Electronic Supplementary Information (ESI)

Direct Sensing of Fluoride in Aqueous Solutions using Boronic Acid Based Sensor

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1. General

All commercial reagents and solvents were used as received. Protocatechuic acid (PCA) was purchased from Energy Chemicals. D-glucose was purchased from Acros. D-fructose was purchased from TCI. 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) was purchased from Aladdin Industrial Inc. Other chemicals were products of Sinopharm Chemical Reagent Co. Ltd. The synthesis of **1** has been reported previously.[1]

Absorption spectra and turbidity measurements were performed on a Varian Cary 300 UV-Vis spectrophotometer. Fluorescence spectra were recorded on Hitachi F-4500 fluorescence spectrophotometer. All spectroscopic measurements were carried out at ambient temperature of 298 K.

2. Experimental

Procedure for sample preparation for spectroscopic measurements

Stock solutions of **1** (10 mM), PCA (1 M, 2 M or 4 M) and catechol (1 M, 2 M, or 4 M) were prepared in MeOH. Stock solutions of NaF (10 mM, 0.1 M or 0.5 M), glucose (1 M) and fructose (1 M) were prepared in water. The NaF solutions were diluted by buffer and water to the desired concentrations. Spectroscopic measurements were carried out in default buffer (pH 2.0 50 mM sodium phosphate buffer with 50 mM NaCl). To 2 mL of the NaF solutions in default buffer was added 20 μL 10 mM MeOH stock solution of **1**, followed by a stock solution of the diol component if a diol was used. The samples were incubated for 20 min and then subject to spectroscopic measurements.

*pH dependence of fluoride sensing by the **1**-PCA ensemble*

The samples for fluorescence measurements were prepared following the general procedure described above, except that different buffering agents (50 mM) were used in place of the sodium phosphate buffer for pH above 2.5. The buffering agents used are H_3PO_4-NaH_2PO4 (pH 1.5-2.5), HCOOH-HCOONa (pH 3.0-3.5), HOAc-NaOAc (pH 4.0-5.0), 4-morpholineethanesulfonic acid (MES, pH 6.0), NaH_2PO_4-Na_2HPO_4 (7.0), HEPES (8.0), $NaHCO_3$-Na_2CO_3 (9.0-10.0).

Determination of fluoride in a commercial mouthwash sample

The mouthwash liquid sample (50 mL) was treated with NaCl (5 mL 0.2M solution, to prevent emulsification) and extracted with chloroform (30 mL × 3), and then diluted 10-fold with default buffer (pH 2.0 50 mM sodium phosphate buffer with 50 mM NaCl). Equal volumes of samples were taken and spiked with NaF so that the concentrations of the added fluoride were 0 mM, 0.5 mM, 1 mM, 1.5 mM and 2 mM, respectively. The samples were subject to fluorescence measurements following the general procedure.

3. Data analysis

Binding constants (K) for 1:3 (host to guest) stoichiometry were calculated by fitting the fluorescence titration data to eq 1, where x denotes the fluoride concentration, y is the fluorescence intensity, y_0 is the fluorescence intensity in the absence of fluoride and y_∞ is the saturated value.

$$y = \frac{y_0 + y_\infty K x^3}{1 + K x^3} \tag{1}$$

Binding constants (K) for 1:1 stoichiometry were calculated by fitting the data to eq 2, where the denotations of x, y and y_0 are the same as in eq 1, c is the concentration of **1**, and a is the proportionality efficient of fluorescence intensity change versus fraction of fluoride-bound **1**.

$$y = y_0 + \frac{a}{2c}(c + x + 1/K - \sqrt{(c + x + 1/K)^2 - 4cx}) \tag{2}$$

Stepwise acid dissociation constants (pK_{a1} and pK_{a2}) for a "diprotic acid (H_2A)" were calculated by fitting the fluorescence-pH titration data to eq 3, where $I_{\text{subscript}}$ is the relative fluorescence intensity of the respective species.

$$y = \frac{I_{H_2A} 10^{pK_{a1}+pK_{a2}-2pH} + I_{HA} 10^{pK_{a2}-pH} + I_A}{10^{pK_{a1}+pK_{a2}-2pH} + 10^{pK_{a2}-pH} + 1} \tag{3}$$

