylanate)-D-glycero-α-D-galacto-2-nonulopyranosid)onate (8)

A mixture of methyl (phenyl 5-amino-9-O-benzyl-5-N,4-O-carbonyl-7,8-O-isopropylidene-3,5-dideoxy-2-thio-D-glycero-β-D-galacto-2-nonulopyranosid)onate (8) (210 mg, 0.396 mmol,) and methyl (8-azidoctyl 5-amino-9-O-benzyl-5-N,4-O-carbonyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosid)onate (7) (109 mg, 0.198 mmol), and pulverized activated MS-3A (200 mg) in dry CH₂Cl₂ (4.00 mL) was stirred at room temperature for 30 min under argon to remove a trace amount of water. Then the reaction mixture was cooled to -78 °C. N-iodosuccinimide (93.7 mg, 0.416 mmol) and a catalytic amount of trifluoromethanesulfonic acid (3.50 mL, 0.0397 mmol) was added to reaction mixture at 0 °C in an argon atmosphere. The mixture was allowed to cool to -78 °C. After being stirred for 1.5 h with being allowed to -60 °C, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate mixture was poured into a mixture of saturated aq. NaHCO₃ and saturated aq. Na₂S₂O₃ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. NaHCO₃ and saturated aq. Na₂S₂O₃ and brine, dried over MgSO₄, filtered, and evaporated in vacuo. The residue was chromatographed on silica gel with 98:2 chloroform-methanol and further purified by gel permeation chromatography (GPC) to give 8 (163 mg, 0.168 mmol, 84%, α only). The α/β ratios were determined by ¹H NMR analysis.

[α]D²¹ -43.7 (c 1.42, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.35 (m, 10H, aromatic), 5.53 (br-s, 1H, NH), 5.36 (br-s, 1H, NH), 4.65 (d, 1H, Bn, J = 12.1 Hz), 4.60 (d, 1H, Bn, J = 12.1 Hz), 4.46-4.53 (m, 3H), 4.16-4.20 (m, 1H), 4.11 (dd, 1H, J = 2.4, 6.8 Hz), 3.94-4.04 (m, 3H), 3.79-3.94 (m, 9H), 3.77 (s, 3H), 3.65 (m, 1H), 3.57 (dd, 1H, J = 10.6, 11.1 Hz), 3.49 (dd, 1H, J = 10.1, 10.6 Hz), 3.19-3.26 (m, 4H), 3.03 (d, 1H, J = 6.3 Hz), 2.96 (dd, 1H, J = 3.4, 12.1 Hz), 2.91 (dd, 1H, J = 3.9, 12.1 Hz), 2.19 (dd, 1H, J = 12.1, 12.6 Hz), 2.02 (dd, 1H, J = 12.1, 12.6 Hz), 1.38 (s, 3H), 1.63 (s, 3H), 1.55-1.60 (m, 4H), 1.29 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 168.7, 168.0, 159.8, 159.8, 137.9, 137.6, 128.6, 128.5, 128.0, 127.8, 127.7, 109.3, (101.8, 100.3, anomeric), 76.6, 76.3, 76.0, 75.4, 75.2, 73.6, 73.6, 7.09, 70.4, 68.5, 65.1, 58.4, 58.2, 53.6, 52.8, 51.5, 37.4, 29.6, 29.3, 29.1, 28.8, 26.8, 26.7, 25.9, 24.9; IR (KBr) 3302, 2937, 2097, 1771, 1371, 1146, 1086, 754 (cm⁻¹); HRMS (ESI-TOF) Calcd for C₇R₆O₆N₅S₀₁₇ [M+H]⁺ 970.4297, found 970.4298.
Methyl (8-azidooctyl 5-amino-5-N,4-O-carbonyl-3,5-dideoxy-8-O-(methyl 5-amino-9-O-benzyl-5-N,4-O-carbonyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-D-glycero-α-D-galacto-2-nonulopyranosidonate) (9)

To a stirred solution 8 (70.4 mg, 0.0726 mmol) in THF (725 mL) and H₂O (150 mL) was added trifluoroacetic acid (580 mL) at room temperature. After being stirred at 40 °C for 1.5 h, the reaction mixture was poured into saturated aq. NaHCO₃ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. NaHCO₃, and brine, dried over MgSO₄, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 97:3 chloroform-methanol to give 9 (42.8 mg, 0.0462 mmol, 64%).

