Electronic Supplementary Material (ESI) for RSC Advances.

A simple supramolecular complex of boronic acid-appended *β*-cyclodextrin and a fluorescent boronic acid-based probe with excellent selectivity for D-glucose in water

Ko Sugita [‡a], Yota Suzuki [‡a], Yuji Tsuchido [a,b], Shoji Fujiwara [a,c], Takeshi Hashimoto [*a], and Takashi Hayashita [*]

a. Department of Materials and Life Sciences, Faculty of Science and Technology, Sophia University, 7-1, Kioi-cho, Chiyoda-ku, Tokyo, 102-8554 (Japan)

b. Department of Life Science and Medical Bioscience, Graduate School of Advanced Science and Engineering, Waseda University (TWIns), Wakamatsu-cho, Shinjuku-ku, Tokyo, 162-8480 (Japan)

c. Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama-shi, Kanagawa 221-8686 (Japan)

‡ These authors contributed equally.

Table of Contents

ICD spectra of *1*/FPB-*β*CyD

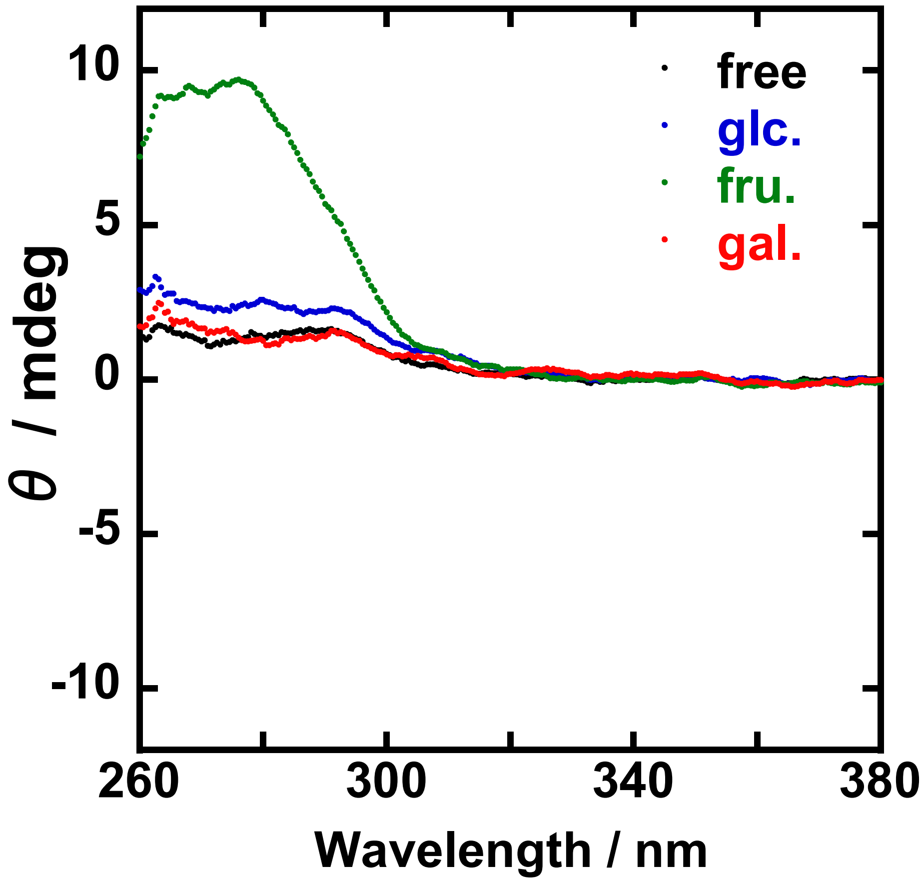


Fig. S1. ICD spectra of ***1*/FPB-*β*CyD** in DMSO/water (2/98 in v/v) in the absence (black, free) and presence of 30 mM saccharides: D-glucose (blue, glc.), D-fructose (green, fru.), and D-galactose (red, gal.); C_{probe} = 10 μM, $C_{\mathbf{FPB}\text{-}\beta\mathbf{CyD}}$ = 0.2 mM, 10 mM of carbonate buffer, pH = 10, T = 25°C and I = 0.10 M.

<u>Fluorescence spectrum of *1*/FPB-*β*CyD</u>

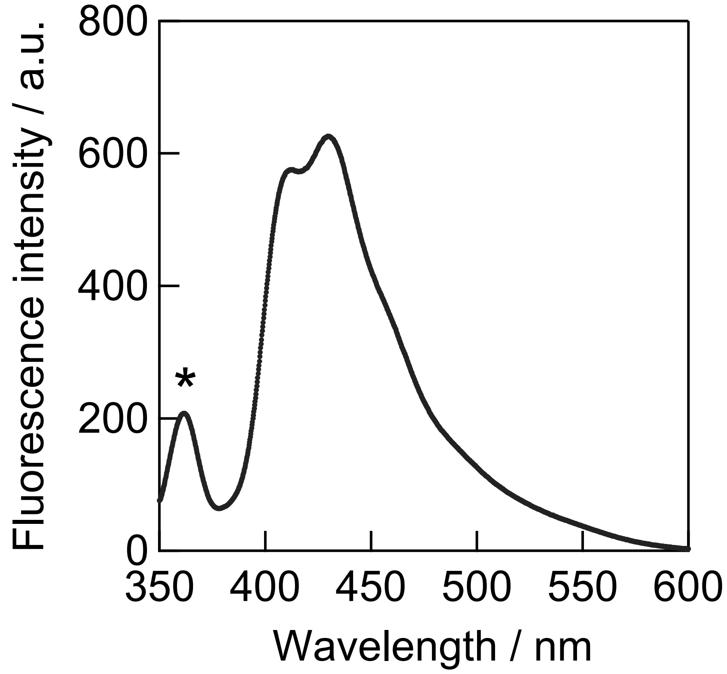


Fig. S2. Fluorescence spectrum of the mixture of ***1*** (10 μM) and **FPB-*β*CyD** (0.2 mM) in DMSO/water (2/98 in v/v): 10 mM of carbonate buffer, pH = 10, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm. * denotes scattered light.

Change in fluorescence spectra of *1*/FPB-*β*CyD with time

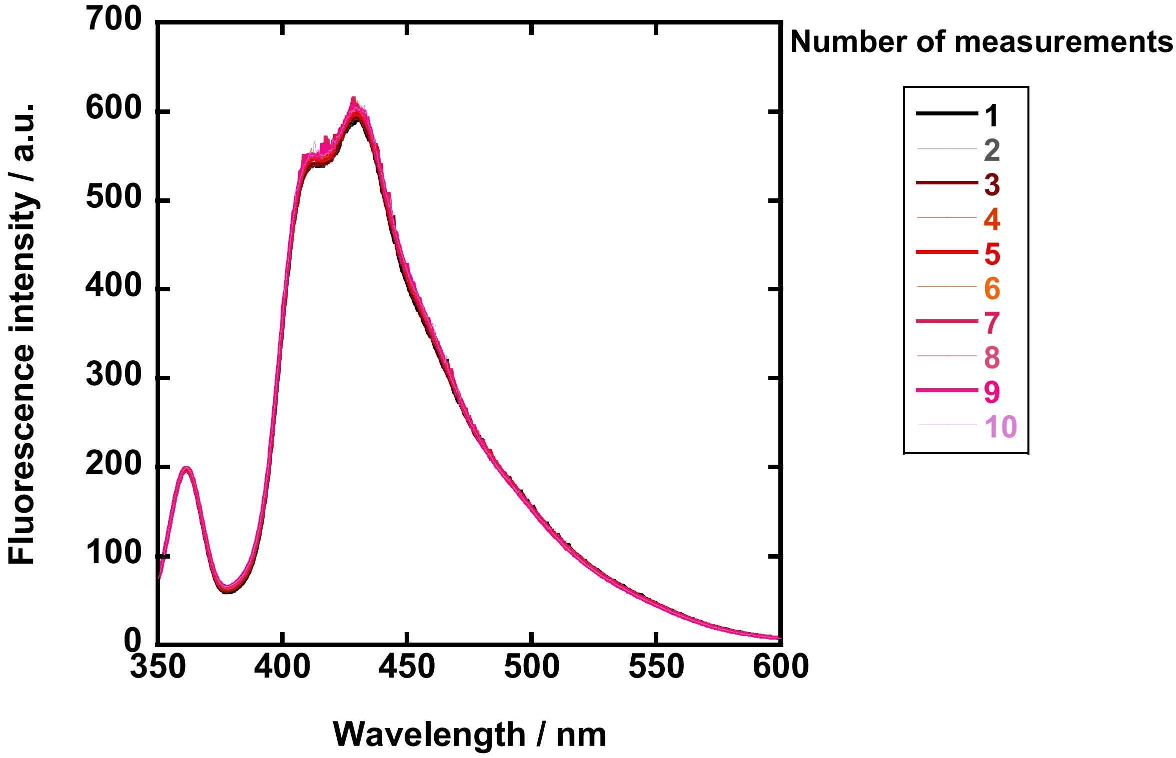


Fig. S3. Change in fluorescence spectra of ***1*/FPB-*β*CyD** in DMSO/water (2/98 in v/v) with time. Each spectrum was measured every 67 seconds: C_{probe} = 10 μM, $C_{\mathbf{FPB}\text{-}\boldsymbol{\beta}\mathbf{CyD}}$ = 0.2 mM, 10 mM of carbonate buffer, pH = 10, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm.

UV-vis specta of 1/FPB-βCyD with/without saccharides

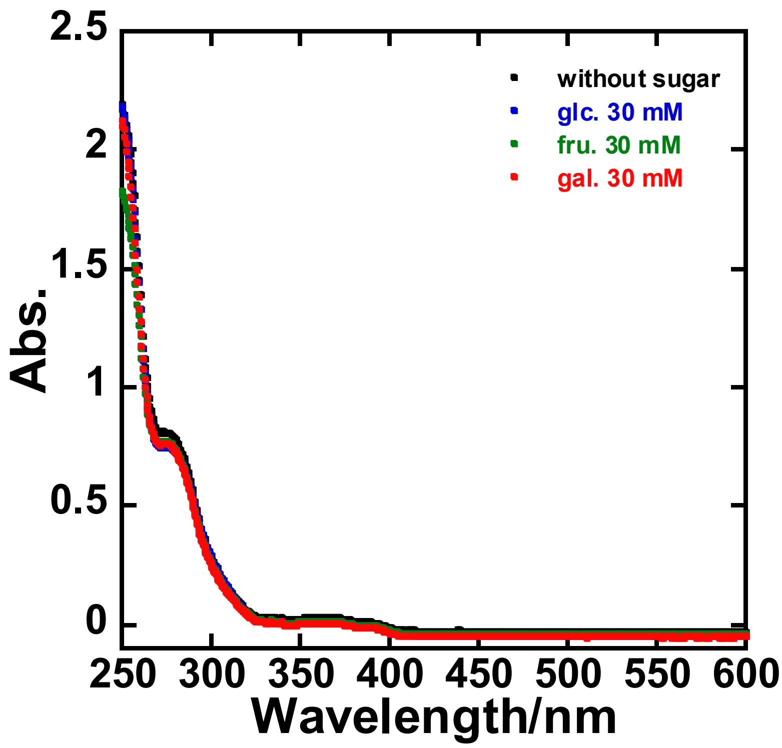


Fig. S4. UV-vis adsorption spectra of the mixture of ***1*** (10 μM) and **FPB-*β*CyD** (0.2 mM) in the absence and presence of 30 mM monosaccharides in DMSO/water (2/98 in v/v): 10 mM of carbonate buffer, pH = 10, T = 25°C, I = 0.10 M. Without monosaccharides (black), D-glucose (blue, glc.), D-fructose (green, fru.), and D-galactose (red, gal.).

