Supporting Information

Simplest Chemosensor Array for Phosphorylated Saccharides

Yui Sasaki,[†] Éric Leclerc,[†,‡] Vahid Hamedpour,[†] Riku Kubota,[†] Shin-ya Takizawa,[§] Yasuyuki Sakai,[‡,∥] and Tsuyoshi Minami[†,‡,*]

Corresponding author: tminami@iis.u-tokyo.ac.jp

[†] Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo, 153-8505, Japan.

[‡] CNRS UMI 2820, Laboratory for Integrated Micro Mechatronic Systems, Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo, 153-8505, Japan.

[§] Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo, 153-8902, Japan.

[∥] Center for International Research on Integrative Biomedical Systems, Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo, 153-8505, Japan.

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1. Examples of UV－vis Titrations

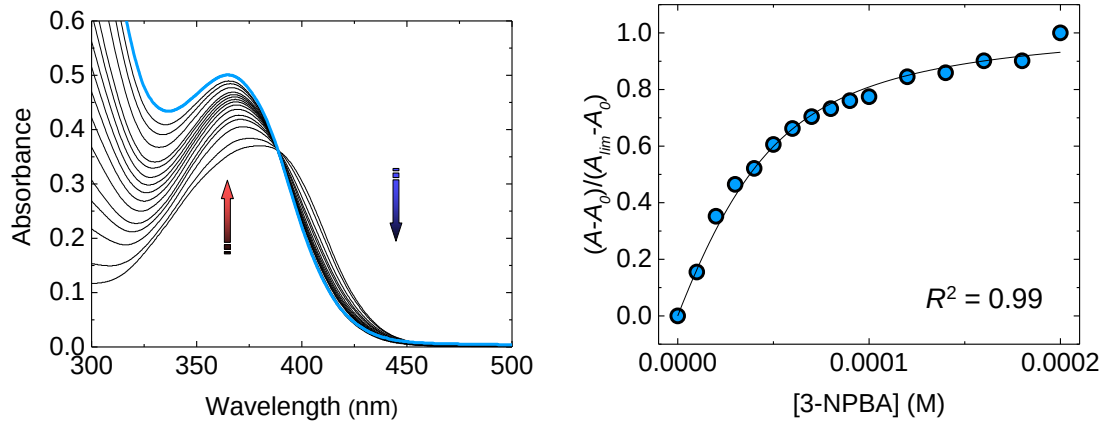


Figure S1. UV－vis spectra of **1** (40 μM) upon the addition of 3-NPBA in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. [3-NPBA] = 0－200 μM.

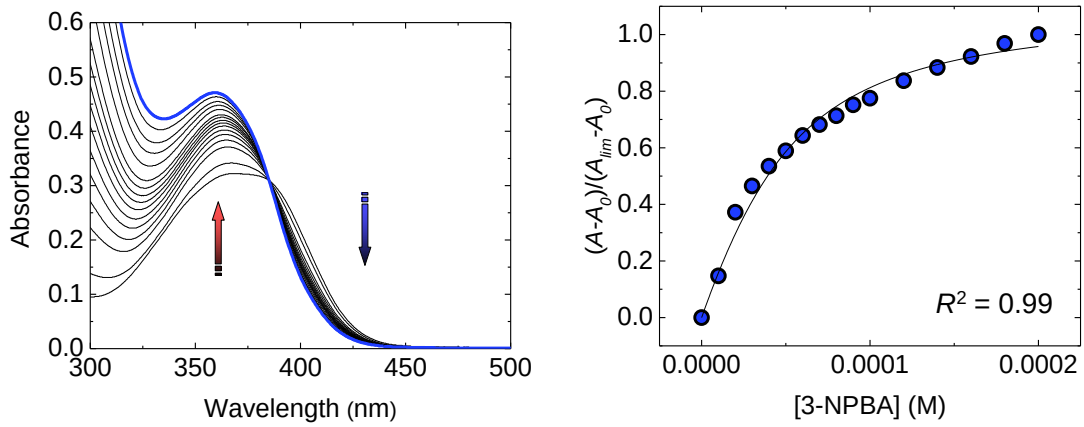


Figure S2. UV－vis spectra of **2** (40 μM) upon the addition of 3-NPBA in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. [3-NPBA] = 0－200 μM.

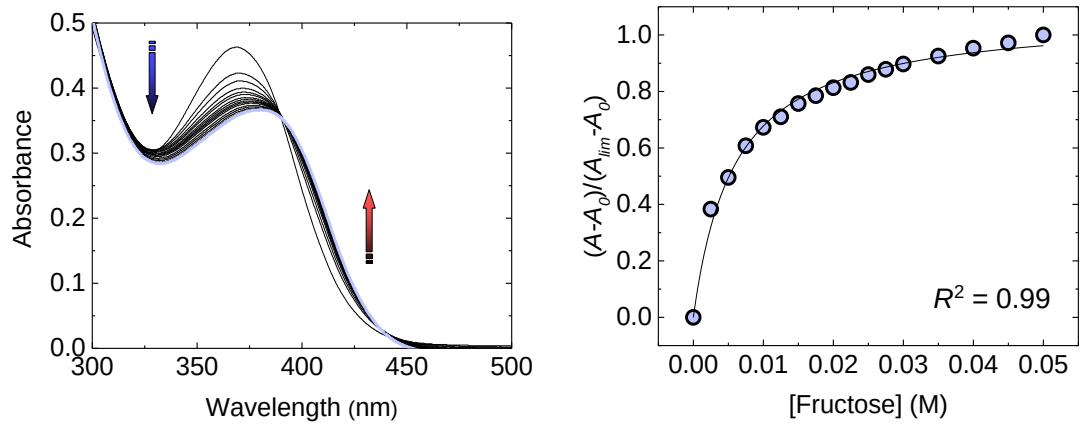


Figure S3. UV－vis spectra spectra of **1** (40 μM)－3-NPBA (80 μM) upon the addition of Fru in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. [Fru] = 0－50 mM.

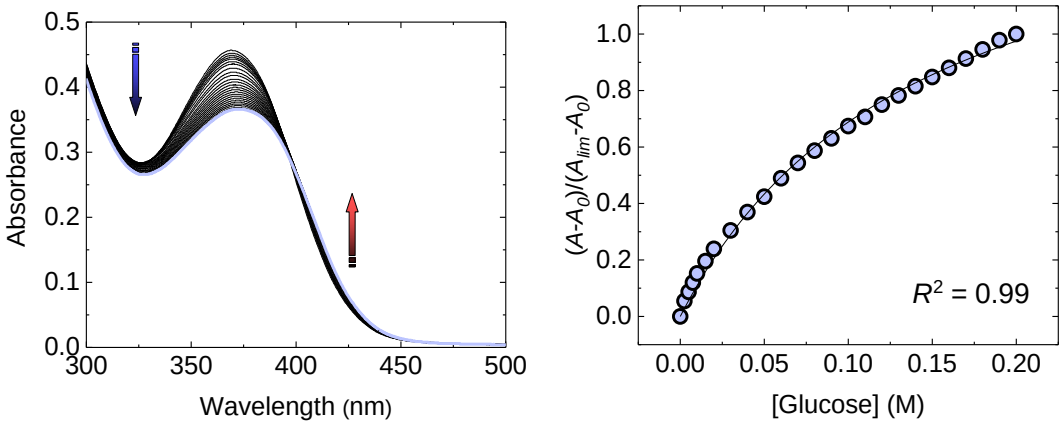


Figure S4. UV－vis spectra of **1** (40 μM)－3-NPBA (80 μM) upon the addition of Glc in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. [Glc] = 0－200 mM.