¹H NMR (400 MHz, CDCl₃) δ 7.27-7.34 (m, 10H), 6.13 (br-s, 1H), 5.92 (br-s, 1H), 4.56 (s, 2H), 4.51 (s, 2H), 4.30-4.31 (m, 1H), 3.94-4.05 (m, 3H), 3.59-3.90 (m, 16H), 3.53 (dd, 1H, J₁ = 9.2, 10.6 Hz), 3.48 (dd, 1H, J₁ = 9.2, 9.7 Hz), 3.42 (d, 1H, J₁ = 4.8 Hz), 3.19-3.26 (m, 4H), 2.96 (dd, 1H, J₁ = 3.4, 12.1 Hz), 2.89 (dd, 1H, J₁ = 3.9, 12.1 Hz), 2.21 (dd, 1H, J₁ = 12.1, 12.6 Hz), 2.03 (dd, 1H, J₁ = 12.1 Hz, 12.6 Hz), 1.50-1.61 (m, 4H), 1.23-1.34 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 168.8, 168.6, 160.5, 160.2, 137.8, 137.6, 128.6, 128.0, 127.9, 127.8, 127.8, 127.8, 127.8, 127.8, 127.8, 127.8, 100.5, 100.4, anomeric) 77.9, 77.8, 77.7, 76.2, 73.7, 71.9, 71.7, 71.2, 70.2, 69.9, 65.3, 58.7, 57.5, 53.7, 53.6, 53.0, 51.5, 37.4, 29.8, 29.6, 29.5, 29.5, 29.4, 29.3, 29.1, 28.9, 26.7, 26.7, 26.1, 26.1, 25.9; IR (KBr) 3398, 2930, 2097, 1749, 1366, 1074, 737 (cm⁻¹); HRMS (ESI-TOF) Calcd for C₄₄H₆₀N₅O₁₇ [M+H]⁺ 930.3984, found 930.3991.

8-aminooctyl 5-acetamido-8-O-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid)-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid (11)

To a stirred solution of 9 (21.7 mg, 0.0234 mmol) in 1,4-dioxane (1.00 mL) and H₂O (1.00 mL) was added LiOH•H₂O (30.0 mg) at room temperature. After being stirred at 80 °C for 40 h, the reaction mixture was evaporated in vacuo. The residue was purified by reverse-phase column chromatography (Bond Elut-C18). The residue was used for the next reaction. To a stirred solution of above residue in H₂O (2.00 mL) was add NaHCO₃ (50.0 mg) acetic anhydride (20.0 mL) at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was evaporated in vacuo. The residue was used for the next reaction without further purification. To a stirred solution of the residue in methanol (2.00 mL) was add NaOMe (20.0 mg) at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was evaporated in vacuo. The residue was purified by reverse-phase column chromatography (Bond Elut-C18). The residue was used for the next reaction. To a stirred solution of above residue in methanol (1.00 mL) and H₂O (1.00 mL) was added
Pd(OH)$_2$(40.0 mg). The reaction mixture was hydrogenolyzed for 3 h under H$_2$ gas atmosphere. The reaction mixture was filtered, and the filtrate was evaporated in vacuo. The residue was purified by reverse–phase column chromatography (Bond Elut-C18) to 11 (12.1 mg, 0.0166 mmol, 4 steps 71%).

$[\alpha]_D^{20}$ +9.31 (c 1.41, H$_2$O); $^1$H NMR (400 MHz, D$_2$O) δ 4.09-4.17 (m, 2H), 3.49-3.70 (m, 13H), 3.40 (dt, 1H, J = 6.8, 9.2 Hz), 2.97 (t, 2H, J = 7.7 Hz), 2.74 (dd, 1H, J = 4.8, 12.6 Hz), 2.62 (dd, 1H, J = 4.3, 12.6 Hz), 2.01 (s, H), 2.04 (s, H), 1.71 (dd, 1H, J = 12.6, 12.1 Hz), 1.51-1.65 (m, 5H), 1.31 (m, 8H); $^{13}$C NMR (100 MHz, D$_2$O, Acetone-d$_6$) δ 175.7, 175.7, 174.1, 174.1, (102.0, 101.2, anomeric), 79.5, 74.9, 73.6, 73.5, 72.5, 70.5, 69.2, 68.7, 65.6, 63.6, 63.5, 62.5, 62.5, 53.3, 52.7, 52.7, 41.4, 40.3, 29.5, 28.7, 27.4, 26.1, 25.7, 23.1, 22.9; IR (KBr) 3436, 2930, 1603, 1437, 1038, 667 (cm$^{-1}$); HRMS (ESI-TOF) Calcd for C$_{36}$H$_{44}$N$_2$O$_{17}$ [M+H]$^+$ 728.3453, found 728.3455.