pH dependence of fluorescence spectra of *1*/FPB-*β*CyD

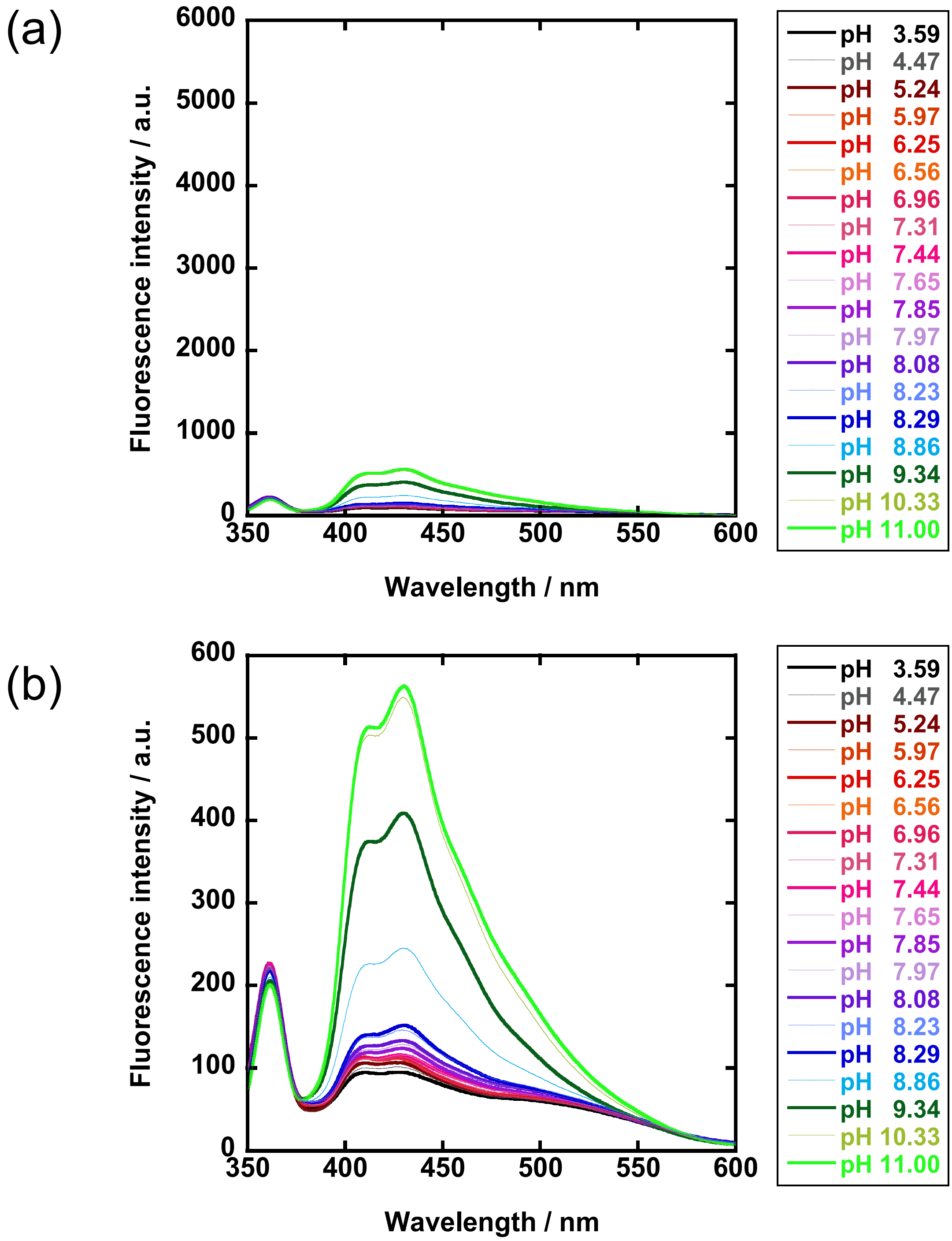


Fig. S5-1. Fluorescence spectra of ***1*/FPB-*β*CyD** in DMSO/water (2/98 in v/v) (a) and enlarged spectra of Fig. S5-1(a) from 0 to 600 region of the fluorescence intensity (b): C_{probe} = 10 μM, $C_{\mathrm{FPB}\text{-}\beta\mathrm{CyD}}$ = 0.2 mM, 10 mM of phosphate buffer, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm.

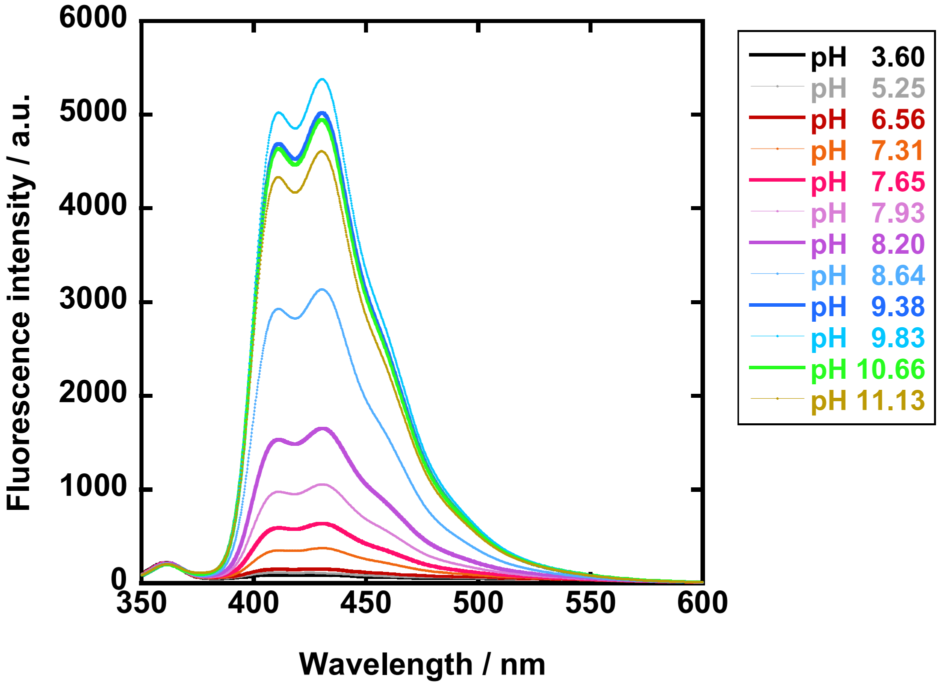


Fig. S5-2. Fluorescence spectra of ***1*/FPB-*β*CyD** in the presence of D-glucose (30 mM) in DMSO/water (2/98 in v/v): C_{probe} = 10 μM, $C_{\textbf{FPB-}\boldsymbol{\beta}\textbf{CyD}}$ = 0.2 mM, 10 mM of phosphate buffer, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm.

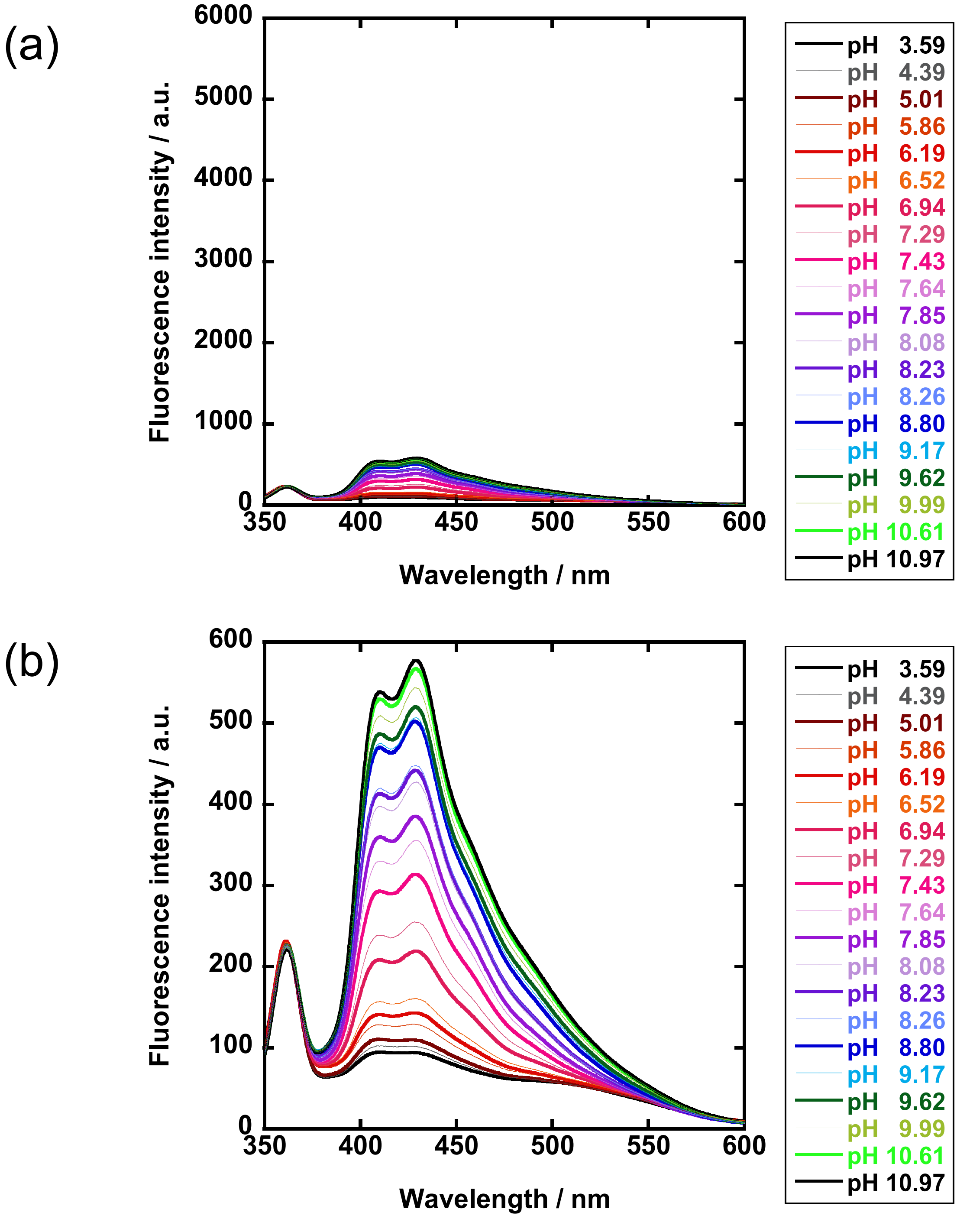


Fig. S5-3. Fluorescence spectra of ***1*/FPB-*β*CyD** in the presence of D-fructose (30 mM) in DMSO/water (2/98 in v/v) (a) and enlarged spectra of Fig. S5-3(a) from 0 to 600 region of the fluorescence intensity (b): C_{probe} = 10 μM, $C_{\textbf{FPB-}\boldsymbol{\beta}\textbf{CyD}}$ = 0.2 mM, 10 mM of phosphate buffer, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm.

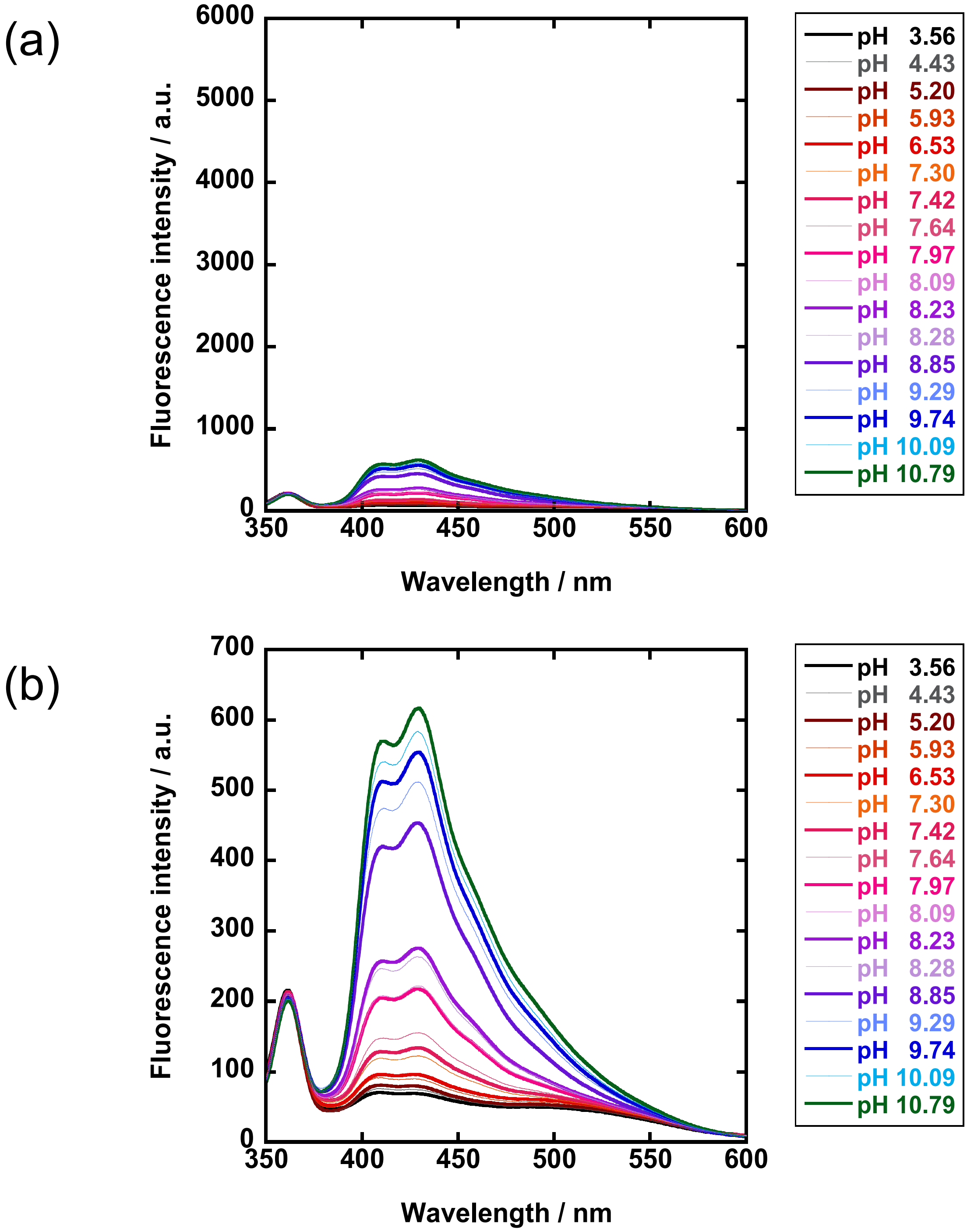
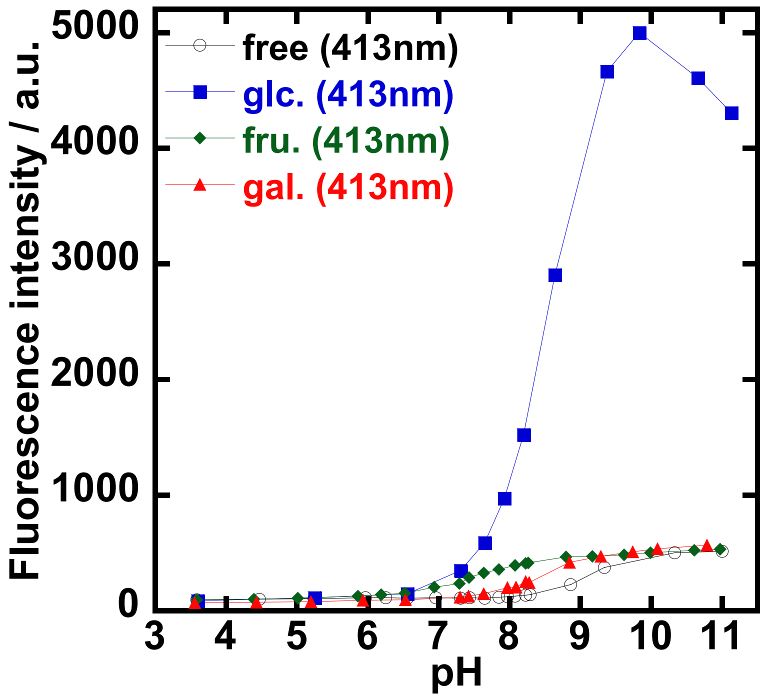


