Electronic Supplementary Information

A pyrophosphate-induced reorganization of reporter-receptor assembly via boronate esterification; new strategy of a turn-on fluorescent detection of multi-phosphates in aqueous solution

Aiko Nonaka,a Shoichi Horie,a Tony D. Jamesb and Yuji Kuboc*

aDepartment of Applied Chemistry, Graduate School of Science and Engineering, Saitama University, 255 Shimo-ohkubo, Sakura-ku, Saitama 338-8570, Japan
bDepartment of Chemistry, University of Bath, Bath, BA2 7AY, UK
cDepartment of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-ohsawa, Hachioji, Tokyo 192-0397, Japan

1. PPI-induced fluorescence enhancement

Fig. S1. Change in fluorescence spectra (λex = 480 nm) for ARS (50 μM) upon addition of PPI (0 – 500 μM) in the presence of 1·Zn (250 μM) in MeOH-10 mM HEPES buffer (1:1 v/v) containing 10 mM NaCl at pH 7.4 at 25 ºC.
2. Fluorescence spectrum of ARS with Zn$^{11}$-DPA-free phenylboronic acid

![Fluorescence spectrum](image)

**Fig. S2.** Change in fluorescence spectra ($\lambda_{ex} = 480$ nm) for ARS (50 μM) upon addition of PPI (0 – 1000 μM) in the presence of phenylboronic acid (250 μM) in MeOH-10 mM HEPES buffer (1:1 v/v) containing 10 mM NaCl at pH 7.4 at 25 °C.

3. $^1$H, $^1$H COSY spectrum of alizarin plus 1-Zn with PPI

![COSY spectrum](image)

**Fig. S3.** $^1$H, $^1$H COSY spectrum in CD$_3$OD–D$_2$O (9:1 v/v) (400 MHz, r.t.). [alizarin] = 2.4 mM, [1-Zn] = 2.4 mM. The spectrum was obtained after (solid (PPI) – liquid (2.4 mM of alizarin and 1-Zn in CD$_3$OD–D$_2$O (9:1 v/v))) two-phase extraction.
3. Fluorescence spectra of ARS upon adding an incremental amount of 3·Zn

Fig. S4. The fluorescence spectra for ARS (50 μM) upon addition of 3·Zn (0 – 250 μM) in MeOH-10 mM HEPES buffer (1:1 v/v) containing 10 mM NaCl at pH 7.4 at 25 °C, λ<sub>ex</sub> = 480 nm.