Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supplementary Information

for

Multilayer films composed of phenylboronic acid-modified dendrimers sensitive to glucose under physiological conditions

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Supplementary Information S1.

An infrared absorption spectrometer (FTIR-8200A, Shimadzu Co., Kyoto, Japan) was used for recording IR spectra of the LbL films. Figure S1 shows IR spectra of $(PVA/3CPBA\text{-}D)_{20}$ and $(PVA/3C5NPBA\text{-}D)_{20}$ films which were prepared on the surface of a As_2Se_3 substrate. The LbL films were prepared at pH 9.0. The spectra exhibited strong absorption bands of amide I and II originating from amide linkages in the dendrimers.

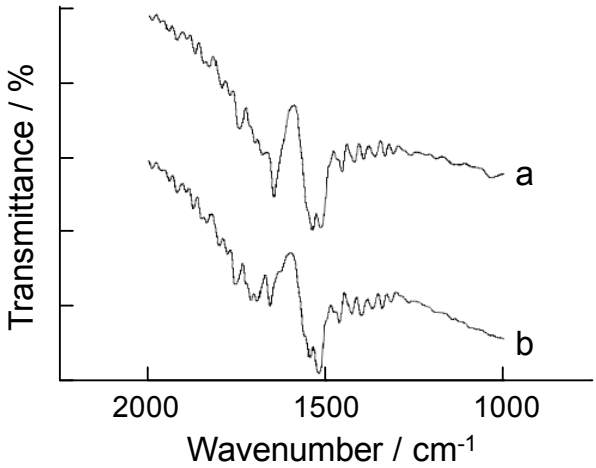

Fig. S1. IR spectra of $(PVA/3CPBA\text{-}D)_{20}$ (a) and $(PVA/3C5NPBA\text{-}D)_{20}$ (b) films deposited on a As_2Se_3 substrate.

Supplementary Information S2

We have used a quartz crystal microbalance (QCM; 440E QCM, BAS Co., Tokyo, Japan) to show that LbL film cannot be constructed by LbL deposition of PVA and unmodified PAMAM dendrimer. An 8 MHz AT-cut quartz resonator coated with a thin gold (Au) layer (geometric surface area, 0.20 cm^2) was used as a probe, in which the adsorption of 1 ng of substrate induces a ca. -0.75 Hz change in the resonance frequency.

The Au surface layer of the quartz resonator was cleaned using a mixture of H_2O_2 and H_2SO_4 (3:1 by volume, piranha solution) and thoroughly rinsed in pure water before use (*CAUTION: Piranha solution should be handled with extreme care*). The cleaned quartz resonator was mounted in a flow-through cell and the surface was exposed alternately to the solutions of PVA and dendrimers (0.1 mg mL^{-1}, in 10 mM CHES buffer containing 150 mM NaCl, pH 9.0).

Fig. S2 shows typical frequency changes (ΔF) in the alternate deposition of PVA and 3CPBA-D or unmodified PAMAM dendrimer. The resonance frequency of the QCM was decreased when the quartz resonator was alternately exposed to PVA and 3CPBA-D solutions, suggesting the successful deposition of PVA/3CPBA-D film. On the other hand, the ΔF was negligibly small when unmodified PAMAM dendrimer was used in place of 3CPBA-D, which shows that LbL did not form from PVA and unmodified PAMAM dendrimer.

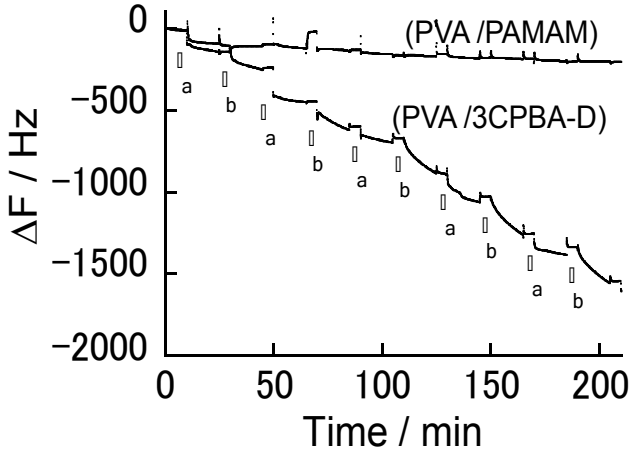

Fig. S2. Typical QCM response for the deposition of PVA/PAMAM and PVA/3CPBA-D films at pH 9.0. The quartz resonator was exposed to (a) PVA and (b) PAMAM or 3CPBA-D.

Supplementary Information S3

Fig. S3 shows typical response of $(PVA/3C5NPBA\text{-}D)_{10}$ film when the film was exposed to 1-100 mM fructose and glucose. The percent of decomposition of the film was approximately 75% in 100 mM fructose, which is higher than that in 100 mM glucose solution. The results suggest that the percent of decomposition depends on the binding affinity of sugar to the boronic acid-modified dendrimer. The binding constants of glucose and fructose to PBA at pH 7.5 are reported to be 4.6 and 210 M^{-1}, respectively.[47]

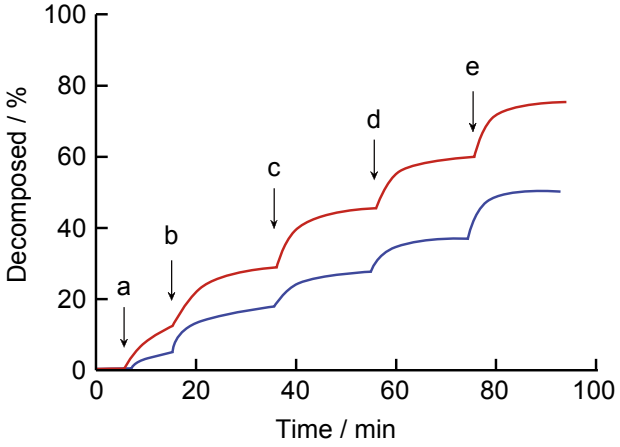

Fig. S3. Decomposition of $(PVA/3C5NPBA\text{-}D)_{10}$ film in 1-100 mM fructose (red line) and glucose (blue line) solutions at pH 7.4 at 23 °C. The concentrations of fructose or glucose in the solution: 1 (a), 5 (b), 10 (c), 30 (d) and 100 mM (e).