Fig. S5-4. Fluorescence spectra of ***1*/FPB-βCyD** in the presence of D-galactose (30 mM) in DMSO/water (2/98 in v/v) (a) and enlarged spectra of Fig. S5-4(a) from 0 to 700 region of the fluorescence intensity (b): C_{probe} = 10 μM, $C_{\mathbf{FPB\text{-}\beta CyD}}$ = 0.2 mM, 10 mM of phosphate buffer, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm.

(a)



(b)

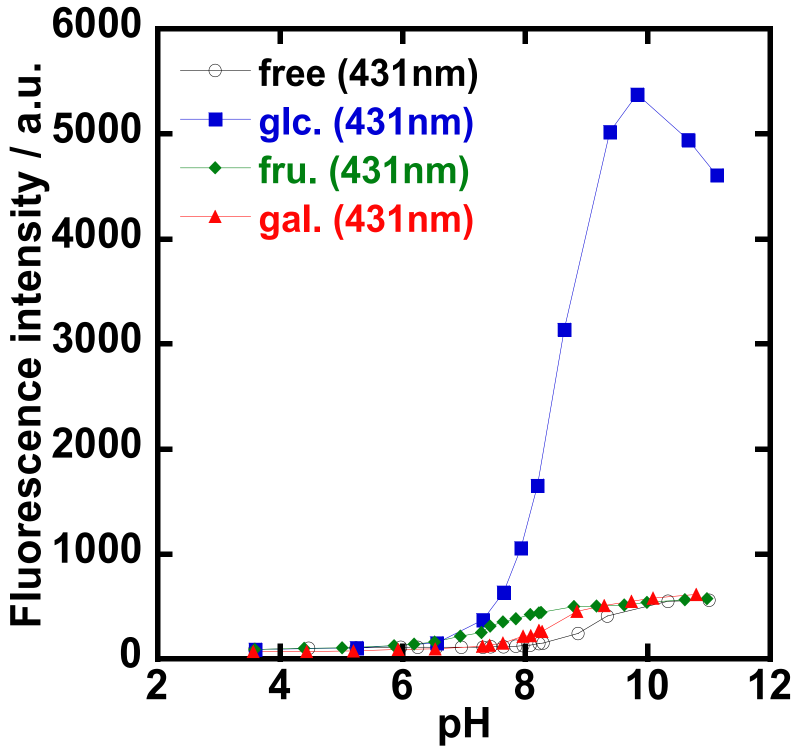
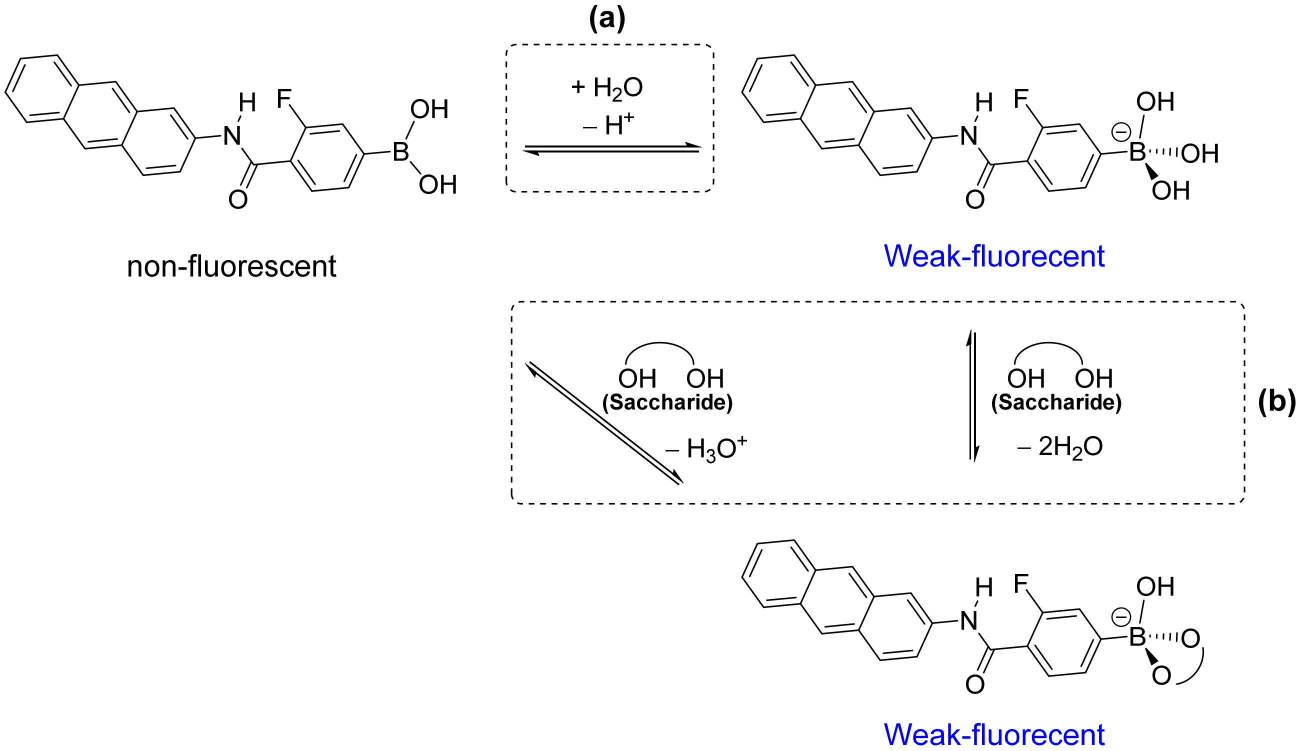


Fig. S5-5. Fluorescence intensities of ***1*/FPB-*β*CyD** at 413 (a) and 431 nm (b) under various pH conditions in the absence (black, free) and presence of saccharides (30 mM) in DMSO/water (2/98 in v/v) in Fig.s S5-1, S5-2, S5-3, and S5-4: D-glucose (blue, glc.), D-fructose (green, fru.), and D-galactose (red, gal.).

Apparent acid dissociation constants of *1*/FPB-*β*CyD



Scheme S1. Acid dissociation equilibrium of ***1*** (a) and the reaction of ***1*** with saccharides (b) in water.

(a)

(b)

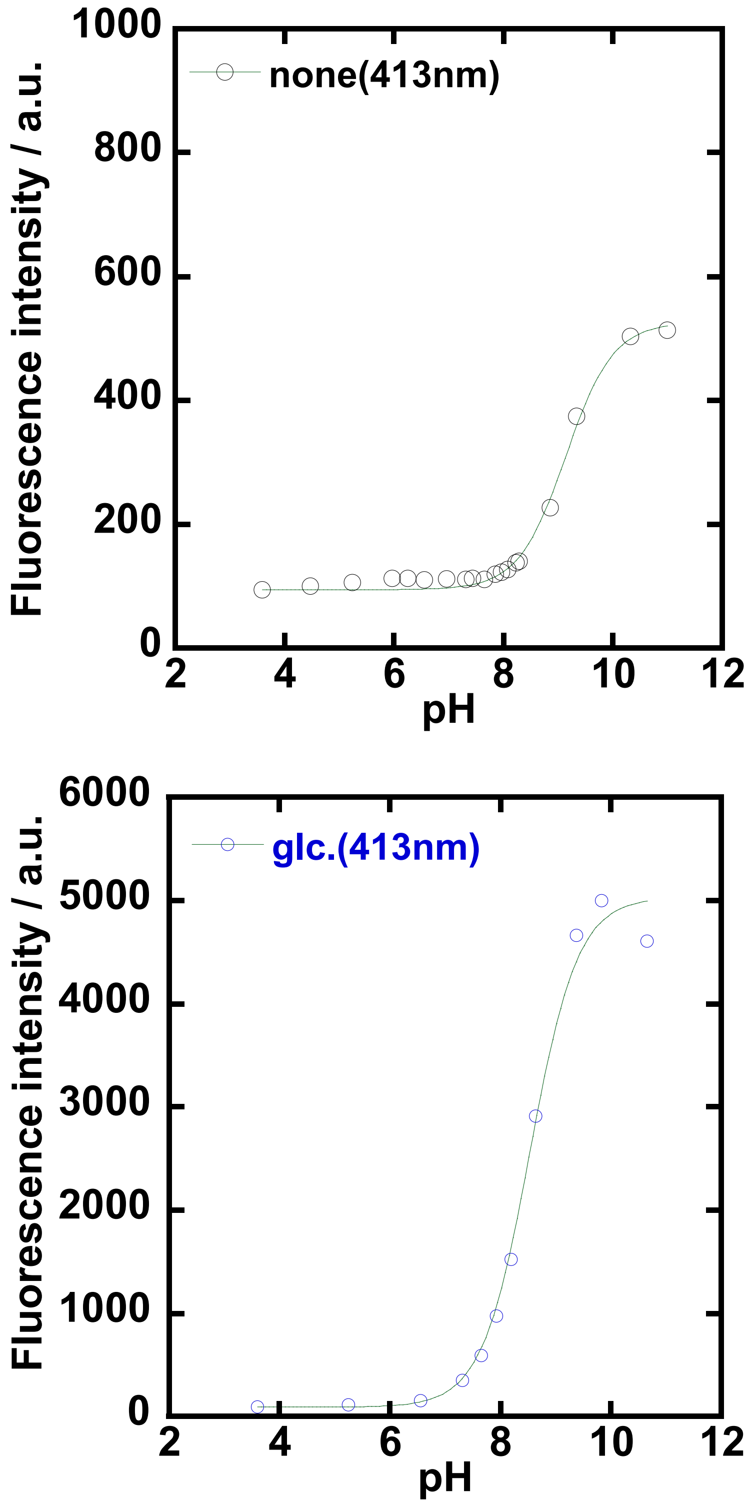
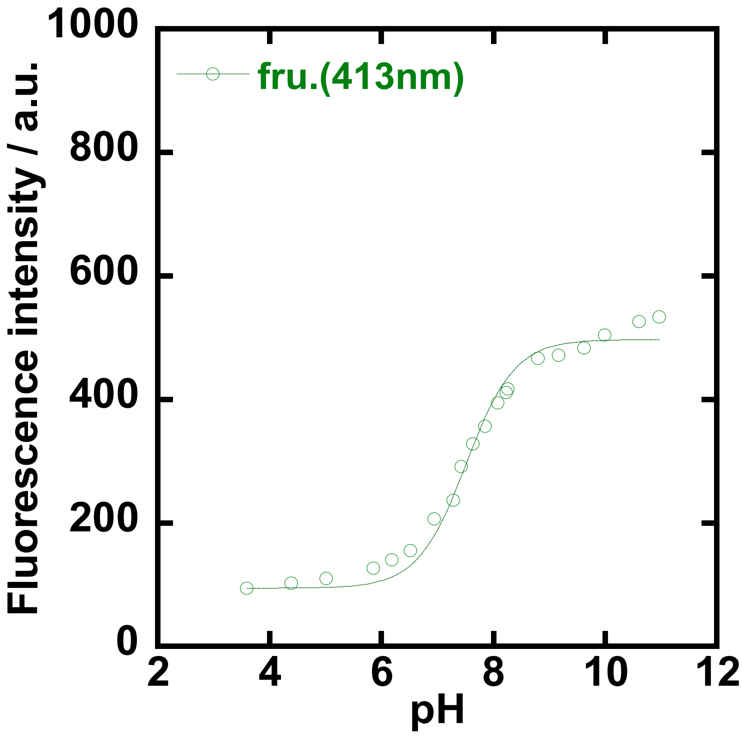


Fig. S6. Fluorescence intensity of ***1*/FPB-*β*CyD** at 413 nm under various pH conditions in the absence (a) and presence of saccharides (30 mM) in DMSO/water (2/98 in v/v): D-glucose (b), D-fructose (c), and D-galactose (d); C_{probe} = 10 μM, $C_{\mathbf{FPB\text{-}\beta CyD}}$ = 0.2 mM, 10 mM of phosphate buffer, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm. Each solid curve indicates a theoretical sigmoidal curve derived from the acid dissociation model of a monobasic acid fitted by non-linear least squares analysis.

