Detection of anions using a fluorescent alizarin-phenylboronic acid ensemble

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**11B NMR study**

**11B** 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$_3$OD (0.5 ml) to prepare a stock solution of (n-Bu)$_4$NF (100 mM). After the CD$_3$CD solution (0.8 mL) of NPBA (1 mM) in a NMR tube was measured (Fig. 1(a)), 40 µL of (n-Bu)$_4$NF solution (100 mM) was added to the solution (Fig. 1(b)). As alternative measurements, a CD$_3$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)$_4$NF solution (100 mM) was added to the tube (Fig. 1(d)).

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**Fig. S1** 11B NMR spectra of NPBA in the absence or presence of alizarin upon addition of (n-Bu)$_4$NF in CD$_3$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 rage 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 µL
portion of MeOH solution of NPBA (240 mM) was added to a 500 µL portion of MeOH solution
of alizarin (4.5 mM). The solution was adjusted to 600 µL portion by adding MeOH; (b) A 50 µL
portion of MeOH solution of NPBA (240 mM) was added to a 500 µL portion of MeOH solution
of alizarin (4.5 mM). And then, a 50 µL portion of MeOH solution of (n-Bu)4NF (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)4NF
(b) in MeOH (a negative mode, glycerin was used as a matrix). [alizarin] = 3.8 mM, [NPBA] = 20 mM,
[(n-Bu)4NF] = 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 \((n = 3)\).

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

\[
K_n = \frac{[\text{PhB(OH)}_3 \beta_2 F_n]}{[\text{PhB(OH)}_2 ][F^-]^n}
\]

![Graph showing change in fluorescence intensity of NPBA at 333 nm upon adding KF in MeOH; [NPBA] = 2 mM, \(\lambda_{ex} = 268\) nm.]

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

**1H NMR spectra**

1H NMR spectra were taken on a Bruker DRX400 (400 MHz) spectrometer. Chemical shifts \((\delta)\) are reported downfield from the initial standard Me4Si.

1) NPBA upon adding \((n\text{-Bu})_4\text{NF}\)
**Fig. S4** $^1$H NMR spectra (400 MHz, CD$_3$OD, 24 °C) of NPBA (20 mM) upon adding (n-Bu)$_4$NF: (a) NPBA, (b) NPBA + 1 equiv. of [(n-Bu)$_4$NF].

2) alizarin plus NPBA upon adding (n-Bu)$_4$NOAc

**Fig. S5** $^1$H NMR spectrum of alizarin (3.8 mM) plus NPBA (20 mM) upon adding (n-Bu)$_4$NOAc (20 mM) in CD$_3$OD at 24 °C.