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Lactotriaose-containing carbosilane dendrimers: Syntheses and lectin-binding activities

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Abstract—Carbosilane dendrimers periphery-functionalized with lactotriaose (GlcNAcβ1–3Galβ1–4Glc) with valencies of three, four, six, and twelve were prepared for use in a lectin-binding assay. A lactotriaose derivative was prepared from D-glucosamine and D-lactose derivatives. The *N*-Troc-protected glucosamine glycosyl donor and 3′-O-unprotected lactose glycosyl acceptor were condensed in the presence of silver trifluoromethanesulfonate and methylsulfenyl bromide to provide corresponding trisaccharide with new β-1-3 linkages in 92% yield. The protection group of the trisaccharide was transformed into an acetyl group. The 4-pentenyl glycoside was prepared from the acetate via glycosyl bromide. The alkene was converted into acetyl sulfide by addition of thioacetic acid under radical conditions. The lactotriaose unit was linked with carbosilane dendrimers to afford acetyl-protected glycodendrimers. De-O-acetylation of the dendrimers was carried out in the presence of sodium methoxide and then aq NaOH to give the desired lactotriaose clusters using a carbosilane dendrimer backbone. Their biological activities toward WGA were evaluated by fluorescence methods. The binding constants of free lactotriaose and trivalent, tetravalent, hexavalent, and dodecavalent glycodendrimers to WGA were determined to be 1.1×10^3, 4.4×10^4, 5.1×10^4, 2.8×10^6, and 1.3×10^6 M^{-1}, respectively. The hexavalent glycodendrimer showed a 2500-fold larger binding effect than that of free lactotriaose.

1. Introduction

It is known that carbohydrate substructures of cell surface glycoconjugates constitute important binding sites for a variety of pathogen infections.[1] Multivalent carbohydrate–protein interactions are often observed in biological systems and they appear to enhance affinity. This event due to multivalency has also been called the *glycoside cluster effect*.[2] Artificial multivalent carbohydrate ligands have been synthesized, and some of them have shown remarkable enhancement effects.[3] We have also reported syntheses of some glycodendrimers having globotriaose,[4] galabiose,[5] sialyllactose,[6] mannobiose,[7] and functional saccharides[8] in which carbosilane dendrimers were employed as the scaffolds of carbohydrate, and we have described the biological activities of some of these glycodendrimers.[5,9] The hexavalent glycodendrimer periphery-functionalized with globotriaose (Galα1–4Galβ1–4Glcβ1–) neutralized Vero toxin-producing *Escherichia coli* O157:H7 with high affinity in in vivo experiments using mice.[9a]

Recently, syntheses of lacto-*N*-neotetraose (Galβ1–4GlcNAcβ1–3Galβ1–4Glc) clusters targeting dengue virus have been reported.[10] Dengue virus is involved in dengue fever and dengue hemorrhagic fever. The incidence of these viral infections is increasing in many

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countries located in tropical and subtropical areas. However, no effective vaccines or anti-dengue agents have yet been developed. Suzuki et al. discovered that dengue virus preferentially adheres to lacto-*N*-neotetraose located on the surfaces of eukaryotic cells. Synthesized hexavalent lacto-*N*-neotetraose cluster inhibited dengue virus infection of BHK-21 cells, thus demonstrating the potential therapeutic usefulness of lacto-*N*-neotetraose cluster compounds as dengue virus inhibitors.[11]

It would be interesting to investigate why hexavalent clusters are so effective between different types of donors and acceptors. The biological activities of many artificial glycoclusters have been evaluated by using lectins. Lectins are thought to be ideal models for studying carbohydrate–protein interactions with glycoclusters. To investigate the binding activities of lactotriaose clusters, we selected the wheat germ agglutinin (WGA), which specifically recognizes *N*-acetyl glucosamine. It is known that fluorescence methods can be used for binding experiments with WGA and saccharide derivatives.[12]

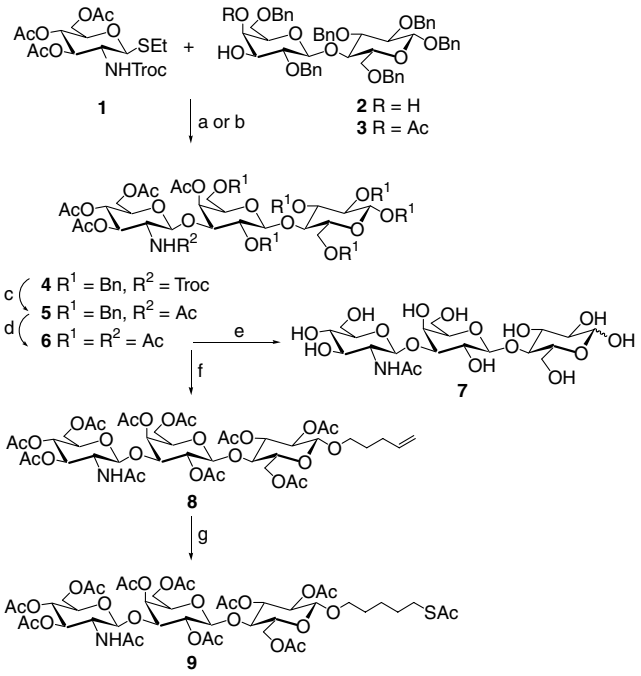
Herein, we describe the syntheses of lactotriaose dendrimers and the specific binding properties of families of lactotriaose dendrimers with WGA.

Furthermore, chemical synthesis of a lacto-*N*-neotetraose residue and clusters requires many reaction steps. It is important to improve the synthetic problems for the practical use of a carbosilane dendrimer having lacto-*N*-neotetraose. A lactotriaose (GlcNAcβ1–3Galβ1–4Glc) cluster is one of the precursors for the efficient synthesis of a lacto-*N*-neotetraose cluster. Since the synthesis of a lactotriaose cluster is easier than that of a lacto-*N*-neotetraose cluster, and the trisaccharide can be easily converted into the tetrasaccharide by using enzymatic glycosylation, Zanini and Roy[13] reported successful enzymatic conversion of GlcNAc to LacNAc on a synthetic dendrimer. Moreover, Narvor and coworkers[14] reported enzymatic synthesis of lacto-*N*-neotetraose using dendrimeric polyethylene glycol. Lacto-*N*-neotetraose was obtained by using β-(1–4)-galactosyl transferase with a chemo-enzymatically synthesized lactotriaose cluster using dendrimeric polyethylene glycol. Therefore, carbosilane dendrimers having lactotriaose are expected to be candidates for improving the synthetic problems of the dengue virus inhibitor, having lacto-*N*-neotetraose.

