Supporting Information

Aggregation of Alzheimer Amyloid β Peptide (1–42) on the Multivalent Sulfonated Sugar Interface

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1. Materials, Measurements and Methods

1-1. Materials

These compounds were respectively confirmed by ^{1}H-NMR, ^{13}C-NMR and mass spectroscopy. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded using a Varian Gemini 2000 (Varian Inc., Palo Alto, CA) equipped with a Sun workstation (Oracle Corp., Redwood Shores, CA) and $CDCl_3$, DMF-d_7, CD_3OD and D_2O were selected as deuterated solvents. Mass spectra were measured by MALDI-TOF-MS (Voyager, Applied Biosystems, Foster City, CA), FAB-MS (VG Autospec, Manchester, UK) and ESI-MS (LCQ Deca xp, Thermo Fisher Scientific, Waltham, MA).

The following reagents were used as received: 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) and lithium aluminum hydride 1.0 M solution in THF (Sigma-Aldrich Corp., St. Louis, MO), acetone, chloroform ($CHCl_3$), copper (0) powder, copper (II) sulfate pentahydrate, dichloromethane, *N*,*N*-dimethylformamide (DMF), ethanol (EtOH), ethyl acetate (EtOAc), *n*-hexane, hydrochloric acid (HCl), iodomethane, methanol (MeOH), potassium bromide, potassium carbonate, sodium *L*-ascorbate, sodium azide, sodium chloride, sodium hydride, sodium hydrogen carbonate ($NaHCO_3$), sodium hydroxide (sulfuric acid, tetrahydrofuran (THF), thionyl chloride and trichloroisocyanuric acid (Kanto Chemical co., Inc., Tokyo, Japan), palladium/charcoal (Pd/C) and sulfurtrioxide trimethylamine complex (Merck, NJ), amyloid β protein (human, 1-42) (Aβ (1-42), 2-(7-aza-1H-benzotriazole-1-yl)-1,1,3,3-tetramethyl uronium hexafluorophosphate (HATU) (Peptide Institute Inc., Osaka, Japan), 2-[2-(2-chloroethoxy)ethoxy]ethanol, *N*,*N*-diisopropylethylamine (DIEPA), 3-bromo-1-propyne, 3,5-dihydroxybenzoic acid and gallic acid (3,4,5-trihydroxybenzoic acid) (Tokyo Chemical Industry .co., ltd., Tokyo, Japan). Ion-exchange resin, Dowex was bought from Muromachi Technos Co. Ltd. (Tokyo, Japan), and was prepared to exchange from H^+ form into Na^+ form.

The following buffer solution were used as received and prepared; NaOH-50 buffer was bought from GE Healthcare Bioscience (Chalfont St. Giles, U.K.), and 50mM potassium phosphate buffer (pH=7.4) as follow conventional method.

p-Nitrophenyl *N*-acetyl-D-glucosamine were synthesized by conventional methods (B. G. Davis, A. J. Fairbanks, Carbohydrate Chemistry; Oxford Univ. Press: London 2002) from *N*-acetyl-D-glucosamine). The obtained *p*NP pyranosides were used for a synthesis of 6-sulfo-N-acetyl-D-glucosamine (6S-GlcNAc).

1-2. Measurements

The functional SAMs were prepared on the gold coated glass substrates. The substrate purchased from Moritex Co. (Tokyo, Japan) was used for dynamic mode-atomic force microscope (D-AFM), FTIR-RAS, ellipsometry, X-ray photoelectron spectroscopy (XPS) and water contact angle goniometry, while Au-Kit, the substrate provided by GE Healthcare Bio-Science, was used for SPR analysis. Before the preparation, each gold substrate was prepared to be exposed to UV/ozone (UV.TC.NA.003, Bioforce Nanoscience Inc., Ames, IA) and was rinsed with EtOH several times. The surface functional groups were confirmed using FTIR-RAS (Perkin Elmer Inc., Winter Street Waltham, MA) equipped with an RAS attachment (Reflector 2, Harrick Scientific Products Inc., Pleasantville, NY). The surface was investigated by XPS, which was recorded by Ulvac Phi 5600 (Ulvac Inc. Kanagawa, Japan). Water contact angle was measured by DropMaster300 (Kyowa Interface Science Co., Ltd., Saitama, Japan) and the thicknesses of the SAMs were estimated using an ellipsometer (PZ2000, Royal Philips Electronics, Eindhoven, Netherlands). The analysis methods of SPR, AFM and FTIR-RAS were applied for Aβ (1-42) analyses. SPR binding analysis was carried out by BIACORE 3000 and Au-Kit as probe chip, and all products were provided by GE Healthcare Bio-Sciences co.. On the other hand, D-AFM observation was accomplished using SPI3800N (Seiko Instruments Inc., Chiba, Japan) which equipped with SPA400 as a probe station, and the cantilever of DF40P was used as a cantilever. Secondary structure of Aβ (1-42) by FTIR-RAS was measured by same systems as SAMs characterization.

1-3. Methods for Preparation of Functional SAMs

Acetylenyl-functionalized layers were immobilized by the formation of a self-assembled monolayer (SAM). Disulfides with hydroxyl- (**S1**) and acetylenyl- (**S2**) terminals were dissolved in molar ratio

S1:**S2**=5:1 (total 10mM) in EtOH. After the gold substrate was immersed in the solution for 12 h, and then it rinsed with EtOH several times. Subsequently, azide terminated 6S-GlcNAc derivatives (**1-3**) were reacted with acetylenyl terminated SAM via click chemistry. Each reactive solution was prepared from 5.0mM 6S-GlcNAc solutions, 0.10mM $CuSO_4$, 0.50mM sodium *L*-ascorbate and 0.01wt% copper (0) powder in mixture solution of EtOH:H_2O=1:2 (v/v), and dropped on the acetylenyl terminated SAMs under N_2 gas. 12h later, each substrate was washed by EtOH and distilled repeatedly and characterized by FTIR-RAS, ellipsometry, XPS and water contact angle goniometry.

1-4. Interaction Analyses of Aβ (1-42) on Multivalent 6S-GlcNAc Immobilized Interfaces

Aβ (1-42) (200μM) was dissolved in 0.02% aqueous NH_3 solution into being an unfolded. Dissolved Aβ (1-42) solution was separated into certain volumes in plastic vial. After each vial was frozen by liquid N_2 rapidly, they were stored at -80ºC. These freezing stock samples were diluted to appropriate buffer solution just before usage. The sample which was prepared from same batch was used for assay between subsequent measurements.

1-4-1. SPR Analysis

Binding analysis of Aβ (1-42) on multivalent 6S-GlcNAc immobilized surface was kinetically estimated by SPR. Running buffer with 0.1M-NaCl, 20mM-pottassium phosphate buffer (pH 7.4) and 0.008% aqueous NH_3 solution was used for the measurement. The freezing stock sample was diluted to the solution buffer at the same ratio as running buffer solution just before measurement, in order to equalize NH_{3aq} content in each measurement, and then various concentrations of Aβ (1-42) (2.5, 5, 10, 20 and 40μM) were prepared as the sample solution. Measurement was carried out at flow rate of 5μL/min. The sample solution from 2.5μM to 40μM was interacted with no sugar modified (**S1** and **S2**), monovalent 6S-GlcNAc **1**, divalent 6S-GlcNAc **2,** and trivalent 6S-GlcNAc **3** immobilized substrate for 25min. The deposited Aβ (1-42) on the substrate was dissociated by 15μL of NaOH-50 three times, and the measurement was carried out from a sample of lower concentration.

1-4-2. D-AFM Observation

Morphology of Aβ (1-42) aggregation on the substrate was observed by dynamic mode AFM (D-AFM) measurement. 10μM sample solution of Aβ (1-42) was produced by the same method as the method using 1-4. The prepared substrates were immersed in 400μL of Aβ (1-42) sample solution 12h at 25ºC in static state. After incubation, carefully excess adherent of Aβ (1-42) on the surface was rinsed with H_2O several times and was dried by N_2. Aggregate image on each surface was displayed by D-AFM. The parameter of cantilever as follow; resonant frequency was 330kHz and the spring constant was 40N/m. The parameter of systems as follows; applied voltage was 1.0V and scanning frequency was 1Hz.

1-4-3. Secondary Structure Analyses Using FTIR-RAS Measurements

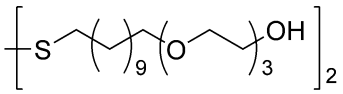
Each secondary structure of Aβ (1-42) on the substrates was investigated by FTIR-RAS measurement. For the estimation of conformation of Aβ (1-42), the sample substrate which used for D-AFM analysis was used. Measurement was carried out using MCT-N detector under the circumstance where fulfilled by the dry air, and the power of peak resolution was applied to $4.0cm^{-1}$.

2. Syntheses

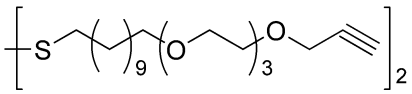
All compounds were identified by ^{1}H and ^{13}C-NMR, and mass spectroscopy (ESI-MS, FAB-MS or MALDI-TOF-MS).

2-1. Self-Assembled Monolayers

Hydroxyl- (**S1**) and acetylenyl- (**S2**) terminated disulfides were synthesized following a literature (Lee, J. K. et al, (2004) *Langmuir 20*, 3844-3847.) and its synthetic procedures were abbreviated.