2. Examples of Fluorescence Titrations

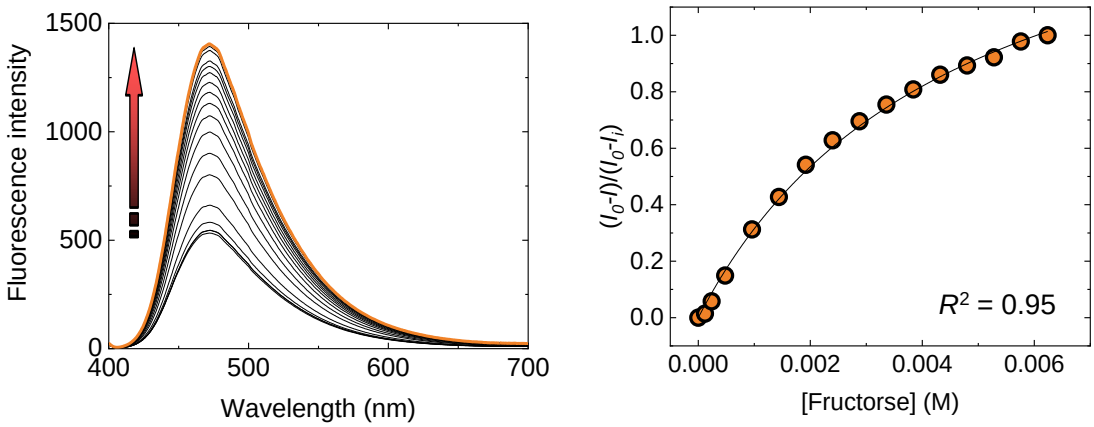


Figure S5. Fluorescence spectra of **1** (4 μM)－3-NPBA (240 μM) upon the addition of Fru in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. λ_{ex} = 388 nm. [Fru] = 0－6240 μM.

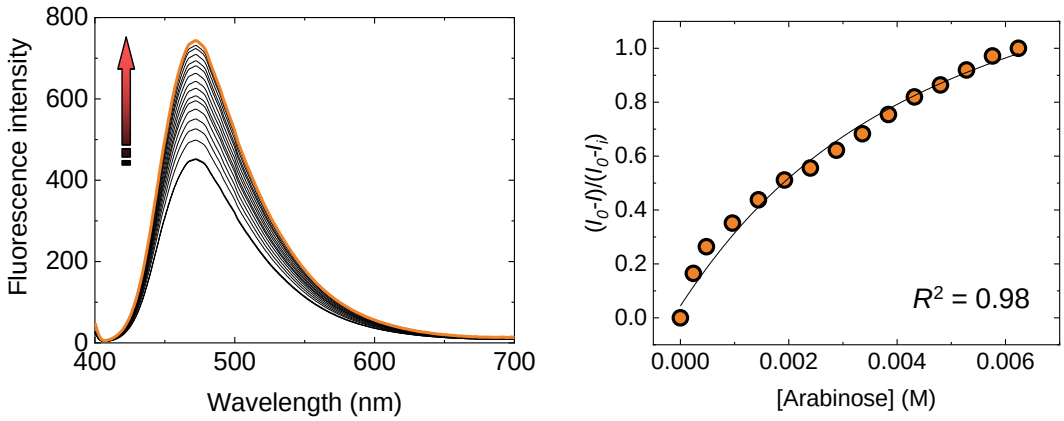


Figure S6. Fluorescence spectra of **1** (4 μM)－3-NPBA (240 μM) upon the addition of Ara in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. λ_{ex} = 388 nm. [Ara] = 0－6240 μM.

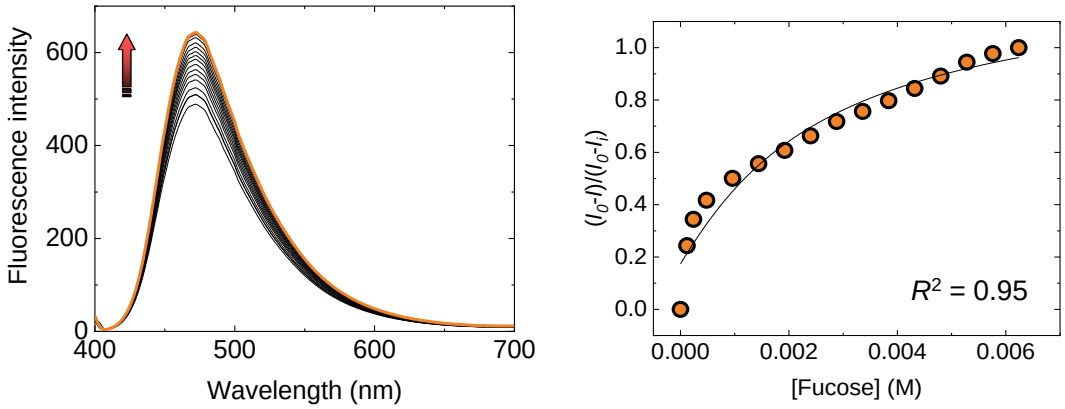


Figure S7. Fluorescence spectra of **1** (4 μM)－3-NPBA (240 μM) upon the addition of Fuc in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. λ_{ex} = 388 nm. [Fuc] = 0－6240 μM.

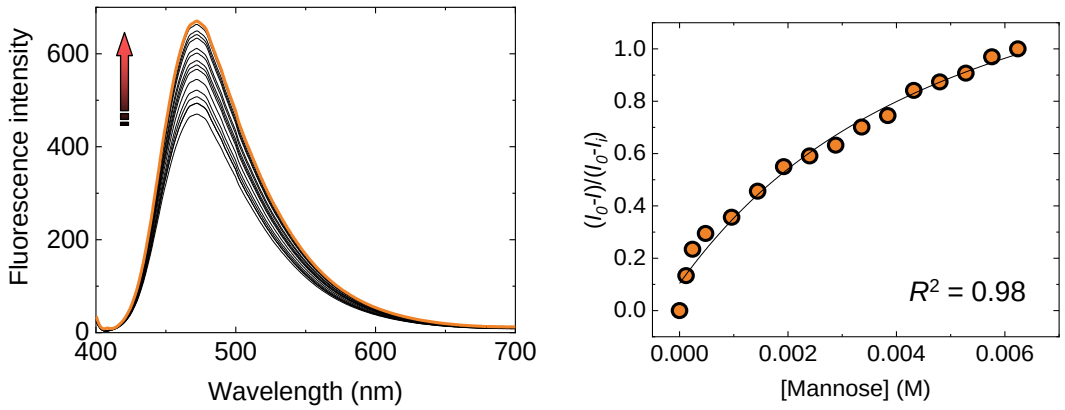


Figure S8. Fluorescence spectra of **1** (4 μM)－3-NPBA (240 μM) upon the addition of Man in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. λ_{ex} = 388 nm. [Man] = 0－6240 μM.