2. Results and discussion

2.1. Syntheses of glycodendrimers

The known *N*-Troc-protected thioglycoside (**1**)[15] was prepared from glucosamine hydrochloride. Glycosylation of the known 3′,4′-O-unprotected acceptor (**2**)[16] with donor **1** under promotion of methylsulfenyl bromide (MeSBr)[17] and silver trifluoromethanesulfonate (AgOTf) in CH_2Cl_2 for 15 h at −78 °C, followed by O-acetylation, furnished trisaccharide (**4**) in 43% yield, and about 28% of the 3′,4′-O-acetylated glycosyl acceptor was recovered (Scheme 1). A trace amount of 3′,4′-



Scheme 1. Reagents and conditions: (a) **2**, AgOTf, MeCN, CH_2Cl_2, −78 °C, 10 min, then MeSBr, $ClCH_2CH_2Cl$, −78 °C, 15 h, then Ac_2O, pyridine, 2 h (43%); (b) **3**, AgOTf, MeCN, CH_2Cl_2, −60 °C, 20 min, then MeSBr, $ClCH_2CH_2Cl$, −60 to −30 °C, 1 h (92%); (c) Zn, AcOH, 30 min, then Ac_2O, pyridine 7.5 h (97%); (d) H_2, $Pd(OH)_2$/C, MeOH, 16 h, then Ac_2O, DMAP, pyridine, 7 h (quant); (e) NaOMe, MeOH, 2 h, then aqueous NaOH, 4 h (82%); (f) HBr/AcOH, 16 h, then 4-pentene-1-ol, Ag_2CO_3, MS 4 Å, I_2, CH_2Cl_2, 2 days (50%); (g) AcSH, AIBN, 1,4-dioxane, 80 °C, 3 h (87%).

O-glycosylated tetrasaccharide was obtained as a by-product. Consequently, 3′-O-unprotected lactose derivative (**3**)[18] was chosen as another glycosyl acceptor. The compound **3** could be readily obtained from compound **2** by treatment with methyl orthoacetate and then with acetic acid. Glycosylation of **1** with 3′-O-unprotected derivative **3** under promotion of MeSBr and AgOTf in CH_2Cl_2 for 1 h at −60 to −30 °C furnished trisaccharide **4** in 92% yield; no stereoisomeric glycosides could be isolated from the reaction mixture. The β-glucosamine linkage was confirmed by the ^1H NMR signal at δ 4.67 ppm ($J_{1''2''} = 8.7$ Hz, H-1″) and the ^{13}C NMR signals at δ 102.42, 101.91, and 100.92 ppm (C-1, C-1′, and C-1″, respectively). Elemental analysis and FAB-MS spectrum ($[M+H]^+$ 1386.7) also support the trisaccharide structure. The *N*-Troc group of **4** was transformed into an acetamido group by zinc powder in acetic acid, followed by N-acetylation, to give *N*-Ac-protected glycoside (**5**)[19] in 97% yield. Compound **5** was de-O-benzylated by hydrogenolysis in methanol, and the crude product was O-acetylated by acetic anhydride and a catalytic amount of 4-dimethylaminopyridine in pyridine to furnish acetate (**6**)[19] (mixture of α and β anomers) in quantitative yield. De-O-acetylation of **6** with sodium methoxide in methanol and then saponification yielded lactotriaose (**7**)[20] in 82% yield after gel filtration. The 4-pentenyl glycoside (**8**) was prepared via glycosyl bromide by treatment with silver carbonate in 50% yield. Treatment of **8** with thioacetic acid and AIBN gave 5-acetylthiopentyl glycoside (**9**) in 87% yield. The struc-

ture of **9** was confirmed by ^{1}H and ^{13}C NMR spectra, FAB-MS spectrum, and elemental analysis. The signals at 2.83 (t, 2H, $J = 7.3$ Hz, CH_2SAc) and 2.31 (s, 3H, CH_2SAc) ppm in the ^{1}H NMR spectrum of **9** prove the formation of acetylthio function.

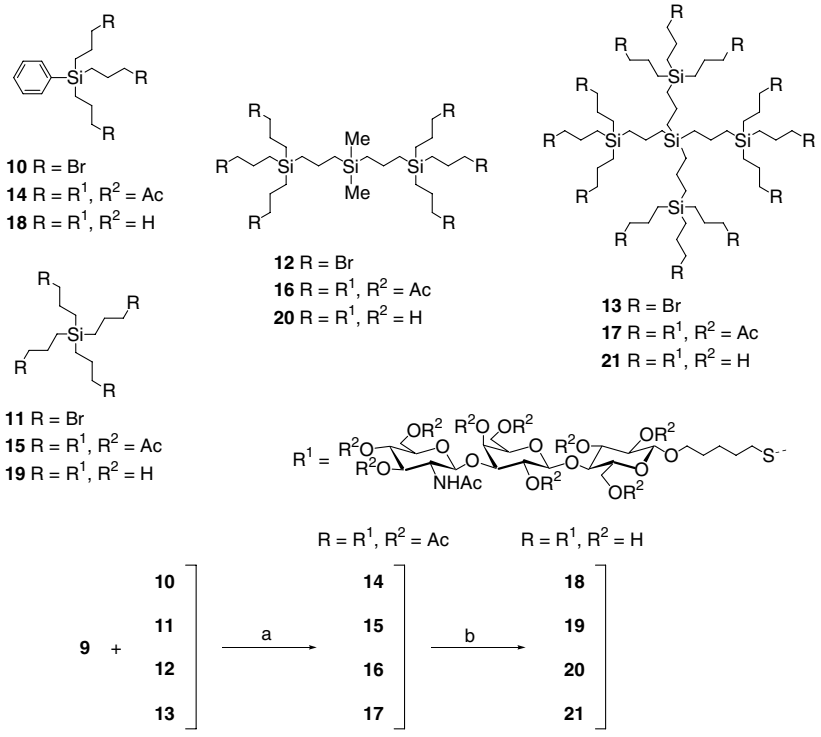
Carbosilane dendrimers **10** and **11** were synthesized by a previously described method.[4b,c] Lactotriaose derivative **9** was attached to tri- (**10**), tetra- (**11**), hexa- (**12**), and dodecavalent dendritic carbosilane scaffolds (**13**) (Scheme 2). Compound **9** (1.4 equiv per bromine functionality) was coupled in good yields to the respective (poly)bromide dendrimers by treatment with sodium methoxide in a mixture of methanol and DMF. The crude product was O-acetylated by acetic anhydride with a catalytic amount of 4-dimethylaminopyridine in pyridine. The resultant products were purified by a recycling preparative HPLC to give acetylated glycodendrimers **14** (66%), **15** (45%), **16** (61%), and **17** (73%). All acetylated glycodendrimers were examined by means of ^{1}H and ^{13}C NMR spectra. Finally, de-O-acetylation of the acetylated glycodendrimers with sodium methoxide in methanol and then saponification gave lactotriaose-coated carbosilane dendrimers trivalent **18** (68%), tetravalent **19** (81%), hexavalent **20** (54%), and dodecavalent **21** (89%). These glycodendrimers were identified by ^{1}H and ^{13}C NMR spectra. Further evidence of the synthesized glycodendrimers was obtained by high-resolution mass spectroscopy (Table 1). The results showed good agreement with the calculated values for the expected structures. The molecular weight of the acetylated and de-O-acetylated dodecavalent dendrimers (**17** and **21**) was too great to measure with high-resolution mass spectra.