(c)



(d)

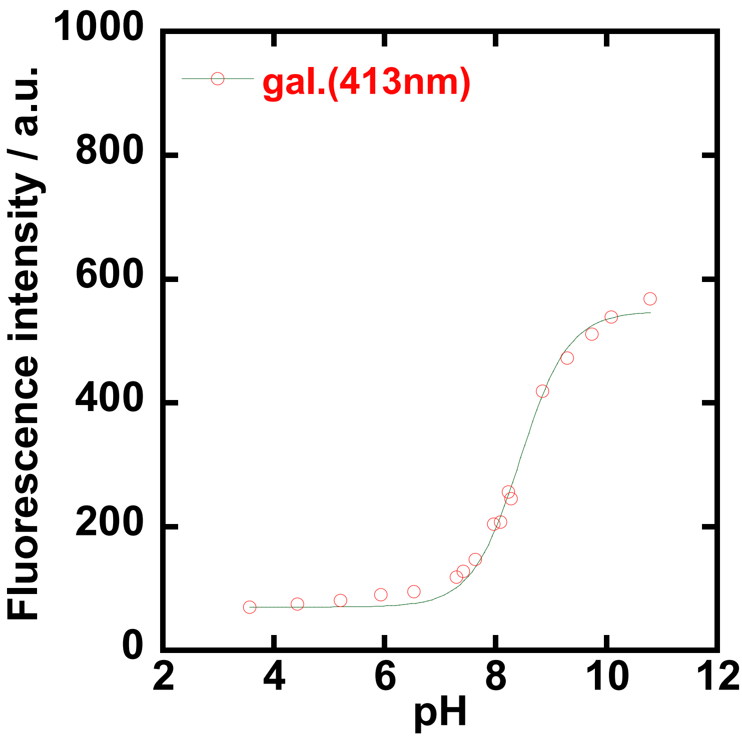


Fig. S6. Fluorescence intensity of ***1*/FPB-*β*CyD** at 413 nm under various pH conditions in the absence (a) and presence of saccharides (30 mM) in DMSO/water (2/98 in v/v): D-glucose (b), D-fructose (c), and D-galactose (d); C_{probe} = 10 μM, $C_{\mathbf{FPB\text{-}\beta CyD}}$ = 0.2 mM, 10 mM of phosphate buffer, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm. Each solid curve indicates a theoretical sigmoidal curve derived from the acid dissociation model of a monobasic acid fitted by non-linear least squares analysis. (Continued)

Fluorescence spectra of *1*/FPB-*β*CyD at various saccharide concentrations

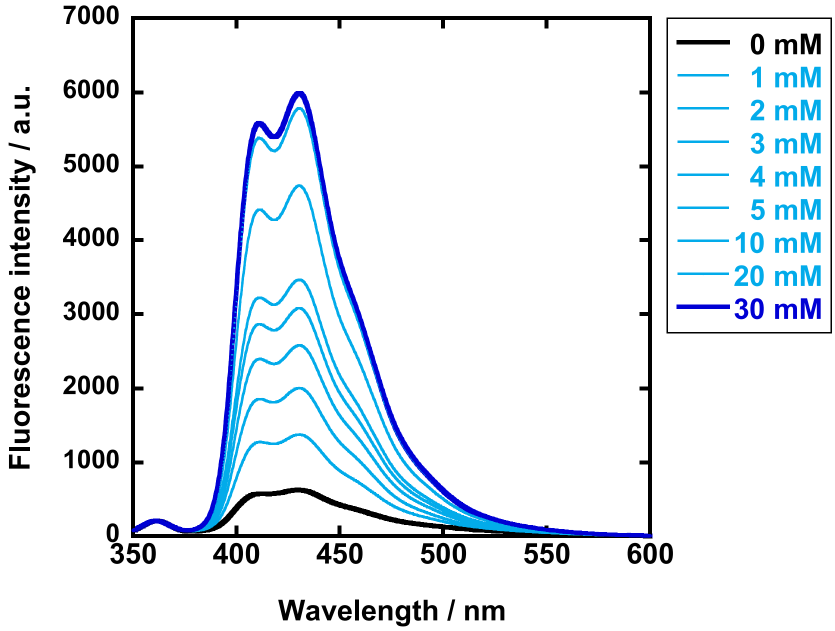
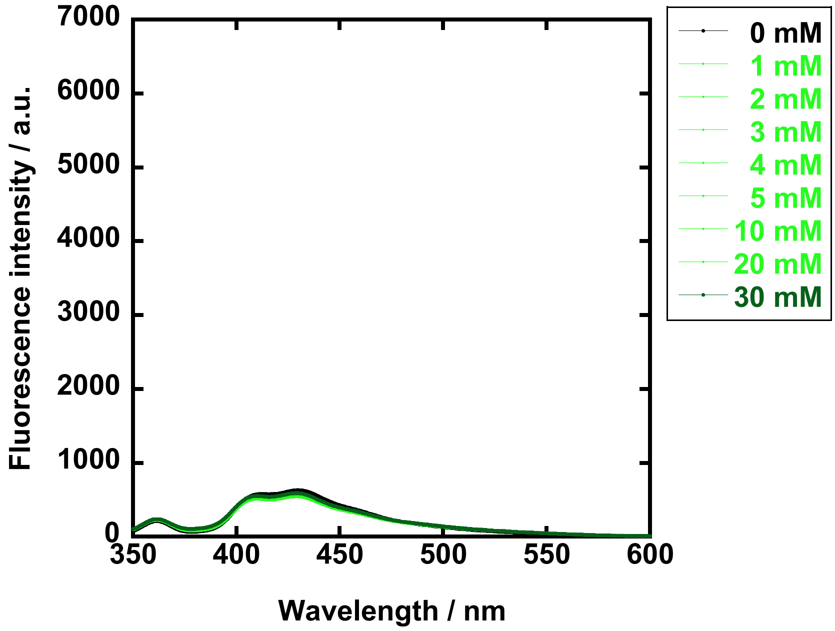


Fig. S7-1. Fluorescence spectra of ***1*/FPB-*β*CyD** at various D-glucose concentrations in DMSO/water (2/98 in v/v): C_{probe} = 10 μM, $C_{\mathbf{FPB\text{-}\beta CyD}}$ = 0.2 mM, 10 mM of carbonate buffer, pH 10, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm.

(a)



(b)

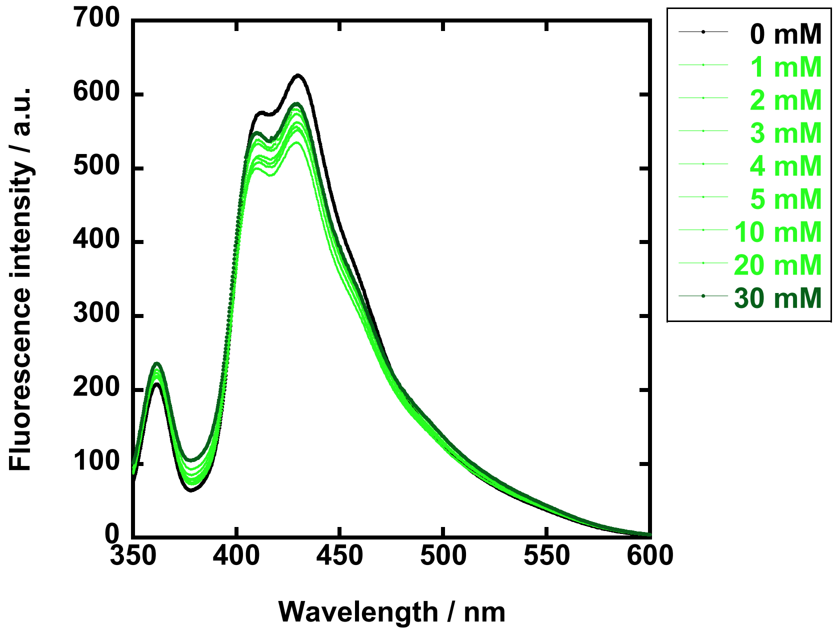


Fig. S7-2. Fluorescence spectra of ***1*/FPB-*β*CyD** at various D-fructose concentrations in DMSO/water (2/98 in v/v) (a) and enlarged spectra of Fig. S7-2(a) from 0 to 700 region of the fluorescence intensity (b): C_{probe} = 10 μM, $C_{\mathrm{FPB}\text{-}\beta\mathrm{CyD}}$ = 0.2 mM, 10 mM of carbonate buffer, pH 10, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm.