S1



S2

Fig.S1. Hydroxyl- and acetylenyl- terminated disulfides.

Hydroxyl-terminated disulfide (**S1**)

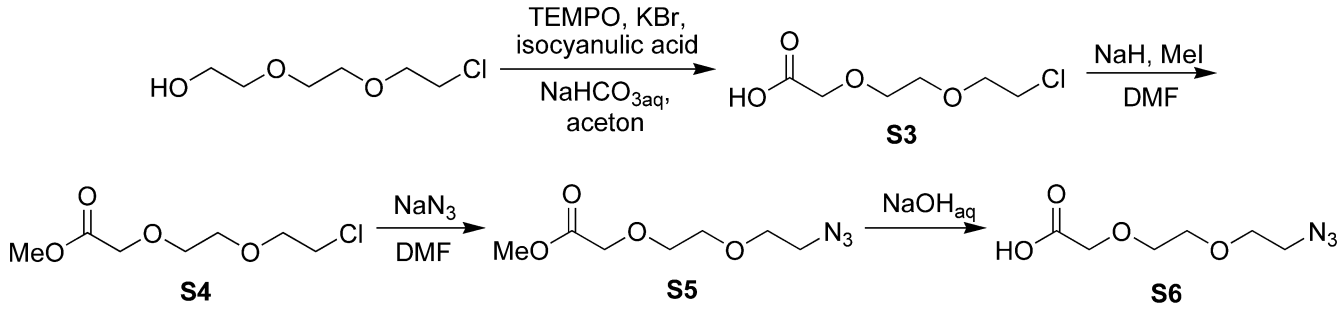
^{1}H-NMR (300MHz, $CDCl_3$, ppm): δ 3.55-3.72 (24H, m, -(OCH_2CH_2)$_3$OH)), 3.44 (4H, br, *J*=12.5 and 4.8Hz, -CH_2 (OCH_2CH_2)$_3$OH), 2.66 (4H, t, *J*=7.5Hz, -$SSCH_2$-), 2.15 (2H, s, -OH), 1.69-1.51 (8H, m, -$CH_2(CH_2)_7CH_2CH_2$(OCH_2CH_2)$_3$OH), 1.25 (28H, br, -$S(CH_2)_2(CH_2)_8$-). ^{13}C-NMR (75MHz, $CDCl_3$, ppm): δ 72.1 (-$OCH_2CH_2OCH_2CH_2OCH_2CH_2$OH), 71.2 (-$CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2$OH), 70.2(-$OCH_2CH_2OCH_2CH_2OCH_2CH_2$OH), 70.0 (-$OCH_2CH_2OCH_2CH_2OCH_2CH_2$OH), 69.6 (-$OCH_2CH_2OCH_2CH_2OCH_2CH_2$OH), 61.4 (-$OCH_2CH_2OCH_2CH_2OCH_2$OH), 38.8 (-$SCH_2CH_2CH_2CH_2$-), 29.2 (-$CH_2CH_2CH_2OCH_2CH_2O$-), 29.1 (-$SCH_2(CH_2)_3(CH_2)_4$-), 28.9 (-$S(CH_2)_3CH_2$-), 28.2 (-$S(CH_2)_2CH_2CH_2$-), 25.7 (-$CH_2CH_2CH_2OCH_2CH_2O$-). MALDI-TOF-MS [positive]: 693.5 $[M+Na^+]^+$ (calculated), 693.7 $[M+Na^+]^+$ (observed).

Acetylenyl terminated disulfide (**S2**)

^{1}H-NMR (300MHz, $CDCl_3$, ppm): δ 4.19 (4H, m, -CH_2CCH), 3.67-3.54 (24H, m, -(OCH_2CH_2)$_3OCH_2CCH$), 3.42 (4H, t, *J*=6.9Hz, -CH_2(OCH_2CH_2)$_3OCH_2CCH$)), 2.65 (4H, t, *J*=7.8Hz, -

SC$\underline{H_2}$-), 2.41 (2H, m, -CC$\underline{H}$), 1.53-1.67 (8H, m, -C$\underline{H_2}$CH$_2$(OCH$_2$CH$_2$)$_3$OCH$_2$CCH and –SCH$_2$C$\underline{H_2}$-), 1.25 (28H br, -S(CH$_2$)$_2$($\underline{CH_2}$)$_7$-). ^{13}C-NMR (75MHz, $CDCl_3$, ppm): δ 74.1 (-C$\underline{C}$H), 71.2 (-$\underline{C}$H$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CCH), 70.3 (-OCH$_2\underline{C}$H$_2$O$\underline{C}$H$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CCH), 70.2 (-OCH$_2$CH$_2$OCH$_2$CH$_2$O$\underline{C}$H$_2$CH$_2$OCH$_2$CCH), 70.0 (-O$\underline{C}$H$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CCH), 69.7 (-O$\underline{C}$H$_2$CH$_2$OCH$_2$CCH), 68.8 (-OCH$_2\underline{C}$H$_2$OCH$_2$CCH), 58.0 (-O$\underline{C}$H$_2$CCH), 38.9 (-S$\underline{C}$H$_2$CH$_2$CH$_2$CH$_2$-), 29.3 (-CH$_2\underline{C}$H$_2$CH$_2$OCH$_2$CH$_2$O-), 29.2 (-S$\underline{C}$H$_2$(CH$_2$)$_3$($\underline{C}$H$_2$)$_4$-), 28.9 (-SCH$_2$CH$_2$CH$_2\underline{C}$H$_2$-), 28.2 (-SCH$_2$CH$_2\underline{C}$H$_2$CH$_2$-), 25.7 (-$\underline{C}$H$_2$CH$_2$CH$_2$OCH$_2$CH$_2$O-). MALDI-TOF-MS [positive]: 769.7 [M+Na$^+$]$^+$ (calculated), 769.1[M+Na]$^+$ (observed).

2-2. A Linker



Scheme S1. Synthesis of a linker for sugar microarray.

2-[2-(2-Chloro-ethoxy)ethoxy]acetic acid (**S3**)

2-[2-(2-Chloroethoxy)ethoxy]ethanol (6.60g, 39.0mmol), potassium bromide (936mg, 7.80mmol) and TEMPO (120mg, 1.20mmol) were dissolved in acetone (90mL) and sat. $NaHCO_{3aq}$ (120mL), and were stirred at 0ºC. Subsequently, trichloroisocyanulic acid (18.3mg, 78.6mmol) was gradually added to the solution. One day later, after the completion of the reaction was confirmed by TLC (EtOAc:n-hexane=3:1), the compound was extracted with $CHCl_3$. Organic layer was washed with 1N-HCl_{aq}, sat.$NaHCO_{3aq}$, and distilled water. After the solution was dried over with $MgSO_4$, the solution was evaporated and then the colorless oil was yielded (7.02g, 98%).

^{1}H-NMR (300MHz, $CDCl_3$, ppm): δ 4.14 (2H, s, -C$\underline{H_2}$COOH), 3.74 and 3.72 (2H×2, m, -OC$\underline{H_2}$C$\underline{H_2}$O-), 3.66 (2H, br, -OC$\underline{H_2}$CH$_2$Cl), 3.61 (2H, dd, *J*=10.2 and 5.1Hz -OCH$_2$C$\underline{H_2}$Cl), 2.14 (1H, br, -COO$\underline{H}$).

^{13}C-NMR (75MHz, $CDCl_3$, ppm): δ 172.8(-CH_2<u>C</u>OOH), 72.1, 70.9 and 69.8 (-<u>C</u>H_2-), 42.3 (-<u>C</u>H_2Cl). ESI-MS [negative]: 181.0 $[M-H^+]^-$ (calculated), 181.2 $[M-H^-]^-$ (observed).

<u>Methyl [2-(2-chloroethoxy)ethoxy]acetate (**S4**)</u>

After **S3** (8.56g, 47.0mmol) was dissolved in DMF, sodium hydride (1.40g, 58.0mmol) was added at 0ºC and stirred for 30min. Then, iodomethane (7.64mL, 87.8mmol) was dropped therein. After 12h, the reaction completion was confirmed by TLC (EtOAc:n-hexane=1:3). Following evaporation, the product was extracted by EtOAc, and washed 1N-HCl, sat.$NaHCO_{3aq}$, and sat.$NaCl_{aq}$. The solution was evaporated to the crude solution, and then purified by silica gel-column chromatography (EtOAc:n-hexane=1:3). At last, the solution was dried up with $MgSO_4$, and then evaporated to yield the yellowish oil (4.97g, 65%).

^{1}H-NMR (300MHz, $CDCl_3$, ppm): δ4.15 (2H, s, CH_2), 3.71 (2H×2, d, *J*=7.2Hz, CH_2), 3.54-3.63 (2H×4 and 3H, m, CH_2 and CH_3). ^{13}C-NMR (75MHz, $CDCl_3$, ppm): δ 170.8(-CH_2<u>C</u>OOMe), 71.3, 70.9 and 70.7 (-O<u>C</u>H_2-), 68.7 (-<u>C</u>H_2COOMe), 51.8 (-CH_2COO<u>Me</u>), 42.7 (-<u>C</u>H_2Cl). ESI-MS [positive]: 219.4 $[M+Na^+]^+$ (calculated), 219.1 $[M+Na^+]^+$ (observed).

