

## Electronic supplementary information

### Detection of anions using a fluorescent alizarin-phenylboronic acid ensemble

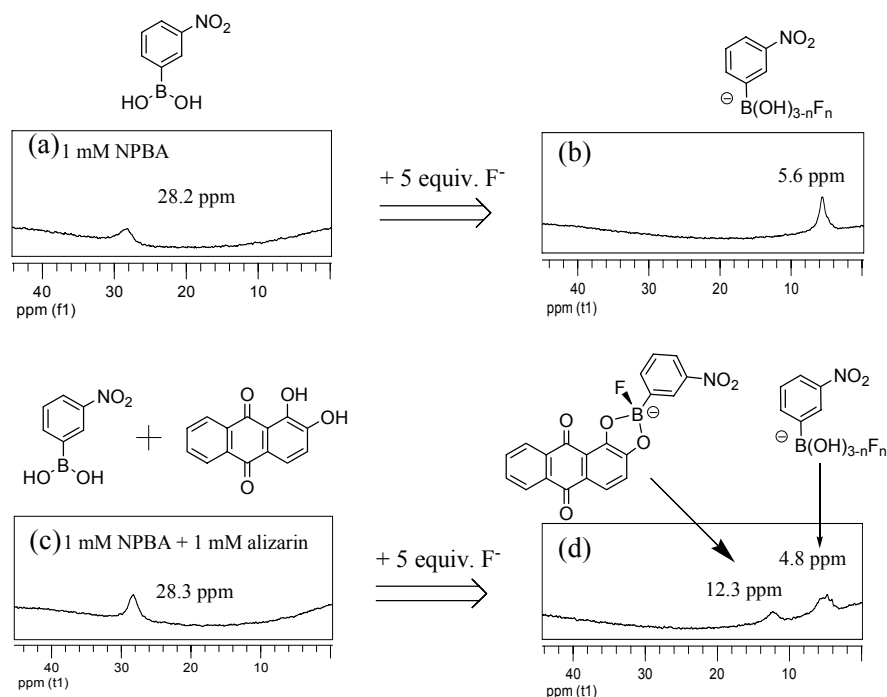
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#### <sup>11</sup>B NMR study

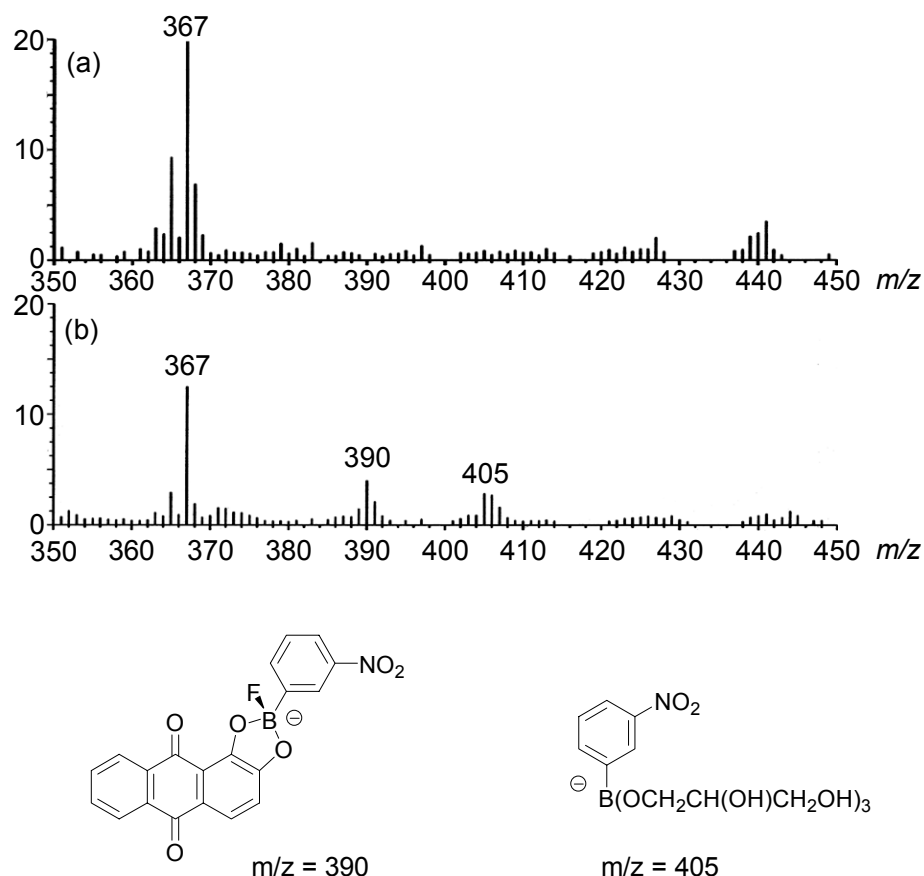
<sup>11</sup>B NMR (96.3 MHz, 296 K) spectra were measured with a Bruker Avance 300 using boron trifluoride diethyl etherate, as external reference. Tetra *n*-butylammonium fluoride trihydrate (16 mg) was dissolved in CD<sub>3</sub>OD (0.5 ml) to prepare a stock solution of (*n*-Bu)<sub>4</sub>NF (100 mM). After the CD<sub>3</sub>OD solution (0.8 mL) of NPBA (1 mM) in a NMR tube was measured (Fig. 1(a)), 40 μL of (*n*-Bu)<sub>4</sub>NF solution (100 mM) was added to the solution (Fig. 1(b)). As alternative measurements, a CD<sub>3</sub>OD solution (0.8 mL) involving NPBA (1 mM) and alizarin (1 mM) was prepared in a NMR tube and measured (Fig. 1(c)). Subsequently, 40 μL of (*n*-Bu)<sub>4</sub>NF solution (100 mM) was added to the tube (Fig. 1(d)).