2.2. Interaction of glycodendrimers with WGA

The versatility of lactotriaose cluster compounds was investigated by determining the binding specificity of these glycoclusters with WGA. Fluorescence methods have been used extensively to study the specific interaction of WGA with sugars[12] and glycopolymers.[21] It is known that the values of binding constants of WGA with chitin oligomers [(Glc*p*NAc)$_n$] increase with increase in the length of these oligomers. Privat et al.[12b] reported that changes in tryptophan fluorescence by addition of a chitin oligomer depend on the ligand size and that oligomers produced a 10-nm shift toward shorter wavelength and 46% enhancement of fluorescence intensity. The binding constants of chitin oligomers to WGA were determined to be 6.9×10^2 (Glc*p*NAc), 4.5×10^3 [(Glc*p*NAc)$_2$], 2.0×10^4 [(Glc*p*NAc)$_3$], and 2.3×10^4 M^{-1} [(Glc*p*NAc)$_4$]. Nishimura et al.[21a] reported that a synthesized glycopolymer carrying a GlcNAc residue effectively bound to WGA and that the polymer produce a 6-nm shift toward a shorter wavelength and 43% enhancement of fluorescence intensity.

Synthesized carbosilane dendrimers having lactotriaose, in contrast to glycopolymers, have a monodispersed and well-defined structure. Therefore, tests of binding activities of the dendrimers with WGA are expected to give clearer results.

Figure 1 shows the emission spectra of WGA and its complexs with monovalent saccharide **7** (Fig. 1A) and dodecavalent dendrimer **21** (Fig. 1B) at pH 7.8. The monovalent **7** showed no enhancing effect on fluorescence intensity in the range of micromolar



Scheme 2. Reagents and conditions: (a) NaOMe, MeOH, DMF, 3 h, then Ac_2O, DMAP, pyridine, 50 °C, 3 h (66% for **14**, 45% for **15**, 61% for **16**, and 73% for **17**); (b) NaOMe, MeOH, then aqueous NaOH (68% for **18**, 81% for **19**, 54% for **20**, and 89% for **21**).

Table 1. HRMS (ESI) of the glycodendrimers

Compound	Formula	*m/z* (calculated)	*m/z* (found)
Acetylated-trivalent (**14**)	$C_{144}H_{209}N_3O_{75}S_3Si+2Na^+$	1675.0674	1675.0668
Acetylated-tetravalent (**15**)	$C_{184}H_{272}N_4O_{100}S_4Si+3Na^+$	1454.1550	1454.1552
Acetylated-hexavalent (**16**)	$C_{284}H_{426}N_6O_{150}S_6Si_3+4Na^+$	1672.0773	1672.0805
Acetylated-dodecavalent (**17**)	$C_{564}H_{840}N_{12}O_{300}S_{12}Si_5+Na^+$	13136.8[a]	13135.5[b]
Trivalent (**18**)	$C_{90}H_{155}N_3O_{48}S_3Si+2Na^+$	1107.9248	1107.9281
Tetravalent (**19**)	$C_{112}H_{200}N_4O_{64}S_4Si+2Na^+$	1413.5477	1413.5525
Hexavalent (**20**)	$C_{176}H_{318}N_6O_{96}S_6Si3+3Na^+$	1465.5832	1465.5858
Dodecavalent (**21**)	$C_{348}H_{624}N_{12}O_{192}S_{12}Si_5+4Na^+$	2164.9	2166.5

[a] The value is average mass.
[b] The value is from MALDI-TOFMS.

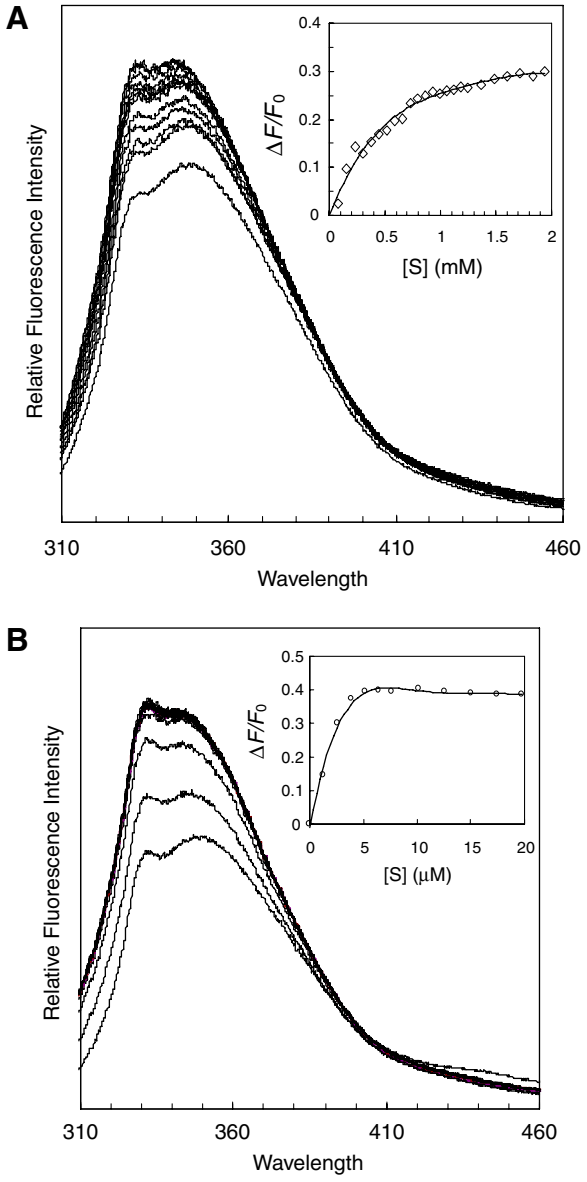


Figure 1. Changes in fluorescence spectrum of WGA (0.69 μM, 3.0 mL of Tris–HCl buffer-containing 1.25 M NaCl and 25 mM $CaCl_2$, pH 7.8, 5.0 °C) upon addition of (A) 40-μL aliquots of the monovalent saccharide **7** (11.6 mM) and (B) 10-μL aliquots of the dodecavalent dendrimer **21** (0.32 mM). ΔF is change in the fluorescence intensity at fluorescence maximum wavelength of a solution containing the lectin obtained by exciting at 295 nm with a total ligand concentration [S], and F_0 is the fluorescence intensity of lectin alone.