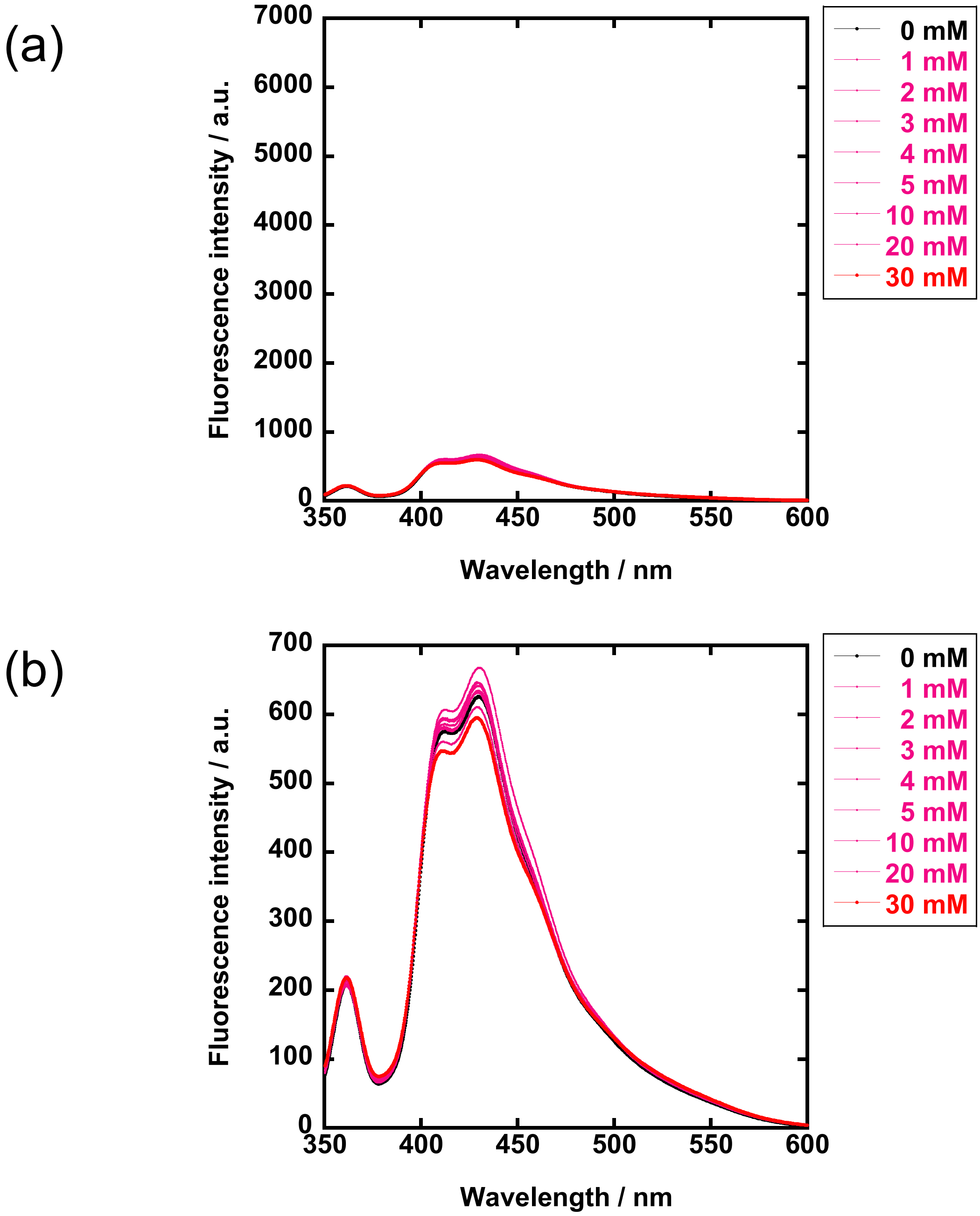
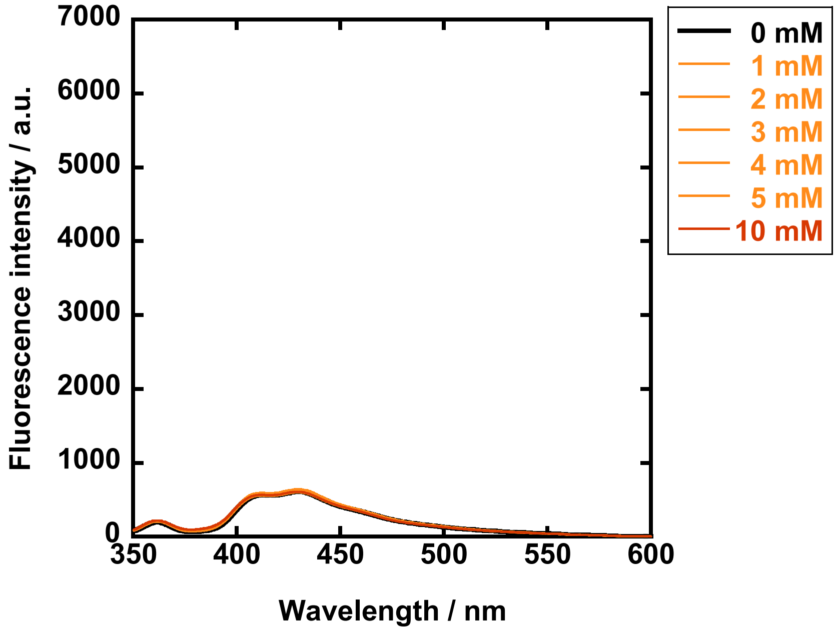


Fig. S7-3. Fluorescence spectra of ***1*/FPB-*β*CyD** at various D-galactose concentrations in DMSO/water (2/98 in v/v) (a) and enlarged spectra of Fig. S7-3(a) from 0 to 700 region of the fluorescence intensity (b): C_{probe} = 10 μM, $C_{\mathbf{FPB}\text{-}\boldsymbol{\beta}\mathbf{CyD}}$ = 0.2 mM, 10 mM of carbonate buffer, pH 10, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm.

(a)



(b)

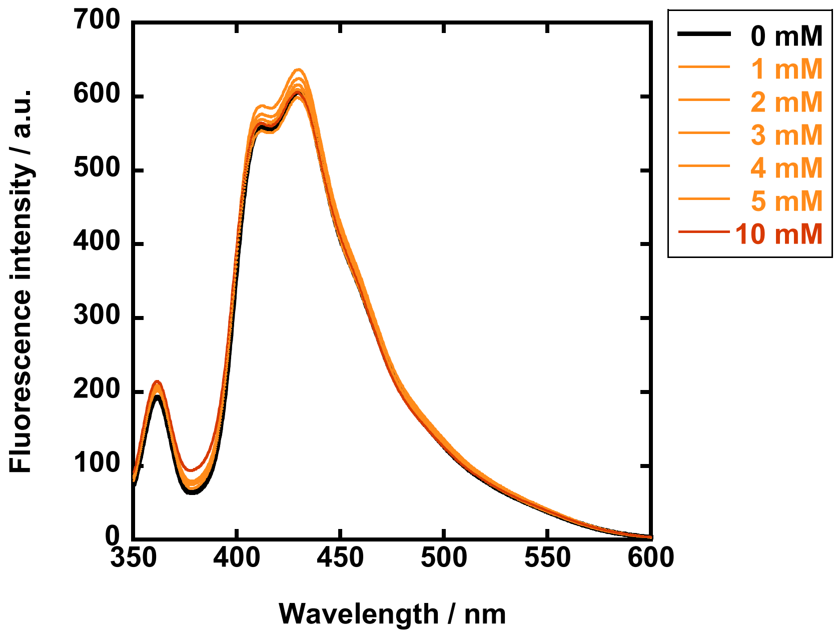


Fig. S7-4. Fluorescence spectra of ***1*/FPB-*β*CyD** at various D-mannose concentrations in DMSO/water (2/98 in v/v) (a) and enlarged spectra of Fig. S7-4(a) from 0 to 700 region of the fluorescence intensity (b): C_{probe} = 10 μM, $C_{\mathbf{FPB\text{-}\beta CyD}}$ = 0.2 mM, 10 mM of carbonate buffer, pH 10, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm.

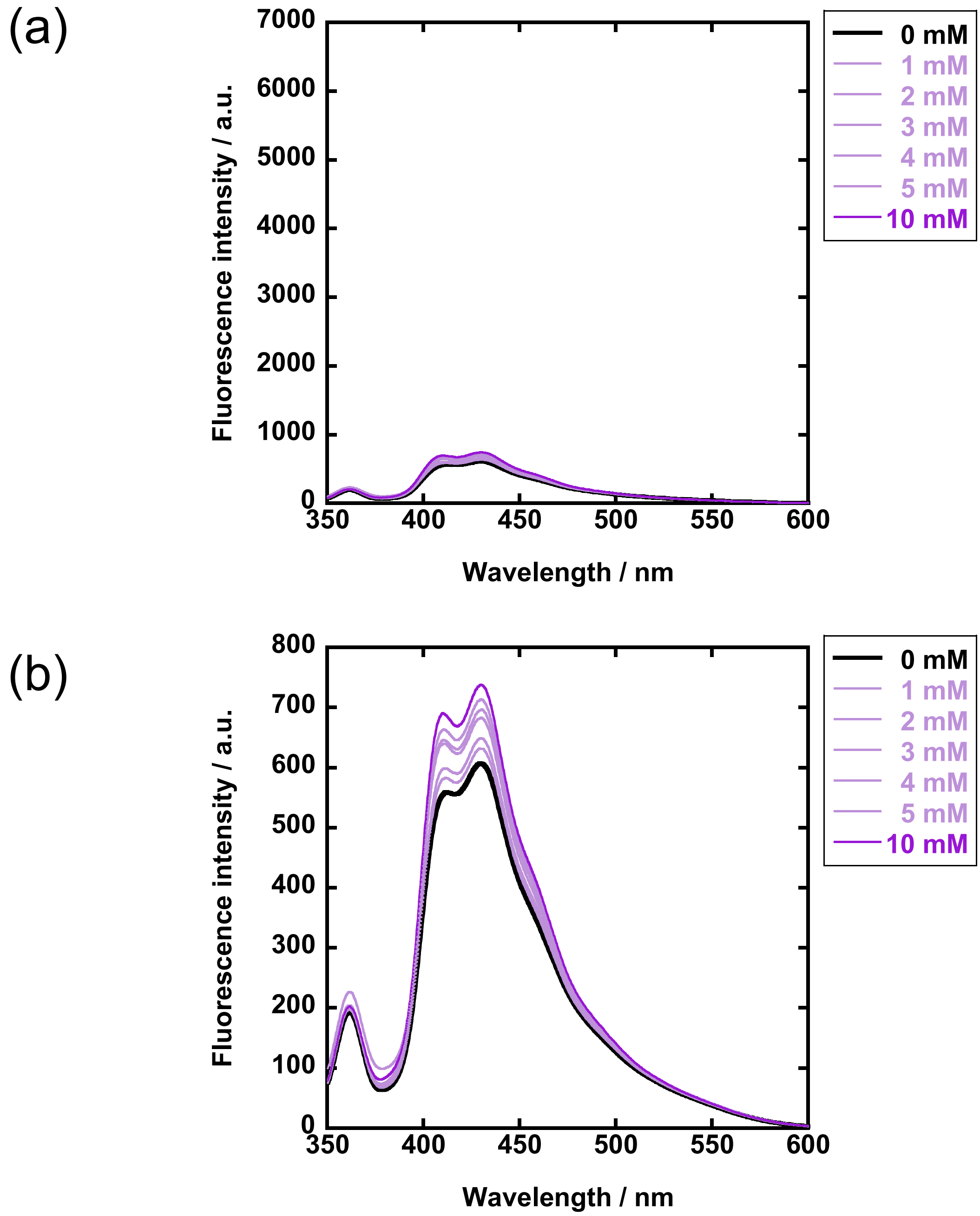


Fig. S7-5. Fluorescence spectra of ***1*/FPB-*β*CyD** at various D-ribose concentrations in DMSO/water (2/98 in v/v) (a) and enlarged spectra of Fig. S7-5(a) from 0 to 800 region of the fluorescence intensity (b): C_{probe} = 10 μM, $C_{\mathbf{FPB\text{-}\beta CyD}}$ = 0.2 mM, 10 mM of carbonate buffer, pH 10, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm.

(a)

(b)

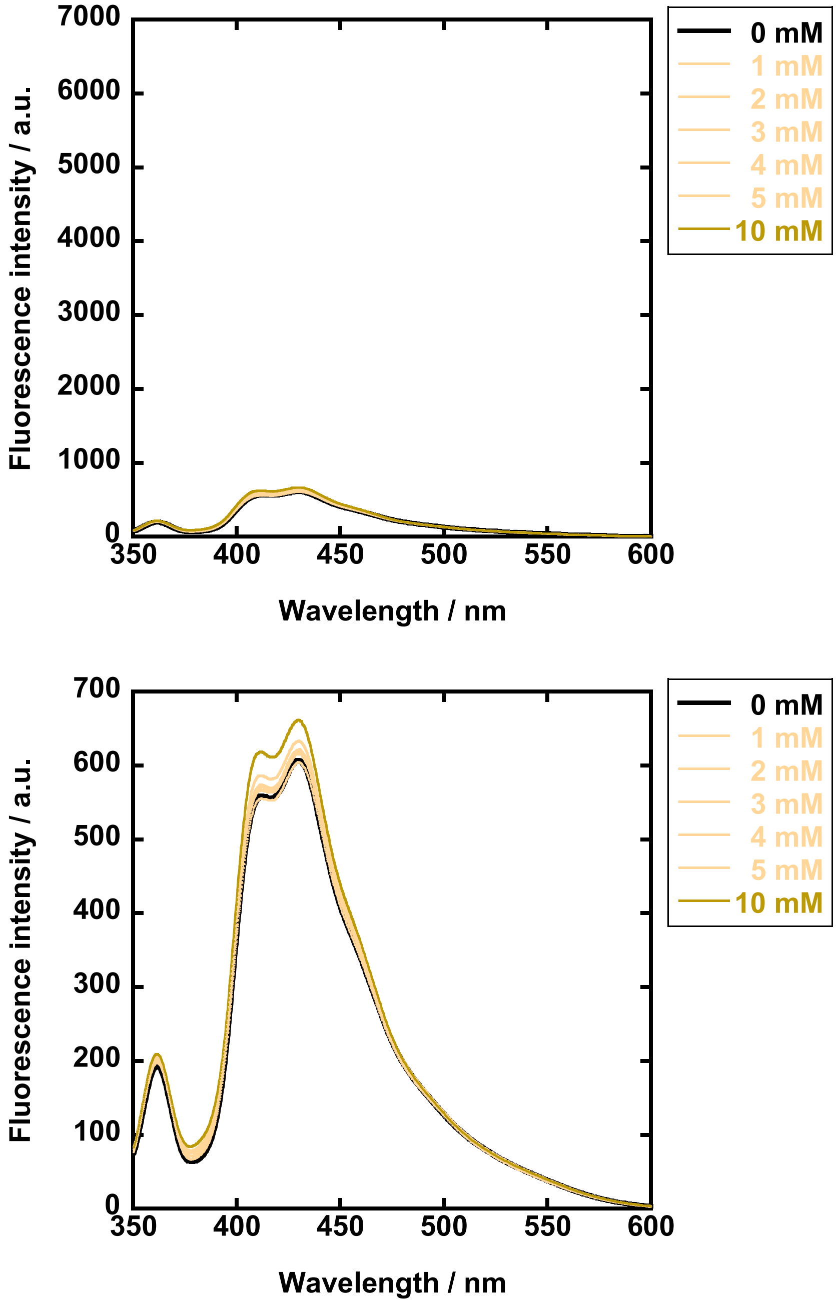


Fig. S7-6. Fluorescence spectra of ***1*/FPB-*β*CyD** at various D-xylose concentrations in DMSO/water (2/98 in v/v) (a) and enlarged spectra of Fig. S7-6(a) from 0 to 700 region of the fluorescence intensity (b): C_{probe} = 10 μM, $C_{\mathbf{FPB\text{-}\beta CyD}}$ = 0.2 mM, 10 mM of carbonate buffer, pH 10, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm.