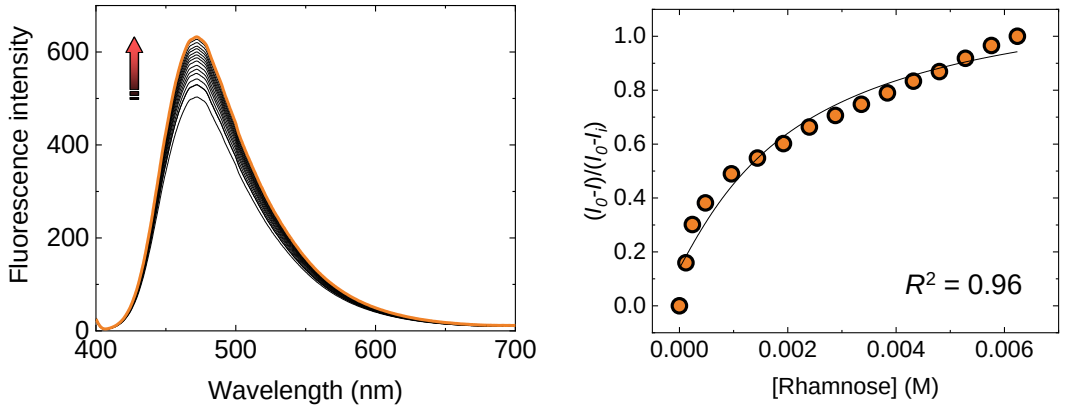


Figure S9. Fluorescence spectra of **1** (4 μM)－3-NPBA (240 μM) upon the addition of Rha in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. λ_{ex} = 388 nm. [Rha] = 0－6240 μM.

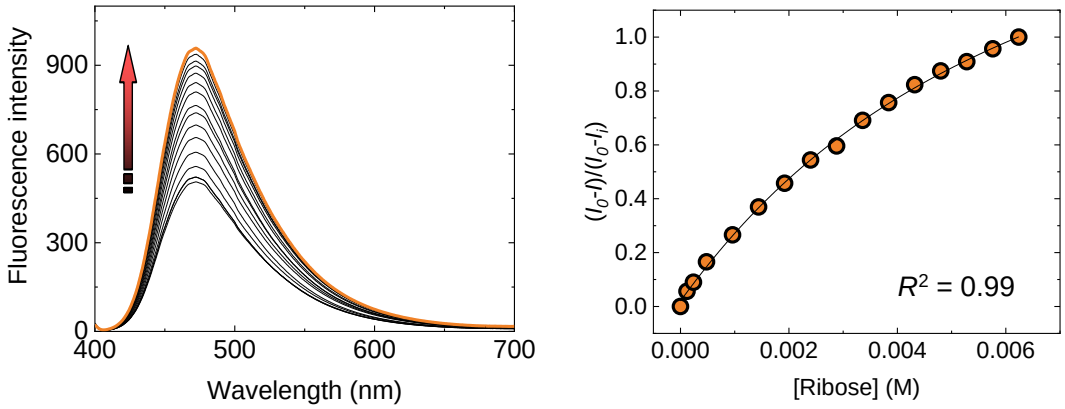


Figure S10. Fluorescence spectra of **1** (4 μM)－3-NPBA (240 μM) upon the addition of Rib in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. λ_{ex} = 388 nm. [Rib] = 0－6240 μM.

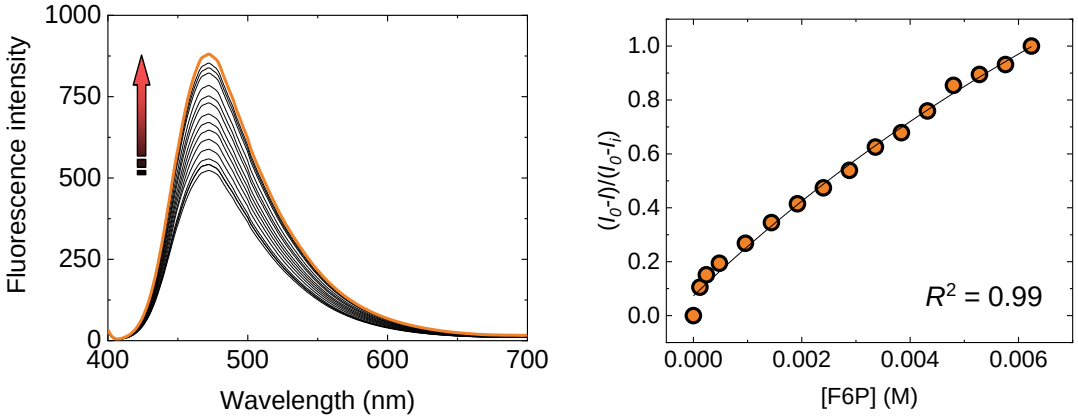


Figure S11. Fluorescence spectra of **1** (4 μM)－3-NPBA (240 μM) upon the addition of F6P in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. λ_{ex} = 388 nm. [F6P] = 0－6240 μM.

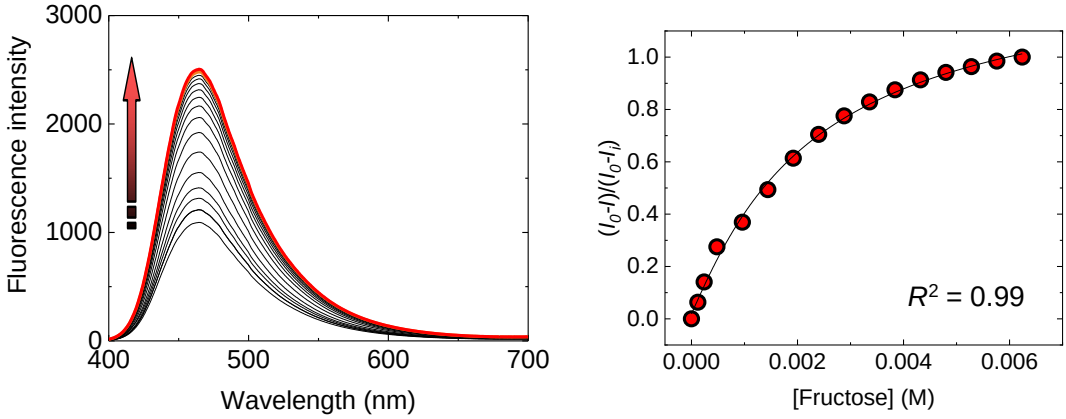


Figure S12. Fluorescence spectra of **2** (4 μM)－3-NPBA (240 μM) upon the addition of Fru in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. λ_{ex} = 381 nm. [Fru] = 0－6240 μM.