Table 2. K_a values of the glycodendrimers with WGA

Compound	K_a[a] (M^{-1})	Relative potency
Monovalent (**7**)	1.1×10^3	1
Trivalent (**18**)	4.4×10^4	40
Tetravalent (**19**)	5.1×10^4	46
Hexavalent (**20**)	2.8×10^6	2500
Dodecavalent (**21**)	1.3×10^6	1200

[a] K_a values are calculated from Steck–Wallack plot analyses.

concentrations. However, in the range of millimolar concentrations of **7**, maximum fluorescence intensity was enhanced by 30% and the emission maximum was shifted from 349 to 345 nm (Fig. 1A). In contrast, when lectin was saturated with dodecavalent **21**, maximum fluorescence intensity was enhanced by 40% and the emission maximum was shifted from 350 to 344 nm (Fig. 1B). Three other dendrimers also showed enhancement of fluorescence intensities and 8-nm shifts of the emission maximum. The intensity was enhanced by 33% (**18**), 30% (**19**), and 44% (**29**). The K_a values of these clusters and monomeric lactotriaose to WGA were determined by Steck–Wallack plot analysis (Table 2). The K_a value of trivalent glycocluster **18** was similar to that of tetravalent **19**. The **18** and **19** were 40 times and 46 times more potent, respectively, than lactotriaose monomer **7**. The hexavalent cluster **20** showed the maximum K_a value (2.8×10^6 M^{-1}) in the clusters, the K_a value being 2500 times larger than that of monovalent **7**. Interestingly, dodecavalent cluster **21** showed less potency than hexavalent **20**, which could be attributed to the over-crowding of the poorly accessible surface saccharide moieties of the dendrimer **21**. These results clearly indicate that lactotriaoses supported on the hexavalent glycodendrimer are suitable for binding to WGA.

3. Conclusion

High stereo-selective synthesis of a lactotriaose derivative in high yield was accomplished by using the 3′-O-unprotected lactose derivative **3** and *N*-Troc-protected glucosamine derivative **1**. A series of new carbosilane dendrimers periphery-functionalized with lactotriaose was successfully synthesized. The hexavalent glycodendrimer showed a 2500-fold larger binding effect than that of free lactotriaose, though the dodecavalent one exhibited only a 1200-fold larger binding effect.

4. Experimental

4.1. General methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 400, at 400 MHz for proton and at 100 MHz for carbons, respectively. Proton chemical shifts are given in ppm with use of tetramethylsilane (0 ppm) or residual solvent peaks as internal standard. NMR signals were assigned by ^{1}H, ^{13}C, HH, and HC COSY measurements. FAB mass spectra were obtained with a JEOL JMS-HX110A spectrometer. Optical rotations were recorded on a JASCO DIP-1000 digital polarimeter at ambient temperature, using a 10-cm micro cell. Recycling preparative HPLC was performed with a LC-908 or LC-918W (Japan Analytical Industry Co., Ltd) connected to an RI detector RI-5.

4.1.1. Benzyl *O*-[3,4,6,-tri-*O*-acetyl-2-deoxy-2-(2,2,2,-trichloroethoxycarbonylamino)- β-D-glucopyranosyl]-(1 → 3)-*O*-(2,6-di-*O*-benzyl-4-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (4).

4.1.1.1. Prepared from 1 and 2. A solution of AgOTf (135.1 mg, 0.526 mmol) in MeCN (0.9 mL) was added to a mixture of glycosyl donor **1**[15] (123.0 mg, 0.234 mmol) and acceptor **2**[16] (139.1 mg, 0.158 mmol) in CH_2Cl_2 (1.75 mL) at −78 °C under Ar. After 10 min, a 4 M solution of methylsulfenyl bromide in 1,2-dichloroethane (98.8 μL)[17] was added during 5 min. The reaction mixture was stirred for 15 h at same temperature, diisopropylamine (1.0 mL) was added, and the mixture was stirred for 30 min. After concentration of the reaction mixture, $CHCl_3$ was added to the residue. The mixture was filtered and concentrated, and the residue was treated with pyridine (4 mL) and Ac_2O (2 mL) for 2 h. The resulting solution was concentrated, and the residue was purified by a recycling preparative HPLC (column, JAIGEL-1H and 2H; solvent, chloroform) to give compound **4** (93.4 mg, 43%).

4.1.1.2. Prepared from 1 and 3. A solution of AgOTf (16.64 g, 64.8 mmol) in MeCN (90 mL) was added to a mixture of glycosyl donor **1** (16.40 g, 31.2 mmol) and acceptor **3**[18] (19.16 g, 20.7 mmol) in CH_2Cl_2 (190 mL) at −60 °C under Ar. After 20 min, a 4 M solution of methylsulfenyl bromide in 1,2-dichloroethane (13.1 mL) was added during 40 min. The temperature was gradually raised to −30 °C during 1 h, diisopropylamine (50 mL) was added, and the mixture was stirred for 15 min at −30 °C. After concentration of the reaction mixture, $CHCl_3$ was added to the residue. The mixture was filtered and concentrated, and the residue was purified by column chromatography on silica gel (3:7 then 2:3 EtOAc/hexane) to give compound **4** (26.47 g, 92%). $[\alpha]_D^{26}$ −9.2° (*c* 1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 7.42–7.18 (m, 30H, aromatic), 5.41 (d, 1H, J = 3.5 Hz, H-4′), 5.00 (t, 1H, J = 9.6 Hz, H-4″), 4.97 (d, 1 H, J = 10.4 Hz, CH_bPh), 4.93 (d, 1 H, J = 12.3 Hz, CH_bPh), 4.90 (d, 1 H, J = 11.2 Hz, CH_bPh), 4.87 (d, 1 H, J = 13.5 Hz, CH_aPh), 4.69–4.78 (m, 4H, H-3″, CH_aPh, CH_bPh × 2), 4.67 (d, 1H, $J_{1'',2''}$ = 8.7 Hz, H-1″), 4.62–4.68 (m, 3H, OCH_2CCl_3, CH_aPh), 4.58 (d, 1H, J = 12.0 Hz, CH_aPh), 4.49 (d, 1H, J = 11.6 Hz, NH), 4.48 (d, 1H, $J_{1',2'}$ = 7.7 Hz, H-1′), 4.46 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 4.39–4.45 (m, 2H, CH_aPh, CH_bPh), 4.27 (d, 1H, J = 11.8 Hz, CH_aPh), 4.20 (d, 2H, J = 3.4 Hz, H-6″ab), 4.06 (t, 1H, J = 9.4 Hz, H-4), 3.80 (dd, 1H, J = 2.8 Hz, J = 10.4 Hz, H-6b), 3.66–3.71 (m, 2H, H-6a, H-3′), 3.45–3.61 (m, 6H, H-2, H-3, H-2′, H-5′, H-2″, H-5″), 3.31–3.35 (m, 3H, H-5, H-6′ab), 2.06 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.96 (s, 3H, OAc). ^{13}C NMR ($CDCl_3$) δ 170.71, 170.50, 169.78, 169.24, 153.79, 138.97, 138.52, 138.13, 137.96, 137.40, 128.65, 128.37, 128.32, 128.30, 128.22, 128.08, 127.99, 127.90, 127.85, 127.83, 127.68, 127.62, 127.57, 127.50, 127.30, 126.85, 102.42 (C-1), 101.91 (C-1′), 100.92 (C-1″), 95.53, 82.63, 81.59, 80.89, 75.83, 75.26, 74.97, 74.84, 74.20, 73.53, 73.42, 72.51, 71.82, 71.66, 70.87, 69.37, 68.47, 67.94, 67.84, 61.85, 55.98, 20.70, 20.67, 20.56, 20.52; Anal. Calcd for $C_{71}H_{78}Cl_3NO_{21}$: C, 61.45; H, 5.67; N, 1.01. Found: C, 61.33; H, 5.59; N, 0.94. FAB-MS: $[M+H]^+$ 1386.7.