\[N\text{-5,6-heptadienylcarbonylaminooctyl 5-acetamido-8-O-(5-acetamido-3,5-dideoxy-D-glycero-\(\alpha\)-D-galacto-2-nonulopyranosylonic acid)-3,5-dideoxy-D-glycero-\(\alpha\)-D-galacto-2-nonulopyranosylonic acid (3-12)}\]

To a stirred solution of 8-aminoctyl 5-acetamido-8-O-(5-acetamido-3,5-dideoxy-D-glycero-\(\alpha\)-D-galacto-2-nonulopyranosylonic acid)-3,5-dideoxy-D-glycero-\(\alpha\)-D-galacto-2-nonulopyranosylonic acid (3-10) (5.73 mg, 7.58 µmol, 1.00 eq.) in H$_2$O (500 µL) was added 2,5-dioxo pyrrolidin-1-yl 5,6-heptadienoate (3-11) (3.38 mg, 15.2 µmol, 2.00 eq.) in 1,4-dioxane (500 µL) at room temperature. After being stirred at the same temperature for 17 h, the reaction mixture was evaporated in vacuo. The residue was purified by reverse-phase column chromatography (Bond Elut-C18) to give N-5,6-heptadienylcarbonylaminooctyl 5-acetamido-8-O-(5-acetamido-3,5-dideoxy-D-glycero-\(\alpha\)-D-galacto-2-nonulopyranosylonic acid)-3,5-dideoxy-D-glycero-\(\alpha\)-D-galacto-2-nonulopyranosylonic acid (3-12) (5.00mg, 5.98 µmol, 79%).

$[\alpha]_D^{21}$ +0.206 (c 0.225, MeOH); $^1$H NMR (400 MHz, D$_2$O) δ 5.12 (tt, 1H, J = 6.6 Hz), 4.69 (dt, 2H, J = 6.6 Hz), 4.09-4.16 (m, 2H), 3.53-3.88 (m, 13H), 3.38 (dt, 1H, J = 7.2, 8.7 Hz), 3.07 (m, 2H), 3.12 (m, 2H), 2.73 (dd, 1H, J = 4.4, 12.1 Hz), 2.60 (dd, 1H, J$_{3eq,4}$ = 4.4, 12.1 Hz), 2.23 (m, 2H), 1.99 (s, 6H), 2.02 (s, 6H), 1.84-1.92 (m, 2H), 1.71 (t, 1H, J = 12.1 Hz), 1.50-1.58 (m, 3H), 1.10-1.26 (m, 10H); $^{13}$C NMR (100 MHz, D$_2$O) δ 215.5, 208.4, 176.0, 175.1, 175.1, 173.4, 101.4, 100.6, 89.4, 78.7, 75.2, 774.2, 72.8, 71.8, 70.0, 68.5, 68.4, 68.0, 65.2, 62.8, 61.8, 52.6, 52.0, 40.6, 39.5, 35.3, 29.2, 28.9, 28.7, 28.6, 28.6, 27.2, 26.3, 25.5, 25.4, 25.0, 22.6, 22.5, 22.3; HRMS (ESI-TOF) Calcd. for C$_{37}$H$_{62}$N$_2$O$_{18}$ [M+H]$^+$ 836.4028, found 836.3994.
diSia-Bn ester monomer 16

To a stirred solution of 5 (137 mg, 0.164 mmol) in DMF (1.64 mL) was added BnBr (58.5 µL, 0.492 mmol), Cs₂CO₃ (214 mg, 0.656 mmol) and a catalytic amount of TBAI at room temperature. After being stirred at 60 °C for 24 h, the reaction mixture was evaporated in vacuo. The residue was purified by column chromatography on silica gel with 90:10 chloroform:methanol to give diSia-Bn monomer 6 (93.8 mg, 0.103 mmol, 61%).

