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Supporting Information

For

A selective glucose sensor: cooperative effect by monboronic acid-modified

poly(amidoamine) dendrimers

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General Consideration.

PAMAM dendrimers were purchased from Dendritech. Co. Chemicals were purchased from Acros, Merck and Sigma-Aldrich Co. Analytical thin-layer chromatography were pre-coated and detected at 254 nm by UV lamp. MALDI-Mass spectra were recorded from Autoflex III MALDI-TOF system (Bruker Daltonics). NMR spectra were obtained on a Varian 400MHz spectrometer and JOEL 400MHz spectrometer. UV-Vis spectra were collected by Agilent 8453. Fluorescence spectra were collected by Varian. Gel permeation chromatography (GPC) experiments were obtained using an Agilent HPLC system (1100 series) and performed using TSK G2000sw column (7.5x 300 mm, 10µm size).

Preparation and characterization of boronic acid modified PAMAM dendrimers *Boronic acid modified PAMAM dendrimers (1a-1e)*

Scheme S 1 Synthesis of CPBA functionalized 2nd to 6th PAMAM dendrimers.



(G:2)-dendri-PAMAM-(CPBA)14(1a)

The solution of PyBOP (51 mg, 0.98 mmol), CPBA (163 mg, 0.98 mmol), Et₃N (0.13 mL, 0.98 mmol) in dry DMF (10 mL), was stirred for 20 min. To the resulting mixture was added the solution of (G:2)-*dendri*-PAMAM-(NH₂)₁₆ (100 mg, 0.03 mmol) in 10 % EtOH/DMF (11 mL) and stirred at 40°C for 2 days. The solid were filtrated and dissolved in MeOH (5 mL) for the following column chromatography purification. (Sephadex LH20, 3.5 x 60 cm, eluted by MeOH) to give the white solid. (110 mg, 70 %). ¹H NMR (400 MHz, CD₃OD, ppm) δ : 7.80 (br s, 56H), 3.60 (m, 26H), 3.50 (m, 72H), 3.38 (m, 46H), 3.15 (m, 20H), 2.83 (m, 18H), 2.74 (m, 46H); ¹³C NMR (100 MHz, CD₃OD, ppm) δ : 173.6, 172.8, 170.3, 138.7, 136.7, 135.0, 127.5, 53.8, 51.4, 40.4, 35.9, 30.2; ¹¹B NMR (133 MHz, CD₃OD, ppm) δ : 24.7 Mass (MALDI, m/z, sinapinic acid (SA): **1a**=20:1): Calculated for C₂₄₀H₃₅₈B₁₄N₅₈O₇₀ Na₁[M+Na]⁺: 5350.

Mass (MALDI, m/z, sinapinic acid (SA): 1a=20(1): Calculated for C240H358B14N58O70 Na1 [M+Na] (5350, PDI : 1.16)



Figure S 1 ¹H NMR spectra of dendrimer **1a**.



Figure S 2 ¹³C NMR spectra of dendrimer **1a**.



Figure S 3 ¹¹B NMR spectra of dendrimer **1a**.



Figure S 4 MALDI-TOF MS spectra of dendrimer 1a.

(G:3)-dendri-PAMAM-(CPBA)30 (1b)

The procedure used to synthesize **1a** was applied to synthesized **1b** (112 mg, 68%). ¹H NMR (400 MHz, CD₃OD, ppm) δ : 7.80 (br s, 120H), 3.62 (m, 116H), 3.50 (m, 152H), 3.38 (m, 74H), 2.88 (m, 62H), 2.77 (m, 80H); ¹³C NMR (100 MHz, CD₃OD, ppm) δ : 173.4, 172.5, 170.3, 138.6, 136.8, 135.1, 127.4, 53.7, 51.4, 40.4, 35.6, 30.7, 29.9; ¹¹B NMR (133 MHz, CD₃OD, ppm) δ : 25.1

Mass (MALDI, m/z, SA: **1b**=20:1): Calculated for C511H756B30N122O150K1 [M+K]⁺: 11386. Found: 11386, PDI :1.16



Figure S 5 ¹H NMR spectra of dendrimer **1b**.