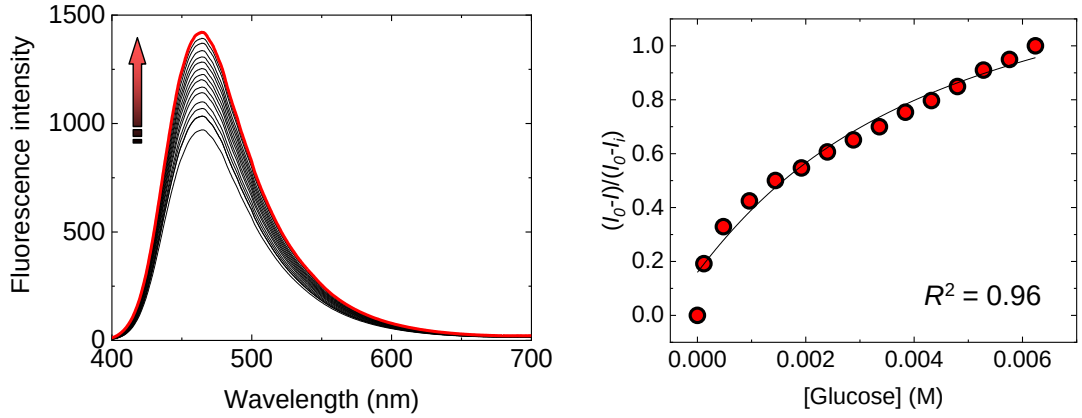


Figure S13. Fluorescence spectra of **2** (4 μM)－3-NPBA (240 μM) upon the addition of Glc in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. λ_{ex} = 381 nm. [Glc] = 0－6240 μM.

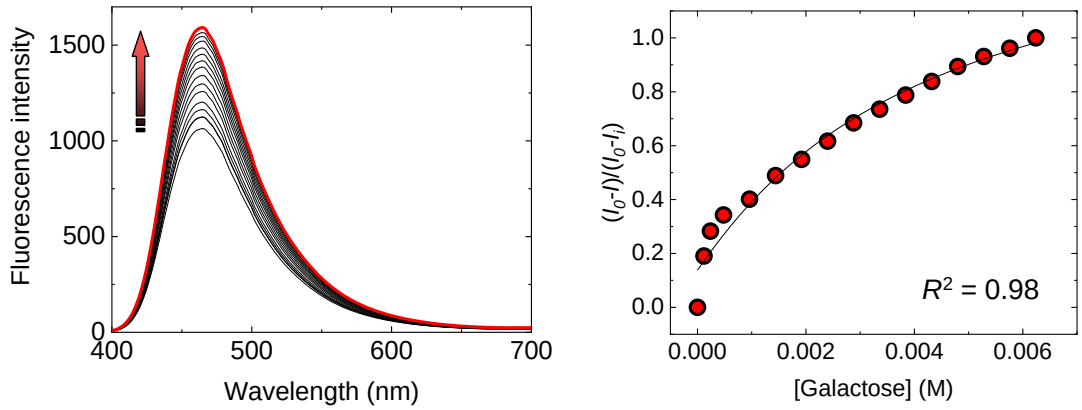


Figure S14. Fluorescence spectra of **2** (4 μM)－3-NPBA (240 μM) upon the addition of Gal in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. λ_{ex} = 381 nm. [Gal] = 0－6240 μM.

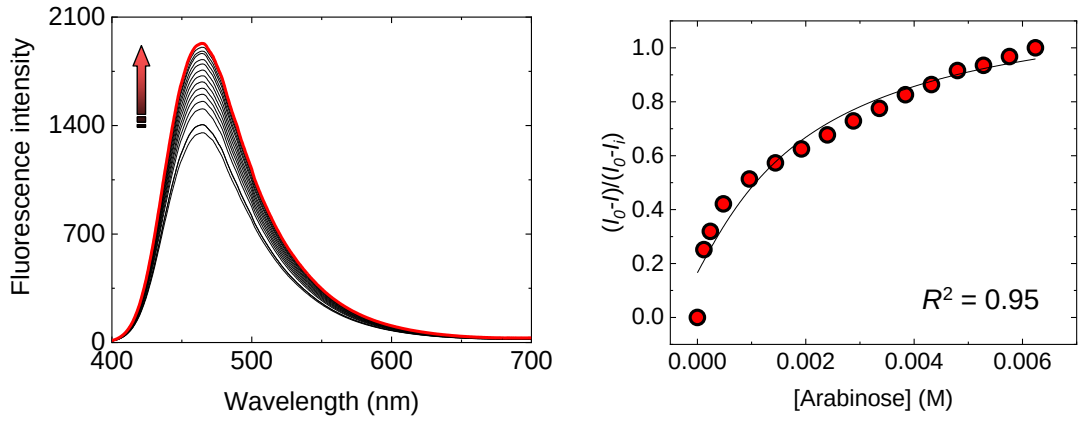


Figure S15. Fluorescence spectra of **2** (4 μM)－3-NPBA (240 μM) upon the addition of Ara in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. λ_{ex} = 381 nm. [Ara] = 0－6240 μM.

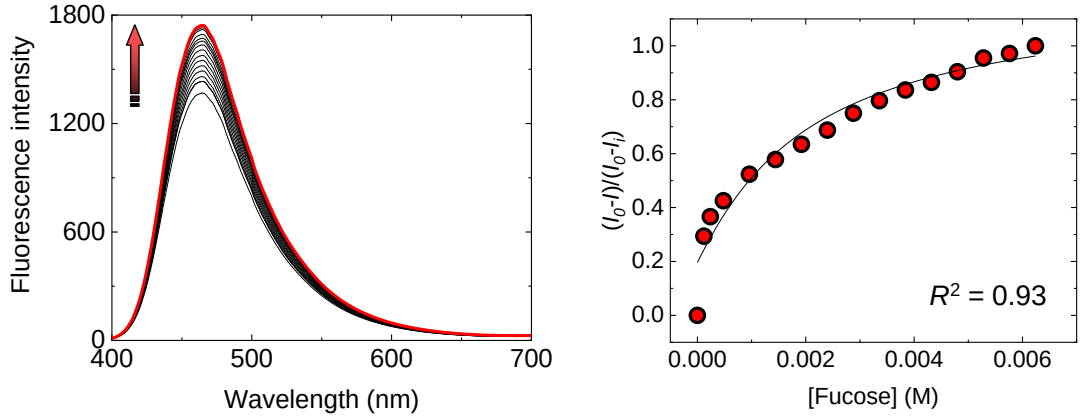


Figure S16. Fluorescence spectra of **2** (4 μM)－3-NPBA (240 μM) upon the addition of Fuc in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. λ_{ex} = 381 nm. [Fuc] = 0－6240 μM.

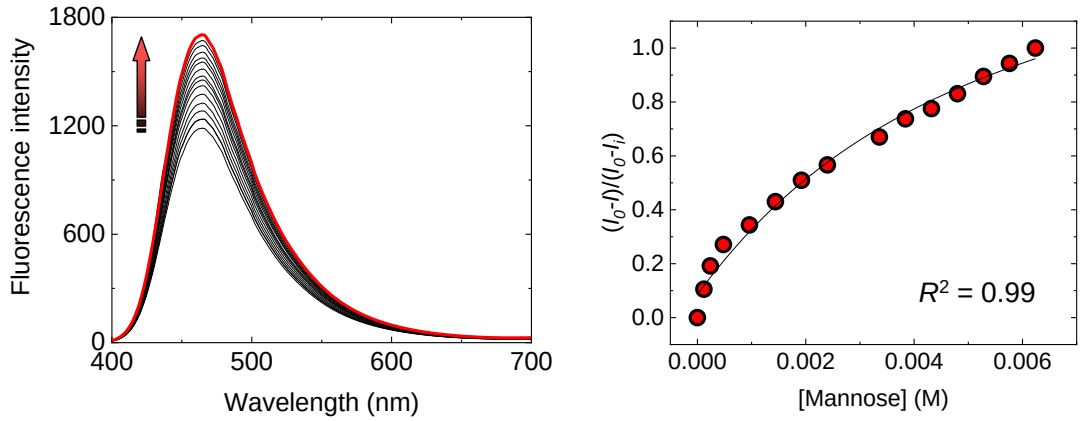


Figure S17. Fluorescence spectra of **2** (4 μM)－3-NPBA (240 μM) upon the addition of Man in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. λ_{ex} = 381 nm. [Man] = 0－6240 μM.