4. Spectral traces

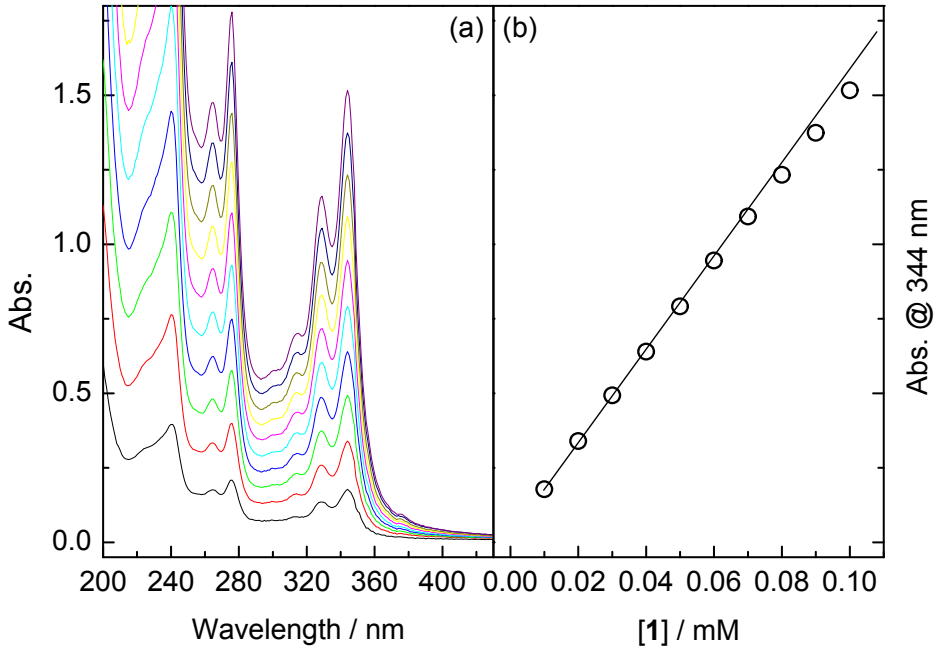


Fig. S1 (a) Absorption spectra of **1** at varying concentrations (10 μM – 0.1 mM) in default buffer. (b) Absorbance of **1** at 344 nm vs concentration of **1**.

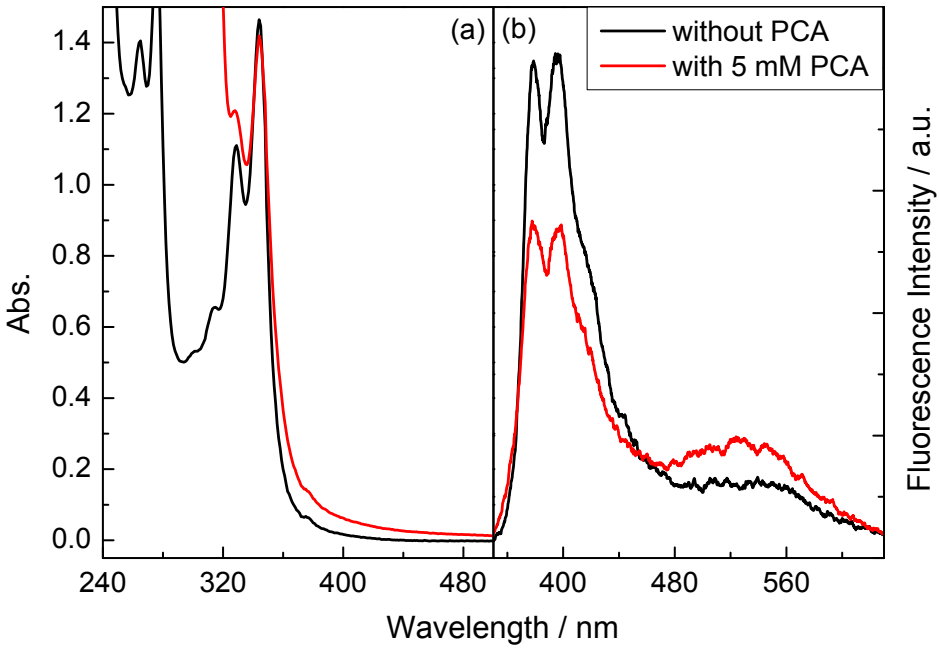


Fig. S2 Absorption (a) and fluorescence spectra (b) of **1** (0.1 mM) in the absence and presence of 5 mM PCA in default buffer. λ_{ex} = 328 nm.

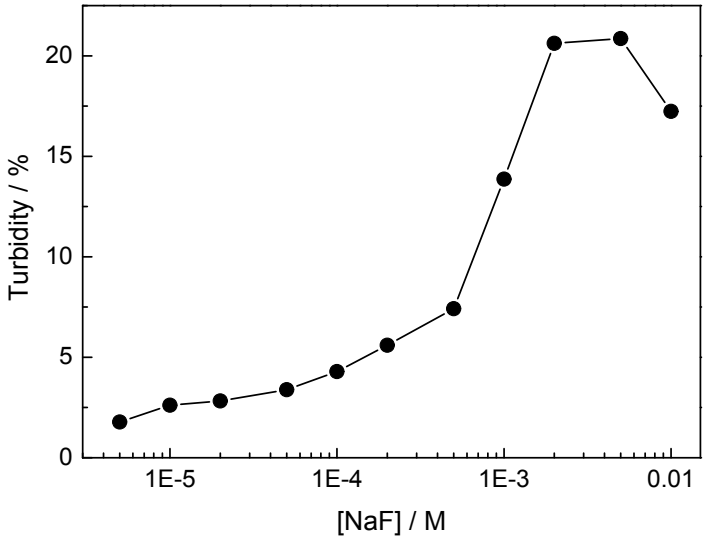


Fig. S3 Turbidty of solution of **1** (0.1 mM) and PCA (5 mM) with increasing concentration of NaF (0-10 mM) in default buffer.