Figure S 6 ¹³C NMR spectra of dendrimer **1b**.



Figure S 7¹¹B NMR spectra of dendrimer **1b**.



Figure S 8 MALDI-TOF MS spectra of dendrimer 1b.

(G:4)-*dendri*-PAMAM-(CPBA)58 (1c)

The procedure used to synthesize **1a** was applied to synthesized **1c**. (115 mg, 72 %). ¹H NMR (400 MHz, CD₃OD, ppm) δ : 7.76 (br s, 232H), 3.48 (m, 160H), 3.38 (m, 216H), 3.09 (m, 254H) , 2.91 (m, 120H);, 2.52 (m, 246H); ¹³C NMR (100 MHz, CD₃OD, ppm) δ : 173.9, 170.3, 138.5, 136.6, 134.9, 127.4, 53.4, 51.3, 40.6, 37.2, 32.0; ¹¹B NMR (133 MHz, CD₃OD, ppm) δ : 24.4

Mass (MALDI, m/z, SA: 1c=20:1): Calculated for C1028H1539B58N250O298 [M+H]⁺: 22797 Found: 22797, PDI :1.25



Figure S 9 ¹H NMR spectra of dendrimer **1c**.



Figure S 10¹³C NMR spectra of dendrimer **1c**.



Figure S 11 ¹¹B NMR spectra of dendrimer 1c.



Figure S 12 MALDI-TOF MS spectra of dendrimer 1c.

(G:5)-dendri-PAMAM-(CPBA)119 (1d)

The procedure used to synthesize **1a** was applied to synthesized **1d**. (112 mg, 70 %). ¹H NMR (400 MHz, CD₃OD, ppm) δ : 7.78 (br s, 476H), 3.49 (m, 626H), 3.38 (m, 566H), 3.24 (m, 332H), 2.70 (m, 496H); ¹³C NMR (100 MHz, CD₃OD, ppm) δ : 173.6, 172.9, 170.3, 138.6, 136.7, 135.1, 127.5, 53.7, 51.3, 40.4, 36.1, 30.8; ¹¹B NMR (133 MHz, CD₃OD, ppm) δ : 23.2

Mass (MALDI, m/z, SA: **1d**=20:1): Calculated for C2095H3124B119N506O609 [M+H]⁺: 46432. Found: 46432, PDI :1.16



Figure S 13 ¹H NMR spectra of dendrimer **1d**.



Figure S 14 ¹³C NMR spectra of dendrimer **1d**.



Figure S 15 ¹¹B NMR spectra of dendrimer **1d**.



Figure S 16 MALDI-TOF MS spectra of dendrimer 1d.

(G:6)-dendri-PAMAM-(CPBA)205 (1e)

The procedure used to synthesize **1a** which was also applied to synthesized **1e**. (88 mg, 58 %). ¹H NMR (400 MHz, CD₃OD, ppm) δ : 7.79 (br s, 820H), 3.48 (m, 1364H), 3.38 (m,1476H), 2.74 (m, 1228H); ¹³C NMR (100 MHz, CD₃OD, ppm) δ : 173.3, 172.6, 170.3, 138.6, 136.7, 135.1, 127.4, 53.6, 51.2, 40.4, 35.8, 30.4; ¹¹B NMR (133 MHz, CD₃OD, ppm) δ : 23.1

Mass (MALDI, m/z, SA: **1e**=20:1): Calculated for C₃₉₇₀H₆₁₀₈B₂₀₄N₁₀₁₈O₁₁₂₀K₆ [(M+6K⁺) /6]: 14768 Found: 14768, PDI :1.13



Figure S 17 ¹H NMR spectra of dendrimer **1e**.



Figure S 18 ¹³C NMR spectra of dendrimer **1e**.



Figure S 19¹¹B NMR spectra of dendrimer **1e**.



Figure S 20 MALDI-TOF MS spectra of dendrimer 1e.