<u>Methyl [2-(2-azide-ethoxy)ethoxy]acetate (**S5**)</u>

S4 (4.97g, 25.3mmol, 1eq) and sodium azide (9.87g, 152mmol, 6eq) were dissolved in DMF 250mL. The solution was stirred at 70ºC. After a day, the reaction was stopped and the solvent was evaporated. The solution was extracted by $CHCl_3$ and washed by 1N-HCl_{aq}, sat.$NaHCO_{3aq}$ and sat.$NaCl_{aq}$. The solution was dried over with $MgSO_4$ and evaporated to the yellowish oil (4.82g, 93%).

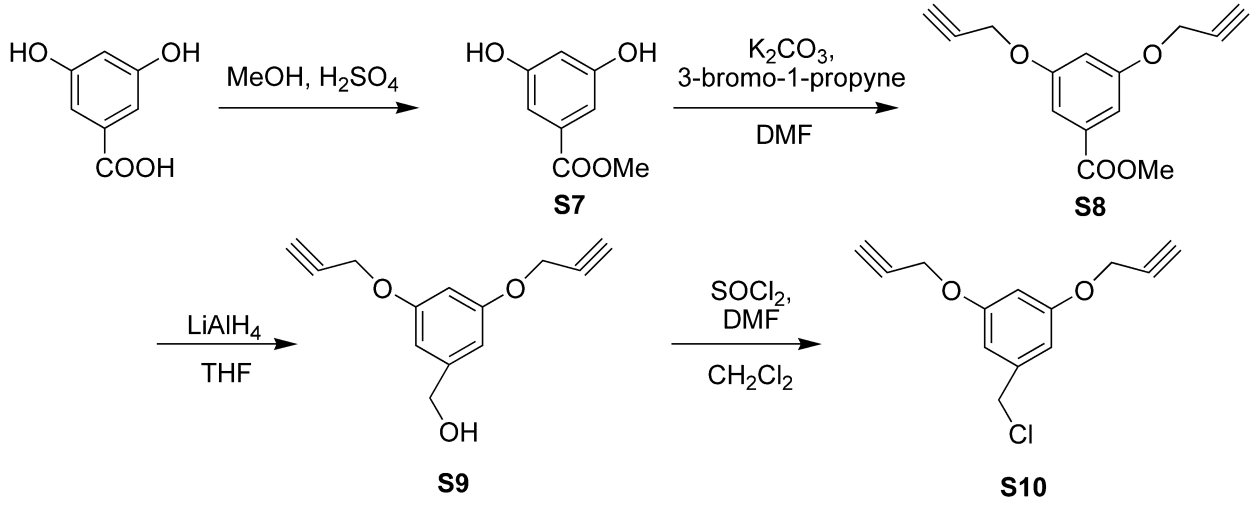
^{1}H-NMR (300MHz, $CDCl_3$, ppm): δ4.17 (2H, s, -OC<u>H</u>$_2$CO-), 3.75 (3H, m, CH_3), 3.66-3.75 (2H×3, overlap, CH_2×3), 3.39 (2H, t, *J*=5Hz, -CH_2N_3). ^{13}C-NMR (75MHz, $CDCl_3$, ppm): δ 170.4 (-CH_2<u>C</u>OO CH_3), 70.6, 70.3 and 69.6 (-O<u>C</u>H_2-), 68.2 (-<u>C</u>H_2COOMe), 51.3 (-<u>C</u>H_2N_3), 50.2 (-CH_2COO<u>Me</u>). ESI-MS [positive]: 226.1 $[M+Na^+]^+$ (calculated), 226.1 $[M+Na^+]^+$ (observed).

<u>[2-(2-Azide-ethoxy)ethoxy]acetate (**S6**)</u>

S5 (4.38g, 21.6mmol) was dissolved in 1N-$NaOH_{aq}$ 330mL, and was stirred at room temperature. After a day, we confirmed the reaction by TLC (EtOAc:n-hexane=1:3) and the compound was extracted by $CHCl_3$. The solution was dried over with $MgSO_4$ and evaporated to the yellowish oil (4.38g, >100%).

^{1}H-NMR (300MHz, $CDCl_3$, ppm): δ 4.20 (2H, s, -OCH_2CO-), 3.78 (2H, m, CH_2), 3.70 (2H×2, m, CH_2×2), 3.42 (2H, t, *J*=5.0Hz, -CH_2N_3). ^{13}C-NMR (75MHz, $CDCl_3$, ppm): δ 173.1 (-CH_2<u>C</u>OOH), 70.9, 70.1, 69.7 and 68.1(-<u>CH_2</u>-), 50.2(-<u>CH_2</u>N_3). ESI-MS [negative]: 188.1 $[M\text{-}H^+]^-$ (calculated), 188.6 $[M\text{-}H^+]^-$ (observed).

2-3. Di-branched Dendron



Scheme S2. Synthesis of the di-branched dendron.

<u>Methyl 3, 5-dihydroxybenzoate (**S7**)</u>

3, 5-dihydroxy benzoic acid (3.08g, 20mmol) was dissolved in MeOH (50mL), and conc. H_2SO_{4aq} (2mL) was added to the solution. The solution was refluxed at 80ºC for a half day. This reaction was confirmed by TLC (EtOAc:n-hexane=1:3), and was evaporated to the crude solid under reduced pressure. After the solid was extracted with EtOAc, the solution was washed by sat.$NaHCO_{3aq}$, and dried over with $MgSO_4$. The solution was evaporated to the white powder (3.59g, >100%).

^{1}H-NMR (300MHz, CD_3OD-d_4, ppm): δ 6.92 (2H, br, ArH, ortho to benzoate), 6.46 (1H, br, ArH, para to benzoate), 3.85 (3H, s, -Me). ^{13}C-NMR (75MHz, CD_3OD-d_4, ppm): δ 167.8 (-<u>C</u>OO-), 158.9 (ArC, meta to benzoate), 132.1 (ArC, ipso to benzoate), 107.9 (ArC, ortho to benzoate), 107.3 (ArC,

para to benzoate), 51.6 (-Me). FAB-MS [positive]: 169.1 $[M+H^+]^+$ (calculated), 169 $[M+H^+]^+$ (observed).

Methyl 3, 5-bis(propargyloxy)benzoate (**S8**)

S7 (1.50g, 8.94mmol, 1.0eq) and potassium carbonate (3.72g, 27.0mmol, 3eq) were dissolved in DMF. The solution was added 3-bromo-propyne (2.02mL, 27.0mmol, 3.0eq) and reacted at 80ºC under nitrogen for a day. After confirmation by TLC (EtOAc:n-hexane=1:3), the solution was extracted by $CHCl_3$, and washed by distilled water. The solution was evaporated to the crude solution, and then purified by silica gel-column chromatography (EtOAc:n-hexane=1:1). The white powder was isolated (1.10g, 51%).

^{1}H-NMR (300MHz, $CDCl_3$, ppm): δ 7.28 (2H, br, ArH, ortho to benzoate), 6.80 (1H, t, *J*=2.1Hz, ArH, para to benzoate), 4.70(2H×2, d, *J*=2.7Hz, -CH_2-), 3.89 (3H, s, -Me), 2.52 (1H×2, t, *J*=2.4Hz, -CH). ^{13}C-NMR (75MHz, $CDCl_3$, ppm) δ 166.0 (-COO-), 158.2 (ArC, meta to benzoate), 131.7 (ArC, ipso to benzoate), 108.5 (ArC, ortho to benzoate), 107.2 (ArC, para to benzoate), 77.6 (-CCH), 75.6 (-CCH), 55.8 (-OCH_2-), 52.0 (-Me). FAB-MS [positive]: 245.1 $[M+H^+]^+$ (calculated), 245 $[M+H^+]^+$ (observed).

3, 5-Bis(propagyloxy) benzyl alcohol (**S9**)

S8 (1.13g, 4.62mmol) was dissolved in THF, and then 1.5 M-$LiAlH_4$ in THF (6mL) was added. Then 1.5M-$LiAlH_4$ in THF (5mL) was added a half hour later, since the reaction was not finished. 10 minutes later, after we confirmed that the reaction was terminated by TLC (EtOAc:n-hexane =1:1), the reaction was quenched by distilled water, and the solvent was dried over by $MgSO_4$. After purification by silica gel-column chromatography (EtOAc:n-hexane=2:1), the white powder was isolated (1.02g, 97%).