**Fig. S1** <sup>11</sup>B NMR spectra of NPBA in the absence or presence of alizarin upon addition of (*n*-Bu)<sub>4</sub>NF in CD<sub>3</sub>OD at 23 °C.

### FAB mass spectra

Negative-ion FAB Mass spectra were recorded on a JEOL JMS-DX 303, where Xe was used as the atom beam accelerated 3 keV, with a mass range of  $m/z$  80-1200. Calibration was performed using ULTRAMARK 1621 ranging from 93-1194. Spectra were obtained with a magnet scan rate of 5 sec per scan. FAB mass solutions were prepared by the following procedures: (a) a 50  $\mu\text{L}$  portion of MeOH solution of NPBA (240 mM) was added to a 500  $\mu\text{L}$  portion of MeOH solution of alizarin (4.5 mM). The solution was adjusted to 600  $\mu\text{L}$  portion by adding MeOH; (b) A 50  $\mu\text{L}$  portion of MeOH solution of NPBA (240 mM) was added to a 500  $\mu\text{L}$  portion of MeOH solution of alizarin (4.5 mM). And then, a 50  $\mu\text{L}$  portion of MeOH solution of (*n*-Bu)<sub>4</sub>NF (240 mM) was added to the solutions. A few drops of the solution were mixed with one drop of glycerin matrix on a FAB probe tip.



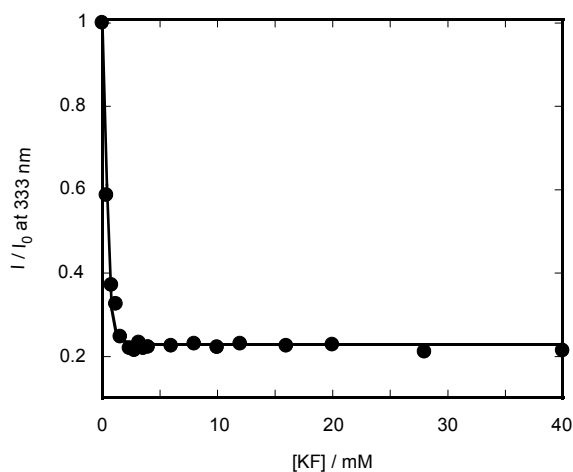
**Fig. S2** FAB mass spectra of alizarin plus NPBA (a) and alizarin plus NPBA upon adding (*n*-Bu)<sub>4</sub>NF (b) in MeOH (a negative mode, glycerin was used as a matrix). [alizarin] = 3.8 mM, [NPBA] = 20 mM, [(*n*-Bu)<sub>4</sub>NF] = 20 mM.

### Fluorescence titrations of NPBA with KF in MeOH

Fluorescence spectra were measured by a JASCO FP-6300 spectrophotometer. The experimental curve (Fig. S3) could be reproduced in terms of eqn. (1) assuming the formation of a trifluoro tetrahedral boronate ( $n = 3$ ).

$$I = \frac{I_0 + I_\infty K_n [F^-]^n}{1 + K_n [F^-]^n} \quad \text{eqn. (1)}$$

$$K_n = \frac{[\text{PhB(OH)}_{3-n}\text{F}_n]}{[\text{PhB(OH)}_2][F^-]^n}$$



**Fig. S3** Change in fluorescence intensity of NPBA at 333 nm upon adding KF in MeOH; [NPBA] = 2 mM,  $\lambda_{\text{ex}} = 268$  nm.

### <sup>1</sup>H NMR spectra

<sup>1</sup>H NMR spectra were taken on a Bruker DRX400 (400 MHz) spectrometer. Chemical shifts ( $\delta$ ) are reported downfield from the initial standard Me<sub>4</sub>Si.

- 1) NPBA upon adding (*n*-Bu)<sub>4</sub>NF