(G:4)-dendri-PAMAM-(NHAc)11 (10a)

The Et₃N (5.35 µL, 38.46 µmol) was added in the solution of (G:4)-*dendri*-PAMAM-(NH₂)₁₆ (71 mg, 4.99 µmol) in MeOH (15 mL), and stirred for 30 min. To the resulting mixture was added acetic anhydride (3.30 µL, 34.96 µmol) dropwise and the reaction was stirred for overnight at room temperature. After stirring overnight, MeOH was removed and purified by column chromatography. (Sephadex LH20, 3.5 x 60 cm, eluted by MeOH) to give the colorless thickness solid. (56 mg, 78 %). ¹H NMR (400 MHz, CD₃OD, ppm) δ : 3.59 (m, 228H), 3.44 (m, 232H), 3.30 (m, 162H), 3.19 (m, 118H), 2.82 (m, 256H), 1.99 (m, 33H); ¹³C NMR (100 MHz, CD₃OD, ppm) δ : 174.0, 173.7, 173.3, 54.0, 53.6, 51.3, 51.1, 41.2, 41.0, 40.2, 39.9, 38.3, 36.6, 31.8, 31.4, 23.0



Figure S 21 ¹H NMR spectra of dendrimer 10a.



Figure S 22 ¹³C NMR spectra of dendrimer **10a**.

(G:4)-*dendri*-PAMAM-(NHAc)15 (10b)

The procedure used to synthesize **10a** was applied to synthesized **10b** (62 mg, 65 %). ¹H NMR (400 MHz, CD₃OD, ppm) δ : 3.56 (m, 130H), 3.50 (m, 138H), 3.18 (m, 322H), 3.05 (m, 138H), 2.68 (m, 268H), 1.98 (s, 45H); ¹³C NMR (100 MHz, CD₃OD, ppm) δ : 174.8, 174.3, 53.9, 53.6, 51.2, 41.0, 40.2, 39.9, 38.2, 37.4, 32.8, 23.1



Figure S 23 ¹H NMR spectra of dendrimer **10b**.



Figure S 24 ¹³C NMR spectra of dendrimer **10b**.

(G:4)-*dendri*-PAMAM-(NHAc)20 (*10c*)

The procedure used to synthesize **10a** was applied to synthesized **10c** (83 mg, 69 %). ¹H NMR (400 MHz, CD₃OD, ppm) δ : 3.28 (m, 556H), 3.05 (m, 110H), 2.84 (m, 96H), 2.57 (m, 234H), 1.84 (s, 132H); ¹³C NMR (100 MHz, CD₃OD, ppm) δ : 175.6, 173.3, 172.6, 53.7, 51.3, 41.0, 39.5, 38.2, 35.8, 30.3, 22.0



Figure S 25 ¹H NMR spectra of dendrimer **10c**.



Figure S 26 ¹³C NMR spectra of dendrimer **10c**.

(G:4)-*dendri*-PAMAM-(NHAc)44 (10d)

The procedure used to synthesize **10a** was applied to synthesized **10d** (95 mg, 87 %). ¹H NMR (400 MHz, CD₃OD, ppm) δ : 3.53 (m, 40H), 3.35 (m, 116H), 3.29 (m, 178H), 3.14 (m, 52H) , 2.94 (m,240H), 2.75 (m, 128H) , 2.47 (m, 242H), 1.98 (m, 132H); ¹³C NMR (100 MHz, CD₃OD, ppm) δ : 175.1, 174.7, 173.5, 53.4, 51.1, 41.4, 40.1, 40.0, 38.6, 34.7, 29.7, 22.9



Figure S 27 ¹H NMR spectra of dendrimer **10d**.



Figure S 28 ¹³C NMR spectra of dendrimer **10d**.

Preparation of boronic acid-modified acetyl G3 PAMAM dendrimers (6a-6d)

Scheme S 3 Synthesis of acetic anhydride and CPBA functionalized 4th PAMAM dendrimers.