^{1}H-NMR (300MHz, CD_3OD-d_4, ppm): δ 6.62 (2H, br, ArH, ortho to benzyl), 6.52 (1H, t, *J*=3.2Hz, ArH, para to benzyl), 4.70 (2 H, m, -CH_2OH), 4.54 (2H, s, -OCH_2CCH), 2.93 (1H×2, t, *J*=2.4Hz, -OCH_2CCH). ^{13}C-NMR (75MHz, CD_3OD-d_4, ppm): δ 159.4 (ArC, meta to benzyl), 144.5 (ArC, ipso to benzyl), 106.4 (ArC, ortho to benzyl), 101.2 (ArC, para to benzyl), 78.9 (-OCH_2CCH), 75.8 (-

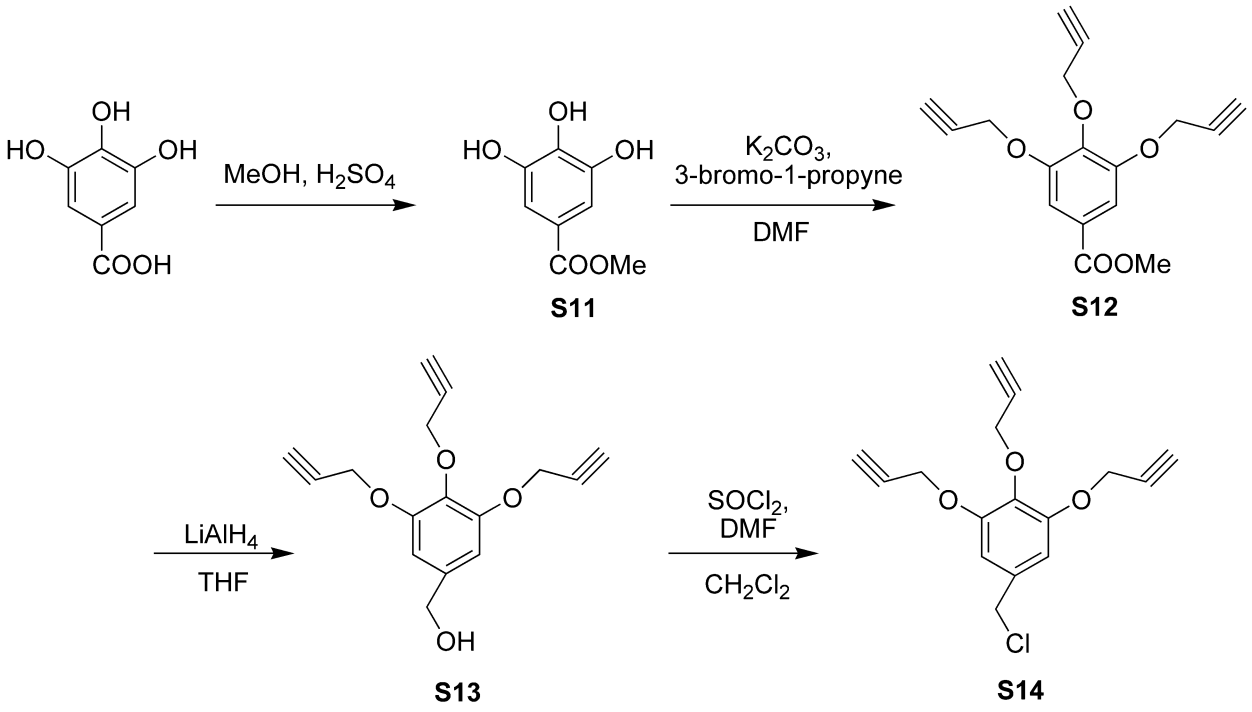
$OCH_2C\underline{C}H$), 64.1 (-$\underline{C}H_2OH$), 55.8 (-$O\underline{C}H_2CCH$). FAB-MS [positive]: 217.1 $[M+H^+]^+$ (calculated), 217 $[M+H^+]^+$ (observed).

3, 5-Bis(propagyloxy)benzyl chloride (**S10**)

S9 (500mg, 2.31mmol, 1.0eq) was dissolved in dichloromethane, and a few drops of DMF was added. Then, thionyl chloride (252μL, 3.47mmol, 5.0eq) was added to the solution at 0ºC and the solution was stirred for a half day. The reaction was confirmed by TLC (EtOAc:n-hexane=1:1) and the solvent was removed by evaporation. The crude compound was purified to the white powder (539mg, 99%) by silica gel-column chromatography (EtOAc:n-hexane=1:1).

^{1}H-NMR (300MHz, $CDCl_3$, ppm): δ 6.63 (2H, d, *J*=2.1Hz, ArH, ortho to benzyl), 6.53 (1H, t, *J*=3.2Hz, ArH, para to benzyl), 4.66 (2 H×2, d, *J*=2.4Hz, -CH_2-), 4.05 (2H, s, -CH_2-Cl), 2.50 (1H×2, t, *J*=2.4Hz, -CH). ^{13}C-NMR (75MHz, DMF-d_7, ppm) δ 159.0 (ArC, meta to benzyl), 140.4 (ArC, ipso to benzyl), 108.5 (ArC, ortho to benzyl), 102.0 (ArC, para to benzyl), 79.1 (-$OCH_2\underline{C}CH$), 77.5 (-$OCH_2C\underline{C}H$), 55.9 (-$O\underline{C}H_2CCH$), 46.2 (-$\underline{C}H_2Cl$).

2-4. Tri-branched Dendron



Scheme S3. Synthesis of the tri-branched dendron.

Methyl 3, 4, 5-dihydroxybenzoate (**S11**)

Gallic acid (3.00g, 17.6mmol) and dissolved in MeOH (50mL). Then, conc. H_2SO_{4aq} (2mL) was added to the solution and was stirred refluxing at 80ºC for 12h. Reaction end was confirmed by TLC (EtOAc:n-hexane=1:1), and was evaporated to the crude solid. After extraction with EtOAc, the solution was washed by saturated $NaHCO_3$aq and distilled water, and dried over with $MgSO_4$. The solution was evaporated and then purified silica gel-column chromatography (EtOAc:n-hexane=1:1). A white powder was yielded (2.66g, 96%).

^{1}H-NMR (300MHz, CD_3OD-d_4, ppm): δ 7.03 (2H, br, ArH, ortho to benzoate), 3.81 (3H, s, -Me). ^{13}C-NMR (75MHz, CD_3OD-d_4, ppm): δ168.1 (-COO-), 145.6 (ArC, meta to benzoate), 138.8 (ArC, para to benzoate), 120.6 (ArC, ipso to benzoate), 110.3 (ArC, ortho to benzoate), 51.4 (-Me). ESI-MS [positive]: 207.0 $[M+Na^+]^+$ (calculated), 208.7 $[M+Na^+]^+$ (observed).

Methyl 1, 3, 5-tris(propargyloxy)benzoate (**S12**)

S11 (1.50g, 5.43mmol, 1.0eq) and potassium carbonate (6.34g, 45.3mmol, 8.3eq) were dissolved in DMF. This solution was added to 3-bromo-propyne (4.0mL, 45.3mmol, 8.3eq) and stirred at 80ºC under nitrogen for a day. After confirmation by TLC (EtOAc:n-hexane=1:3), the solution was extracted by $CHCl_3$, and washed by distilled water twice. The solution was evaporated to the crude solution, and then purified by silica gel-column chromatography (EtOAc:n-hexane=1:1). The white powder was isolated (1.95g, 80%).

^{1}H-NMR (300MHz, $CDCl_3$, ppm): δ 7.47 (2H, br, ArH, ortho to benzoate), 4.83-4.80 (2H×3, d, *J*=2.7Hz, -CH_2-), 3.92 (3H, s, Me), 2.54 (1H×2, t, *J*=1.6Hz, -CH (meta to benzoate)), 2.46 (1H, t, *J*=1.6Hz, -CH (para to benzoate)). ^{13}C-NMR (75MHz, $CDCl_3$, ppm): δ 165.9 (COOMe), 150.9 (ArC, meta to COOMe), 140.7 (ArC, para to benzoate), 125.4 (ArC, ipso to benzoate), 109.4 (ArC, ortho to benzoate), 78.3 (CH_2CCH (meta to benzoate)), 77.5 (CH_2CCH (para to benzoate)), 75.8 (CH_2CCH (meta to benzoate)), 75.2 (CH_2CCH (para to benzoate)), 59.9 (CH_2CCH (para to benzoate)), 56.7

($\underline{CH_2}$CCH (meta to benzoate)), 52.0 (COO$\underline{Me}$). ESI--MS [positive]: 321.1 $[M+Na^+]^+$ (calculated), 321.3 $[M+Na^+]^+$ (observed). ESI-MS [positive]: 321.1 $[M+Na^+]^+$ (calculated), 321.0 $[M+Na^+]^+$ (observed).

3, 4, 5-Tris(propagyloxy) benzyl alcohol (**S13**)

S12 (520mg, 1.74mmol) was dissolved in THF, and then 1.5 M-$LiAlH_4$ in THF (4mL) was added. Then 1.5M-$LiAlH_4$ in THF (5mL) was added a half hour later, since the reaction was not completed. 10 minutes later, after we confirmed that the reaction end by TLC (EtOAc:n-hexane =1:1), the reaction was quenched by 10mL of distilled water, and the solvent was dried over by $MgSO_4$. After purification by silica gel-column chromatography (EtOAc:n-hexane=2:1), the white powder was isolated (384mg, 82%).

^{1}H-NMR (300MHz, $CDCl_3$, ppm): δ 6.79 (2H, br, ArH, ortho to benzyl), 4.77 (2H×2, d, *J*=2.1 Hz, -CH_2- (meta to benzyl)), 4.73 (2H, d, *J*=2.4 Hz, -CH_2- (para to benzyl)), 4.58 (2H, d, *J*=5.7 Hz, -$\underline{CH_2}$OH), 2.52 (1H×2, t, *J*=2.1 Hz, -CCH (meta to benzyl)), 2.46 (1H, t, *J*=2.4Hz, -CCH (para to benzyl)). ^{13}C-NMR (75MHz, $CDCl_3$, ppm): δ 151.3 (ArC, meta to benzyl), 136.8 (ArC, ipso to benzyl), 110.2 (ArC, para to benzyl), 106.6 (ArC, ortho to benzyl), 78.1 (-$OCH_2\underline{C}CH$), 74.8 (-$OCH_2C\underline{CH}$), 64.8 (-CH_2OH), 59.9 (-$\underline{CH_2}$CCH (para to benzyl)), 56.6 (-$\underline{CH_2}$CCH (meta to benzyl)). ESI-MS [positive]: 293.1 $[M+Na^+]^+$ (calculated), 293.0 $[M+Na^+]^+$ (observed).