Change in fluorescence spectra of *1*/FPB-*β*CyD with time in the presence of saccharides

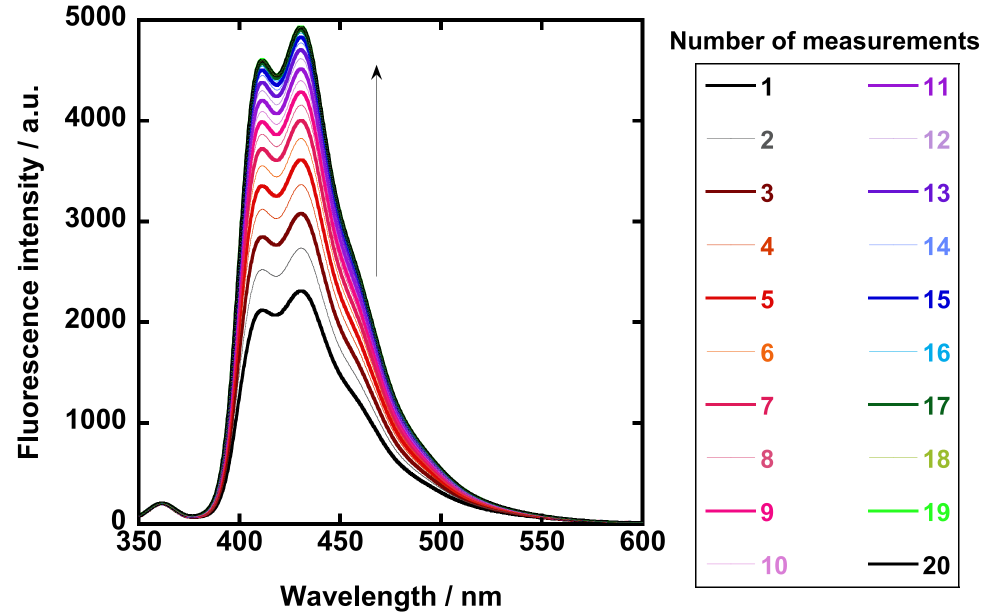


Fig. S8-1. Change in fluorescence spectra of ***1*/FPB-*β*CyD** with time after the addition of D-glucose in DMSO/water (2/98 in v/v): C_{probe} = 10 μM, C_{Dglu} = 30 mM, $C_{\mathbf{FPB}\text{-}\boldsymbol{\beta}\mathbf{CyD}}$ = 0.2 mM, 10 mM of carbonate buffer, pH 10, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm. Each spectrum was measured every 67 seconds.

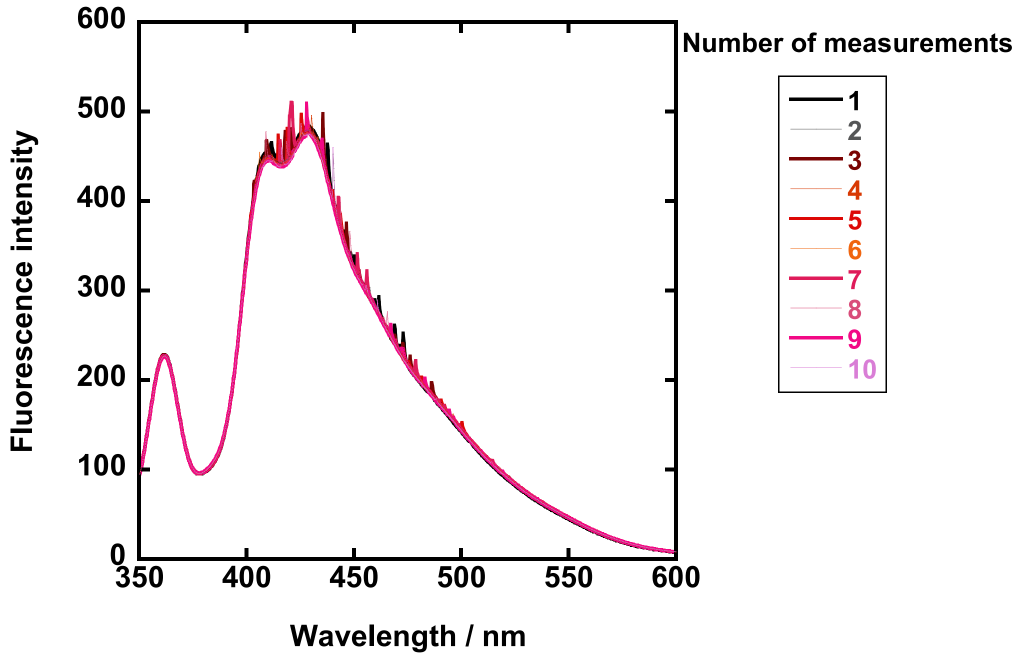


Fig. S8-2. Change in fluorescence spectra of ***1*/FPB-*β*CyD** with time after the addition of D-fructose in DMSO/water (2/98 in v/v): C_{probe} = 10 μM, C_{Dfru} = 30 mM, $C_{\mathbf{FPB}\text{-}\boldsymbol{\beta}\mathbf{CyD}}$ = 0.2 mM, 10 mM of carbonate buffer, pH 10, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm. Each spectrum was measured every 67 seconds.

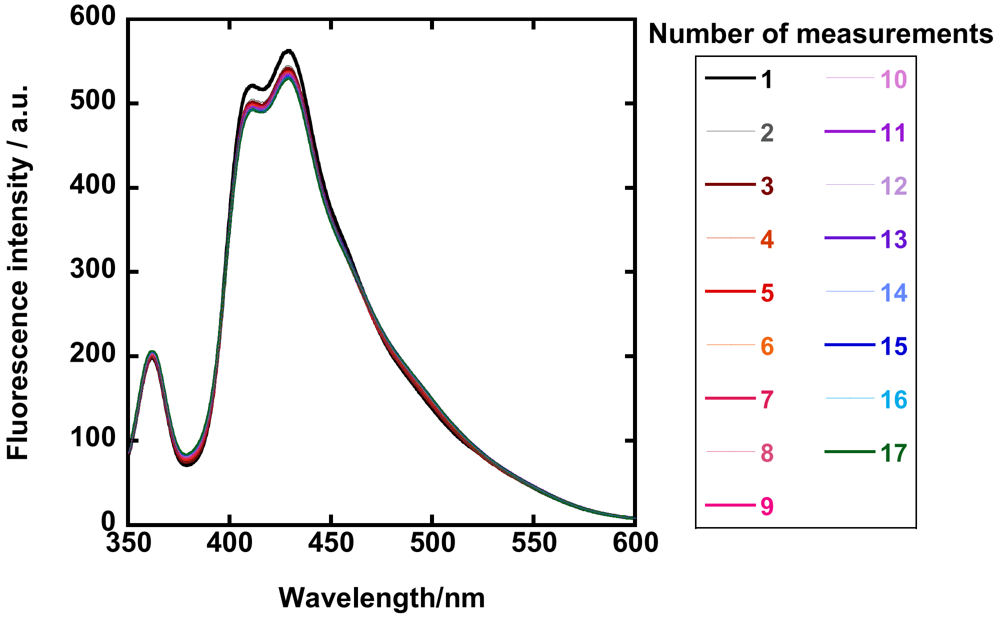


Fig. S8-3. Change in fluorescence spectra of ***1*/FPB-*β*CyD** with time after the addition of D-galactose in DMSO/water (2/98 in v/v): C_{probe} = 10 μM, C_{Dgal} = 30 mM, $C_{\mathbf{FPB}\text{-}\boldsymbol{\beta}\mathbf{CyD}}$ = 0.2 mM, 10 mM of carbonate buffer, pH 10, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm. Each data was measured every 67 seconds.

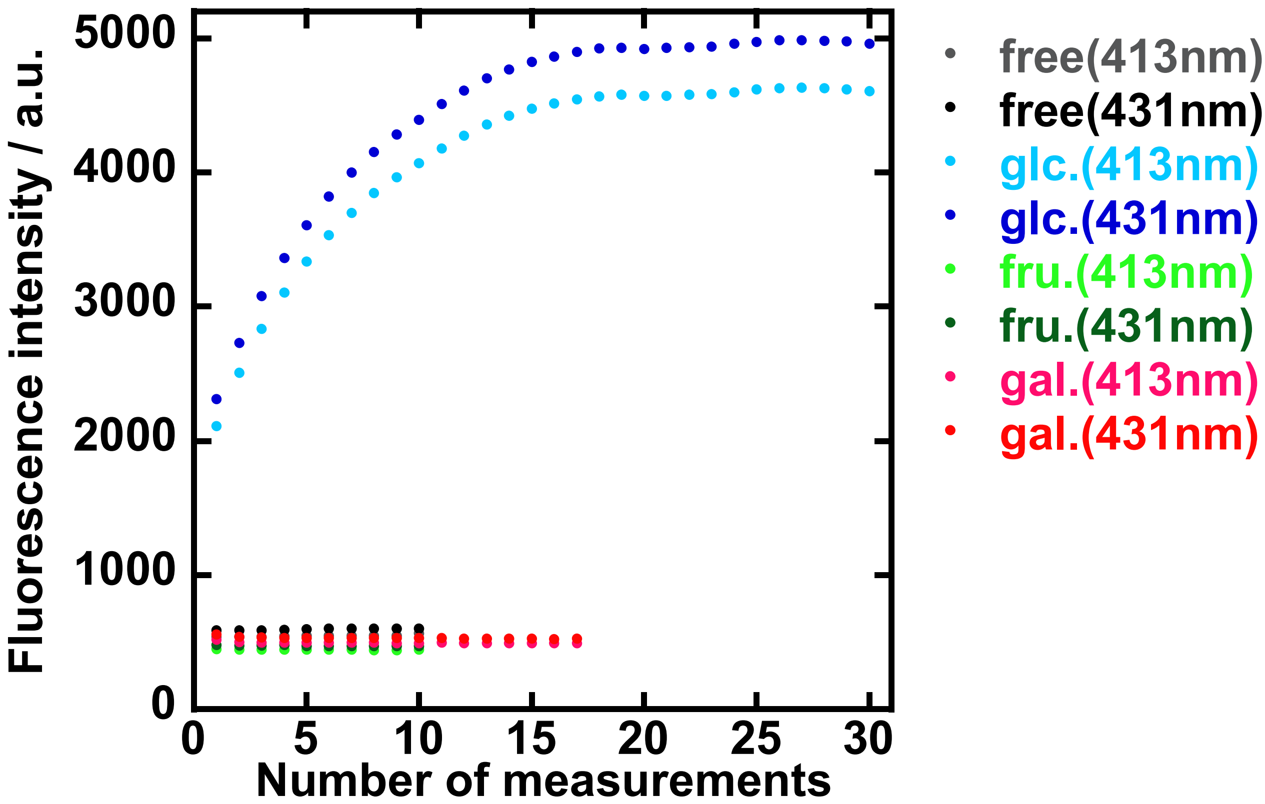


Fig. S8-4. Changes in fluorescence intensities of ***1*/FPB-βCyD** at 413 and 431 nm with time after the addition of saccharides in DMSO/water (2/98 in v/v): C_{probe} = 10 μM, $C_{\mathbf{FPB\text{-}\beta CyD}}$ = 0.2 mM, 10 mM of carbonate buffer, pH 10, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm. Each data was measured every 67 seconds. The data were taken from Fig.s S3, S8-1, S8-2, and S8-3.