(G:4)-dendri-PAMAM-(NHAc)11-(CPBA)46 (6a)

The solution of PyBOP (160.68 mg, 0.31 mmol), CPBA (51.24 mg, 0.31 mmol), Et₃N (0.04 mL, 0.31 mmol) in dry DMF (10 mL), was stirred for 20 min. To the mixture was added the solution of **10a** (40.0 mg, 2.76 µmol) in 10 % EtOH/DMF (11 mL). After the addition, the mixture was stirred at 40°C for 1 day. The reaction was concentrated and then was dissolved in MeOH for column chromatography puffication. (Sephadex LH20, 3.5 x 60 cm, eluted by MeOH) to give the colorless thickness solid. (37 mg, 61 %). ¹H NMR (400 MHz, CD₃OD, ppm) δ : 7.78 (brs, 184H), 3.49 (m, 238H), 3.38 (m, 114H), 3.25 (m, 220H), 3.08 (m, 154H), 2.61 (m,270 H), 1.92 (m, 33H); ¹³C NMR (100 MHz, CD₃OD, ppm) δ : 173.6, 173.0, 170.3, 138.6, 136.6, 134.9, 127.5, 53.7, 53.4, 51.3, 40.5, 40.4, 39.6, 36.3, 30.7, 23.1; ¹¹B NMR (133 MHz, CD₃OD, ppm) δ : 23.4

Mass (MALDI, m/z, SA: **6a**=20:1): Calculated for C₉₆₆H₁₅₅₇B₄₆N₂₅₀O₂₇₃ Na₁ [M+Na]⁺ : 21506. Found: 21506, PDI : 1.20



Figure S 29 ¹H NMR spectra of dendrimer **6a**.



Figure S 30 13 C NMR spectra of dendrimer **6a**.



Figure S 31 ¹¹B NMR spectra of dendrimer **6a**.



Figure S 32 MALDI-TOF MS spectra of dendrimer 6a.

(G:4)-dendri-PAMAM-(NHAc)15-(CPBA)43 (6b)

The procedure used to synthesize **6a** was applied to synthesized **6b** (57 mg, 51 %). ¹H NMR (400 MHz, CD₃OD, ppm) δ : 7.79 (br s, 172H), 3.49 (m, 286H), 3.38 (m, 204H), 3.29 (m, 210H), 2.68 (m, 296H), 1.96 (s, 45H); ¹³C NMR (100 MHz, CD₃OD, ppm) δ : 173.7, 173.3, 170.3, 136.8, 135.1, 127.5, 53.7, 51.3, 40.4, 40.0, 36.6, 31.3, 23.0; ¹¹B NMR (133 MHz, CD₃OD, ppm) δ : 24.3

Mass (MALDI, m/z, SA: **6b**=20:1): Calculated for C₉₅₂H₁₅₅₁B₄₃N₂₅₀O₂₆₈ Na₁ [M+Na]⁺: 21230. Found: 21230, PDI : 1.19



Figure S 33 ¹H NMR spectra of dendrimer **6b**.



Figure S 34 ¹³C NMR spectra of dendrimer **6b**.



Figure S 35 ¹¹B NMR spectra of dendrimer **6b**.



Figure S 36 MALDI-TOF MS spectra of dendrimer 6b.

(G:4)-dendri-PAMAM-(NHAc)20-(CPBA)40 (6c)

The procedure used to synthesize **6a** was applied to synthesized **6c** (63.6 mg, 55 %). ¹H NMR (400 MHz, CD₃OD, ppm) δ : 7.80 (br s, 160H), 3.51 (m, 460H), 3.40 (m, 178H), 3.26 (m, 98H), 2.88 (m, 108H), 2.79 (m, 152H), 1.97 (s, 60H); ¹³C NMR (100 MHz, CD₃OD, ppm) δ : 173.6, 172.6, 170.3, 138.7, 136.7, 135.1, 127.5, 53.7, 51.3, 40.4, 39.8, 35.8, 30.1, 23.1; ¹¹B NMR (133 MHz, CD₃OD, ppm) δ : 24.5

Mass (MALDI, m/z, SA: **6c**=20:1): Calculated for C₉₂₂H₁₅₄₈B₄₀N₂₅₀O₂₆₄K₁ [M+K]⁺: 21013. Found: 21013 [M+K]⁺, PDI :1.17



Figure S 37 ¹H NMR spectra of dendrimer 6c.



Figure S 38 ¹³C NMR spectra of dendrimer **6c**.



Figure S 39 ¹¹B NMR spectra of dendrimer **6c**.



Figure S 40 MALDI-TOF MS spectra of dendrimer 6c.