[α]D –20.3 (c 1.61, CHCl₃); ¹H NMR (400 MHz, CD₃OD) δ 7.30–7.50 (m, 5H), 5.29 (d, 1H, J = 12.2 Hz), 5.19 (d, 1H, J = 12.2 Hz), 5.09 (dt, 1H, J = 12.2 Hz), 4.85 (dd, 1H, J = 12.2 Hz), 4.63-4.68 (m, 2H), 4.59 (dd, 1H, J = 4.9, 12.2 Hz), 4.34 (dt, 1H, J = 5.4, 10.8 Hz), 4.23 (dt, 1H, J = 11.7 Hz), 4.07 (dd, 1H, J = 7.3, 14.6 Hz), 3.45-3.89 (m, 13H), 3.14 (dd, 2H, J = 6.8, 7.3 Hz), 2.67 (dd, 1H, J₁₆ = 4.9, 12.7 Hz), 2.38 (dd, 1H, J₁₆ = 5.4, 12.2 Hz), 2.21 (dd, 2H, J₁₆ = 7.4, 7.8 Hz), 1.90-2.15 (m, 8H), 1.55-1.76 (m, 4H), 1.37-1.55 (m, 4H), 1.27-1.35 (m, 6H); ¹³C NMR (100 MHz, CD₃OD) δ 210.9, 176.6, 176.3, 175.8, 170.4, 168.6, 137.7, 135.1, 132.8, 131.2, 130.6, 130.5x2, 130.4x2, (101.5, 98.3, anomeric), 90.7, 75.8, 75.3, 75.2, 73.3, 72.9, 72.5, 70.6, 70.4, 69.5, 69.4, 69.1x2, 66.3, 65.9, 54.6, 54.3, 42.9, 42.6, 41.3, 41.2, 37.2, 31.5, 31.2, 31.1, 29.6, 28.7, 27.8, 27.7, 27.3, 23.7, 23.4; IR (KBr) 3272, 2931, 1742, 1638, 1557, 1456, 1375, 1182, 1125, 1040, 700, 613 (cm⁻¹); HRMS (ESI-TOF) Calcd. for C₄₄H₆₂N₃O₁₇ [M+H]+ 908.4392, found 908.4419.

Polymrization of the lactone monomer 16 to 17a and 17b

Bis(1,5-cyclooctadiene)nickel (0.1 M solution of toluene), 10-azido-3-trifluoroacetyl-1-decene (14) (0.1 M solution of toluene) and Monomer (1.00 eq.) in solvent were placed under a nitrogen atmosphere in a test tube equipped with a three way tap and a magnetic stirrer bar. The mixture was stirred at room temperature for reaction time. After complete conversion of the monomer (monitored by TLC analysis), the solution was precipitated with solvent and concentrated in vacuo to give Polymer.

20 mer 17a

According to the general procedure 2 with the following amounts: Bis(1,5-cyclooctadiene) nickel (41.2 µL, 4.12 µmol, 0.0500 eq.), 10-azido-3-trifluoroacetyl-1-decene (14) (41.2 µL, 4.96 µmol, 0.0600 eq.) was added a solution of diSia-Bn monomer (16) (75.0 mg, 82.6 µmol, 1.00 eq.) in MeOH (500 µL) at room temperature for 3 days to give
azido-poly-disia-Bn ester 20 mer 17a (73.1 mg, 97%).

$^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 7.20-7.45 (m, 5H), 5.10-5.40 (m, 2H), 4.50-4.67 (br-m), 4.20-4.40 (br-m, 1H), 4.00-4.12 (dt, 1H, $J = 5.4, 11.7$ Hz), 3.40-3.95 (br-m, 1H), 3.00-3.40 (br-m, 4H), 2.47-2.79 (br-m, 2H, H-3eq., H-3’eq.), 1.80-2.46 (br-m, 10H), 1.03-1.80 (br-m, aliphatic); IR (KBr) 3442, 2095, 1640, 611 (cm$^{-1}$).

50 mer 17b

According to the general procedure 2 with the following amounts: Bis(1,5-cyclooctadiene) nickel (13.0 µL, 1.30 µmol, 0.0200 eq.), 10-azido-3-trifluoroacetyl-1-decene (14) (13.0 µL, 1.56 µmol, 0.0240 eq.) was added a solution of diSia-Bn monomer 16 (59.0 mg, 65.0 µmol, 1.00 eq.) in MeOH (500 µL) at room temperature for 3 days to give azido-poly-disia-Bn ester 50 mer 17b (52.3 mg, 89%).

$^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 7.15-7.42 (m, 5H, aromatic), 5.10-5.40 (m, 2H), 4.45-4.70 (br-m), 4.18-4.40 (br-m, 1H), 4.00-4.15 (br-m, 1H), 3.42-3.97 (br-m, 1H), 3.00-3.40 (br-m, 4H), 2.47-2.79 (br-m, 2H), 1.03-2.46 (br-m, H-3ax., H-3’ax., Acx2, NHC(O)C$_2$H$_2$, aliphatic); IR (KBr) 3291, 2108, 1743m 1641, 1559, 1126, 1072, 1038 (cm$^{-1}$).