4.1.2. Benzyl *O*-(2-acetoamido-3,4,6,-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-*O*-(2,6-di-*O*-benzyl-4-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (5). Compound **4** (5.03 g, 3.62 mmol) was dissolved in AcOH (50 mL), and Zinc powder (10.25 g) was added. The mixture was stirred for 30 min, filtered through Celite, and concentrated. The residue was treated with pyridine (15 mL) and Ac_2O (7 mL) at room temperature for 7.5 h. The mixture was co-concentrated with toluene. The residue was dissolved in EtOAc, washed with 1 M HCl aq, saturated $NaHCO_3$ solution, and brine. The organic layer was dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography on silica gel (1:1 EtOAc/hexane then EtOAc) to give compound **5**[19] (4.39 g, 97%).

4.1.3. *O*-(2-Acetoamido-3,4,6,-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl acetate (6). A mixture of compound **5** (4.12 g, 3.28 mmol) and 20% $Pd(OH)_2$/C (1.0 g) in MeOH (15 mL) was stirred under hydrogen gas for 16 h at room temperature and then filtered through Celite. The filtrate was concentrated. The residue was treated with pyridine (30 mL), Ac_2O (20 mL), and 4-dimethylaminopyridine (28 mg) at room temperature for 7 h. The mixture was co-concentrated with toluene. The residue was dissolved in EtOAc, washed with 1 M HCl aq, saturated $NaHCO_3$ solution, and brine. The organic layer was dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography on silica gel (EtOAc) to give compound **6**[19] (3.16 g, quant).

4.1.4. *O*-(2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-*O*-(β-D-galactopyranosyl)-(1 → 4)-D-glucopyranose (7). A solution of **6** (567.8 mg, 0.588 mmol) in MeOH (5 mL) was treated with NaOMe (31.7 mg, 0.587 mmol) at room temperature for 2 h. The mixture was concentrated, and 0.1 M NaOH aq (4 mL) was then added to the residue. After 4 h, the solution was neutralized by Amberlite IR120B (H^+) resin. The resin was filtered off and filtrate was concentrated to dryness. Purification of the

crude product by gel permeation chromatography (Sephadex G50, 5% HOAc aq eluent) gave **7**[20] (263.3 mg, 82%) as white powder after lyophilization.

4.1.5. 4-Pentenyl (2-acetoamido-3,4,6,-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (8). To a suspension of compound **6** (6.64 g, 6.87 mmol), AcOH (30 mL) was added 33% HBr/AcOH (3.66 mL, 20.62 mmol) at 0 °C. The mixture was stirred for 16 h at room temperature under darkness. The mixture was poured into ice-water and extracted with $CHCl_3$. The solution was washed with water, saturated $NaHCO_3$ solution, and brine. The organic layer was dried ($MgSO_4$) and concentrated. The crude product was dissolved in CH_2Cl_2 (66 mL), and 4 Å molecular sieves powder (6.78 g) and 4-pentene-1-ol (3.55 mL, 34.37 mmol) were added successively. The mixture was stirred for 1 h at room temperature. Ag_2CO_3 (4.75 g, 17.23 mmol) and I_2 (39.4 mg) were added to the mixture at 0 °C. After stirring under the dark at room temperature for 2 days, the mixture was filtered through Celite and concentrated. The residue was purified by column chromatography on silica gel (9:1 EtOAc/toluene) to give compound **8** (3.39 g, 50%). $[\alpha]_D^{26}$ +13.9° (*c* 1.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 5.72–5.83 (m, 1H, –C*H* = CH_2), 5.48 (dd, 1H, *J* = 9.3 Hz, *J* = 10.5 Hz, H-3″), 5.40 (d, 1H, *J* = 5.4 Hz, NH), 5.33 (d, 1H, $J_{3',4'}$ = 3.4 Hz, H-4′), 5.17 (t, 1H, *J* = 9.4 Hz, H-3), 4.95–5.07 (m, 5H, H-2′, H-1″, H-4″, –CH=C*H*$_2$), 4.89 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 4.45 (dd, 1H, $J_{5,6b}$ = 1.7 Hz, $J_{6a,6b}$ = 11.6 Hz, H-6b), 4.44 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 4.38 (dd, 1H, *J* = 2.5 Hz, *J* = 12.3 Hz, H-6′b), 4.35 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1′), 4.12 (dd, 1H, $J_{5,6b}$ = 5.4 Hz, $J_{6a,6b}$ = 11.9 Hz, H-6a), 4.04–4.08 (m, 3H, H-6′a, H-6″ab), 3.81–3.87 (m, 1H, one of OCH_2), 3.72–3.80 (m, 3H, H-4, H-3′, H-5′), 3.64–3.68 (m, 1H, H-5″), 3.57–3.61 (m, 1H, H-5), 3.45–3.50 (m, 1H, one of OCH_2), 3.25–3.31 (m, 1H, H-2″), 1.91–2.36 (m, 32H, Ac, $OCH_2CH_2CH_2$ CH=CH_2), 1.62–1.70 (m, 2H, $OCH_2CH_2CH_2$ CH=CH_2); ^{13}C NMR ($CDCl_3$) δ 170.65, 170.49, 170.45, 170.32, 169.81, 169.56, 169.49, 169.39, 169.68, 137.71 (–*C*H=CH_2), 115.00 (–CH=*C*H_2), 100.64 (C-1′), 100.54 (C-1), 99.49 (C-1″), 75.96, 75.71, 72.60, 72.53, 71.61, 71.56, 71.10, 70.90, 69.22, 68.80, 68.63, 62.11, 61.56, 61.06, 56.51, 29.73, 28.50, 23.21, 20.79, 20.67, 20.61, 20.57; Anal. Calcd for $C_{43}H_{61}NO_{25}$: C, 52.07; H, 6.20; N, 1.41. Found: C, 51.87; H, 6.24; N, 1.41. FABMS: $[M+H]^+$ 992.7; $[M+Na]^+$ 1014.7.