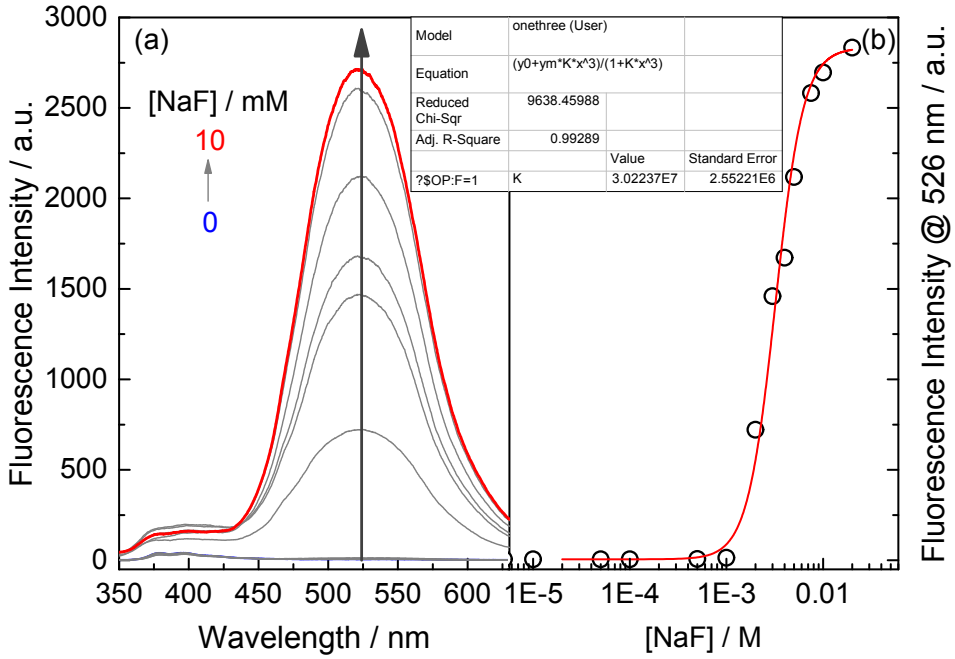


Fig. S4 (a) Fluorescence spectra of **1** (0.1 mM) in the presence of NaF over 0-10 mM in default buffer. (b) Fluorescence intensity of **1** at 526 nm vs NaF concentration and the curve fit (line) using eq 1. λ_{ex} = 328 nm.