(G:4)-dendri-PAMAM-(NHAc)44-(CPBA)18 (6d)

The procedure used to synthesize **6a** was applied to synthesized **6d** (53.1 mg, 48 %). ¹H NMR (400 MHz, CD₃OD, ppm) δ : 7.83 (s, 72H), 3.65 (m, 160H), 3.51 (m, 244H), 3.32 (m, 164H), 3.29 (m, 162H), 2.85 (m, 110H), 2.77 (m, 156H), 1.97 (s, 132H); ¹³C NMR (100 MHz, CD₃OD, ppm) δ : 173.6, 172.7, 170.3, 138.7, 136.8, 135.1, 127.5, 53.8, 51.4, 40.3, 39.9, 36.0, 30.7, 30.4, 23.1; ¹¹B NMR (133 MHz, CD₃OD, ppm) δ : 27.5

Mass (MALDI, m/z, SA: **6d**=20:1): Calculated for C₈₂₉H₁₄₈₂B₁₇N₂₅₀O₂₁₉Na₁ [M+Na]⁺: 18603. Found: 18603, PDI :1.19



Figure S 41 ¹H NMR spectra of dendrimer 6d.



Figure S 42 ¹³C NMR spectra of dendrimer **6d**.



Figure S 43 ¹¹B NMR spectra of dendrimer **6d**.



Figure S 44 MALDI-TOF MS spectra of dendrimer 6d.

Gel Permeation Chromatography.

GPC traces for dendrimer **1a-1e**, **6a-6d** in TSK G2000SW column (7.5 x 300 mm, 10 μ m size) in Agilent HPLC system (1100 series). The experiments were conducted at 25°C at a flow rate of 1 mL/min with 50% methanol and 50% water with 0.1 % TFA as eluent and detected at 220 nm. The results of filtration were followed with the figures that **1a** (7.06 min), and **1b** (6.43 min), and **1c** (5.98 min), and **1d** (5.69 min), and **1e** (5.28 min), and **6a** (5.95 min), and **6b** (5.89 min), and **6c** (5.93 min), and **6d** (5.97 min) are discovered. The PDI value were calculated using (G:2-6)-*dendri*-PAMAM-(NH₂)_n as standard.







Figure S 46 GPC traces for dendrimers a.) 6a b.) 6b c.) 6c d.) 6d.

Measurement of binding constant

K_b of ARS in the solution of 40% Ethanol in 30 mM PBS (pH 4.96 and 7.50)

An 83.2 µM solution of ARS in 50% Ethanol in 40 mM PBS (pH 5.92 and 7.60) as solution A. An 83.2 µM solution of 1b was prepared in 50% Ethanol in 40 mM PBS (pH 5.92 and 7.60) as solution B. A 0.25 mL of solution A (83.2 µM) was added 0.25 mL solvent to obtain 0.5 mL ARS (41.6 µM) in cuvette for fluorescence measurement. 0.25 mL of solution B (83.2 µM) was added 0.25 mL solvent to obtain 0.5 mL **1b** (41.6 µM) in cuvette for fluorescence measurement. 0.25 mL of solution B (83.2 µM) was added 0.25 mL of solution A to obtain 0.5 mL ARS-1b (41.6 µM) in cuvette for fluorescence measurement.

K_b of ARS in DMF

An 83.2 µM solution of ARS in DMF as solution A. An 83.2 µM solution of **1b** was prepared in DMF (with 10% MeOH) as solution B. A 0.25 mL of solution A (83.2 µM) was added 0.25 mL solvent to obtain 0.5 mL ARS (41.6 µM) in cuvette for fluorescence measurement. 0.25 mL of solution B (83.2 µM) was added 0.25 mL solvent to obtain 0.5 mL **1b** (41.6 µM) in cuvette for fluorescence measurement. 0.25 mL of solution B (83.2 µM) was added 0.25 mL of solution A to obtain 0.5 mL ARS-1b (41.6 µM) in cuvette for fluorescence measurement.