Determination of the conditional equilibrium constant

The fluorescence intensity at 431 nm was measured at various D-glucose concentrations. The data were analyzed by using KaleidaGraph programme according to a theoretical equation derived from the 1:1 binding model (Eq. S1).

$$I - I_0 = \frac{I_{\mathrm{lim}} - I_0}{2C_{\mathrm{probe}}}\left\{C_{\mathrm{probe}} + C_{\mathrm{glucose}} + \frac{1}{K'} - \left[\left(C_{\mathrm{probe}} + C_{\mathrm{sugar}} + \frac{1}{K'}\right)^2 - 4C_{\mathrm{probe}} \cdot C_{\mathrm{glucose}}\right]^{\frac{1}{2}}\right\} \qquad \text{(S1)}$$

where C_{glucose} is the total concentration of D-glucose; I and I_0 represent the fluorescence intensity at 431 nm in the presence and absence of D-glucose, respectively; I_{lim} is the fluorescence intensity at 431 nm when the change of I (= ΔF.I. = $I - I_0$) reaches saturation; K' is the conditional equilibrium constant for the reaction of ***1*/FPB-*β*CyD** with D-glucose.

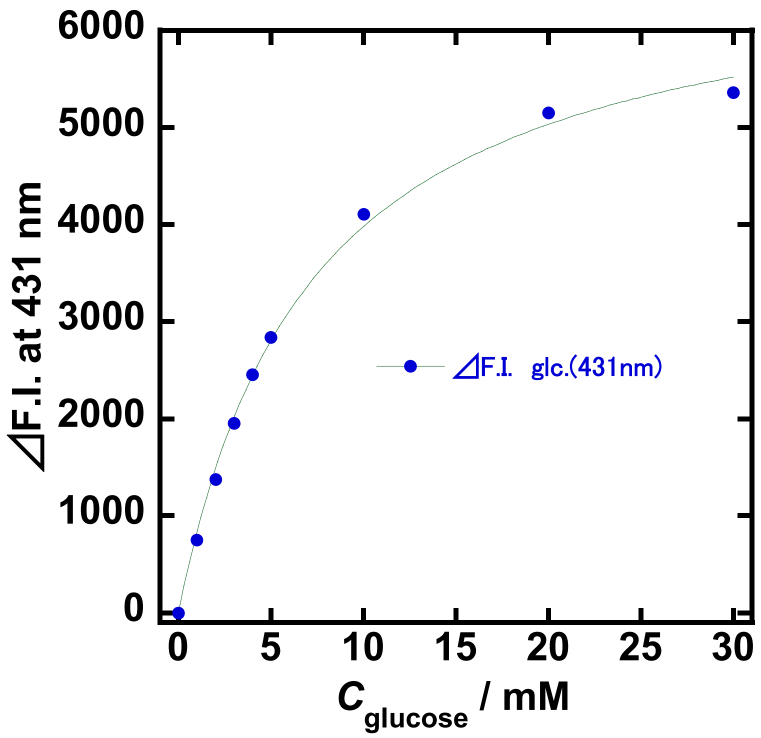


Fig. S9. Difference in the fluorescence intensity of ***1*/FPB-*β*CyD** at 431 nm (ΔF.I. = $I - I_0$) at various D-glucose concentrations in DMSO/water (2/98 in v/v): C_{probe} = 10 μM, $C_{\mathbf{FPB\text{-}\beta CyD}}$ = 0.2 mM, 10 mM of carbonate buffer, pH 10, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm. I and I_0 denote the fluorescence intensities at 431 nm in the presence and absence of saccharides, respectively.

Competitive experiments

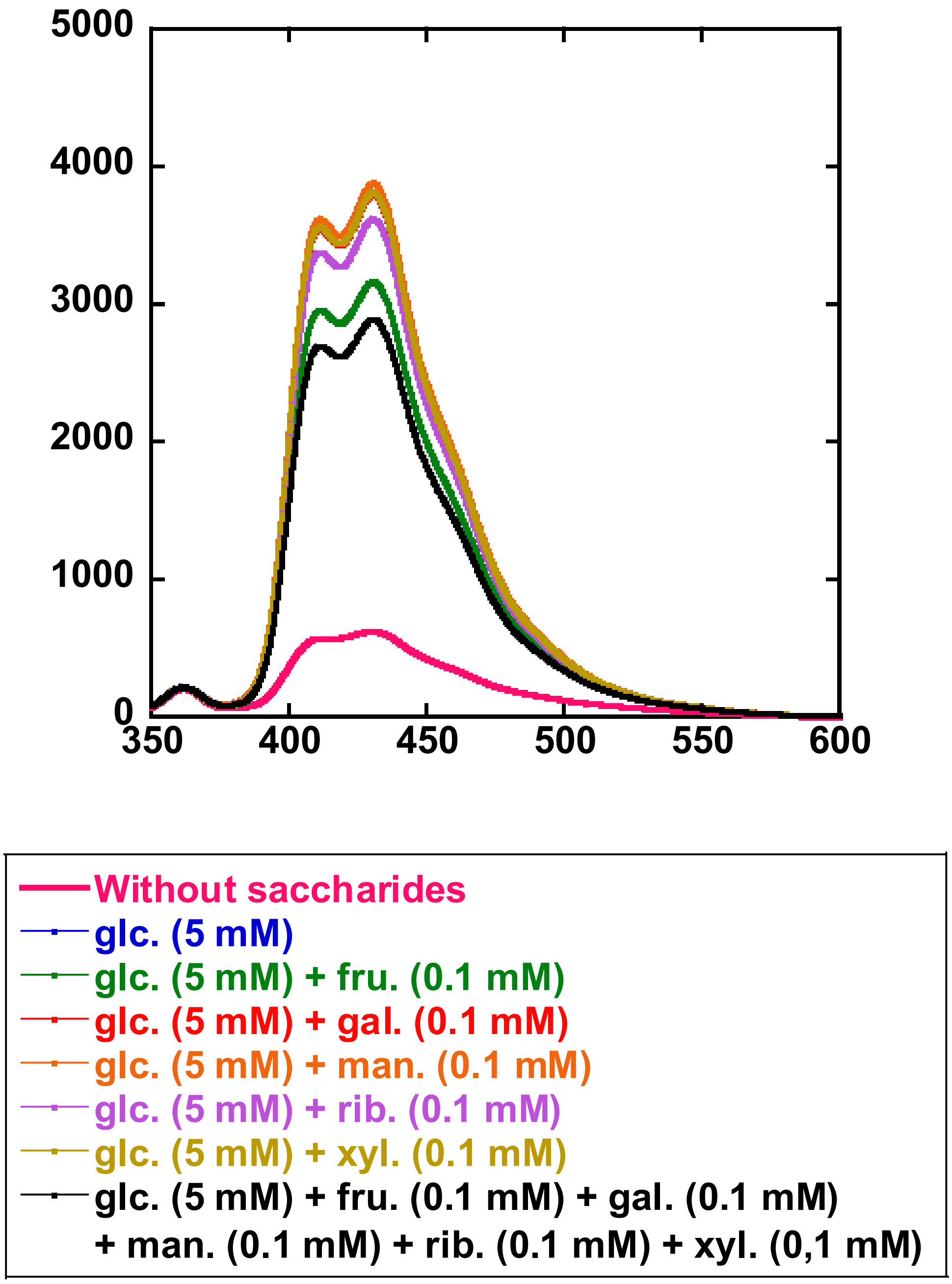


Fig. S10-1. Fluorescence spectra of ***1*/FPB-*β*CyD** with 5 mM D-glucose in the presence of various 0.1 mM saccharides in DMSO/water (2/98 in v/v). The spectra of ***1*/FPB-*β*CyD** without saccharides was also shown: C_{probe} = 10 μM, $C_{\mathrm{FPB\text{-}\beta CyD}}$ = 0.2 mM, 10 mM of carbonate buffer, pH 10, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm. I and I_0 denote the fluorescence intensities in the presence and absence of saccharides, respectively. The abbreviations, glc., fru., gal., man., rib., and xyl., denote D-glucose, D-fructose, D-galactose, D-mannose, D-ribose, and D-xylose, respectively.

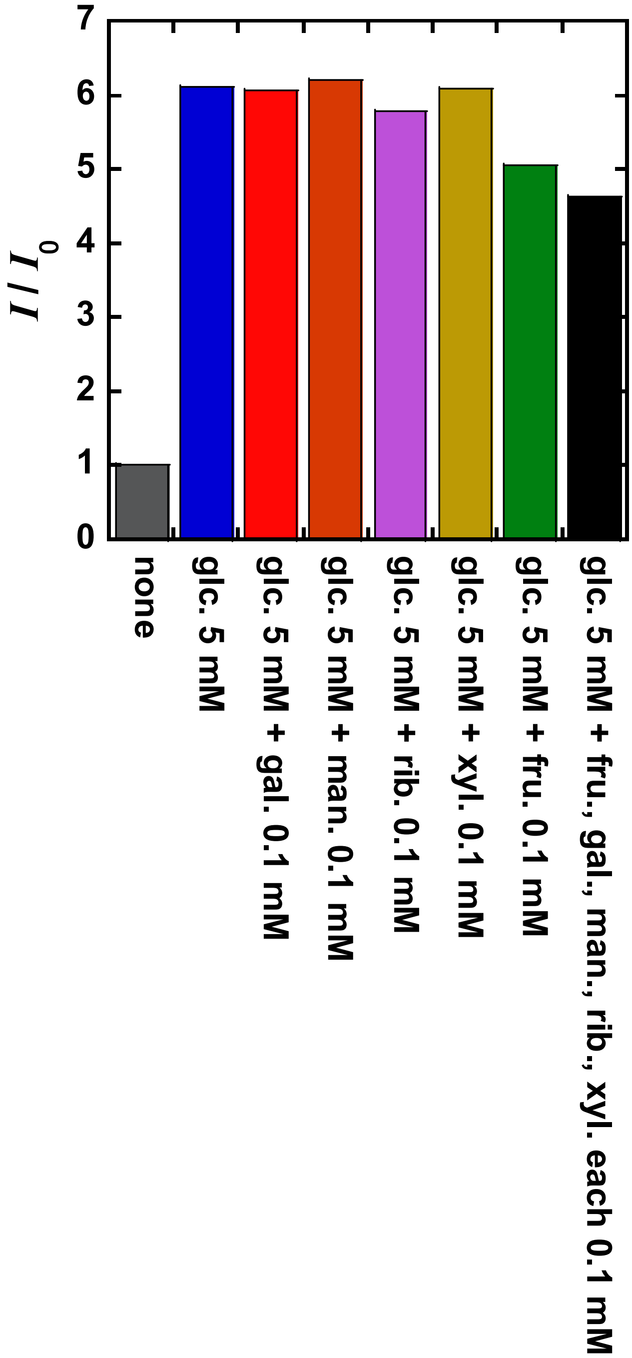


Fig. S10-2. The ratio of fluorescence intensities of ***1*/FPB-*β*CyD** (I/I_0) with 5 mM D-glucose in the presence of various 0.1 mM saccharides in Fig. S10-1. I and I_0 denote the fluorescence intensities at 431 nm in the presence and absence of saccharides, respectively.