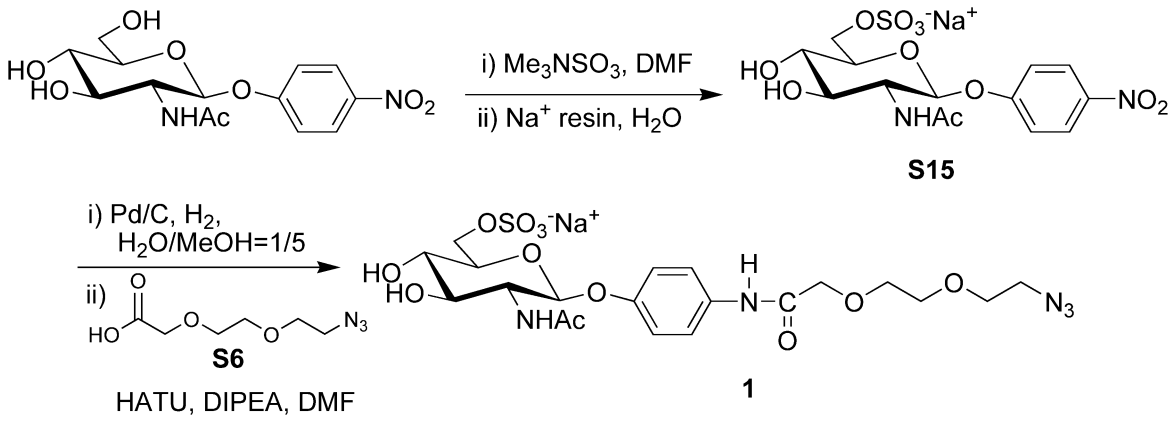
3, 4, 5-Tris(propagyloxy)benzyl chloride (**S14**)

S13 (360mg, 1.33mmol, 1.0eq) was dissolved in dichloromethane, and a few drops of DMF was added. Then, thionyl chloride (420μL, 5.78mmol, 4.3eq) was added to the solution at 0ºC and the solution was stirred for 12h. Reaction end was confirmed by TLC (EtOAc:n-hexane=1:1) and the solvent was removed under reduced pressure. The crude compound was purified by silica gel-column chromatography (EtOAc:n-hexane=3:1), to the white powder (320mg, 86%).

^{1}H-NMR (300MHz, $CDCl_3$, ppm): δ 6.80 (2H, br, ArH, ortho to benzyl), 4.77 (2H×2, d, *J*=2.4Hz, -$\underline{CH_2}$CCH (meta to benzylchloride)), 4.73 (2H, d, *J*=2.4Hz, -$\underline{CH_2}$CCH (para to benzylchloride)), 4.55 (2H, s, -CH_2Cl), 2.54 (1H×2, t, *J*=2.4Hz, -CCH (meta to benzylchloride)), 2.46 (1H, t, *J*=2.4Hz, -CCH

(para to benzylchloride)). ^{13}C-NMR (75MHz, CDC_{l3}, ppm): δ 151.3 (ArC, meta to benzyl), 133.0 (ArC, ipso to benzyl), 108.6 (ArC, para to benzyl, ortho to benzyl), 77.9 (-OCH_2CCH), 74.9 (-OCH_2CCH), 60.0 (-CH_2CCH (meta to benzylchloride)), 56.7 (-CH_2CCH (para to benzylchloride)), 46.0 (-CH_2Cl). ESI-MS [positive]: 311.1 $[M+Na^+]^+$ (calculated), 310.9 $[M+Na^+]^+$ (observed).

2-6. Monovalent 6-Sulfo-N-acetyl-D-glucosamine (6S-GlcNAc)



Scheme S4. Synthesis of monovalent 6S-GlcNAc **1**.

pNP-6-sulfo-*N*-acetyl-D-glucosamine (pNP-6S-GlcNAc) (**S15**)

*p*NP-*N*-acetyl-D-glucosamine (1.537g, 4.494 mmol) was dissolved in 120mL of DMF and stirred at 40ºC. Sulfurtrioxide trimethylamine complex (whole mass was 1.801g, 12.96mmol 3eq) was separated into three batches and they were added into the reactive solution slowly by 6hours. 24 hours later, the reaction end was confirmed by rev. TLC (H_2O:MeOH=3:1), and quenched by 50mL of MeOH. After the solvent was removed by aspiration, the crude compound was purified by rev. silica-gel column chromatography (H_2O:MeOH =10:1) and then white powder (1.100g, 51%) was yielded. The white powder (106mg) was dissolved in 10mL of distilled water. After 100 mg of ion-exchange resin (Na^+ ion stored) was added in the solution, the solution was slowly stirred for 12h and $NHMe^{3+}$ ion was exchanged into Na^+ ion. The white powder (52mg, 53%) was yielded by the removal of the resin and evaporation of the filtrate.

^{1}H-NMR (300MHz, D_2O, ppm): δ 8.13 (2H, d, *J*=9.0 Hz, ArH, ortho to nitro), 7.07 (2H, d, *J*=9.3 Hz, ArH, meta to nitro), 5.20 (1H, d, *J*=8.4 Hz, H-1), 4.29 (1H, dd, *J*=2.3 and 11.7 Hz, H-6_{proR}), 4.13 (1H, dd, *J*=5.6 and 11.4 Hz, H-6_{proS}), 3.94 (1H, dd, *J*=8.4 and 11.2 Hz, H-2), 3.82 (1H, ddd, *J*=2.1, 5.6 and 9.5 Hz, H-5), 3.59 (1H, t, *J*=9.3 Hz, H-3), 3.50 (1H, t, *J*=9.1 Hz, H-4), 1.90 (3H, s, Ac). ^{13}C-NMR (75MHz, D_2O (ref. $CDCl_3$), ppm) 177.7 (NH<u>C</u>OCH_3), 164.5 (ArC, para to nitro), 145.6 (ArC, ipso to nitro), 129.0 (ArC, ortho to nitro), 119.4 (ArC, meta to nitro), 101.5 (C-1), 77.0 (C-5), 76.1 (C-4), 72.3 (C-3), 69.8 (C-6), 58.1 (C-2), 25.0 (NHCO<u>C</u>H_3). ESI-MS [negative]: 421.1[M-Na^+]$^-$ (calculated), 421.1 [M-Na^+]$^-$ (observed).

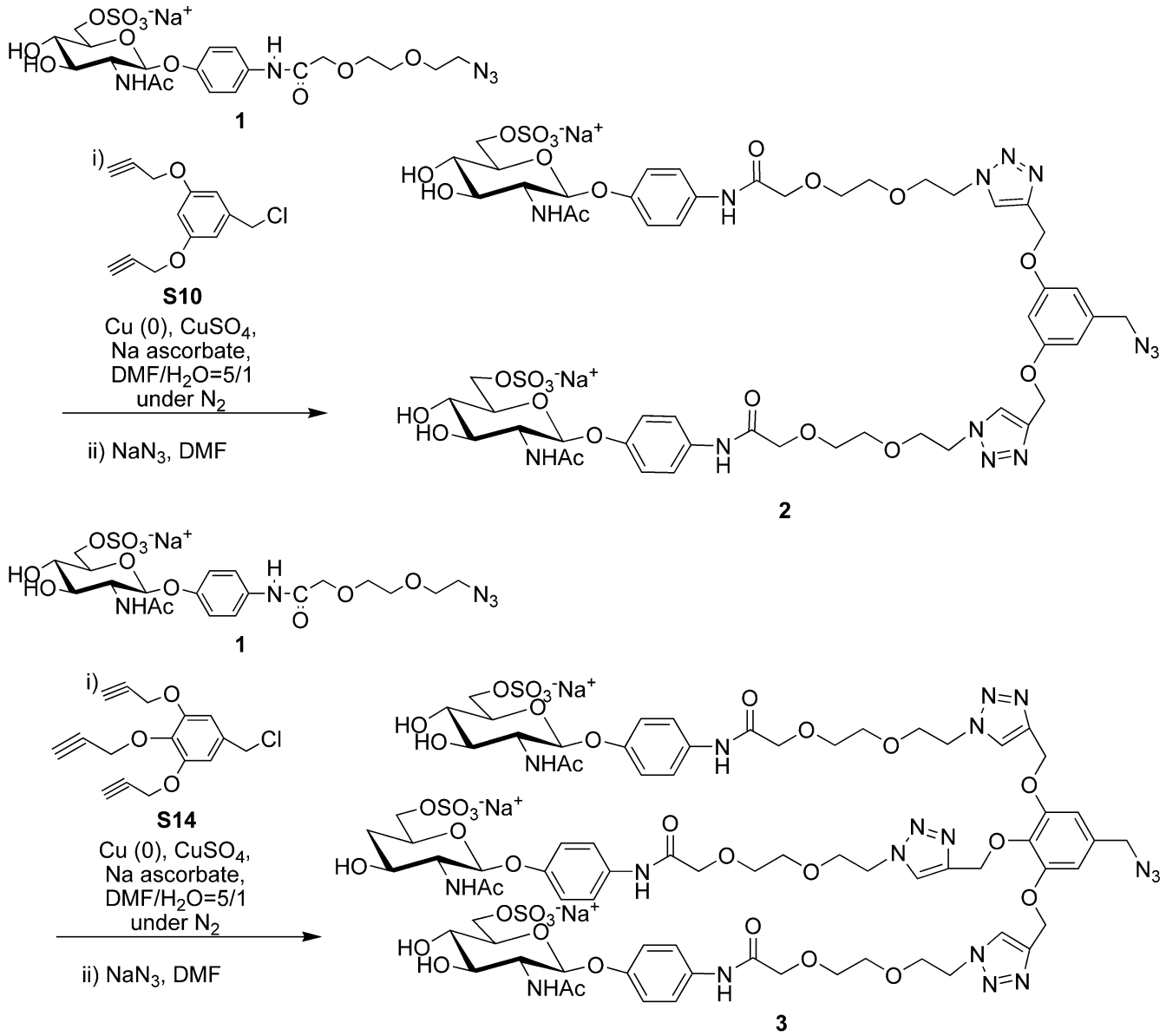
<u>*p*-(*N*-(2-(2-Azide-ethoxy)ethoxy)amido)phenyl 6-sodium sulfo-*N*-acetyl-β-*D*-glucosamine (monovalent-6S-GlcNAc (**1**))</u>