4.1.6. 5-Acetylthiopentyl (2-acetoamido-3,4,6,-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (9). A solution of compound **8** (479.9 mg, 0.484 mmol) in 1,4-dioxane (0.5 mL) was treated with thioacetic acid (0.69 mL, 9.676 mmol) and AIBN (158.8 mg, 0.968 mmol) at 80 °C for 3 h under Ar. Cyclohexene (98 μL, 0.968 mmol) was added with stirring for 10 min. The resulting solution was purified by column chromatography on silica gel (1:1 EtOAc/hexane then EtOAc) to yield compound **9** (449.7 mg, 87%). $[\alpha]_D^{29}$ +9.9° (*c* 1.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 5.44–5.49 (m, 2 H, H-3″, NH), 5.31 (d, 1H, $J_{3',4'}$ = 3.3 Hz, H-4′), 5.15 (t, 1H, *J* = 9.4 Hz, H-3), 4.97–5.05 (m, 3H, H-2′, H-1″, H-4″), 4.86 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 4.42–4.46 (m, 2H, H-1, H-6b), 4.33–4.38 (m, 2H, H-1′, H-6′b), 4.10 (dd, 1H, *J* = 5.4 Hz, *J* = 11.9 Hz, H-6a), 4.00–4.07 (m, 3H, H-6′a, H-6″ab), 3.70–3.84 (m, 4 H, H-4, H-3′, H-5′, one of OCH_2), 3.64–3.68 (m, 1H, H-5″), 3.58–3.59 (m, 1H, H-5), 3.41–3.47 (m, 1H, one of OCH_2), 3.24–3.31 (m, 1H, H-2″), 2.83 (t, 2H, *J* = 7.3 Hz, SCH_2), 2.31 (s, 3H, SAc), 2.11 (s, 3H, Ac), 2.10 (s, 3H, Ac), 2.09 (s, 3H, Ac), 2.08 (s, 3H, Ac), 2.07 (s, 3H, Ac), 2.03 (s, 3H, Ac), 2.01 (s, 3H, Ac), 2.00 (s, 3H, Ac), 1.95 (s, 3H, Ac), 1.90 (s, 3H, Ac), 1.52–1.57 (m, 4H, $OCH_2CH_2CH_2CH_2CH_2S$), 1.32–1.42 (m, 2H, OCH_2-$CH_2CH_2CH_2CH_2CH_2S$). ^{13}C NMR ($CDCl_3$) δ 195.76, 170.58, 170.44, 170.39, 170.27, 169.74, 169.52, 169.43, 169.33, 169.01, 100.58, 100.39, 99.44, 75.97, 75.63, 72.55, 72.46, 71.53, 71.45, 71.06, 70.79, 69.58, 68.73, 68.58, 62.04, 61.53, 61.02, 55.92, 39.18, 35.01, 30.48, 29.01, 28.76, 28.71, 24.86, 23.13, 20.73, 20.60, 20.55, 20.51; Anal. Calcd for $C_{43}H_{61}NO_{25}$: C, 50.60; H, 6.13; N, 1.31. Found: C, 50.29; H, 6.09; N, 1.29. FABMS: $[M+H]^+$ 1068.5; $[M+Na]^+$ 1090.5.

4.1.7. Acetylated trivalent glycodendrimer (14). A mixture of **10** (37.5 mg, 79.6 μmol) and **9** (360.2 mg, 337.3 μmol) was dissolved in a mixture of DMF (0.4 mL) and MeOH (0.3 mL), and the solution was treated with 28% NaOMe methanolic solution (82 μL, 337.3 μmol) at room temperature for 3 h. AcOH (0.5 mL) was then added to the mixture, and the resulting solution was evaporated under reduced pressure. The residue was treated with pyridine (10 mL), AcOH (5 mL), and 4-dimethylaminopyridine (10.1 mg) at 50 °C for 3 h. The resulting solution was poured into ice-water and extracted with EtOAc. The organic solution was washed with 1 M HCl aq, saturated $NaHCO_3$ aq, and brine. Organic phase was dried ($MgSO_4$) and concentrated. Purification by recycling preparative HPLC (column, JAIGEL-2.5H and 3H; solvent, chloroform) afforded **14** (172.9 mg, 66%). $[\alpha]_D^{22}$ +10.7° (*c* 0.8, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 7.43–7.45, 7.32–7.33 (2m, 5H, SiPh), 5.44–5.49 (m, 6H, H-3″, NH), 5.32 (s, 3H, H-4′), 5.15 (t, 3H, *J* = 9.4 Hz, H-3), 4.97–5.05 (m, 9H, H-2′, H-1″, H-4″), 4.86 (dd, 3H, $J_{1,2}$ = 8.1 Hz, $J_{2,3}$ = 9.3 Hz, H-2), 4.42–4.46 (m, 6H, H-1, H-6b), 4.33–4.38 (m, 6H, H-1′, H-6′b), 4.04–4.11 (m, 12H, H-6a, H-6′a, H-6″ab), 3.65–3.82 (m, 15H, H-4, H-3′, H-5′, H-5″, one of OCH_2), 3.55–3.61 (m, 3H, H-5), 3.39–3.46 (m, 3H, one of OCH_2), 3.24–3.31 (m, 3H, H-2″), 2.48 (t, 6H, *J* = 7.1 Hz, SCH_2), 2.42 (t, 6H, *J* = 7.1 Hz, SCH_2), 1.90–2.11 (m, 90H, Ac), 1.49–1.60 (m, 18H, $OCH_2CH_2CH_2CH_2CH_2S$), 1.33–1.40 (m, 6H, $SiCH_2$-CH_2CH_2S), 0.87–0.91 (m, 6H, $SiCH_2$). ^{13}C NMR ($CDCl_3$) δ 170.50, 170.36, 170.30, 170.25, 169.67, 169.48, 169.35, 169.24, 168.92, 136.07, 133.79, 128.94, 127.68, 100.55, 100.37, 99.41, 76.11, 75.59, 72.49, 72.40, 71.40, 71.03, 70.66, 69.68, 68.62, 68.53, 62.01, 61.52, 60.98, 55.80, 35.67, 31.77, 29.14, 28.83, 24.92, 23.84, 23.11, 20.70, 20.51, 11.67; HRMS(ESI) Anal. Calcd for $C_{144}H_{209}N_3O_{75}S_3Si[M+2Na]^{2+}$: 1675.0674. Found: 1675.0668.