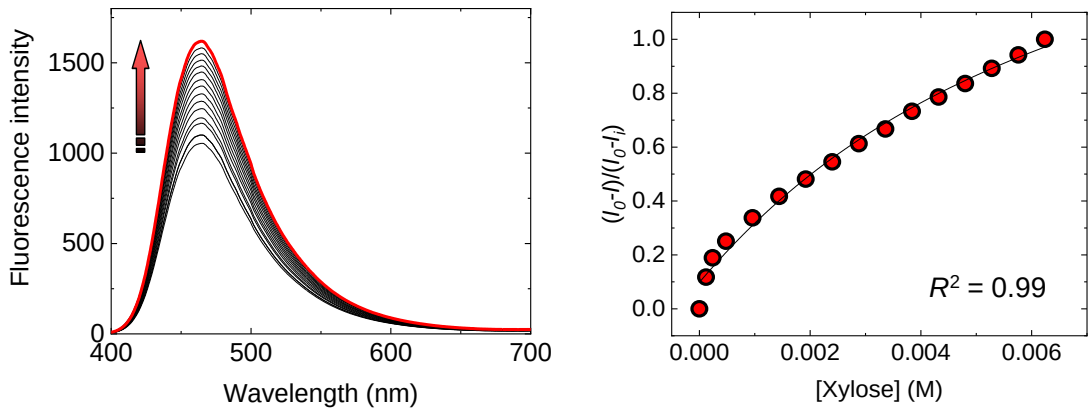


Figure S18. Fluorescence spectra of **2** (4 μM)－3-NPBA (240 μM) upon the addition of Xyl in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. λ_{ex} = 381 nm. [Xyl] = 0－6240 μM.

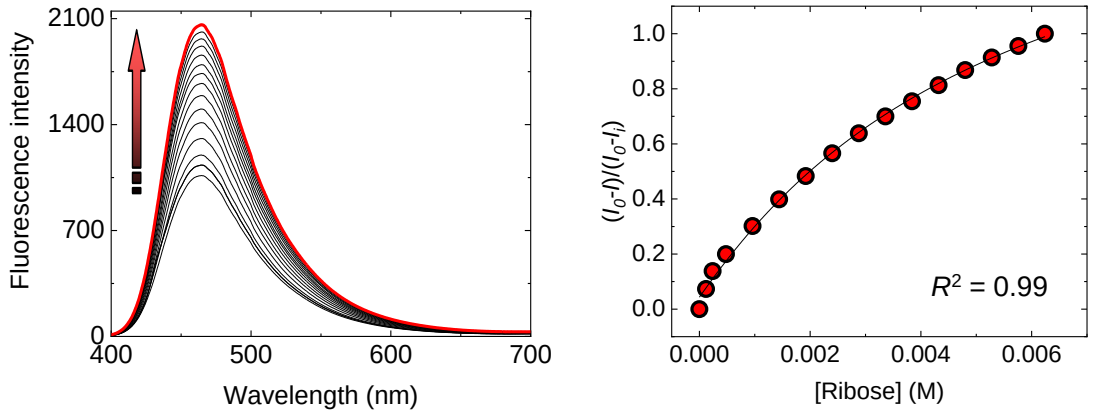


Figure S19. Fluorescence spectra of **2** (4 μM)－3-NPBA (240 μM) upon the addition of Rib in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. λ_{ex} = 381 nm. [Rib] = 0－6240 μM.

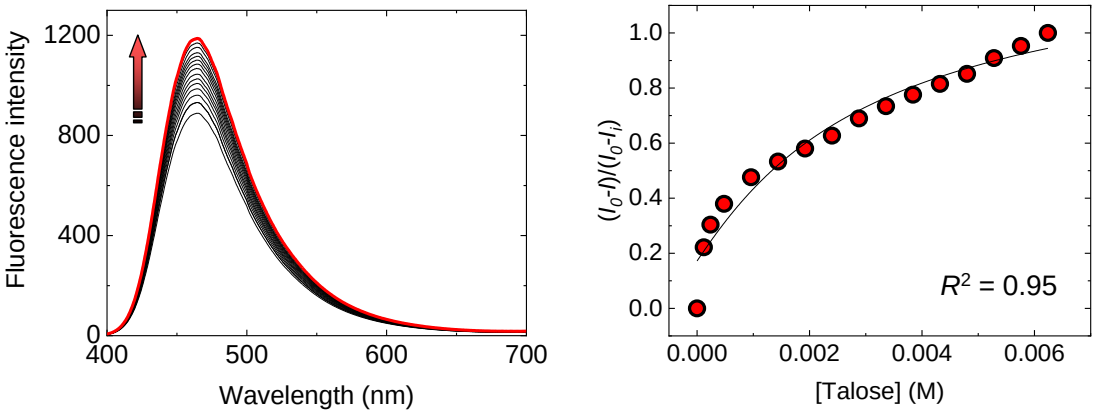


Figure S20. Fluorescence spectra of **2** (4 μM)－3-NPBA (240 μM) upon addition of Tal in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. λ_{ex} = 381 nm. [Tal] = 0－6240 μM.

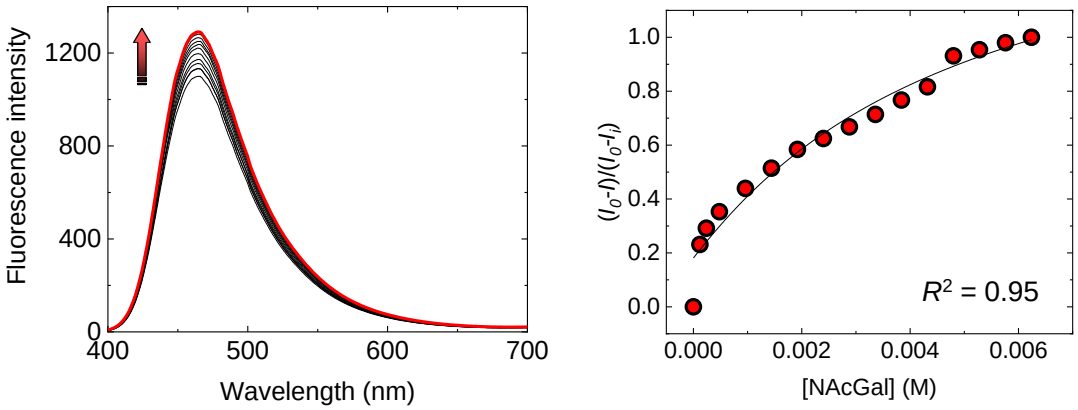


Figure S21. Fluorescence spectra of **2** (4 μM)－3-NPBA (240 μM) upon the addition of NAcGal in a HEPES buffer solution (50 mM) at pH 7.4 at 25 °C. λ_{ex} = 381 nm. [NAcGal] = 0－4320 μM.