S15 (775mg, 1.91mmol, 1.0eq) and Pd/C (100mg) were dissolved in MeOH (50mL) and were stirred under hydrogen at room temperature. An hour later, Pd/C was removed and the solution was evaporated to the brownish solid (717mg). Subsequently, the compound and **S6** (545mg, 2.88mmol, 1.5eq) were dissolved in DMF (50mL) and were stirred at 0ºC. Then, HATU (746mg, 1.96mmol, 1.0eq) and DIPEA (500μl, 2.88mmol, 1.5eq) were added to the solution. 8 hours later, the product was confirmed the reaction by rev. TLC (MeOH:H_2O=1:8) and the solution was evaporated to the crude product. The crude product was purified by rev. chromatography (H_2O:MeOH=10:1), and the white powder was isolated (1.032g, 99%).

^{1}H-NMR (300MHz, D_2O, ppm): δ 7.27 (2H, d, *J*=9.0Hz, ArH, meta to 6S-GlcNAc), 6.98 (2H, d, *J*=9.3Hz, ArH, ortho to 6S-GlcNAc), 5.02 (1H, d, *J*=8.1Hz, H-1), 4.27 (1H, dd, *J*=2.0 and 11.3Hz, H-6_{proR}), 4.12 (1H, dd, *J*=4.7 and 11.2 Hz, H-6_{proS}), 4.11 (2H, s, -NHCO-<u>CH_2</u>-), 3.87 (1H, t, *J*=9.5Hz, H-2), 3.76-3.45 (7H, m, H-3, H-4, H-5 and –O<u>CH_2CH_2</u>O-), 3.04 (2H, t, *J*=4.8Hz, -O<u>CH_2</u>CH_2N_3), 3.07 (2H, q, *J*=7.4Hz, OCH_2<u>CH_2</u>N_3), 1.90 (3H, s, Ac). ^{13}C-NMR (75MHz, DMF-d_7, ppm): δ 169.9 (-NH<u>CO</u>CH_3), 168.1 (-NHCO-), 154.4 (ArC, ipso to 6S-GlcNAc), 133.4 (ArC, para to 6S-GlcNAc), 121.1 (ArC, meta to 6S-GlcNAc), 116.9 (ArC, ortho to 6S-GlcNAc), 100.2 (C-1), 75.6 (C-5), 74.8 (C-4), 70.0 (-

NHCO$\underline{CH_2}$O-, C-3), 69.8 (-$CH_2O\underline{CH_2}CH_2N_3$), 66.1 (C-6), 56.2 (C-2), 54.5 (-$NHCOCH_2OCH_2\underline{CH_2}O$-), 54.4 (-$NHCOCH_2O\underline{CH_2}CH_2O$-), 50.6 (-$CH_2OCH_2\underline{CH_2}N_3$), 22.7(-$NHCO\underline{CH_3}$). ESI-MS [negative]: 562.2 $[M\text{-}Na^+]^-$ (calculated), 562.3 $[M\text{-}Na^+]^-$ (observed).

2-7. Divalent and Trivalent 6S-GlcNAc



Scheme S5. Syntheses of divalent **2** and trivalent **3** 6S-GlcNAc derivatives.

Divalent 6S-GlcNAc (**2**)

1 (266mg, 0.455mmol, 3.4eq) and **S10** (31mg, 0.133mmol, 1.0eq) were dissolved in DMF while sodium *L*-ascorbate (18mg, 0.091mmol, 0.7eq) and copper (II) sulfate pentahydrate (7mg, 0.047mmol, 0.3eq) were dissolved in distilled water. The reactive solution was prepared by mixing each solution and the addition of copper (0) powder (0.4mg), and was stirred under nitrogen at room temperature for a day. The object production was confirmed by rev. TLC (H_2O:MeOH = 8:1). Copper rest was removed by centrifugation and water layer was removed under reduced pressure. The crude compound was dissolved in DMF, and sodium azide (67mg, 1.03mmol, 7.7eq) was added. After the stirring reaction mixture at 70ºC for a day, the solution was evaporated and purified by rev. chromatography (H_2O:MeOH=8:1). The white powder was yielded (41mg, 22%).

^{1}H-NMR (300MHz, D_2O, ppm): δ 7.91 (2H, s, cyclictriazole), 7.03 (2H, d, *J*=8.7Hz, ArH, meta to 6S-GlcNAc), 6.79 (2H, d, *J*=9.0 Hz, ArH, ortho to 6S-GlcNAc), 6.39 (2H, s, ArH, cyclictriazole (ortho to benzylazide)), 6.24 (1H, s, ArH, cyclictriazole (para to benzylazide)), 4.92 (2H, d, *J*=8.4 Hz, H-1), 4.87 (4H, s, -O$\underline{CH_2}$-cyclictriazole), 4.49 (4H, t, *J*=4.6Hz, -NHCO-$\underline{CH_2}$-), 4.22 (2H, dd, J=1.7 and 11.3Hz, H-6_{proR}), 4.10 (2H, s, -ArCH_2N_3), 4.08 (2H, dd, *J*=5.4 and 11.4 Hz, H-6_{proS}), 3.90-3.81 (2H, m, H-2), 3.87 (4H, t, *J*=5.1Hz, -$CH_2\underline{CH_2}$-cyclictriazole-, 3.84 (4H, t, *J*=4.5Hz, -$\underline{CH_2}CH_2$-cyclictriazole-), 3.71-3.59 (2H, m, H-5), 3.56- 3.37 (2H+2H+2H×4, m, H-3, H-4 and -O$\underline{CH_2}\underline{CH_2}$O-), 1.89 (3H×2, s, Ac). ^{13}C-NMR (75MHz, DMF-d_7, ppm): δ169.9 (-NH$\underline{CO}CH_3$), 168.1(-NHCO-), 160.1 (ArC, meta to benzylazide), 154.3 (ArC, ipso to 6S-GlcNAc), 143.1 (-N(linker)-N=N-$\underline{C}$(CH_2O-benzylazide)=C-), 138.4 (ArC, ipso to benzylazide), 133.4 (ArC, para to 6S-GlcNAc), 125.2 (-N(linker)-N=N-C(CH_2O-benzylazide)=$\underline{C}$-), 121.1 (ArC, meta to 6S-GlcNAc), 116.9 (ArC, ortho to 6S-GlcNAc), 107.7 (ArC, ortho to benzylazide), 101.3 (C-1), 100.3 (ArC, para to benzylazide), 75.8 (C-5), 74.8 (C-4), 71.2 (-N(linker)-N=N-C($\underline{CH_2}$O-benzylazide)=C-), 70.7 (-NHCO$\underline{CH_2}$O-), 69.9 (C-3), 66.0 (C-6), 61.7 (-O$\underline{CH_2}\underline{CH_2}$-cyclictriazole), 56.2 (C-2), 53.8 (-O$\underline{CH_2}CH_2$-cyclictriazole), 54.1 (ArCH_2N_3), 49.8 (-$CH_2OCH_2\underline{CH_2}$-cyclictriazole), 22.7(-NHCO$\underline{CH_3}$). MALDI-TOF-MS [negative]: 1388.4 $[M\text{-}Na^+]^-$ (calculated), 1388.5 $[M\text{-}Na^+]^-$ (observed).