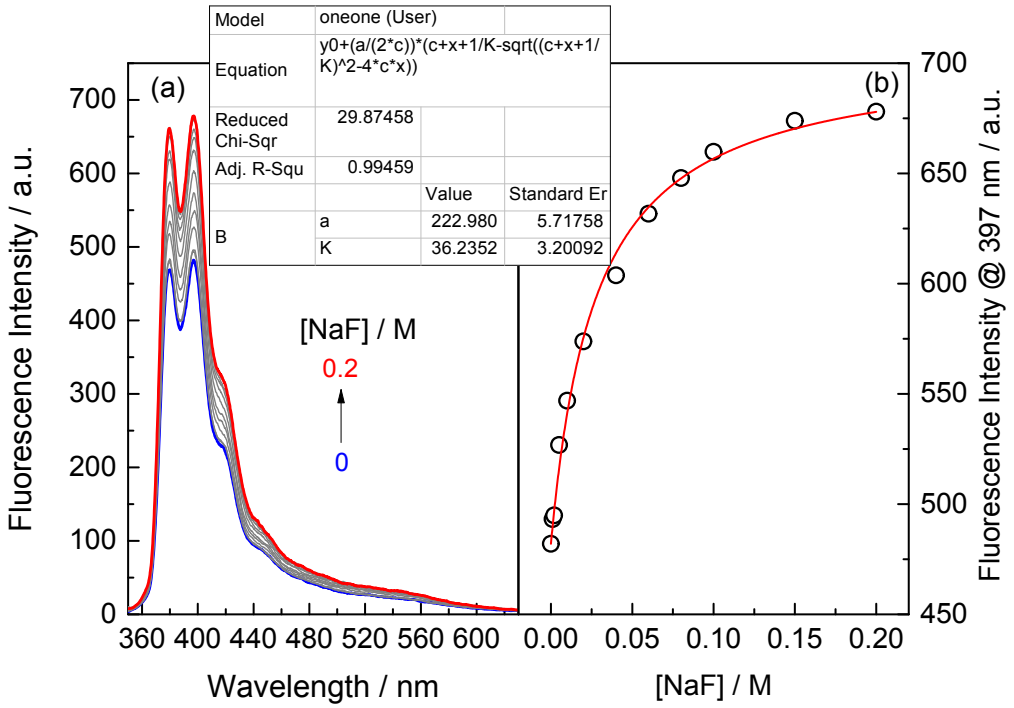


Fig. S5 (a) Fluorescence spectra of **1** (0.1 mM) in the presence of NaF (0-0.2 M) in default buffer with 2 mM CTAB. Note that CTAB micelles solubilize **1** and prevent its aggregation, as no excimer emission is observed and **1** shows enhancement of the pyrene monomer fluorescence with addition of fluoride. (b) Fluorescence intensity of **1** at 526 nm vs NaF concentration and the curve fit (line) using eq 2. λ_{ex} = 328 nm.

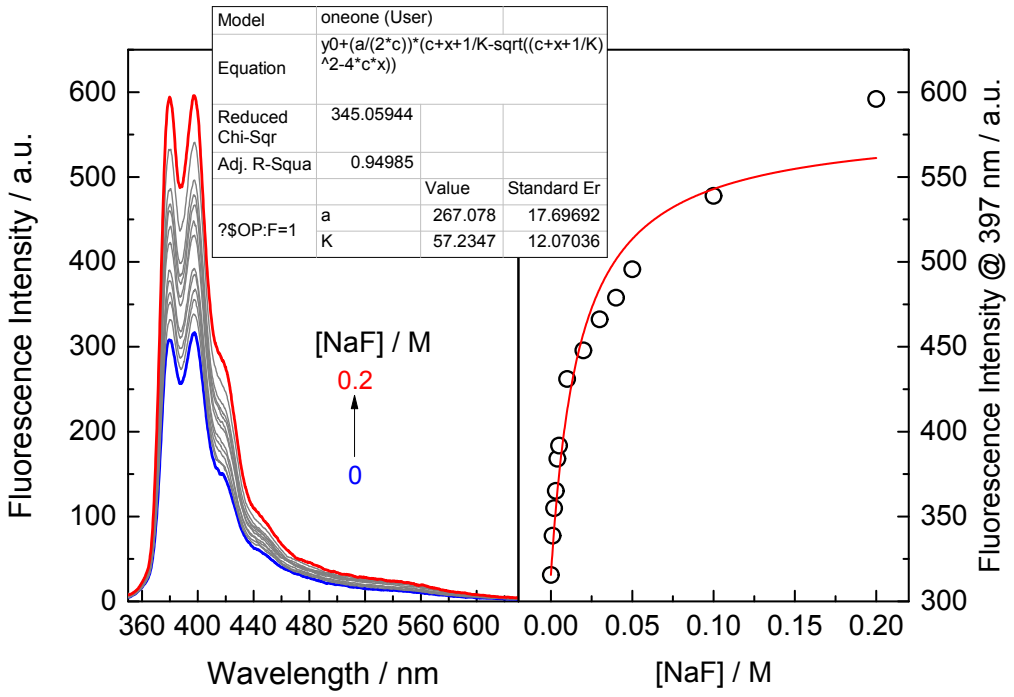


Fig. S6 (a) Fluorescence spectra of **1** (0.1 mM) in the presence of PCA (10 mM) and NaF (0-0.2 M) in default buffer with 2 mM CTAB. (b) Fluorescence intensity of **1** at 526 nm vs NaF concentration. λ_{ex} = 328 nm. Fluorescence intensity of **1** at 526 nm vs

NaF concentration and the curve fit (line) using eq 2, which gives a poor fitting of the data. λ_{ex} = 328 nm. Note that the fluoride titration curve shows two distinct regions, likely due to the formation of both ternary **1**-PCA-fluoride complex and binary **1**-fluoride complex.