3. Quantum Yield and Emission Lifetime

Table S1. The quantum yield and emission lifetime of **1** and its complexes

	1	**1**－3-NPBA	**1**－3-NPBA +Fru
Quantum yield (%) at λ_{ex} = 380 nm	7	1	3
Emission lifetime (ns) at λ_{ex} = 365 nm	2.23	2.24	2.22

[**1**] = 4 μM, [3-NPBA] = 240 μM, [Fru] = 6000 μM. Measurements were conducted in a HEPES buffer solution (50 mM) at pH 7.4 at r.t.

Table S2. The quantum yield and emission lifetime of **2** and its complexes

	2	**2**－3-NPBA	**2**－3-NPBA +Fru
Quantum yield (%) at λ_{ex} = 360 nm	14	1	3
Emission lifetime (ns) at λ_{ex} = 365 nm	2.66	2.67	2.60

[**2**] = 4 μM, [3-NPBA] = 240 μM, [Fru] = 6000 μM. Measurements were conducted in a HEPES buffer solution (50 mM) at pH 7.4 at r.t.

4. pH Titrations

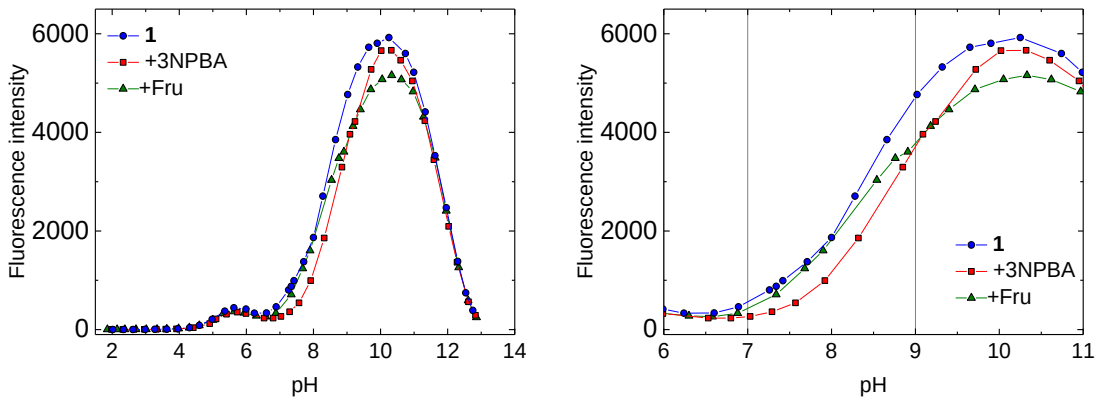


Figure S22. pH-Dependent fluorescence intensity of **1** (●); **1** plus 3-NPBA (■); **1** plus 3-NPBA with Fru (▲) in water. λ_{ex} = 388 nm. [**1**] = 4 μM, [3-NPBA] = 240 μM, [Fru] = 6.0 mM.

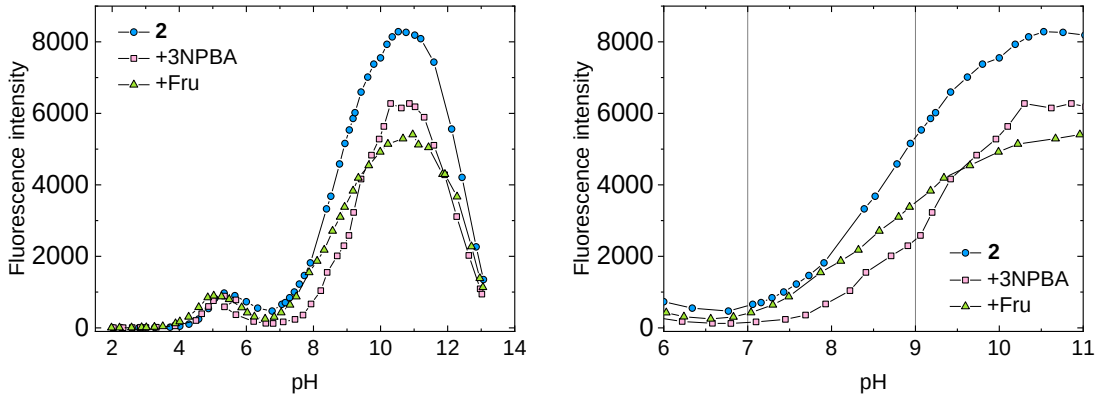


Figure S23. pH-Dependent fluorescence intensity of **1** (●); **1** plus 3-NPBA (■); **1** plus 3-NPBA with Fru (▲) in water. λ_{ex} = 381 nm. [**2**] = 4 μM, [3-NPBA] = 240 μM, [Fru] = 6.0 mM.

5. ESI MS Analysis

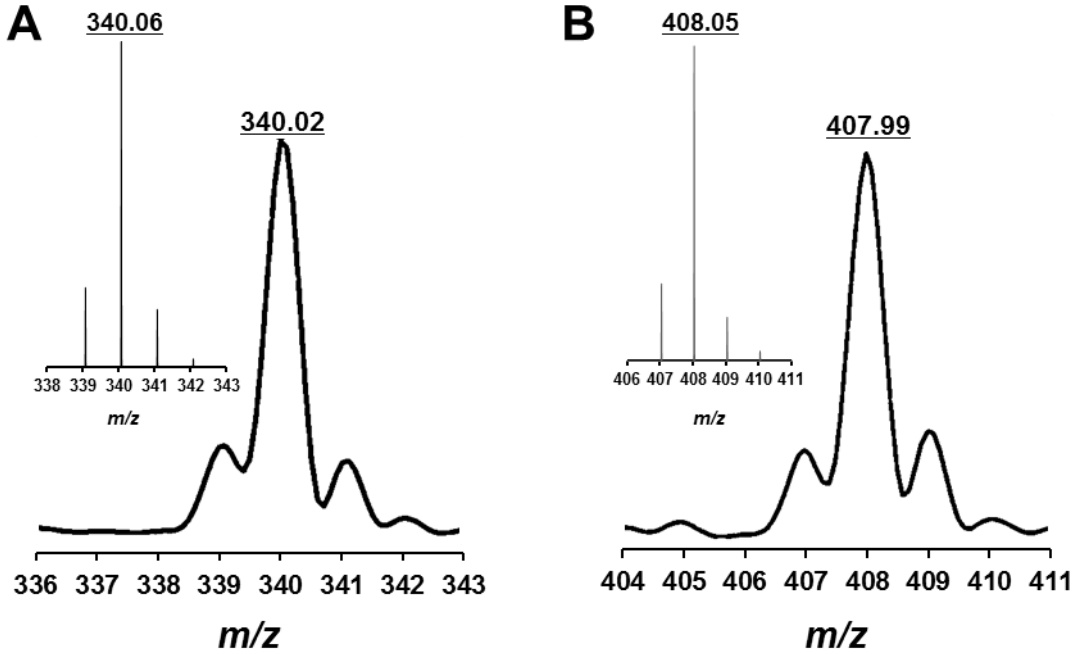


Figure S24. ESI mass spectra (negative) of (A) **2** − 3-NBPA complex. Inset: Calculated isotope pattern for [**2** − $2H_2O$+3-NPBA+OH]$^-$. (B) F6P − 3-NBPA complex. Inset: Calculated isotope pattern for [F6P − $2H_2O$+3-NPBA+OH]$^-$