pH dependence of fluorescence spectra of *1*/PB-*β*CyD

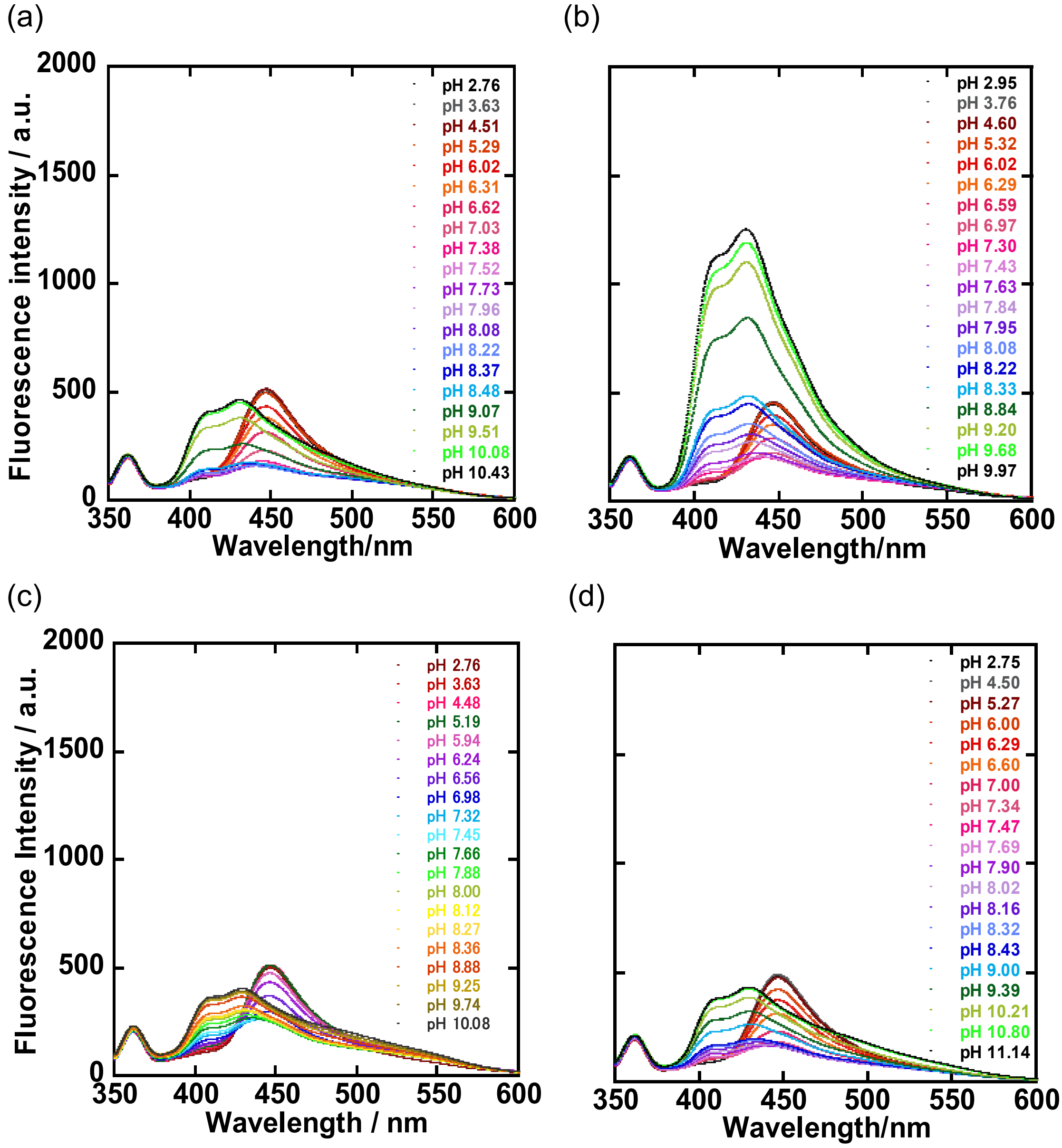


Fig. S11-1. Fluorescence spectra of ***1*/PB-*β*CyD** under various pH conditions in the absence (a) and presence of saccharides (30 mM) in DMSO/water (2/98 in v/v): D-glucose (b), D-fructose (c), and D-galactose (d); C_{probe} = 10 μM, $C_{\mathbf{FPB}\text{-}\beta\mathbf{CyD}}$ = 0.2 mM, 10 mM of phosphate buffer, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm.

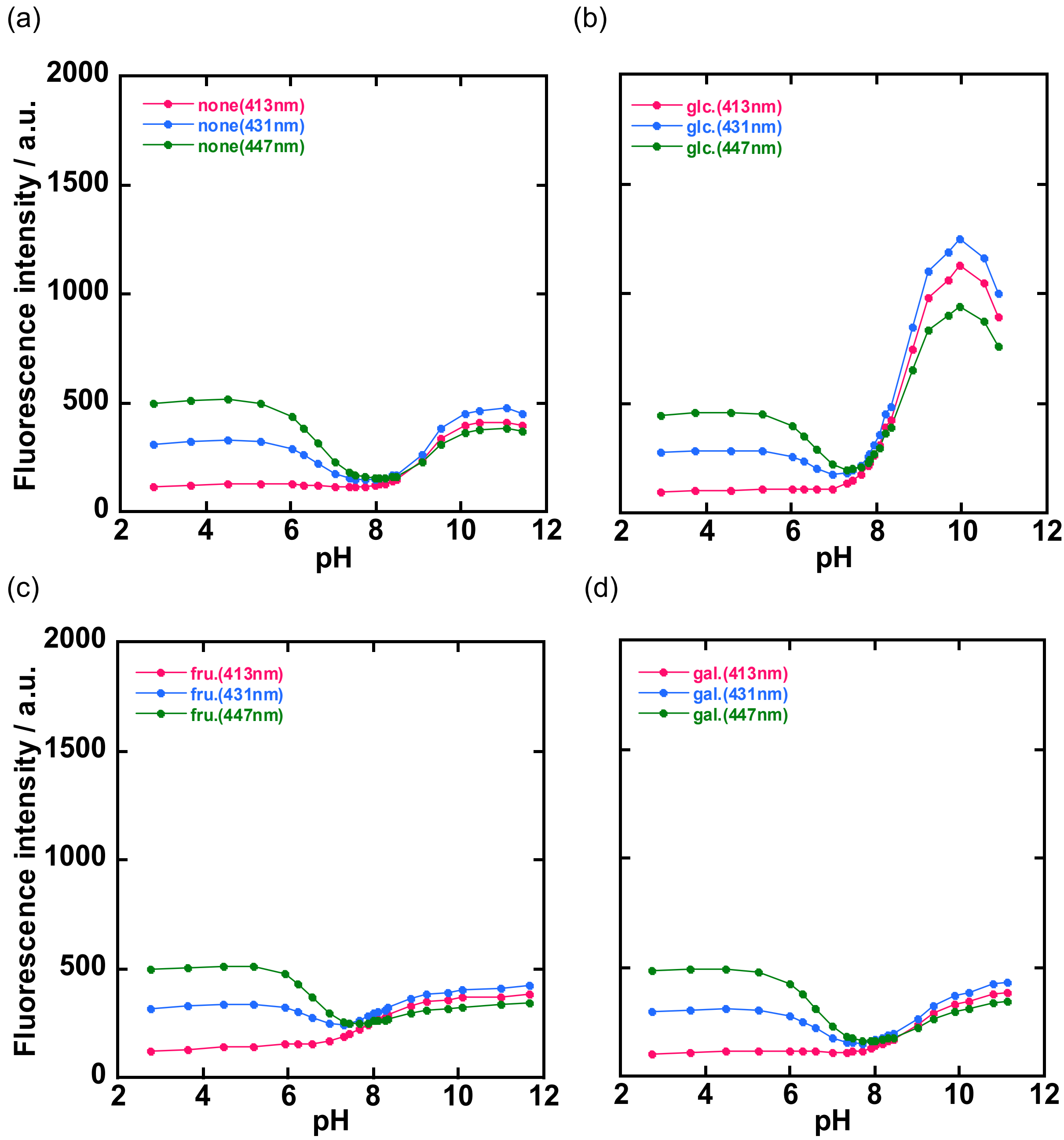
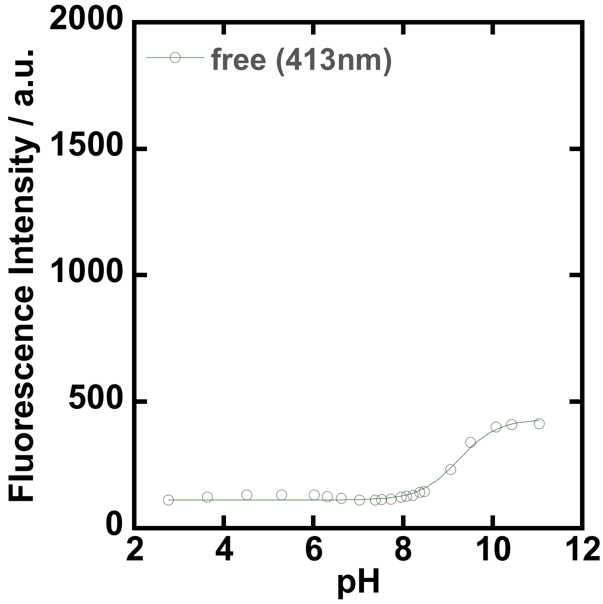


Fig. S11-2. Fluorescence intensities of ***1*/PB-βCyD** at 413, 431 and 447 nm under various pH conditions in the absence (a) and presence of saccharides (30 mM) in DMSO/water (2/98 in v/v): D-glucose (b), D-fructose (c), and D-galactose (d): C_{probe} = 10 μM, $C_{\mathbf{FPB\text{-}\beta CyD}}$ = 0.2 mM, 10 mM of phosphate buffer, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm.

Apparent acid dissociation constants of *1*/PB-*β*CyD

(a)



(b)

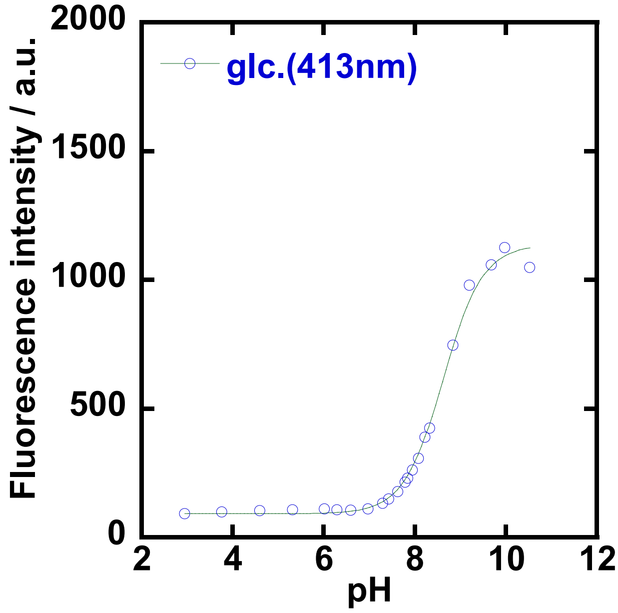
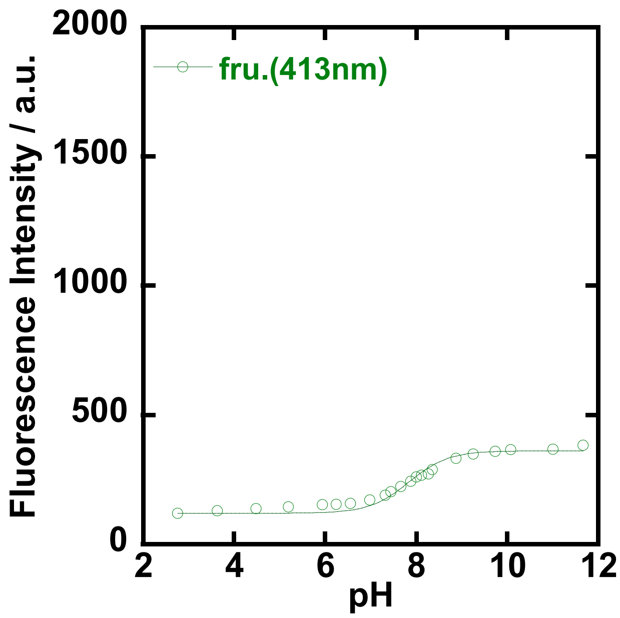


Fig. S12. Fluorescence intensity of ***1*/PB-*β*CyD** at 413 nm under various pH conditions in the absence (a) and presence of saccharides (30 mM) in DMSO/water (2/98 in v/v): D-glucose (b), D-fructose (c), and D-galactose (d); C_{probe} = 10 μM, $C_{\mathbf{FPB\text{-}\beta CyD}}$ = 0.2 mM, 10 mM of phosphate buffer, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm. Each solid curve indicates a theoretical sigmoidal curve derived from the acid dissociation model of a monobasic acid fitted by non-linear least squares analysis.

(c)



(d)

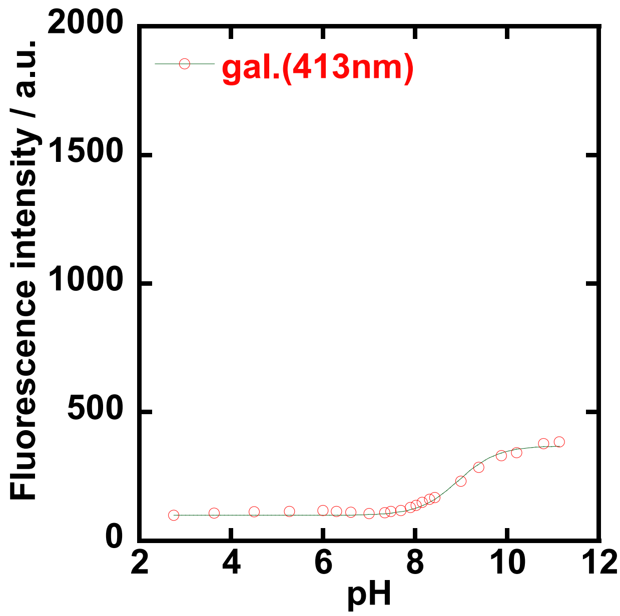


Fig. S12. Fluorescence intensity of ***1*/PB-*β*CyD** at 413 nm under various pH conditions in the absence (a) and presence of saccharides (30 mM) in DMSO/water (2/98 in v/v): D-glucose (b), D-fructose (c), and D-galactose (d); C_{probe} = 10 μM, $C_{\mathbf{FPB}\text{-}\boldsymbol{\beta}\mathbf{CyD}}$ = 0.2 mM, 10 mM of phosphate buffer, T = 25°C, I = 0.10 M, and λ_{ex} = 323 nm. Each solid curve indicates a theoretical sigmoidal curve derived from the acid dissociation model of a monobasic acid fitted by non-linear least squares analysis. (Continued)