**Hirololysis of the Glycopolymers 17a and 17b**

20 mer 3a

To a stirred solution of azido-poly-disia-Bn ester 20 mer 17a (24.3 mg, 1.34 µmol, 1.00 eq.) in H$_2$O (500 µL) and 1,4-dioxane (500 µL) was added LiOH·H$_2$O (0.561 mg, 13.4 mmol, 10.0 eq.) at room temperature. After being stirred at 60 °C for 1 day, the reaction mixture was evaporated in vacuo. The residue was purified with PD-10 to give 20mer 3a (22.0 mg, quant.). DP and PDI of the purified polymer 17a were estimated by a size-exclusion chromatography (SEC: TSKgel-α2500 and TSKgel-α3000) eluted with 0.1% CHO$_2$H in H$_2$O solution to be 26 and 1.09, respectively. Mn was determined relative to a PEG standard samples

$^1$H NMR (400 MHz, D$_2$O) $\delta$ 5.00-5.30 (br-s, 0.7 H), 3.88-4.20 (br-m, 2H, H-8, H-9a), 3.40-3.90 (br-m, 14H, H-4, H-5, H-6, H-7, H-9b, H-4’, H-5’, H-6’, H-7’, H-8’, OCH$_2$X2), 3.30 (br-s, 1H, OCH$_2$CH$_2$), 2.90-3.10 (br-s, 1H, OCH$_2$CH$_2$), 2.44-2.70 (br-m, H-3eq., H-3’eq.), 1.70-2.20 (br-m, 10H, H-3ax., H-3’aix., Acx2, NHC(O)CH$_2$), 0.95-1.70 (br-m, aliphatic)

**GPC-HPLC chart of 3a**
50 mer 3-29c

To a stirred solution of azido-poly-disia-Bn ester 50 mer 17b (17.3 mg, 0.381 µmol, 1.00 eq.) in H$_2$O (500 µL) and 1,4-dioxane (500 µL) was added LiOH · H$_2$O (0.160 mg, 3.81 µmol, 10.0 eq.) at room temperature. After being stirred at 60 °C for 1 day, the reaction mixture was evaporated in vacuo. The residue was purified with PD-10 to give azido-poly-N-5,6-heptadienylcarbonylaminooctyl 5-acetamido-8-O-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid)-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid 50mer 3b (16.5 mg, quant.). DP and PDI of the purified polymer 17b were estimated by a size-exclusion chromatography (SEC: TSKgel-α2500 and TSKgel-α3000) eluted with 0.1% CHOOH in H$_2$O solution to be 42 and 1.14, respectively. Mn was determined relative to a PEG standard samples.

$^1$H NMR (400 MHz, D$_2$O) δ 5.00-5.40 (br-s, 0.5 H), 3.90-4.20 (br-m, H-8, H-9a), 3.20-3.90 (br-m, 15H, H-4, H-5, H-6, H-7, H-9b, H-4’, H-5’, H-6’, H-7’, H-8’, H-9’x2, OCH$_2$x2, OCH$_3$CH$_2$), 3.01 (br-s, OCH$_3$CH$_2$), 2.40-2.75 (br-m, 2H, H-3eq., H-3’eq.), 1.70-2.30 (br-m, 10H, H-3ax., H-3’ax., Acx2, NHC(O)CH$_2$), 0.90-1.70 (br-m, aliphatic).

![GPC-HPLC chart of 3b](image)

**Fluorescent labeling of the glycolymer 3**

20 mer 1a

To a stirred solution of azido-poly-N-5,6-heptadienylcarbonylaminooctyl 5-acetamido-8-O-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid)-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid 20 mer 3-29b (10.2 mg, 5.62 µmol, 1.00 eq.) and TAMRA-alkyne (0.627 mg, 1.12 µmol, 2.00 eq.) in saturated aq. NaHCO$_3$ (500 µL) was added a catalytic amount of 0.5 M aqueous CuSO$_4$ and 0.5 M aqueous Na ascorbate at room temperature. After being stirred at the same temperature for 1 day, the reaction mixture was evaporated in vacuo. The residue was purified with PD-10 to give TAMRA-poly-N-5,6-heptadienylcarbonylaminooctyl 5-acetamido-8-O-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonicacid)-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid 20 mer 3-30b (10.3 mg, quant.).