Trivalent 6S-GlcNAc (**3**)

1 (420 mg, 0.718mmol, 3.9eq) and **S14** (53 mg, 0.227mmol, 1.0eq) were dissolved in DMF while sodium *L*-ascorbate (8.15mg, 0.110mmol, 0.6eq) and copper (II) sulfate pentahydrate (20.0mg, 0.0700mmol, 0.3eq) were dissolved in distilled water. The reactive solution was prepared by mixing each solution and the addition of copper (0) powder (0.05mg), and was stirred under nitrogen at room temperature for a day. The object production was confirmed by rev. TLC (H_2O:MeOH:CH_3COOH = 8:1:1). Copper rest was removed by centrifugation and water layer was removed under reduced pressure. The crude compound was dissolved in DMF, and sodium azide (162mg, 2.48mmol, 5.8eq) was added. After the stirring reaction mixture at 70ºC for a day, the solution was evaporated and purified by rev. chromatography (H_2O:MeOH=8:1). The white powder was yielded (91mg, 20%).

^{1}H-NMR (300MHz, D_2O, ppm): δ 7.91 (2H, s, cyclictriazole (meta to benzylazide)), 7.60 (1H, s, cyclictriazole (para to benzylazide), 7.11 (2H, s, cyclictriazole (ortho to benzylazide)), 7.02 (2H, d, *J*=9.0 Hz, ArH, meta to 6S-GlcNAc (para to benzylazide)), 6.98 (4H, d, *J*=8.7Hz, ArH, meta to 6S-GlcNAc (meta to benzylazide)), 6.79 (2H, d, *J*=9.0 Hz, ArH, ortho to 6S-GlcNAc (para to benzylazide)), 6.76 (4H, d, *J*=8.7 Hz, ArH, ortho to 6S-GlcNAc (meta to benzylazide)), 4.92 (1H, d, *J*=8.7 Hz, H-1 (para to benzylazide)), 4.89 (4H, s, -O$\underline{CH_2}$-cyclictriazole (meta to benzylazide)), 4.89 (2H, d, *J*=8.1 Hz, H-1 (meta to benzylazide)), 4.81 (2H, s, -O$\underline{CH_2}$-cyclictriazole (para to benzylazide), 4.50 (4H, t, *J*=4.7 Hz, -NHCO$\underline{CH_2}$- (meta to benzylazide)), 4.37 (4H, t, *J*=4.4 Hz, -NHCO-$\underline{CH_2}$- (meta to benzylazide)), 4.22 (2H, dd, *J*=2.2 and 13.3 Hz, H-6_{proR}), 4.21 (2H, m, H-6_{proR} (meta and para to benzylazide)), 4.09 (2H, dd, *J*=5.1 and 6.0 Hz, H-6_{proS} (meta to benzylazide)), 4.07 (1H, dd, *J*=5.0 and 6.6 Hz, H-6_{proS} (para to benzylazide)), 3.85 (3H, t, *J*=7.1Hz, H-2), 3.88-3.74 (12H, m, -$\underline{CH_2CH_2}$-cyclictriazole), 3.79 (2H, s, -ArCH_2N_3), 3.67-3.61 (3H, m, H-5), 3.53 (1H, t, *J*=9.0Hz, H-3 (para to benzylazide)), 3.52 (2H, t, *J*=8.6 Hz, H-3 (meta to benzylazide)), 3.51 (1H, t, *J*=8.6H z, H-4 (para to benzylazide)), 3.53-3.42 (2H+12H, t, *J*=8.6Hz, H-4 (para to benzylazide)) 1.88 (3H, s, Ac (para to benzylazide)), 1.87 (3H×2, s, Ac (meta to benzylazide)). ^{13}C-NMR (75MHz, DMF-d_7, ppm): δ169 .9 (-NH$\underline{CO}$$CH_3$), 168.1 (-NHCO-), 154.3 (ArC,

ipso to 6S-GlcNAc), 152.4 (ArC, meta to benzylazide), 143.9 (-N(linker)-N=N-C(CH_2O-benzylazide)=C-), 143.1 (ArC, para to benzylazide), 133.4 (ArC, para to 6S-GlcNAc), 125.2 (-N(linker)-N=N-C(CH_2O-benzylazide)=C-), 125.1 (ArC, ipso to benzylazide), 121.1 (ArC, meta to 6S-GlcNAc), 117.0 (ArC, ortho to 6S-GlcNAc), 109.2 (ArC, ortho to benzylazide), 100.3 (C-1), 75.8 (C-5), 74.8 (C-4), 71.2 (-N(linker)-N=N-C(CH_2O-benzylazide)=C-), 70.7 (-NHCOCH_2O-), 69.9 (C-3), 66.0 (C-6), 62.9 (-$NHCOCH_2OCH_2CH_2O$-), 62.5 (-$NHCOCH_2OCH_2CH_2O$-), 56.2 (C-2), 52.0 (-OCH_2CH_2-cyclictriazole), 49.9 ($ArCH_2N_3$), 49.8 (-$CH_2OCH_2CH_2$-cyclictriazole), 22.7(-NHCOCH_3). ESI-MS [negative]: 1002.3 $[M-2Na^+]^{2-}$ and 660.5 $[M-3Na^+]^{3-}$ (calculated), 1003.9 $[M-2Na^+]^{2-}$ and 661.7 $[M-3Na^+]^{3-}$ (observed).

3. Characterization of 6S-GlcNAc Derivatives Immobilized Interface

3-1. X-Ray Photoelectron Spectroscopy

Immobilization of the functional SAM was investigated by XPS. Pass energy and energy step were 22.75eV and 0.025eV/step in high resolution scan, respectively. Binding energy profiles in C1s and N1s regions were demonstrated in Fig.S2 (i) and (ii), respectively. N-N and N=N bond was formed through click reaction. Absorbance elevation of the divalent and the trivalent 6S-GlcNAc in Fig.S2 (ii) indicated existence of N=N and N-N bond formations. Although the emergence of the peaks was confirmed, the quantitation was never accomplished owing to the poor performance of the system.

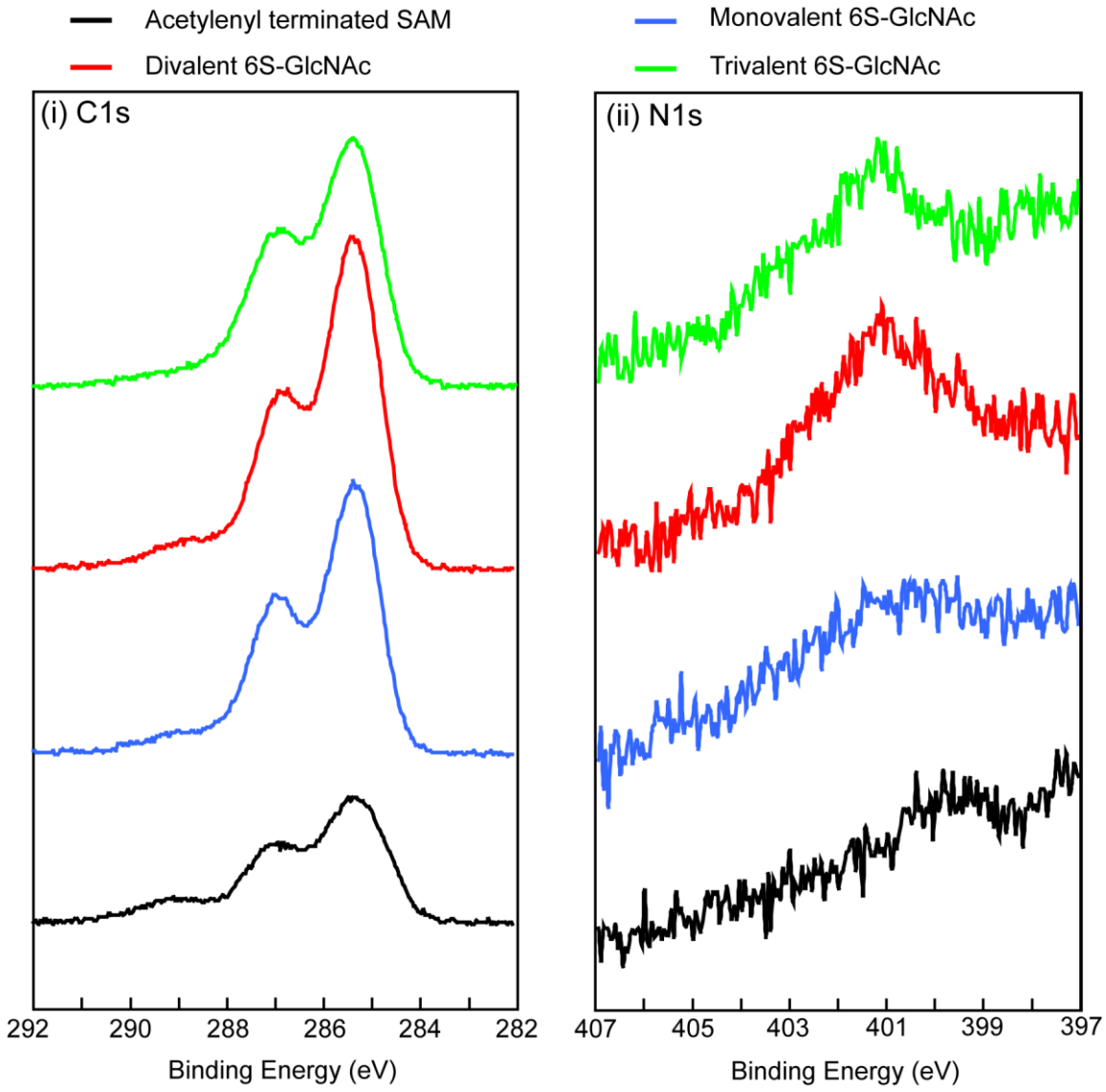


Fig. S2. XPS spectra of the functional SAMs (i) in the region of C1s and (ii) N1s.