K_b of *ARS* at various temperature

An 83.2 µM solution of ARS in DMF as solution A. A 832 µM solution of **1b** was prepared in DMF (with 10% MeOH) as solution B. A 300 µM solution of CPBA was prepared in DMF (with 2.5% MeOH) as solution C. 0.25 mL of solution B (832 µM) was added 0.25 mL solvent A to obtain 0.5 mL ARS-1b (41.6 μM ARS, 416 μM **1b**) in cuvette for fluorescence measurement. 0.25 mL of solution C (300 μM) was added 0.25 mL solvent A to obtain 0.5 mL ARS-CPBA (150 µM) in cuvette for fluorescence measurement. (Figure S 47)



a.)



Figure S 47 Fluorescence intensity of ARS (150 μ M for CPBA, 416 μ M for **1b** in DMF, λ_{ex} = 468 nm) titrated with a.) CPBA (150 μ M) b.) **1b** (416 μ M) c.) Plot of intensity (λ_{en} = 585 nm for CPBA or 565 nm for **1b**) against temperature.

The binding constant of 1a-1e, 6a-6b with ARS

83.2 μ M solution of ARS in DMF as solution A. 2.08-104.0 μ M solution of **1a-1e**, *6a-6b* was prepared in DMF (with 10% MeOH) as solution B. 0.25 mL of solution A (83.2 μ M) was added 0.25 mL solvent to obtain 0.5 mL ARS (41.6 μ M) in cuvette for fluorescence measurement. 0.25 mL of solution B (83.2 μ M) was added 0.25 mL solvent to obtain 0.5 mL **1a-1e**, *6a-6b* (41.6 μ M) in cuvette for fluorescence measurement. 0.25 mL of solution A to obtain 0.5 mL ARS-(**1a-1e**, *6a-6b*) (41.6 μ M) in cuvette for fluorescence measurement. The experiments were conducted at bandwidth in 10 (nm) and PMT med environment. The excitation wavelength was set at 468 nm. The intensity of the emission was recorded at 565 nm upon ARS mixture with dendrimer **1a-1e**, *6a-6b*. The fluorescence spectra result of **1a-1e**, *6a-6b* with ARS fit to Besesi-Hildebrand equation to give the binding constant.

Besesi-Hildebrand equation:

$$\frac{1}{\Delta I_{\rm f}} = \frac{1}{\Delta k_{p0} I_0 K_{eq1}} \frac{1}{[L]} + \frac{1}{\Delta k_{p0} I_0} \qquad (\rm{eq.1})$$
$$\frac{[S_0]}{P} = \frac{K_{eq1}}{K_{eq}} Q + 1 \qquad (\rm{eq.2})$$

$$P = [L_0] - \frac{1}{QK_{eq1}} - \frac{[I_0]}{(Q+1)} \qquad (eq.3)$$





Figure S 48 Binding constant of ARS with a.) **1a**. b.) **1b**. c.) **1c**. d.) **1d**. e.) **1e**. f.) **6a**. g.) **6b**. The binding constant studies are in ARS (41.6 μ M) with various concentration of boronic acid modified PAMAM dendrimers in 2.5% MeOH in DMF ($\lambda_{ex} = 468$ nm, $\lambda_{em} = 565$ nm, 30°C).

The binding constant of CPBA to glucose

A 166.4 μ M solution of ARS in DMF as solution A. A 4992 μ M solution of CPBA was prepared in DMF as solution B. An 832-83200 μ M solution of saccharides was prepared in DMF as solution C. 0.125 mL of solution A (166.4 μ M) was added 0.375 mL solvent to obtain 0.5 mL ARS (41.6 μ M) in cuvette for fluorescence measurement. 0.125 mL of solution B (4992 μ M) was added 0.375 mL solvent to obtain 0.5 mL CPBA (41.6 μ M) in cuvette for fluorescence measurement. 0.125 mL of solution A (166.4 μ M) and 0.125 mL of solution B (4992 μ M) was added into solvent (0.25 mL) to obtain 0.5 mL mixture solution ARS- CPBA (41.6 μ M ARS, 1248 μ M CPBA). 0.125 mL solution B was added into solution C (0.25 mL) in order to make mixture solution BC, and stand for 30 min. Then 0.125 mL solution A was added into mixture solution BC (0.375 mL) to obtain 0.5 mL mixture solution ABC. A 0.5 mL of the mixture ABC was transferred into a cuvette for fluorescence measurement. The experiments were conducted at bandwidth in 10 (nm) and PMT med environment. he fluorescence spectra result of CPBA with glucose fit to Besesi-Hildebrand equation to give the binding constant.