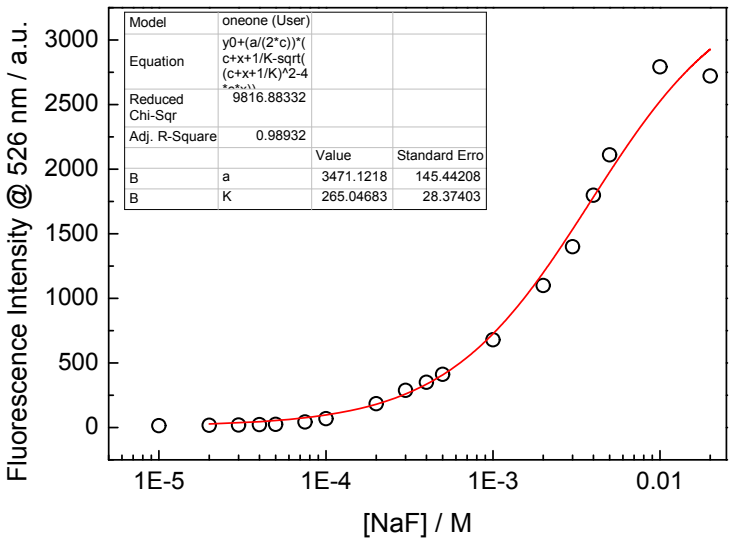


Fig. S7 Fluorescence intensity of **1** (0.1 mM) at 526 nm vs NaF concentration over 0-20 mM in the presence of 5 mM PCA in default buffer and curve fit (line) using eq 2, which gives a poor fitting of the data. λ_{ex} = 328 nm.

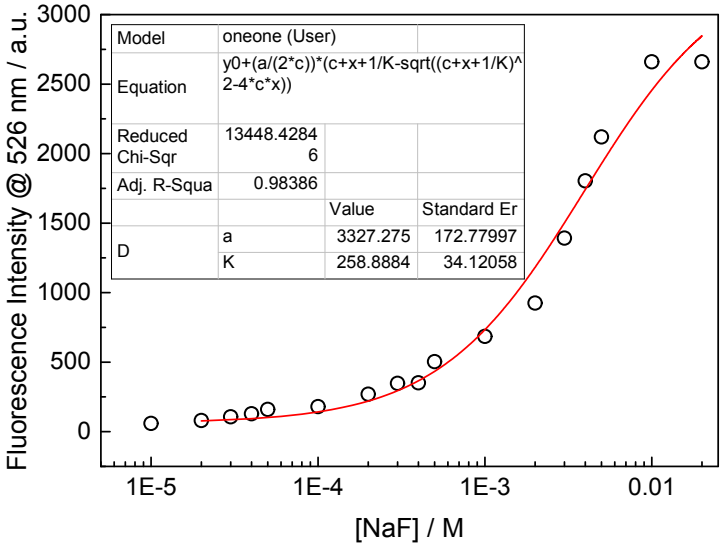


Fig. S8 Fluorescence intensity of **1** (0.1 mM) at 526 nm vs NaF concentration over 0-20 mM in the presence of 10 mM PCA in default buffer and curve fit (line) using eq 2, which gives a poor fitting of the data. λ_{ex} = 328 nm.

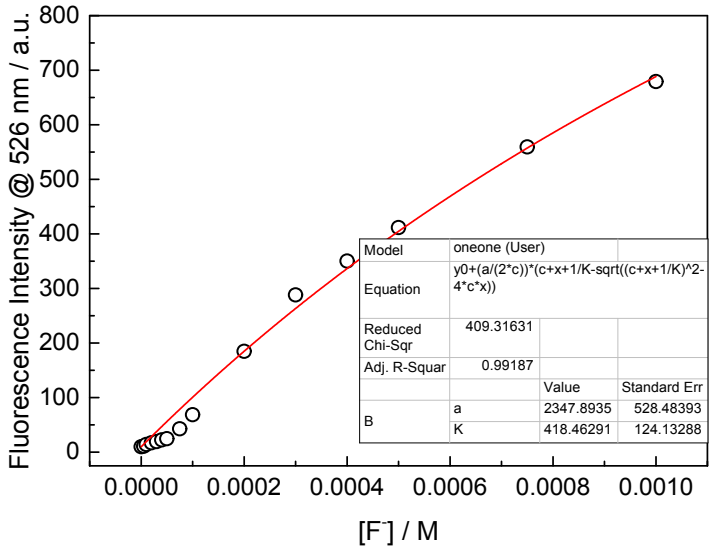


Fig. S9 Fluorescence intensity of **1** (0.1 mM) at 526 nm vs NaF concentration over 0-1 mM in the presence of 5 mM PCA in default buffer and the curve fit (line) using eq 2. λ_{ex} = 328 nm.

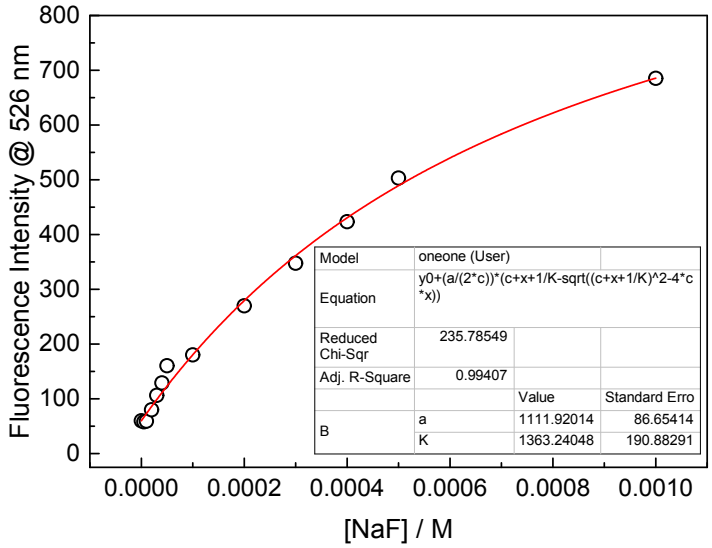


Fig. S10 Fluorescence intensity of **1** (0.1 mM) at 526 nm vs NaF concentration over 0-1 mM in the presence of 10 mM PCA in default buffer and curve fit (line) using eq 2. λ_{ex} = 328 nm.