6. Linear Discriminant Analysis (LDA)

Table S3. The jackknifed classification matrix of qualitative assay

Jackknifed Classification Matrix																
	Ara	F6P	Fru	Fuc	G6P	NAc Gal	NAc Glc	Gal	Glc	Man	Rha	Rib	Tal	Xyl	control	% correct
Ara	20	0	0	0	0	0	0	0	0	0	0	0	0	0	0	100
F6P	0	20	0	0	0	0	0	0	0	0	0	0	0	0	0	100
Fru	0	0	20	0	0	0	0	0	0	0	0	0	0	0	0	100
Fuc	0	0	0	20	0	0	0	0	0	0	0	0	0	0	0	100
G6P	0	0	0	0	20	0	0	0	0	0	0	0	0	0	0	100
NAc Gal	0	0	0	0	0	20	0	0	0	0	0	0	0	0	0	100
NAc Glc	0	0	0	0	0	0	20	0	0	0	0	0	0	0	0	100
Gal	0	0	0	0	0	0	0	20	0	0	0	0	0	0	0	100
Glc	0	0	0	0	0	0	0	0	20	0	0	0	0	0	0	100
Man	0	0	0	0	0	0	0	0	0	20	0	0	0	0	0	100
Rha	0	0	0	0	0	0	0	0	0	0	20	0	0	0	0	100
Rib	0	0	0	0	0	0	0	0	0	0	0	20	0	0	0	100
Tal	0	0	0	0	0	0	0	0	0	0	0	0	20	0	0	100
Xyl	0	0	0	0	0	0	0	0	0	0	0	0	0	20	0	100
control	0	0	0	0	0	0	0	0	0	0	0	0	0	0	20	100
Total	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	100

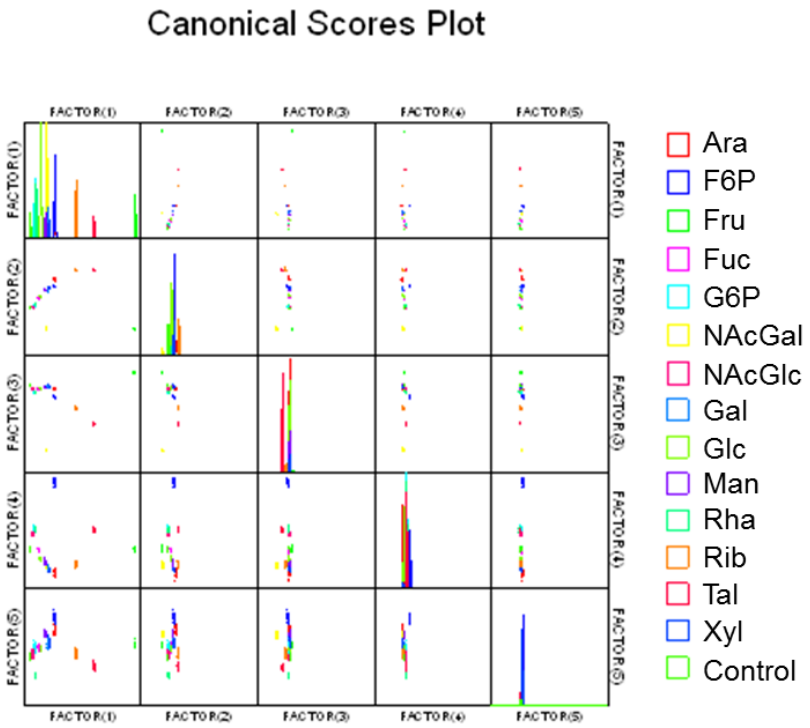
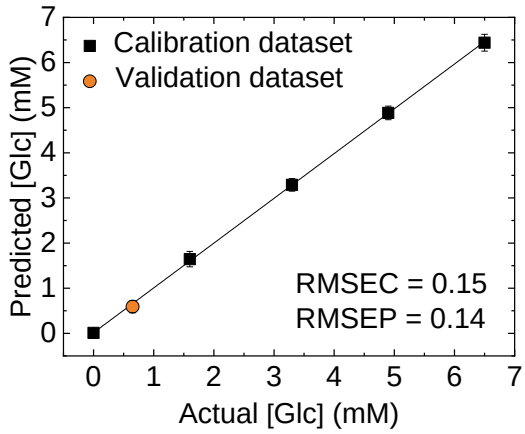


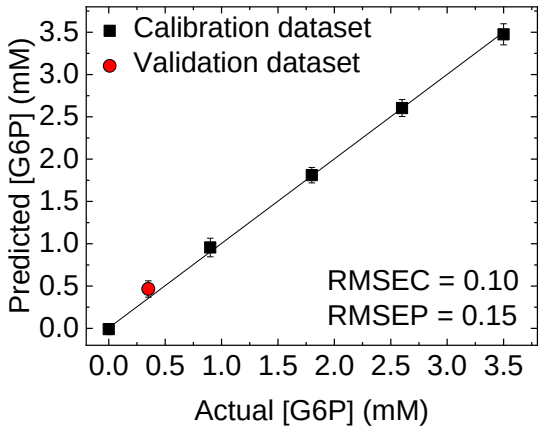
Figure S25. The canonical score plot of qualitative assay for saccharides.

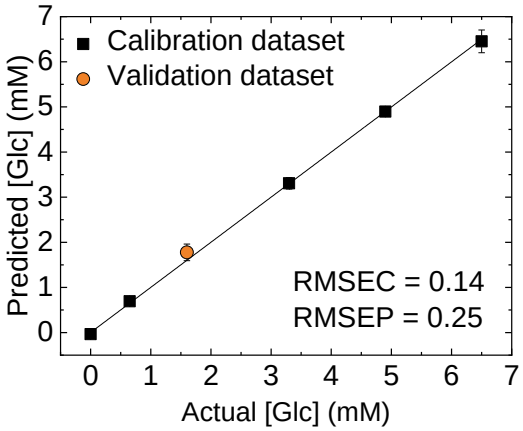
7. Regression Analysis: Support Vector Machine (SVM)

Table S4. Concentration conditions in the quantitative assay of the mixtures

Glc (mM)	G6P (mM)	F6P (mM)
0.0	0.0	0.0
0.65	0.35	0.10
1.6	0.90	0.30
3.3	1.8	0.50
4.9	2.6	0.80
6.5	3.5	1.0


Calibration dataset
Validation dataset
RMSEC = 0.15
RMSEP = 0.14
Predicted [Glc] (mM)
Actual [Glc] (mM)