Figure S 49 Binding constant of CPBA with glucose. The binding constant studies are in CPBA (1248 μ M) with various concentration of saccharides in 2.5% MeOH in DMF ($\lambda_{ex} = 468$ nm, $\lambda_{em} = 565$ nm, 30°C).

The binding constant of 1a-1e, 6a-6d to saccharides using fluorescence spectra

Dendrimer 1a-1e, 6a-6d with glucose, 1a with galactose, lactose, and fructose

A 166.4 μ M solution of ARS in DMF as solution A. A 166.4 μ M solution of boronic acid-modified PAMAM dendrimer (**1a-1e**, **6a-6d**) was prepared in DMF (with 10% MeOH) as solution B. An 832-83200 μ M solution of saccharides was prepared in DMF as solution C. 0.125 mL of solution A (166.4 μ M) was added 0.375 mL solvent to obtain 0.5 mL ARS (41.6 μ M) in cuvette for fluorescence measurement. 0.125 mL of solution B (166.4 μ M) was added 0.375 mL solvent to obtain 0.5 mL ARS (41.6 μ M) in cuvette for fluorescence measurement. 0.125 mL of solution A (166.4 μ M) was added 0.375 mL solvent to obtain 0.5 mL dendrimer **1a-1e**, **6a-6d** (41.6 μ M) in cuvette for fluorescence measurement. 0.125 mL of solution A (166.4 μ M) and 0.125 mL of solution B (166.4 μ M) was added into solvent (0.25 mL) to obtain 0.5 mL mixture solution ARS-(**1a-1e**, **6a-6d**) (41.6 μ M). 0.125 mL solution B was added into solution C (0.25 mL) in order to make mixture solution BC, and stand for 30 min. Then 0.125 mL solution A was added into mixture solution BC (0.375 mL) to obtain 0.5 mL mixture solution ABC. A 0.5 mL of the mixture ABC was transferred into a cuvette for fluorescence measurement. The experiments were conducted at bandwidth in 10 (nm) and PMT med environment. The fluorescence spectra result of **1a-1e**, **6a-6b** with saccharides fit to Besesi-Hildebrand equation to give the binding constant.

Dendrimer 1b-1e with galactose, lactose, and fructose

A 2500 μ M solution of ARS in DMF as solution A. A 2500 μ M solution of boronic acid-modified PAMAM dendrimer (**1a-1e**) was prepared in DMF (with 10% MeOH) as solution B. An 100-200000 μ M solution of saccharides was prepared in DMF as solution C. 2 μ L of solution A (2500 μ M) was added 0.5 mL solvent to obtain 0.5 mL ARS (10.0 μ M) in cuvette for fluorescence measurement. 2 μ L of solution B (2500 μ M) was added 0.5 mL solvent to obtain 0.5 mL dendrimer **1a-1e** (10 μ M) in cuvette for fluorescence measurement. 2 μ L of solution A (5000 μ M) and 2 μ L solution B (5000 μ M) was added into solvent (0.5 mL) to obtain 0.5 mL mixture solution AB (10 μ M). 2 μ L solution B was added into solution C (0.5 mL) in order to make mixture solution BC, and stand for 30 min. Then 2 μ L solution A was added into mixture solution BC (0.5 mL) to obtain 0.5 mL of the mixture ABC was transferred into a cuvette for fluorescence measurement. The experiments were conducted at bandwidth in 10 (nm) and PMT med environment. he fluorescence spectra result of **1a-1e** with saccharides fit to Besesi-Hildebrand equation to give the binding constant.



Figure S 50 Binding constant of **1a** with a.) **2**. b.) **3**. c.) **4**. d.) **5**. The binding constant studies are in **1a** (41.6 μ M) with various concentration of saccharides in 2.5% MeOH in DMF ($\lambda_{ex} = 468 \text{ nm}$, $\lambda_{em} = 565 \text{ nm}$, 30°C).