4.1.8. Acetylated tetravalent glycodendrimer (15). A coupling reaction between **11** (27.7 mg, 53.7 μmol) and **9** (333.1 mg, 311.9 μmol) was carried out in the same manner as described for **14** to give **15** (103.0 mg, 45%). $[\alpha]_D^{22}$ +10.1° (*c* 1.1, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 5.46–5.50 (m, 8H, H-3″, NH), 5.34 (s, 4H, H-4′), 5.17 (t, 4H, J = 9.3 Hz, H-3), 4.99–5.07 (m, 12H, H-2′, H-1″, H-4″), 4.88 (dd, 4H, $J_{1,2}$ = 8.1 Hz, $J_{2,3}$ = 9.4 Hz, H-2), 4.43–4.49 (m, 8H, H-1, H-6b), 4.35–4.40 (m, 8H, H-1′, H-6′b), 4.05–4.13 (m, 16H, H-6a, H-6′a, H-6″ab), 3.72–3.86 (m, 16H, H-4, H-3′, H-5′, one of OCH_2), 3.66–3.68 (m, 4H, H-5″), 3.58–3.62 (m, 4 H, H-5), 3.42–3.48 (m, 4H, one of OCH_2), 3.26–3.32 (m, 4H, H-2″), 2.45–2.50 (m, 16H, SCH_2), 1.91–2.13 (m, 120H, Ac), 1.55–1.62 (m, 24H, $OCH_2CH_2CH_2CH_2CH_2S$), 1.38–1.44 (m, 8H, $SiCH_2CH_2CH_2S$), 0.59–0.64 (m, 8H, $SiCH_2$). ^{13}C NMR ($CDCl_3$) δ 170.61, 170.45, 170.39, 170.30, 169.75, 169.52, 169.45, 169.34, 169.03, 100.62, 100.48, 99.49, 76.04, 75.65, 72.60, 72.49, 71.57, 71.49, 71.09, 70.82, 69.79, 68.73, 68.58, 62.08, 61.52, 61.03, 55.98, 35.94, 32.01, 29.27, 28.96, 25.03, 24.11, 23.20, 20.80, 20.63, 20.61, 20.58, 20.54, 11.86; HRMS(ESI) Anal. Calcd for $C_{184}H_{272}N_4O_{100}S_4Si[M+3Na]^{3+}$: 1454.1550. Found: 1454.1552.

4.1.9. Acetylated hexavalent glycodendrimer (16). A coupling reaction between **12** (36.6 mg, 39.3 μmol) and **9** (351.7 mg, 329.3 μmol) was carried out in the same manner as described for **14** to give **16** (157.8 mg, 61%). $[\alpha]_D^{33}$ +8.8° (*c* 1.2, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 5.45–5.50 (m, 12H, H-3″, NH), 5.33 (s, 6H, H-4′), 5.16 (t, 6H, J = 9.3 Hz, H-3), 4.98–5.06 (m, 18H, H-2′, H-1″, H-4″), 4.87 (dd, 6H, $J_{1,2}$ = 8.2 Hz, $J_{2,3}$ = 9.1 Hz, H-2), 4.43–4.47 (m, 12H, H-1, H-6b), 4.34–4.38 (m, 12H, H-1′, H-6′b), 4.04–4.13 (m, 24H, H-6a, H-6′a, H-6″ab), 3.72–3.81 (m, 24H, H-4, H-3′, H-5′, one of OCH_2), 3.65–3.67 (m, 6 H, H-5″), 3.57–3.62 (m, 6H, H-5), 3.41–3.47 (m, 6H, one of OCH_2), 3.25–3.31 (m, 6H, H-2″), 2.45–2.50 (m, 24 H, SCH_2), 1.90–2.12 (m, 180H, Ac), 1.49–1.60 (m, 36H, $OCH_2CH_2CH_2CH_2CH_2S$), 1.36–1.44 (m, 12H, $SiCH_2CH_2CH_2S$), 1.22–1.30 (m, 4H, $SiCH_2CH_2CH_2Si$), 0.51–0.62 (m, 20H, $SiCH_2$), −0.51 (s, 6H, SiMe). ^{13}C NMR ($CDCl_3$) δ 170.55, 170.40, 170.33, 170.26, 169.70, 169.48, 169.39, 169.29, 168.97, 100.59, 100.43, 99.46, 76.07, 75.62, 72.55, 72.44, 71.51, 71.06, 70.34, 69.74, 68.67, 68.54, 62.03, 61.50, 60.99, 55.90, 35.93, 31.93, 29.23, 28.92, 24.99, 24.14, 23.16, 20.76, 20.57, 20.22, 18.18, 16.94, 11.94, −3.37; HRMS(ESI) Anal. Calcd for $C_{284}H_{426}N_6O_{150}S_6Si_3[M+4Na]^{4+}$: 1672.0773. Found: 1672.0805.

4.1.10. Acetylated dodecavalent glycodendrimer (17). A coupling reaction between **13** (30.7 mg, 17.3 μmol) and **9** (312.5 mg, 291.0 μmol) was carried out in the same manner as described for **14** to give **17** (165.7 mg, 73%). $[\alpha]_D^{21}$ +13.2° (*c* 0.7, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 5.72 (br s, 12H, NH), 5.47 (t, 12H, H-3″), 5.34 (s, 12H, H-4′), 5.17 (t, 12H, J = 9.1 Hz, H-3), 4.99–5.07 (m, 36 H, H-2′, H-1″, H-4″), 4.87 (t, 12H, J = 8.6 Hz, H-2), 4.45–4.48 (m, 24H, H-1, H-6b), 4.36–4.38 (m, 24H, H-1′, H-6′b), 4.05–4.14 (m, 48H, H-6a, H-6′a, H-6″ab), 3.73–3.85 (m, 48H, H-4, H-3′, H-5′, one of OCH_2), 3.66–3.69 (m, 12H, H-5″), 3.59–3.63 (m, 12H, H-5), 3.42–3.48 (m, 12H, one of OCH_2), 3.29–3.33 (m, 12H, H-2″), 2.45–2.50 (m, 48H, SCH_2), 1.91–2.12 (m, 360H, Ac), 1.50–1.62 (m, 72H, $OCH_2CH_2CH_2CH_2CH_2S$), 1.36–1.42 (m, 24H, $SiCH_2CH_2CH_2S$), 1.19–1.25 (m, 8H, $SiCH_2CH_2CH_2Si$), 0.49–0.62 (m, 20H, $SiCH_2$). ^{13}C NMR ($CDCl_3$) δ 170.51, 170.36, 169.67, 169.49, 169.34, 169.22, 168.99, 100.61, 100.41, 99.50, 75.66, 72.46, 71.40, 71.10, 70.62, 69.72, 68.54, 62.06, 61.55, 61.01, 55.95, 55.73, 35.91, 31.96, 29.25, 28.91, 24.99, 24.12, 23.20, 20.79, 20.54, 20.44, 18.26, 17.34, 11.90; MALD-TOFMS Anal. Calcd for $C_{564}H_{840}N_{12}O_{300}S_{12}Si_5[M+Na]^+$: 13136.8 (average mass). Found: 13135.5.