3-2. FTIR-Reflection Absorption Spectroscopy (FTIR-RAS)

FTIR-RAS spectrum of each substrate was measured. The measurements condition was at resolving power of 4.0cm^{-1} using MCT-N detector. Fig. S3 showed that strong bands around 1150-1250, 2820-2900 and 2950-3400 were emerged and individually indicated hemi-acetal, alkyl chain and hydroxyl group.

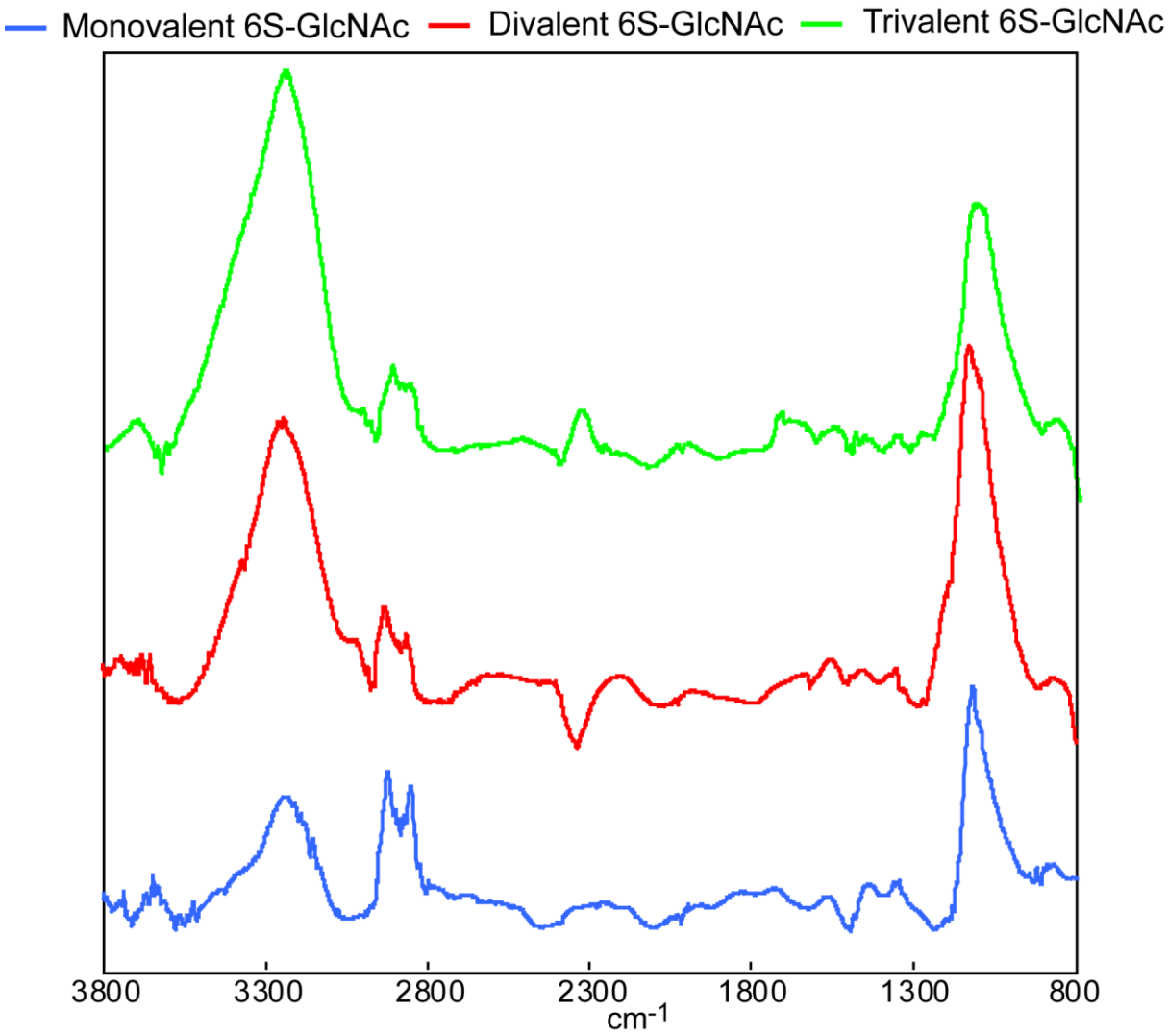


Fig. S3. IR spectra of the functional SAMs.

3-3. Ellipsometry

Thickness of each SAM was calculated by ellipsometer. Average thicknesses were determined in 10 times examination. When the saccharide derivatives such as monovaelent **1**, divalent **2** and trivalent **3** were immobilized on the acetylenyl terminated SAM, their thickness elevations were 14.0 Å, 16.1 Å and 19.0 Å respectively.

3-4. Water Contact Angle Goniometry

Water contact angle on the substrate were evaluated by DropMaster300 (Kyowa Interface Science co., ltd.). Water contact angles were estimated at 25°C with 40% humidity. The measurements were conducted a minute later after dropping. Water contact angles on the monovaelent **1**, divalent **2** and trivalent **3** were 46.3º (standard deviation (SD) =2.5), 41.1º (SD=1.9), 44.8º (SD=1.7) respectively.

4. Analysis of Aβ (1-42) Aggregate on the Sulfonated Sugar Interface

4-1. SPR Curve by Changing the Concentration of Aβ (1-42) Sample Solution

Concentration dependency of Aβ (1-42) for the substrate was measured. No sugar modified (acetylenyl terminated), the monovalent-, the divalent- and trivalent- 6S-GlcNAc immobilized substrates were observed RU changes corresponded to concentrations from 2.5μM to 40μM (Fig. S4).

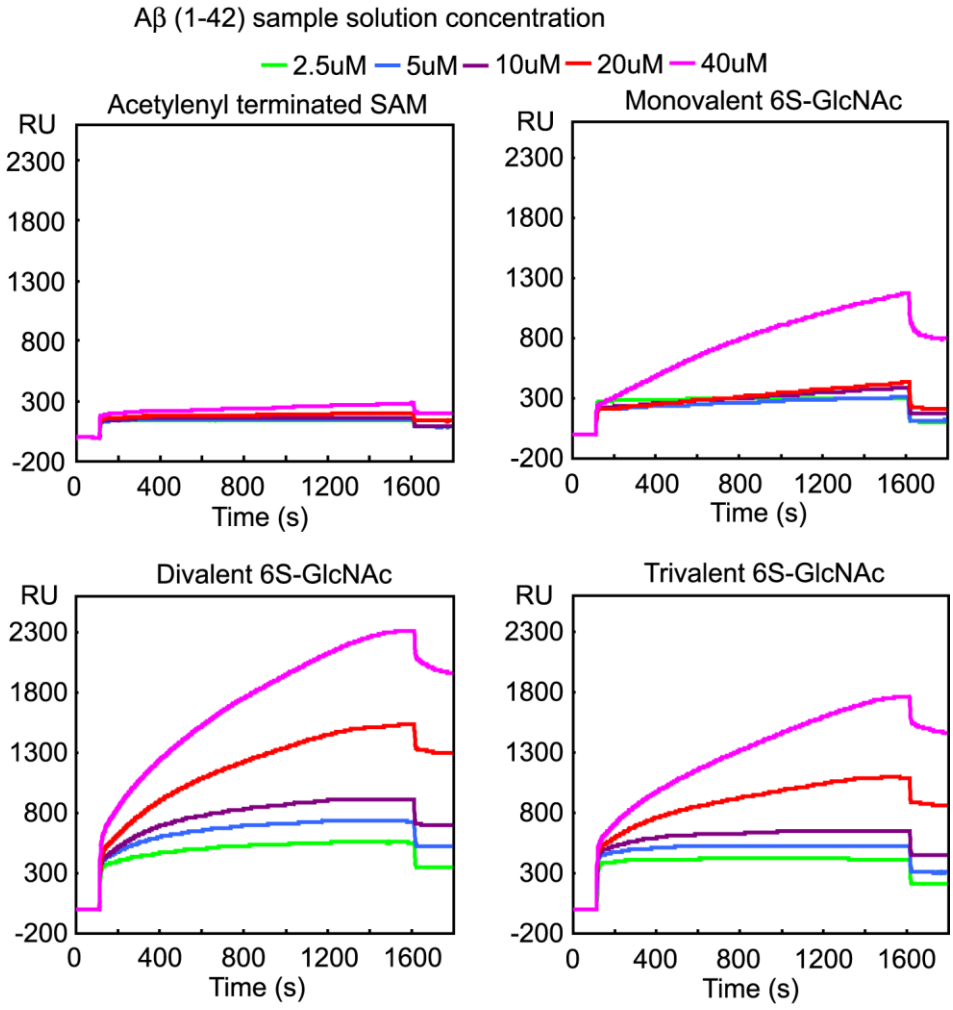


Fig.S4. Aβ (1-42) concentration-dependent curve of RU on each substrate.

Acknowledgement

We thank Dr. Atsushi Hozumi (National Institute of Advanced Industrial Science and Technology (AIST)) for the ellipsometry measurement.