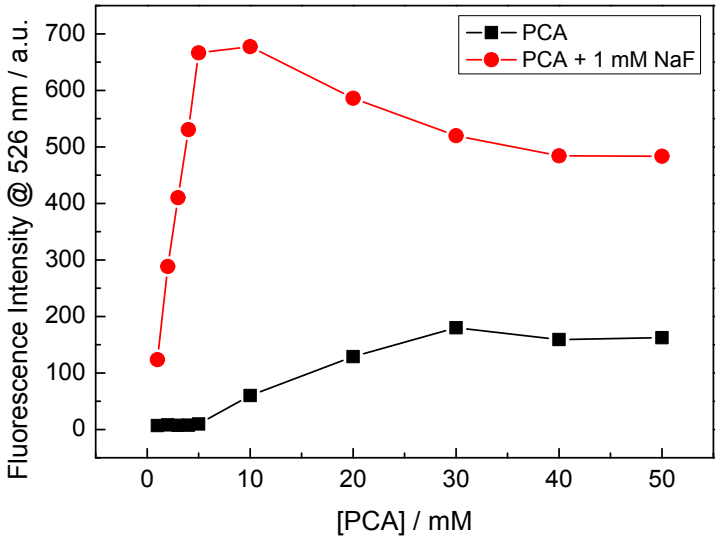


Fig. S11 Fluorescence intensity of **1** (0.1 mM) at 526 nm vs PCA concentration in the absence (black line) and presence (red line) of 1 mM NaF in default buffer. Note that without NaF there is negligible interaction between **1** and PCA with [PCA] ≤ 5 mM. In contrast, in the absence of fluoride, the titration curve almost levels off at PCA concentration of 5 mM, suggesting that binding of PCA and fluoride to **1** occurred in a cooperative manner to form a tetrahedral boronate ester of **1**-PCA-fluoride.

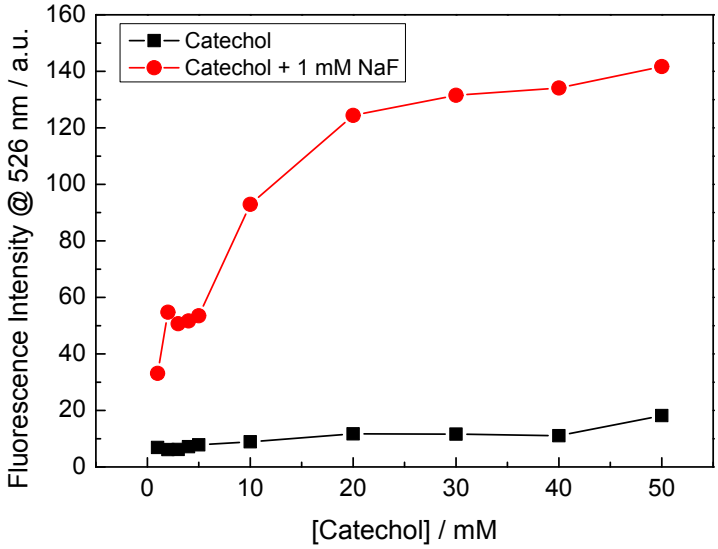


Fig. S12 Fluorescence intensity of **1** (0.1 mM) at 526 nm vs catechol concentration in the absence (black line) and presence (red line) of 1 mM NaF in default buffer.