4.1.11. Trivalent glycodendrimer (18). A solution of **14** (65.9 mg, 19.9 μmol) in MeOH (5 mL) was treated with 28% NaOMe methanolic solution (20 μL) at room temperature for 12 h. The mixture was concentrated, and 0.1 M NaOH aq (5 mL) was then added to the residue. After overnight, the solution was neutralized by Amberlite IR120B (H^+) resin. The resin was filtered off and filtrate was concentrated to dryness. The crude product was purified by recycling preparative HPLC (column, JAIGEL GS-320 and JAIGEL GS-220; solvent, 5% aq HOAc) to give **18** (29.5 mg, 68%) as white powder after lyophilization. $[\alpha]_D^{23}$ −2.3° (*c* 0.9, H_2O). ^1H NMR (D_2O) δ 7.46, 7.29 (2 br s, 5H, Si–Ph), 4.45 (d, 3H, J = 7.6 Hz), 4.40 (d, 3H, J = 7.6 Hz), 4.15 (s, 3 H), 3.55–3.91 (m), 3.46–3.47 (m, 6H), 3.30–3.34 (m, 3H), 2.46 (br s, 12H, SCH_2), 2.05 (s, 9H, NH*Ac*), 1.55–1.62 (m, 18 H, $SCH_2CH_2CH_2CH_2CH_2O$), 1.40 (br s, 6H, $SiCH_2CH_2CH_2S$), 0.89 (br s, 6H, $SiCH_2$). ^{13}C NMR (D_2O) δ 175.44, 137.13, 134.66, 129.90, 128.68, 103.62, 103.41, 102.98, 82.70, 82.36, 79.09, 76.30, 75.51, 75.34, 75.17, 74.22, 73.48, 70.84, 70.61, 70.33, 68.93, 61.60, 61.14, 60.88, 56.34, 36.10, 32.28, 29.99, 29.54, 25.61, 24.56, 23.01, 12.21; HRMS(ESI) Anal. Calcd for $C_{90}H_{155}N_3O_{48}S_3Si[M+2Na]^{2+}$: 1107.9248. Found: 1107.9281.

4.1.12. Tetravalent glycodendrimer (19). Reaction conditions were as described for **18**, with **15** (94.0 mg, 21.9 μmol). The crude product was purified by gel permeation chromatography (Sephadex G50, 5% HOAc aq eluent) to give **19** (49.5 mg, 81%) as white powder after lyophilization. $[\alpha]_D^{27}$ −0.4° (*c* 0.8, H_2O). ^1H NMR (D_2O) δ 4.44 (br s, 8H), 4.15 (s, 4H), 3.55–3.93 (m), 3.46–3.50 (m, 8H), 3.29–3.35 (m, 4H), 2.59 (br s, 16H, SCH_2), 2.05 (s, 12H, NH*Ac*), 1.66 (br s, 24H, $SCH_2CH_2CH_2CH_2CH_2O$), 1.49 (br s, 8H, $SiCH_2CH_2CH_2CH_2S$), 0.74 (br s, 8H, $SiCH_2$). ^{13}C NMR (D_2O) δ 175.49, 103.63, 103.43, 102.96, 82.68, 79.12, 76.33, 75.53, 75.39, 75.18, 74.24, 73.49, 70.91, 70.64, 70.34, 68.96, 61.62, 61.16, 60.86, 56.35, 36.30, 32.35, 30.04, 29.56, 25.64, 24.80, 22.99, 12.42; HRMS(ESI) Anal. Calcd for $C_{112}H_{200}N_4O_{64}S_4Si[M+2Na]^{2+}$: 1413.5477. Found: 1413.5525.

4.1.13. Hexavalent glycodendrimer (20). Reaction conditions were as described for **18**, with **16** (128.0 mg, 19.4 μmol). The crude product was purified by recycling preparative HPLC (column, JAIGEL GS-320 and JAIGEL GS-220; solvent, 5% aq HOAc) to give **20** (45.2 mg, 54%) as white powder after lyophilization.

$[\alpha]_D^{19}$ −1.7° (*c* 0.7, H_2O). ^1H NMR (D_2O) δ 4.45 (br s, 12H), 4.16 (s, 6H), 3.58–3.92 (m), 3.46–3.48 (m, 12H), 3.34 (br s, 6H), 2.58 (br s, 24H, SCH_2), 2.06 (s, 18 H, NH*Ac*), 1.65 (br s, 36H, $SCH_2CH_2CH_2CH_2CH_2O$), 1.49 (br s, 16H, $SiCH_2CH_2CH_2SiCH_2CH_2CH_2S$), 0.71 (br s, 20H, $SiCH_2$), 0.00 (s, 6H, SiMe). ^{13}C NMR (D_2O) δ 175.44, 103.65, 103.43, 103.03, 82.72, 79.15, 78.89, 76.33, 75.54, 75.39, 75.20, 74.25, 73.51, 70.84, 70.64, 70.36, 70.19, 68.96, 61.63, 61.17, 60.92, 56.37, 36.41, 32.44, 30.11, 29.64, 25.70, 24.86, 23.04, 20.93, 19.26, 18.04, 12.51, −1.71; HRMS(ESI) Anal. Calcd for $C_{176}H_{318}N_6O_{96}S_6Si_3[M+3Na]^{3+}$: 1465.5832. Found: 1465.5858.

4.1.14. Dodecavalent glycodendrimer (21). Reaction conditions were as described for **18**, with **17** (142.6 mg, 10.9 μmol). The crude product was purified by gel permeation chromatography (Sephadex G50, 5% HOAc aq eluent) to give **21** (83.1 mg, 89%) as white powder after lyophilization. $[\alpha]_D^{23}$ −0.3° (*c* 1.0, H_2O). ^1H NMR (H_2O) δ 4.46 (br s, 24H), 4.16 (s, 12H), 3.59–3.92 (m), 3.46–3.48 (m, 24H), 3.34 (br s, 12H), 2.61 (br s, 48H, SCH_2), 2.05 (s, 36H, NH*Ac*), 1.67 (br s, 72H, $SCH_2CH_2CH_2CH_2CH_2CH_2O$), 1.50 (br s, 32H, $SiCH_2CH_2CH_2SiCH_2CH_2CH_2S$), 0.74 (br s, 40H, $SiCH_2$). ^{13}C NMR (D_2O) δ 175.41, 103.58, 103.38, 102.955, 82.66, 79.08, 76.27, 75.48, 75.33, 75.14, 74.19, 73.45, 70.82, 70.58, 70.30, 68.90, 61.57, 61.11, 60.85, 56.30, 36.37, 32.42, 30.02, 29.55, 25.63, 24.84, 22.98, 19.43, 18.31, 12.56; HRMS(ESI) Anal. Calcd for $C_{348}H_{624}N_{12}O_{192}S_{12}Si_5[M+4Na]^{4+}$: 2164.8624. Found: 2166.5.

4.2. Fluorescence measurements

Wheat germ agglutinin (lectin from *Triticum vulgaris*, lot No. 054K8925) was purchased from Sigma. Emission spectra of WGA induced by excitation at 295 nm are uncorrected and were recorded with SHIMADZU RF-500PC spectrometer. The solutions were contained in 1 cm quarts cuvettes, mounted in thermostated holders, and the measurements were carried out at 5 °C in order to remove the effect of nonspecific binding on the spectra. The concentration of WGA was estimated to be 0.69 μM by using the absorption coefficient at 280 nm.[22]

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References and notes

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