Calibration dataset
Validation dataset
RMSEC = 0.10
RMSEP = 0.15
Predicted [G6P] (mM)
Actual [G6P] (mM)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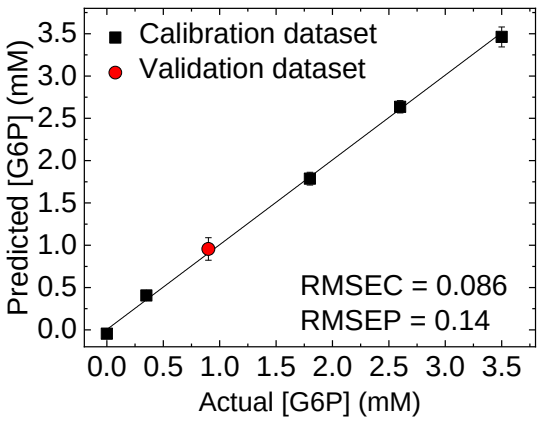
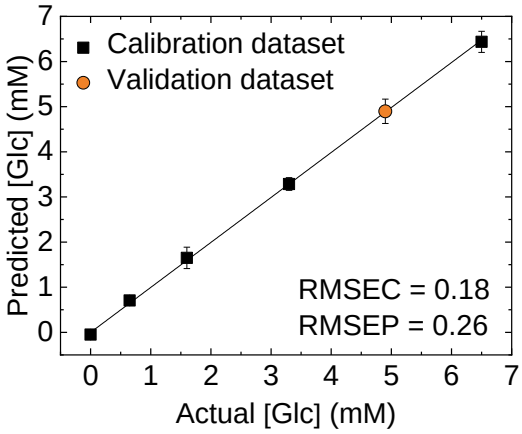
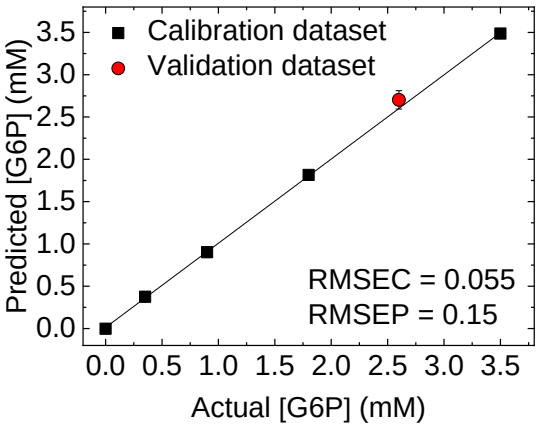
Validation dataset
RMSEC = 0.14
RMSEP = 0.25
Predicted [Glc] (mM)
Actual [Glc] (mM)


Calibration dataset
Validation dataset
RMSEC = 0.086
RMSEP = 0.14
Predicted [G6P] (mM)
Actual [G6P] (mM)


Calibration dataset
Validation dataset
RMSEC = 0.18
RMSEP = 0.26
Predicted [Glc] (mM)
Actual [Glc] (mM)


Calibration dataset
Validation dataset
RMSEC = 0.055
RMSEP = 0.15
Predicted [G6P] (mM)
Actual [G6P] (mM)

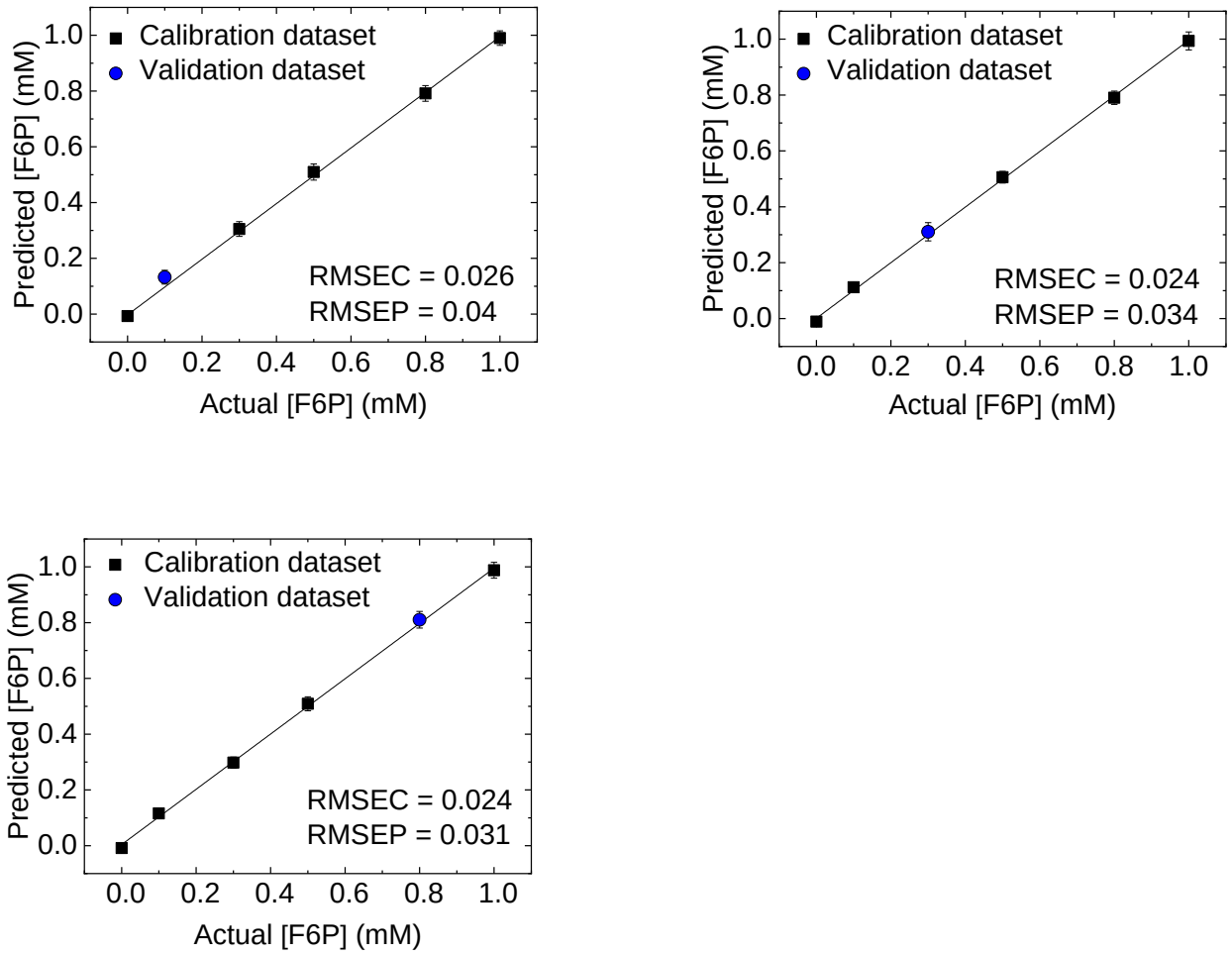


Figure S26. Results of the SVM regression analysis of Glc, G6P, and F6P in mixtures. The values of the root-mean-square of calibration (RMSEC) and prediction (RMSEP) prove high accuracies of the model and its predictive capacity.