$^1$H NMR (400 MHz, D$_2$O) δ 8.34 (s, aromatic), 4.90-5.10 (br-s), 3.90-4.10 (br-m, 2H, H-8, H-9a), 2.80-3.83 (br-m, 19H, H-4, H-5, H-6, H-7, H-9b, H-3’, H-4’, H-5’, H-6’, H-7’, H-8’, H-9’x2, OCH$_3$, OCH$_3$CH$_2$, NHCH$_2$), 2.40-2.70 (br-m, 2H, H-3eq., H-3’eq.), 0.80-2.20 (br-m, H-3ax., H-3’ax., Acx2, aliphatic); IR (KBr) 3437, 1634, 1361, 1121, 837, 769, 669, 620 (cm$^{-1}$); HRMS

50 mer 1b

To a stirred solution of azido-poly-N-5,6-heptadienylcarbonylaminooctyl 5-acetamido-8-O-(5-acetamido-3,5-dIDEOXY-D-GLYCERO-Α-D-GALACTO-2-NONULOPYRANOSYLONIC ACID)-3,5-DIDEOXY-D-GLYCERO-Α-D-GALACTO-2-
nonulopyranosylonic acid 50 mer 3-29c (9.7 mg, 0.214 µmol, 1.00 eq.) and TAMRA-alkyne (0.239 mg, 4.27 µmol, 2.00 eq.) in saturated aq. NaHCO₃ (500 µL) was added a catalytic amount of 0.5 M aqueous CuSO₄ and 0.5 M aqueous Na ascorbate at room temperature. After being stirred at the same temperature for 1 day, the reaction mixture was evaporated in vacuo. The residue was purified with PD-10 to give TAMRA-poly-N-5,6-heptadienylcarbonyl-aminoctyl 5-acetamido-8-O-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid)-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid 50 mer 3-30c (10.0 mg, quant.).

¹H NMR (400 MHz, D₂O) δ 8.32 (br-s, 0.1 H, aromatic), 3.95-4.10 (br-m, 2H, H-8, H-9a), 3.20-3.90 (br-m, 17H, H-4, H-5, H-6, H-7, H-9b, H-3’, H-4’, H-5’, H-6’, H-7’, H-8’, H-9’x2, OCH₂, OCH₂CH₂), 2.90-3.10 (br-s, 2H, NHCH₂), 2.63 (br-dd, 1H, H-3eq. or H-3’ eq., J₃,₄ = 2.9 Hz, J₆,gem = 11.2 Hz), 1.70-2.20 (br-m, 10H, H-3ax., H-3’ax., Acx₂, NHCOCH₃), 1.00-1.70 (br-m, aliphatic).
Dissociating effect of the fluorescent-labelled diSia polymers 1a and 1b and the diSia 18 on the Siglec-7-GD3 interaction

Fc chimaera containing the three N-terminal domains of siglec-7 were purified with Protein A–agarose from tissue culture supernatants of stably transfected CHO cells. 996 well plastic plates were incubated with GD3 in ethanol (30 pmol/well) and solution was dried up for incubation at 37°C for 2h. The immobilized GD3 was a target molecule for Siglec7. Prior to the binding assay, the Fc-chimaeras were complexed with an anti-human IgG+M+A antibody coupled to peroxidase (1:1000 dilution) in 0.1% BSA containing PBS (10 mM phosphate buffer, 150 mM NaCl (pH 7.2)) for 30 min at room temperature. A 50 µl aliquot of this mixture was added per well and incubated for 4 h at room temperature. After five washes with PBS containing 0.05% tween-20 (PBST), the diSia polymer (1a and 1b) or diSia (18) containing PBS or PBS was added to the plate and incubated for 1 h at room temperature. After washing with PBST, 100 µl of the substrate solution was added to the well (100 mM Tris·HCl (pH 6.8), 0.05% o-phenylenediamine, 0.006% H2O2) and the reaction was stopped by adding 100µl of 2N H2SO4. The amount of bound peroxidase was quantified by the measurement of absorbance 490 nm using a microplate reader.

Supplemental figure. Inhibition of the GD3-Siglec7 interaction in the presence or absence of inhibitors.

The GD3-Siglec7 interaction was measured by the ELISA based method. The absorbance in the absence of inhibitors were set to 1.0. Disia-octyl (18), monoSia-octyl, polydiSia (20) (1a) and polydiSia (50) (1b) were used as inhibitors as indicated concentrations. The concentration that lead to 50% inhibition was defined as IC50.
20 mer 3a

50mer 3b