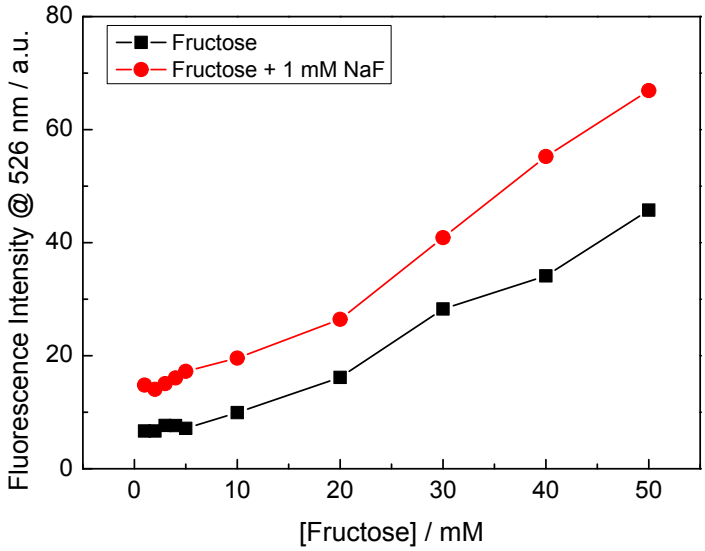


Fig. S13 Fluorescence intensity of **1** (0.1 mM) at 526 nm vs D-fructose concentration in the absence (black line) and presence (red line) of 1 mM NaF in default buffer. Note that the difference between the two curves increases with increasing fructose concentration, indicating that fluoride ion enhances the aggregation of the **1**-fructose complex, although not as pronounced as in the case of PCA (Fig. S6) and catechol (Fig.S7).

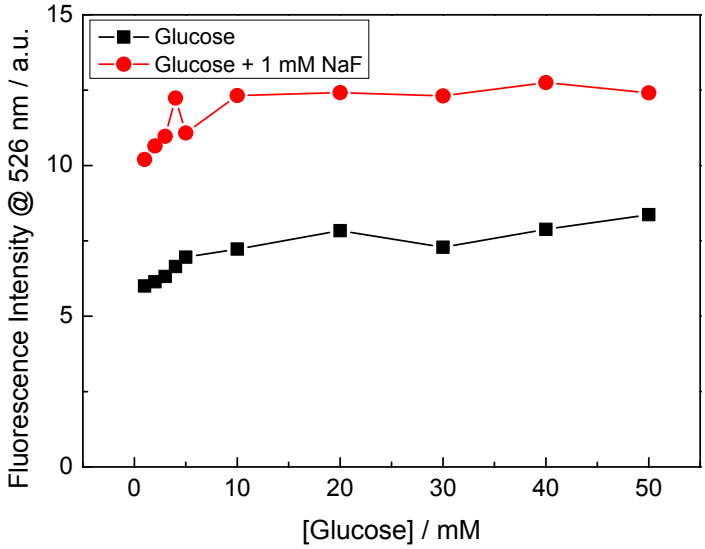


Fig. S14 Fluorescence intensity of **1** (0.1 mM) at 526 nm vs D-glucose concentration in the absence (black line) and presence (red line) of 1 mM NaF in default buffer. Note that the difference between the two curves hardly changes with increasing glucose concentration, indicating that fluoride ion did not enhance the aggregation of the **1**-glucose complex.

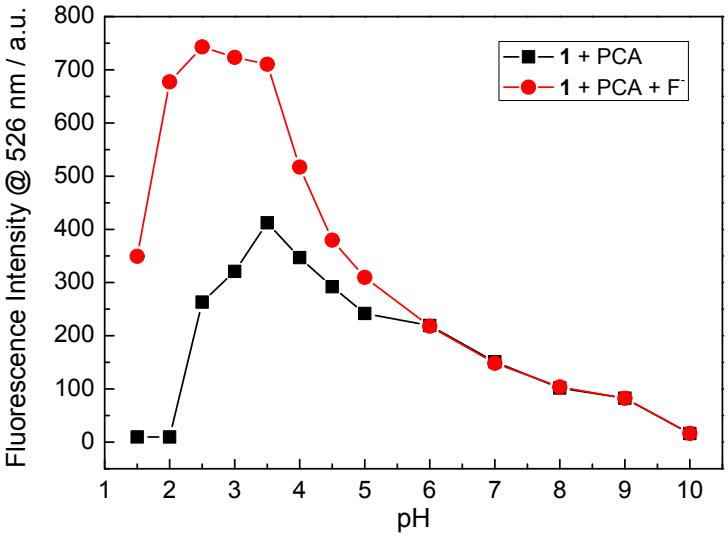
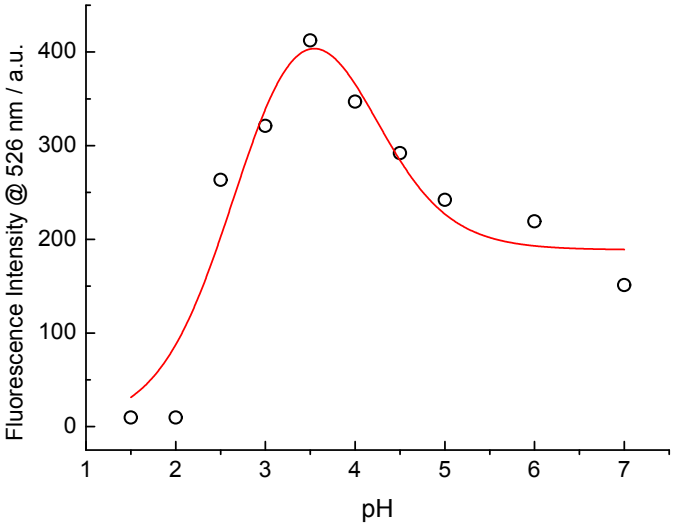


Fig. S15 Fluorescence intensity of **1** (0.1 mM) at 526 nm vs pH with 5 mM PCA in the absence and presence of 1 mM NaF in buffered aqueous solutions. λ_{ex} = 328 nm.