Figure S 51 Binding constant of **1b** with a.) **2**. b.) **3**. c.) **4**. d.) **5**. The binding constant studies are in **1b** (41.6 μ M) with various concentration of saccharides in 2.5% MeOH in DMF ($\lambda_{ex} = 468 \text{ nm}$, $\lambda_{em} = 565 \text{ nm}$, 30°C).



Figure S 52 Binding constant of 1c with a.) 2. b.) 3. c.) 4. d.) 5. The binding constant studies are in 1c (41.6 μ M) with various concentration of saccharides in 2.5% MeOH in DMF ($\lambda_{ex} = 468$ nm, $\lambda_{em} = 565$ nm, 30°C).



Figure S 53 Binding constant of 1d with a.) 2. b.) 3. c.) 4. d.) 5. The binding constant studies are in 1d (41.6 μ M) with various concentration of saccharides in 2.5% MeOH in DMF ($\lambda_{ex} = 468$ nm, $\lambda_{em} = 565$ nm, 30°C).



Figure S 54 Binding constant of **1e** with a.) **2**. a.) **3**. a.) **4**. a.) **5**. The binding constant studies are in **1e** (41.6 μ M) with various concentration of saccharides in 2.5% MeOH in DMF ($\lambda_{ex} = 468$ nm, $\lambda_{em} = 565$ nm, 30°C).



Figure S 55 Binding constant of a.) **6a**. b.) **6b**. with **2**. The binding constant studies are in **6a-6b** (41.6 μ M) with various concentration of **2** in 2.5% MeOH in DMF ($\lambda_{ex} = 468$ nm, $\lambda_{em} = 565$ nm, 30°C).



Figure S 56 Binding constant of **1c** with a.) **8**. b.) **9**. The binding constant studies are in **1c** (41.6 μ M) with various concentration of saccharides in 2.5% MeOH in DMF ($\lambda_{ex} = 468 \text{ nm}$, $\lambda_{em} = 565 \text{ nm}$, 30°C).

| | ARS | | 2 | | 3 | | 4 | | 5 | |
|-------------------|-----------------------|----------------------|--------------------------|-------------------------|---------------------------|------------------------|-------------------|-------------------------|--------------------------|----------------------------------|
| $K_b(M^{-1})$ | Kars-dba ^a | Kars-ba ^b | $K_{Glc\text{-}DBA}{}^a$ | $K_{Glc\text{-}BA}{}^b$ | $K_{Gala\text{-}DBA}{}^a$ | $K_{Gala\text{-}BA}^b$ | $K_{Fru-DBA}{}^a$ | $K_{Fru\text{-}BA}{}^b$ | $K_{Lac\text{-}DBA}{}^a$ | K _{Lac-BA} ^b |
| 1a | 12389 | 880 | 148.6 | 10.6 | 29.2 | 2.1 | 12.2 | 0.9 | 9.1 | 0.7 |
| 1b | 52032 | 1730 | 1963.5 | 65.5 | 27.6 | 0.9 | 20.7 | 0.7 | 1.5 | 0.05 |
| 1c | 80000 | 1380 | 4205.9 | 72.5 | 135.2 | 2.3 | 8.7 | 0.2 | 1.7 | 0.03 |
| 1d | 166700 | 1400 | 6039.8 | 50.7 | 132.4 | 1.1 | 19.5 | 0.2 | 4.7 | 0.04 |
| 1e | 285000 | 1400 | 2947.7 | 14.5 | 771.5 | 3.8 | 666.9 | 3.3 | 51.2 | 0.3 |
| PBA ^c | 670 | | 7.2 | | 38 | | 310 | | ND ^d | |
| CPBA ^e | | | 13 | .9 | | | | | | |

Table S1. Binding constant (M⁻¹) of **1a-1e** with ARS / saccharides.

a: K_b was obtained based on the concentration of dendrimers **1** b: K_b was obtained based on the concentration of boronic acid of each dendrimers **1** c: 9 μ M ARS with 2 mM PBA at pH 8.0 in 0.1 M phosphate buffer.⁶ d : no detection e : the same concentration of boronic acid with **1b** in DMF (with 2.5% MeOH).