Model	twopKas (User)		
Equation	(H2A*10^(pKa1+pKa2-2*x)+HA*10^(pKa2-x)+A)/(10^(pKa1+pKa2-2*x)+10^(pKa2-x)+1)		
Reduced Chi-Sqr	2683.15751		
Adj. R-Square	0.85239		
		Value	Standard Error
B	H2A	0	61.8278
B	HA	517.22286	141.98542
B	A	188.71315	35.21332
B	pKa1	2.69188	0.38221
B	pKa2	4.12196	0.4923

Fig. S16 Curve fit for Fig. S15 (**1** + PCA) using eq 3. The data obtained with higher pH were not used for fitting since appreciable deprotonation of the phenol group of PCA occurs (pK_a 8.83).[2]

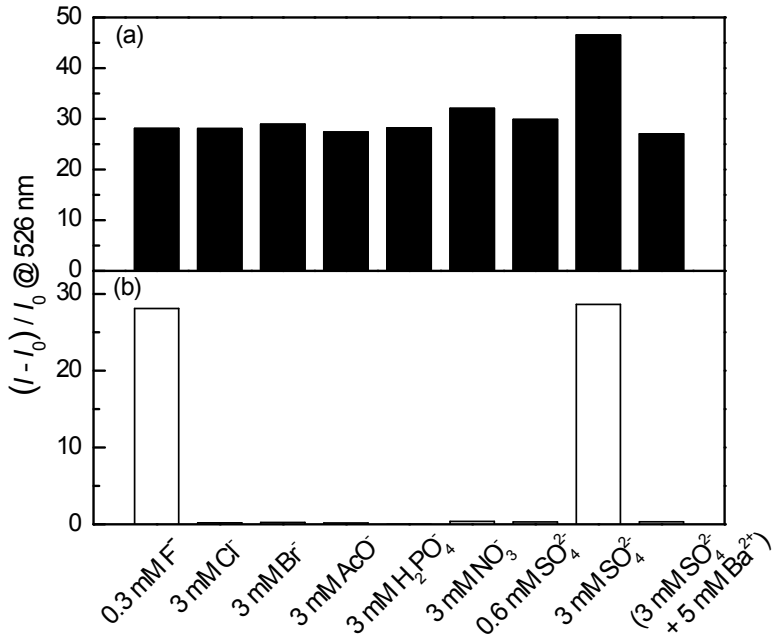


Fig. S17 Enhancement of fluorescence of **1** (0.1 mM) at 526 nm in response to fluoride and other anions alone (b) or in the presence of fluoride coexisting with other anions (a) in the presence of 5 mM PCA in default buffer. λ_{ex} = 328 nm.

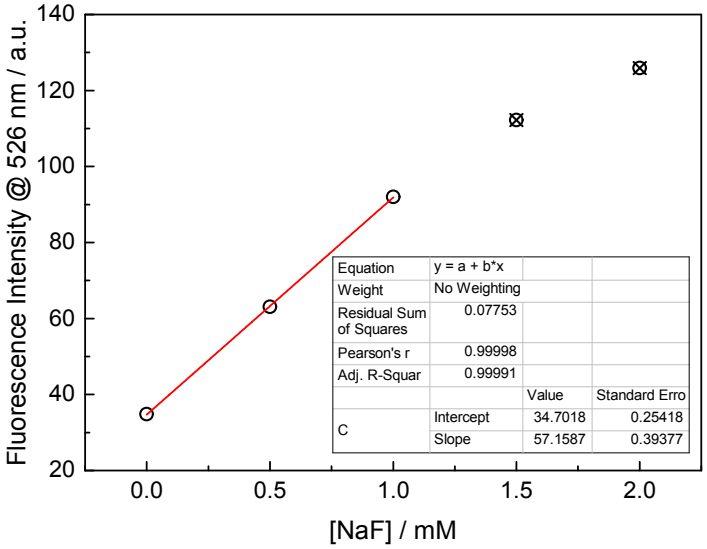


Fig. S18 Determination of fluoride in a mouthwash liquid sample by the standard addition method. The data with [NaF] > 1.0 mM were not used for the fitting since they were deviated from linearity.

Reference

1. Y.-J. Huang, W.-J. Ouyang, X. Wu, Z. Li, J. S. Fossey, T. D. James and Y.-B. Jiang, *J. Am. Chem. Soc.*, 2013, **135**, 1700-1703.
2. R. M. C. Dawson and W. H. Elliott, *Data for Biochemical Research*, Clarendon Press, 1989.